

# **Rate Equations of Polymerization Reactions**

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# Preface

This book is a compilation of rate expressions for industrially important polymerization reactions, which have appeared in major technical journals in both chemistry and chemical engineering. In this text we have selected only homopolymer systems, with the exception of polycondensation systems, although copolymers are more widely used. It is our intention to compile and publish the rate expressions for copolymerization reactions in a subsequent volume.

In the polymer industry rate expressions are vital for the analysis, optimal design, and optimal operation of polymerization reactors. In reacting systems other than polymerization reaction comprehensive summaries of kinetic data have been published on many occasions. For polymerization reactions, however, no extensive compilation of rate expressions has been attempted, even though many useful textbooks have been published for the study of polymerization kinetics.

It is true that computer aided searches of pertinent databases assist chemists and chemical engineers in finding rate expressions needed for their studies. Yet computer surveys of data bases are sometimes time consuming and often costly. We hope that this book will be of service for those who wish to conduct an efficient survey of the rate expressions of interest to them. The contents of the book can be used in a variety of ways. For example, chemists and chemical engineers can estimate polymerization rates for desired polymerization conditions by using the rate expressions assembled here. A comparison of the rates thus estimated against rates determined for a newly developed initiator or catalyst furnishes a useful evaluation of the initiator or catalyst. For the development of polymerization rate models we recommend that investigators modify models on

the basis of their own data. In the area of polymerization reactions it is generally recognized that rate expressions are totally different if the polymerization occurs in the region where diffusion process of reactants and/or products are rate-determining. On some occasions, needless to say, rate expressions reported in the past can be used without modifying the form of the rate equations. However the rate parameters contained in the equations must be reevaluated by using the experimental data gathered by the investigators themselves.

The use of uniform units might be convenient for users of this book. No attempts were made to have such uniformity in order to avoid errors that we might introduce during the process of converting the units.

It should be noted that many important journals issued in Russia, in Eastern Europe and in the People's Republic of China were excluded in our search for rate expressions. This is mainly because some difficulties were experienced in obtaining both the original and the English versions of these journals. However the authors sincerely hope that the publication of this book will encourage other interested persons to collect rate expressions published in the geographical regions mentioned above. Perhaps in this way some collaborative efforts will result in a substantially more complete collection of rate expressions for polymerization reactions.

June, 1997

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Guang-Hui Ma  
Tokyo, Japan

## 1. Free radical polymerization

### 1.1 Acrylonitrile

#### Emulsion polymerization

Emulsifier: sodium lauryl sulfate

Initiator: potassium persulfate

Temperature: 50°C

Maximum conversion: higher than 90%

For  $x \leq x_{cr}$

$$r_p = K A k_d^{1/2} [I]^{1/2} M_0^{1/3} N^{1/6} [M_{pi}]$$

For  $x > x_{cr}$

$$r_p = \frac{K A k_d^{1/2} [I]^{1/2} (M_0 x)^{1/3} N^{1/6} M_0 (1-x)}{A (M_0 x)^{2/3} N^{1/3} + m(1 + B M_0 x)}$$

$$r_{tr} = C_m r_p$$

$$r_i = 2f k_d [I]$$

$$\bar{p} = \frac{r_p}{(1/2)r_i + r_{tr}}$$

$$k_d = 4.46 \times 10^{-3} \text{ [1/hr]}$$

$$m = 5 \times 10^7 \text{ [cm}^2/\text{l]}$$

$$K = 5.8 \times 10^6 \text{ [cm}^2/\text{g-mol}^{1/2} \cdot \text{hr}^{1/2}\text{]}$$

$$C_m = 2.6 \times 10^{-5}$$

$$A: (36\pi)^{1/3} (M_w / \rho_p)^{2/3}, \text{ [cm}^2/\text{g-mol}^{2/3}\text{]}$$

$$B: M_w / 10^3 \rho_p, \text{ [l/g-mol} \cdot \text{cm}^3\text{]}$$

$r_i$ : rate of initiation, [g-mol/l·hr]

$r_{tr}$ : rate of chain transfer, [g-mol/l·hr]

$r_p$ : rate of propagation, [g-mol/l·hr]

$C_m$ : chain transfer coefficient to monomer, [-]

$k_d$ : decomposition rate constant of initiator, [1/hr]

$f$ : efficiency of initiation, [-]

$m$ : distribution coefficient, [cm<sup>2</sup>/l]

$k_{ps}$ : propagation rate constant at polymer surface, [cm<sup>2</sup>/g-mol·hr]

$k_{ts}$ : termination rate constant at polymer surface, [cm<sup>2</sup>/g-mol·hr]

$$K: =k_{ps}f^{1/2}/k_{ts}^{1/2}$$

$M_w$ : molecular weight of acrylonitrile, [g/mol]

$N$ : number of polymer particles in reaction mixture, [1/l]

$x$ : monomer conversion

$x_{cr}$ : value of  $x$ , at which monomer droplets disappear, [g/l]

$$x_{cr}=0.12 \text{ for } \gamma=150/850$$

$$x_{cr}=0.22 \text{ for } \gamma=200/800$$

$$x_{cr}=0.35 \text{ for } \gamma=300/700$$

$\gamma$ : monomer to water ratio, [-]

[I]: concentration of initiator, [g-mol/l]

$M_0$ : initial concentration of monomer, [g-mol/l]

$[M_{pi}]$ :  $=m[M_{wi}]$

$[M_{wi}]$ : =saturated value of  $[M_w]$  with monomer [g-mol/l]

$\rho_p$ : density of polymer, [g/cm<sup>3</sup>]

$\bar{p}$ : degree of polymerization, [-]

Tazawa, A., Omi, S., and Kubota, H., *J. Chem. Eng. Japan*, **5**, 44 (1972).

### Photo-induced bulk polymerization

Sensitizer: 1,1'-azobiscyclohexane carbonitrile

Temperature: 25°C

Conversion: less than 0.1%

$$k_p=52 \text{ [l/mol}\cdot\text{sec]}$$

$$k_t=5.0 \times 10^6 \text{ [l/mol}\cdot\text{sec]}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Bengough, W. I., *Proc. Roy. Soc., London*, **A260**, 205 (1961).

### Photo-induced solution polymerization

Solvent: water

Initiator:  $Fe^{3+}X^-$  ( $X^-$ :  $OH^-$ ,  $Cl^-$ ,  $N_3^-$ )

Temperature: 25°C

Light absorption



Primary dark back reaction

Initiation of polymerization by the primary product  $\text{Fe}^{2+}\text{X}$ 

Separation of the primary product



Secondary dark back reaction



Free radical initiation of polymerization



Propagation of polymerization

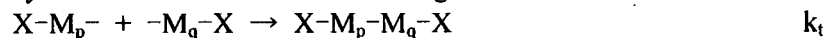


Termination of polymerization

(a) by free radicals



(b) by recombination of active endings



M: monomer.

Ion pair	$k_0/k_i$	$k_p/k_t^{1/2}$ [(l/mol·sec) <sup>1/2</sup> ]
$\text{Fe}^{3+}\text{OH}^-$	$4 \times 10^3$	
$\text{Fe}^{3+}\text{Cl}^-$	$6 \times 10^3$	0.156
$\text{Fe}^{3+}\text{N}_3^-$	$5 \times 10^2$	-

 $k_e$ : the fraction of the light absorbed by  $\text{Fe}^{3+}\text{X}^-$ , [1/sec] $k_d$ : rate constant of primary dark back reaction, [1/sec] $k'_i$ : rate constant of initiation reaction by the primary product  $\text{Fe}^{2+}\text{X}$ , [l/mol·sec] $k_s$ : separation rate constant of the primary product, [1/sec] $k_0$ : rate constant of secondary dark back reaction, [l/mol·sec]



$k_i$ : free radical initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k'_t$ : termination rate constant by free radicals, [l/mol·sec]

$k_t$ : termination rate constant by recombination of active endings, [l/mol·sec]

Evans, M. G., Santappa, M., and Uri, N., *J. Polym. Sci.*, 7, 243 (1951).

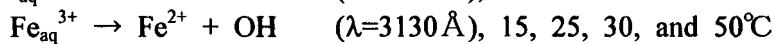
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### Photo-induced solution polymerization

Solvent: water

Initiator: Fenton's reagent ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ )

Photochemical reactions:



Reaction	Rate
Initiation	
$\text{OH} + m_1 \rightarrow \text{S}_1^*$	$R_i$
Aqueous phase propagation	
$m_1 + \text{S}_j^* \rightarrow \text{S}_{j+1}^*$	$k_1[m_1][\text{S}^*]$
Aqueous phase termination	
$\text{S}_j^* + \text{S}_j^* \rightarrow \text{p}$	$k_t[\text{S}^*]^2$
$\text{S}_j^* + \text{Fe(III)} \rightarrow \text{p} + \text{Fe(II)}$	$k_2[\text{S}^*][\text{Fe(III)}]$
Subcritical particle coalescence	
$\text{p} + \text{p} + \dots \rightarrow \text{P}$	rapid
$\text{p} + \text{P} \rightarrow \text{P}$	$\alpha[m_1]f(R_i)$
Very slow, stable particle coalescence	
$\text{P} + \text{P} \rightarrow \text{P}$	$k''_i[\text{P}]^2$
$\text{P} + \text{P}^* \rightarrow \text{P}^*$	$k''_i[\text{P}][\text{P}^*]$
$\text{P}^* + \text{P}^* \rightarrow \text{P}$	$k''_i[\text{P}^*]^2$
Weak adsorption	
$m_1_{\text{aq}} \rightleftharpoons m_1_{\text{ads}}$	very mobile

Particle propagation



Particle activation



Particle termination



$$R_p = R_{aq} + R_s = k_1[m_1][S^*] + k'_p[m_1 \text{ ads}][P^*]$$

Arrhenius parameters

	A [l/mol·sec]	E [kcal/mol]
Propagation ( $k_1$ )	$3.0 \times 10^7$	4.1
Mutual termination ( $k_t$ )	$3.3 \times 10^{13}$	5.4
Termination by Fe(III) ( $k_2$ )	$6.7 \times 10^5$	2.3

$R_i$ : rate of initiation, [mol/l·sec]

$R_{aq}$ : propagation rate in aqueous phase, [mol/l·sec]

$R_s$ : propagation rate in particle, [mol/l·sec]

$k_1$ : propagation rate constant in aqueous phase, [l/mol·sec]

$k_t$ : mutual termination rate constant in aqueous phase, [l/mol·sec]

$k_2$ : termination rate constant with ferric ion in aqueous phase, [l/mol·sec]

$k''_t$ : stable particle coalescence rate constant, [l/mol·sec]

$k'_p$ : particle propagation rate constant, [l/mol·sec]

$k_t$ : particle activation rate constant, [l/mol·sec]

$k'_t$ : particle termination rate constant, [l/mol·sec]

$[m_1]$ : monomer concentration in aqueous phase, [mol/l]

$[m_1 \text{ ads}]$ : monomer concentration adsorbed on particle, [mol/l]

$[S_j^*]$ : concentration of polymer radical with j units in aqueous phase, [mol/l]

$[S^*]$ : total concentration of polymer radicals, [mol/l]

$[p]$ : concentration of dead polymer in aqueous phase, [mol/l]

[P]: concentration of dead particle, [mol/l]

[P\*]: concentration of particle with radical, [mol/l]

Dainton, F. S., Seaman, P. H., James, D. G. L., and Eaton, R. S., *J. Polym. Sci.* **39**, 209 (1959). Copyright © 1959 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Photo-induced solution polymerization

Solvent: water

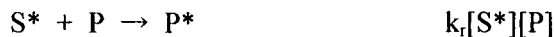
Initiator:  $\text{Fe}^{3+}$ ,  $\text{Fe}^{3+}\text{OH}^-$ ,  $\text{Fe}^{2+}$ ,  $\text{I}^-$

Photochemical reactions:



Reaction	Rate
Initiation	
$\text{Fe}^{3+}\text{OH}^- \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH}$	$R_i = \phi_1 I_{\text{abs}}$
$\text{OH} + m_1 \rightarrow S_1^*$	
Aqueous phase propagation	
$m_1 + S_j^* \rightarrow S_{j+1}^*$	$R_{\text{aq}} = k_p [m_1][S^*]$
Aqueous phase termination	
$2S^* \rightarrow p$	$k_t [S^*]^2$
$S^* + \text{Fe(III)} \rightarrow p + \text{Fe(II)}$	$k_{\text{tf}} [S^*][\text{Fe(III)}]$
Transformation of subcritical particle p to stable particles P	
$p + p \rightarrow P$	rapid
$p + P \rightarrow P$	$\alpha [m_1] f(R_i)$
Slow stable particle coalescence	
$P + P \rightarrow P$	$k''_t [P]^2$
$P + P^* \rightarrow P^*$	$k''_t [P][P^*]$
$P^* + P^* \rightarrow P$	$k''_t [P^*]^2$
Weak adsorption	
$m_{1 \text{ aq}} \rightleftharpoons m_{1 \text{ ads}}$	very mobile
Particle propagation	
$P^* + m_{1 \text{ ads}} \rightarrow P^*$	$R_s = k'_p [P^*][m_{1 \text{ ads}}]$

Particle activation



Particle termination



$$R_p = R_{aq} + R_s = k_p[m_1][S^*] + k'_p[m_1 \text{ ads}][P^*]$$

$$k_p = 1.45 \times 10^4, \text{ [l/mol}\cdot\text{sec]}$$

$$k_t = 2 \times 10^9, \text{ [l/mol}\cdot\text{sec]}$$

$$k_{tf} = 1.3 \times 10^4, \text{ [l/mol}\cdot\text{sec]}$$

$R_i$ : rate of initiation, [mol/l·sec]

$R_{aq}$ : propagation rate in aqueous phase, [mol/l·sec]

$R_s$ : propagation rate in particle, [mol/l·sec]

$k_p$ : propagation rate constant in aqueous phase, [l/mol·sec]

$k_t$ : mutual termination rate constant in aqueous phase, [l/mol·sec]

$k_{tf}$ : termination rate constant with ferric ion in aqueous phase, [l/mol·sec]

$k''_t$ : stable particle coalescence rate constant, [l/mol·sec]

$k'_p$ : particle propagation rate constant, [l/mol·sec]

$k_r$ : particle activation rate constant, [l/mol·sec]

$k'_t$ : particle termination rate constant, [l/mol·sec]

$[m_1]$ : monomer concentration in aqueous phase, [mol/l]

$[m_1 \text{ ads}]$ : monomer concentration adsorbed on particle, [mol/l]

$[S_j^*]$ : concentration of polymer radical with  $j$  units in aqueous phase, [mol/l]

$[S^*]$ : total concentration of polymer radicals, [mol/l]

$[p]$ : concentration of dead polymer in aqueous phase, [mol/l]

$[P]$ : concentration of dead particle, [mol/l]

$[P^*]$ : concentration of particle with radical, [mol/l]

Dainton, F. S. and James, D. G. L., *J. Polym. Sci.*, **39**, 299 (1959).

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### Photo-induced solution polymerization

Solvent: water

Initiator:  $Fe^{3+}OH^-$

Temperature: 15–50°C

Reaction	Rate
Initiation	
$\text{Fe}^{3+}\text{OH}^- \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH}$	$R_i = \phi I_{\text{abs}}$
$\text{OH} + m_1 \rightarrow S_1^*$	
Aqueous phase propagation	
$m_1 + S_j^* \rightarrow S_{j+1}^*$	$R_{\text{aq}} = k_p [m_1][S^*]$
Aqueous phase termination	
$2S^* \rightarrow p$	$k_t [S^*]^2$
$S^* + \text{Fe(III)} \rightarrow p + \text{Fe(II)}$	$k_{\text{tf}} [S^*][\text{Fe(III)}]$
Transformation of subcritical particle p to stable particles P	
$p + p \rightarrow P$	rapid
$p + P \rightarrow P$	$\alpha [m_1] f(R_i)$
Slow stable particle coalescence	
$P + P \rightarrow P$	$k''_t [P]^2$
$P + P^* \rightarrow P^*$	$k''_t [P][P^*]$
$P^* + P^* \rightarrow P$	$k''_t [P^*]^2$
Weak adsorption	
$m_{1 \text{ aq}} \rightleftharpoons m_1 \text{ ads}$	very mobile
Particle propagation	
$P^* + m_1 \text{ ads} \rightarrow P^*$	$R_s = k'_p [P^*][m_1 \text{ ads}]$
Particle activation	
$S^* + P \rightarrow P^*$	$k_t [S^*][P]$
Particle termination	
$S^* + P^* \rightarrow P$	$k'_t [S^*][P^*]$

## Rate constants

Temperature [°C]	$k_t$ [l/mol·sec]	$k_{\text{tr}}$ [l/mol·sec]	$k_p$ [l/mol·sec]
15	$2.8 \times 10^9$	$4.5 \times 10^4$	$2.3 \times 10^4$
25	$3.7 \times 10^9$	$6.2 \times 10^4$	$2.8 \times 10^4$
30	$4.4 \times 10^9$	$6.4 \times 10^4$	$3.25 \times 10^4$

## Arrhenius parameters

	A [l/mol·sec]	E [kcal/mol]
Propagation ( $k_p$ )	$3.0 \times 10^7$	4.1
Mutual termination ( $k_t$ )	$3.3 \times 10^{13}$	5.4
Termination by $\text{Fe}^{3+}\text{OH}^-$ ( $k_{tf}$ )	$6.7 \times 10^5$	2.3

$R_i$ : rate of initiation, [mol/l·sec]

$R_{aq}$ : propagation rate in aqueous phase, [mol/l·sec]

$R_s$ : propagation rate in particle, [mol/l·sec]

$k_p$ : propagation rate constant in aqueous phase, [l/mol·sec]

$k_t$ : mutual termination rate constant in aqueous phase, [l/mol·sec]

$k_{tf}$ : termination rate constant with ferric ion in aqueous phase, [l/mol·sec]

$k''_t$ : stable particle coalescence rate constant, [l/mol·sec]

$k'_p$ : particle propagation rate constant, [l/mol·sec]

$k_r$ : particle activation rate constant, [l/mol·sec]

$k_t'$ : particle termination rate constant, [l/mol·sec]

$[m_1]$ : monomer concentration in aqueous phase, [mol/l]

$[m_1 \text{ ads}]$ : monomer concentration adsorbed on particle, [mol/l]

$[S_j^*]$ : concentration of polymer radical with j units in aqueous phase, [mol/l]

$[S^*]$ : total concentration of polymer radicals, [mol/l]

$[p]$ : concentration of dead polymer in aqueous phase, [mol/l]

$[P]$ : concentration of dead particle, [mol/l]

$[P^*]$ : concentration of particle with radical, [mol/l]

Dainton, F. S. and Eaton, R. S., *J. Polym. Sci.*, **39**, 313 (1959).

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**Photo-induced solution polymerization**

Solvent: dimethyl sulfoxide

Initiator: azobis(isobutyronitrile) (AINB) or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

AINB

Temperature: 25.4–45.9°C

$$R_p = 97 \{ \exp(-4.45 \text{ kcal/RT}) \} I_{ab}^{1/2} [M]$$

H<sub>2</sub>O<sub>2</sub>

Temperature: 25–45°C

$$R_p = 140 \{ \exp\{-4.38 \text{ kcal/RT}\} \} I_{ab}^{1/2} [M] \text{ for } 365 \mu\text{m}$$

$$R_p = 4.20 \{ \exp\{-2.15 \text{ kcal/RT}\} \} I_{ab}^{1/2} [M] \text{ for } 313 \mu\text{m}$$

R<sub>p</sub>: propagation rate, [mol/l·sec]

[M]: monomer concentration, [mol/l]

[I<sub>ab</sub>]: absorbed light intensity, [E/l·sec]Miyama, H., Harumiya, N., and Takeda, A., *J. Polym. Sci.*, **A-1**, **10**, 943 (1972).

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**Solution polymerization**

Solvent: water

Initiator: ammonium persulfate (APS)

Temperature: 35–50°C

Maximum conversion: 80%

$$R_p = k[\text{APS}]^{1/2} [M]^2 = k_2 [M]^2 = \beta k_p (fk_d/k_t)^{1/2} [\text{APS}]^{1/2} [M]^2$$

$$\beta = k / \{ k_p (fk_d/k_t)^{1/2} \} = m V_p^{1/2} / [M]^2$$

$$m = (\beta / V_p^{1/2}) [M]^2$$

$$1/\bar{P}_n = (k_{td} + k_{tc}/2) k_2 V_p / k_p^2 [M]^2 \beta^2 + \text{term related to chain transfer}$$

Temp. [°C]	Initial concentration of APS $\times 10^2$ [mol/l]	$k_2 \times 10^4$ [l/mol·sec]	$\bar{P}_n$ (conversion 45%)	Induction time [min]
35	5.310	3.45	4000	38
35	3.510	2.79	4780	47
35	2.670	2.45	5300	57
35	1.768	1.88	6020	70
35	1.326	1.77	6260	77
35	0.884	1.48	6560	97
35	0.708	1.20	8080	107
40	5.310	5.21	2840	20
40	3.510	4.11	3120	23
40	2.670	3.54	3700	27
40	1.768	2.87	4350	36
40	1.326	2.55	4760	41
40	0.884	2.04	5460	49
40	0.708	1.91	5560	54
50	1.768	5.62	2060	12
50	1.345	4.69	2370	13
50	0.876	3.85	2780	15
50	0.701	3.42	3030	17
50	0.442	2.66	3950	20
50	0.177	1.60	5280	29

Activation energy for polymerization:

$$E = E_d/2 + E_p - E_t/2 + E_B = 13.3 \text{ [kcal/mol]}$$

$$E_d = 31.3, E_p - E_t/2 + E_B = -2.4 \text{ [kcal/mol]}$$

$R_p$ : propagation rate, [mol/l·sec]

$f$ : efficiency of initiation, [-]

$k_d$ : decomposition rate constant of initiator, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

[APS]: concentration of initiator, [mol/l]

$[R_n \cdot]$ : total concentration of polymer radical, [mol/l]



[M]: concentration of monomer, [mol/l]

$V_p$ : efficient volume in polymerization locus, [l]

m: concentration of monomer in polymerization locus, [mol/l]

$\bar{P}_n$ : number-average degree of polymerization

E: activation energy for polymerization, [kcal/mol]

$E_d$ : activation energy for decomposition of initiator, [kcal/mol]

$E_p$ : activation energy for propagation, [kcal/mol]

$E_t$ : activation energy for termination, [kcal/mol]

Kiuchi, H., Yaguchi, S., and Watanabe, M., *Kogyo Kagaku Zashi*, **67**, 1479 (1964).

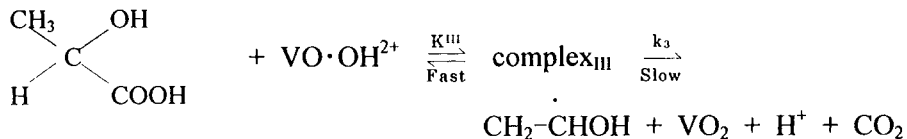
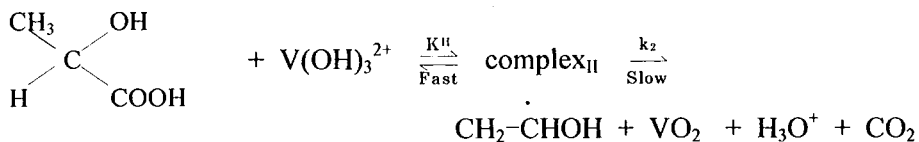
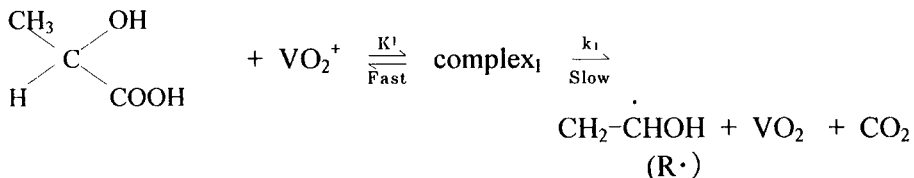
### Solution polymerization

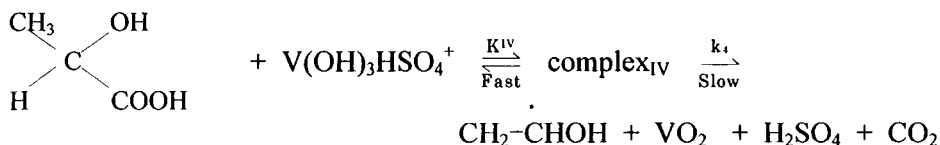
Initiator:  $V^{5+}$ -lactic acid

Solvent: aqueous sulfuric acid

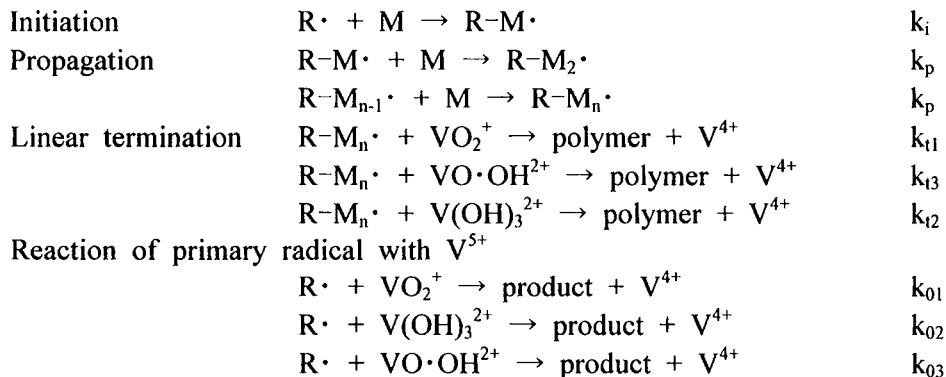
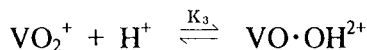
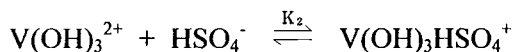
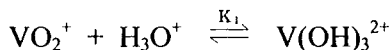
Temperature: 20–35°C

Primary radical production





where



$$R_p = (k_p/k_t)k'[Lac][M]^2/([M] + k_0/k_i[V^{5+}])$$

Rate parameters for  $\text{V}^{5+}$ -lactic acid-acrylonitrile system in aqueous sulfuric acid

Temperature [°C]	$k_p/k_t$		$k_0/k_i$	
	From $1/R_p$ vs. $1/[Lac]$	From $1/R_p$ vs. $[V^{5+}]$	From $1/R_p$ vs. $1/[Lac]$	From $1/R_p$ vs. $[V^{5+}]$
20	-	0.4053	-	13.05
30	0.277	0.281	10.96	11.17

- $k_p$ : propagation rate constant, [l/mol·sec]  
 $k_t$ : termination rate constant, [l/mol·sec]  
 $k_i$ : initiation rate constant, [l/mol·sec]  
 $k_0$ : rate constant for reaction of primary radical with  $V^{5+}$ , [l/mol·sec?]  
 $R_p$ : propagation rate, [mol/l·sec]  
[Lac]: concentration of lactic acid, [mol/l]  
 $[V^{5+}]$ : concentration of vanadate ( $V^{5+}$ ), [mol/l]  
[M]: concentration of monomer, [mol/l]

Saccubai, S. and Santappa, M., *J. Polym. Sci. A-1*, 7, 643 (1969).

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### Solution polymerization

Solvent: dimethyl formamide

Temperature: 50°C

Radical formation	$I \rightarrow R^*$	$k_d$
Initiation	$R^* + M \rightarrow P^*$	$k_i$
Propagation	$P^* + M \rightarrow P^*$	$k_w$
Transfer	$P^* + S \rightarrow S^* + P$	$k_u$
Reinitiation	$S^* + M \rightarrow P^*$	$k_r$
Termination	$P^* + P^* \rightarrow P$	$k_a$

I: initiator,  $R^*$ : radical,  $P^*$ : growing polymer radical, P: dead polymer, S: non-active solvent,  $S^*$ : active solvent.

$$v = k_w(2fk_d/k_a)^{1/2}[M][I]^{1/2}$$

$$1/\bar{P}_n = (2fk_d k_a [I])^{1/2} / k_w [M] + k_a [S] / k_w [M]$$

$$k_d = 2.08 \times 10^{-6} \text{ [1/sec] for AIBN}$$

$$k_d = 2.12 \times 10^{-4} \text{ [1/sec] for APS}$$

$$k_i = 2fk_d$$

$$f = 0.59 \text{ for AIBN}$$

$$f = 0.144 \text{ for APS}$$

$$k_w = 3.28 \times 10^3 \text{ [l/mol·sec]}$$

$$k_r = k_w$$

$$k_w=0.93 \text{ [l/mol}\cdot\text{sec]}$$

$$k_a=1.20 \times 10^9 \text{ [l/mol}\cdot\text{sec]}$$

[i]: concentration of species i, [mol/l]

f: efficiency of initiation, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant, [l/mol $\cdot$ sec]

$k_w$ : propagation rate constant, [l/mol $\cdot$ sec]

$k_{tr}$ : transfer rate constant, [l/mol $\cdot$ sec]

$k_r$ : reinitiation rate constant, [l/mol $\cdot$ sec]

$k_a$ : termination rate constant, [l/mol $\cdot$ sec]

v: rate of polymerization, [mol/l $\cdot$ sec]

$\bar{P}_n$ : number-average degree of polymerization, [-]

Fritzsche, P., Rafler, G., and Tauer, K., *Acta Polymerica*, **40**, 143 (1989).

## 1.2 Butadiene

### Emulsion polymerization

Initiator: hydroperoxide-polyamine

Temperature: 0–30°C

Recipe:

Water	180 parts
Butadiene	100
Soap	5
Potassium chloride	1
Diisopropylbenzene monohydroperoxide	variable
Triethylenetetramine or tetraethylenepentamine	variable

$$-dm/dt = k_p[M]N/2$$

$$k_p = 1.2 \times 10^8 \exp(-9300 \text{ cal}/RT) \text{ [l/mol}\cdot\text{sec]}$$

[M]: monomer concentration in particle, [mol/l]

N: number of particles per ml of water, [1/ml]

-dm/dt: rate of polymerization, [molecules/ml of water·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

Morton, M., Salatiello, P. P., and Landfield, H., *J. Polym. Sci.*, **8**, 215 (1952).

Copyright © 1952 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

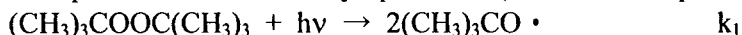
### Photo-induced bulk polymerization

Initiator: di-tert-butyl peroxide and acetone

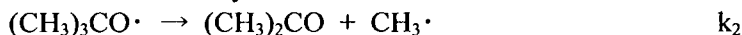
Temperature: 75–95°C for di-tert-butyl peroxide; 60–80°C for acetone

Phase: gas

Photo decomposition of di-tert-butyl peroxide (formation of primary radical)



Deactivation of tert-butoxy radical



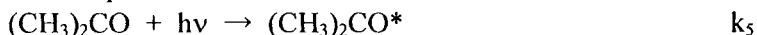
Propagation of tert-butoxy radical



M: monomer.

$$\frac{d[(\text{CH}_3)_2\text{CO}]/dt}{d[(\text{CH}_3)_3\text{COM}]/dt} = \frac{R_A}{R_B} = \frac{k_2}{k_{10}[\text{M}]}$$

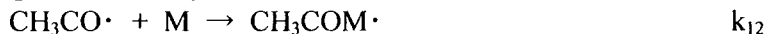
Photo decomposition of acetone



Deactivation of acetyl radical



Propagation of acetyl radical



M: monomer,  $(\text{CH}_3)_2\text{CO}^*$ : photo-activated state.

$$\frac{d[\text{CH}_3\text{COM}]/dt}{d[\text{CO}]/dt} = \frac{R_C}{R_D} = \frac{k_{12}[\text{M}]}{k_8}$$

$$\text{Overall rate equation: } -dP/dt = k_9[\text{M}]$$

Initiator	Activation energy ( $E_9$ ) for $k_9$ [kcal/mol]
Di-tert-butyl peroxide	$5.8 \pm 1.0$
Acetone	$5.0 \pm 1.0$

$$E_2=11.2 \pm 2, E_{10}=5.4, E_8=13.5 \pm 2.0, E_{12}=5.4 \text{ [kcal/mol]}$$

[M]: concentration of butadiene, [mol/l],

$E_9$ : activation energy for overall rate constant  $k_9$ , [kcal/mol]

$E_2$ : activation energy for  $k_2$ , [kcal/mol]

$E_{10}$ : activation energy for  $k_{10}$ , [kcal/mol]

$E_8$ : activation energy for  $k_8$ , [kcal/mol]

$E_{12}$ : activation energy for  $k_{12}$ , [kcal/mol]

Volman, D. H. and Graven, W. M., *J. Am. Chem. Soc.*, **75**, 3111 (1953).

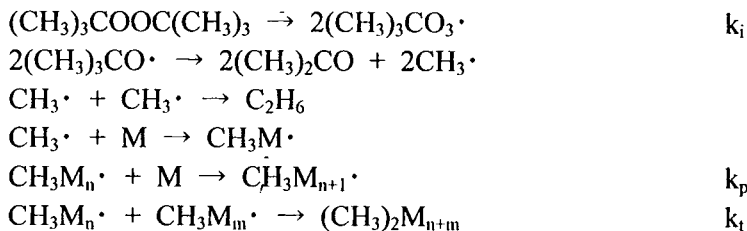
© 1953 American Chemical Society.

**Thermally-induced bulk polymerization**

Initiator: di-tert-butyl peroxide

Temperature: 140–161.2°C

Phase: gas



M: monomer.

$$\begin{aligned}
 d[\text{M}]/dt &= -k_p(k_i/k_t)^{1/2}[\text{M}][\text{C}]^{1/2} \\
 k &= k_p(k_i/k_t)^{1/2}
 \end{aligned}$$

Temperature [°C]	k [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
140.0	0.0289
151.0	0.0548
161.2	0.112

$$E = E_i/2 + E_p - E_t/2 = 22.1 \text{ [kcal/mol]}$$

$$E_i = 39.1, E_p = 2.6, E_t = 0 \text{ [kcal/mol]}$$

[M]: pressure of butadiene, [mmHg], [mol/l]

[C]: pressure of peroxide, [mmHg], [mol/l]

k: overall rate constant, [l/mol·sec]

k<sub>i</sub>: decomposition rate constant of initiator, [1/sec]k<sub>p</sub>: propagation rate constant, [l/mol·sec]k<sub>t</sub>: termination rate constant by combination, [l/mol·sec]

E: activation energy for k, [kcal/mol]

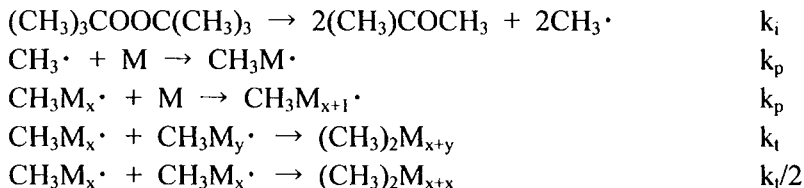
E<sub>p</sub>: activation energy for k<sub>p</sub>, [kcal/mol]E<sub>i</sub>: activation energy for k<sub>i</sub>, [kcal/mol]E<sub>t</sub>: activation energy for k<sub>t</sub>, [kcal/mol]Volman, D. H., *J. Chem. Phys.*, **19**, 668 (1951).

**Thermally-induced bulk polymerization (1,3-butadiene)**

Initiator: di-tert-butyl peroxide

Temperature: 130–165°C

Phase: gas



M: monomer.

$$\begin{aligned}
 -d[\text{M}]/dt &= k_p(2k_i/k_t)^{1/2}[\text{M}][\text{C}]^{1/2} \\
 k &= k_p(2k_i/k_t)^{1/2}
 \end{aligned}$$

Temperature [°C]	k [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
129.4	0.85
140.5	1.93
151.0	3.91
166.2	10.5

$$\begin{aligned}
 k_i &= 1.6 \times 10^6 \exp(-38.4 \text{ kcal}/RT) \text{ [1/sec]} \\
 E_i &= 38.4, E_p = 4.9, E_t = 0, E = 24.1 \text{ [kcal/mol]}
 \end{aligned}$$

[M]: pressure (concentration) of butadiene, [mol/l]

[C]: pressure (concentration) of peroxide, [mol/l]

 $k_i$ : initiation rate constant, [1/sec] $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]

k: overall rate constant, [l/mol·sec]

 $E_i$ : activation energy for  $k_i$ , [kcal/mol] $E_p$ : activation energy for  $k_p$ , [kcal/mol] $E_t$ : activation energy for  $k_t$ , [kcal/mol]

E: activation energy for overall rate constant k, [kcal/mol]

Landers, L. C. and Volman, D. H., *J. Am. Chem. Soc.*, 79, 2996 (1957).

© 1957 American Chemical Society.



### 1.3 Ethylene

#### Bulk polymerization

Initiator:  $\gamma$ -rays, acetoxime, di-tert-butyl peroxide(DTBO), azodi-isobutyronitrile (ADIB), and oxygen

Temperature: 20–260°C

Pressure: 400–2000 atm

Initiator	Overall polymerization rate [mol/l·hr]	Experimental ranges			Exponents and activation energies		
		P [atm]	T [°C]	C [mol/l] $\times 10^3$	P or f	C	E [cal/mol]
-	$1.32 \times 10^{-3} \exp \frac{-30600}{RT} P^{4.9}$ $f^{2.1}$	1200-2000	200-264	-	4.6-5.3	-	26700-34500
Acetoxime	$1.81 \times 10^7 \exp \frac{-31900}{RT} P^{2.6} C^{0.4}$ $f^{1.1}$	1200-2000	180-210	0.85-34.2	2.1-3.0	0.3-0.5	28800-35000
DTBO	$2.37 \times 10^{11} \exp \frac{-29100}{RT} P^{2.2} C^{0.7}$ $f^{1.6}$	380-1050	120-140	1.4-6.8	1.8-2.6	-	16400-41900
ADIB	$\alpha P^{1.2} C^{0.9}$ $f^{0.7}$	400-1200	51	10.2-61.2	1.0-1.3	0.7-1.1	-
Oxygen	$\alpha P^{2.8}$ $f^{1.2}$	1100-1800	230	-	2.1-3.5	-	-
$\gamma$ -Rays	$\alpha \exp \frac{-3300}{RT} P^{2.0} C^{0.9}$ $f^{1.2}$	473-1185	20-125	0.45&4.2 curies	1.4-2.7	0.6-1.2	2100-8800
$\gamma$ -Rays	$\alpha \exp \frac{-13600}{RT} P^{3.1} C^{0.8}$ $f^{1.8}$	675-1375	100-200	0.45&4.2 curies	2.6-3.6	0.04-1.5	7800-18400
					1.4-2.1		

C: catalyst concentration, [mol/l]

P: pressure of monomer, [atm]

T: temperature, [°C] or [°K]

E: activation energy, [cal/mol]

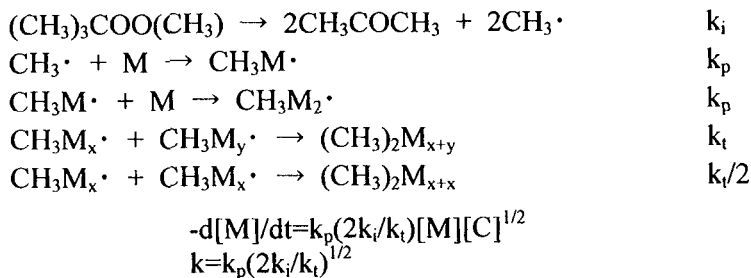
f: ethylene fugacity, [-]

Laird, R. K., Morrell, A.G., and Seed, L., *Faraday Soc. Discussions*, **22**, 126 (1956).

**Bulk Polymerization**

Initiator: di-tert-butyl peroxide

Temperature: 130–165°C



Rate constants

Temperature [°C]	$k \times 10^4$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
131.2	1.86
146.0	6.19
160.1	18.2

Activation energies

Rate constant	Activation energy [kcal/mol]
k	27.4
k <sub>i</sub>	38.4
k <sub>p</sub>	8.2
k <sub>t</sub>	0

$$k_i = 1.6 \times 10^6 \exp(-38.4 \text{ cal/RT})$$

[M]: concentration of monomer, [mol/l]

[C]: concentration of initiator, [mol/l]

k<sub>i</sub>: initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Landers, L. C. and Volman, D. H., *J. Am. Chem. Soc.*, **79**, 2996 (1957).

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### Bulk polymerization

Initiator: in first stage AIBN, in second stage no initiator

Temperature: 20–80°C

Pressure: 160–400 kg/cm<sup>2</sup>

In second stage:

$$R_p = k_p [R \cdot] f_M^2, \quad R_{tr} = k_{tr} [R \cdot] f_M^2, \quad R_b = k_b [R \cdot] f_M^2$$

	Activation energy [kcal/mol]	Activation entropy difference [cal/mol·sec]
Propagation ( $k_p$ )	5.7	$\Delta S_{tr} - \Delta S_p = 38.2$
Transfer ( $k_{tr}$ )	23.4	
Short-chain branching ( $k_b$ )	10.9	$\Delta S_b - \Delta S_p = 19.7$

$$P_n = k_p / k_{tr}$$

$R_p$ : overall propagation rate, [mol/l·sec]

$R_{tr}$ : rate of transfer reaction, [mol/l·sec]

$R_b$ : rate of short-chain branching, [mol/l·sec]

$k_p$ : overall propagation rate constant, [l/mol·sec]

$k_{tr}$ : transfer rate constant, [l/mol·sec]

$k_b$ : short-chain branching rate constant, [l/mol·sec]

$P_n$ : number-average degree of polymerization, [-]

$f_M$ : fugacity of ethylene, [-]

$[R \cdot]$ : total concentration of polymer radicals, [mol/l]

Machi, S., Kise, S., Hagiwara, M., and Kagiya, T., *J. Polym. Sci. A-1*, **5**, 3115 (1967). Copyright © 1967 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Bulk polymerization**

Initiator: di-tert-butyl peroxide

Temperature: 100–300°C

Initiation	$I \rightarrow 2R_1(0)$	$\alpha$
Propagation	$R_i(x) + M \rightarrow R_i(x+1)$	$\beta$
Termination by combination	$R_i(x) + R_j(y) \rightarrow P_{i+j-1}(x+y)$	$\gamma$
Termination by thermal degradation ( $\beta$ -scission)	$R_i(x) \rightarrow P_i(x) + R_1(0)$	$\varepsilon$
Chain transfer to polymer	$R_i(x) + P_j(y) \rightarrow P_i(x) + R_{j+1}(y)$	$y\xi$

I: initiator,  $R_1(0)$ : primary radical, M: monomer,  $R_i(x)$ : radical of chain length x with i branches,  $P_i(x)$ : polymer of chain length x with i branches.

$$\Phi = \Phi_0 \exp(-E_\Phi/RT)$$

	$\alpha$	$\beta$	$\gamma$	$\varepsilon$	$\xi$
$\Phi_0$	$1.6 \times 10^{16}$	$2.95 \times 10^7$	$1.60 \times 10^9$	$2.72 \times 10^{11}$	$9.0 \times 10^5$
$E_\Phi$	38400	7091	2400	20000	9000

$\Phi_0$ : frequency factor, [l/mol·sec] for  $\beta, \gamma, \xi$ , [1/sec] for  $\alpha, \varepsilon$

$E_\Phi$ : activation energy, [cal/mol]

Chen, C. H., Vermeychuk, J. G., Howell, J. A., and Ehrlich, P., *AIChE Journal*, **22**, 463 (1976).

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**Bulk polymerization**

Initiator: di-tert-butyl peroxide (DTBP)

Temperature: 130–165°C

Pressure: up to 3 kbar

$$r_i = k_i C_{DTBP}$$

$$r_p = k_p C_{Radical} C_{Ethylene}$$

$$r_t = k_t C_{Radical}^2$$

$$-dC_{DTBP}/dt = k_d(P, T) \cdot C_{DTBP}$$

$$\begin{aligned}dC_{\text{Ethylene}}/dt &= r_0 = k_p k_t^{-1/2} k_i^{1/2} C_{\text{Ethylene}} C_{\text{DTBP}}^{1/2} \\ r_p &= r_0 \text{ (approximation)} \\ k_0 &= k_p k_t^{-1/2} k_i^{1/2}\end{aligned}$$

$$k_d(P, T) = 1.41 \times 10^{15} \exp\{(-18226 - 0.121 \cdot P)/T\}, \text{ [1/sec]}$$

$$k_0(P, T) = 5.85 \times 10^{11} \exp\{(-12898 + 0.120(P - 1000))/T\}, \text{ [l}^{1/2}/\text{mol}^{1/2} \cdot \text{sec]}$$

$$r_0(P, T) = 5.85 \times 10^{11} \exp\{(-12898 + 0.120(P - 1000))/T\} C_{\text{Ethylene}} C_{\text{DTBP}}^{1/2}, \text{ [mol/l} \cdot \text{sec]}$$

$$k_p/k_t^{1/2} = 11.02 \times 10^3 \exp\{(-3724 + 0.272(P - 1000))/T\}, \text{ [l}^{1/2}/\text{mol}^{1/2} \cdot \text{sec}^{1/2}]$$

$$E_0 = E_p - E_t/2 + E_i/2,$$

$$E_0 = 107.2 \pm 7.5, \quad E_p - E_t/2 = 31 \pm 8$$

$$\Delta V_0 = \Delta V_p - \Delta V_t/2 + \Delta V_i/2$$

$$\Delta V_0 = -17.5 \pm 5.0, \quad \Delta V_p - \Delta V_t/2 = -22.6 \pm 6$$

$r_i$ : initiation rate, [mol/l·sec]

$r_p$ : propagation rate, [mol/l·sec]

$r_t$ : termination rate, [mol/l·sec]

$r_0$ : overall polymerization rate, [mol/l·sec]

$k_d$ : decomposition rate constant of DTBP, [1/sec]

$k_i$ : initiation rate constant, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_0$ : overall polymerization rate constant, [l/mol·sec]

$C_{\text{DTBP}}$ : concentration of initiator, [mol/l]

$C_{\text{Radical}}$ : concentration of total polymer radicals, [mol/l]

$C_{\text{Ethylene}}$ : concentration of monomer, [mol/l]

P: pressure, [bar]

T: temperature, [°K]

$E_t$ : activation energy for termination, [kJ/mol]

$E_p$ : activation energy for propagation, [kJ/mol]

$E_0$ : overall activation energy, [kJ/mol]

$\Delta V_t$ : volume change for termination, [cm<sup>3</sup>/mol]

$\Delta V_p$ : volume change for propagation, [cm<sup>3</sup>/mol]

$\Delta V_0$ : overall volume change, [cm<sup>3</sup>/mol]

**Bulk polymerization**

Initiator: tert-butyl perneodecanoate

Temperature: 449–569°C

Pressure: 1700 bar

Decomposition of initiator	$I \rightarrow 2R^*$	$k_d$
Initiation	$R^* + A \rightarrow R_1 \cdot$	$k_s$
Chain propagation	$R_j + A \rightarrow R_{j+1}$	$k_p$
Chain termination by disproportionation	$R_j + R_k \rightarrow P_j + P_k$	$k_{t1}$
Chain termination by combination	$R_j + R_k \rightarrow P_{j+k}$	$k_{t2}$
Chain transfer to monomer	$R_j + A \rightarrow P_j + R_1$	$k_{tr1}$
Chain transfer to a modifier X	$R_j + X \rightarrow P_j + R_1$	$k_{tr2}$
Chain transfer to a polymer molecule $P_j$	$R_k + P_j \rightarrow P_k + R_j$	$k_{tr3(j)}$
Intramolecular chain transfer	$R_j \rightarrow R_j$	$k_{tr4}$

$$k_{tr3(j)} = k_{tr3(j=1)}(a+b)$$

I: initiator,  $R^*$ : primary radical, A: monomer,  $R_j$ : growing polymer radical with j units,  $P_j$ : dead polymer with j units.

**Kinetic constants**

Rate constant	$k_0$	E [kJ/mol]
$k_d$	$7.0 \times 10^{12}$	121.4
$k_p$	$4.8 \times 10^4$	37.0
$k_{t1}$	$9.7 \times 10^5$	3.0
$k_{t2}$	$9.7 \times 10^5$	3.0
$k_{tr1}$	–	–
$k_{tr3}$	$1.7 \times 10^3$	19.5
$k_{tr4}$	$4.6 \times 10^3$	27.5

$$\Phi = a/b = 1200$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_s$ : initiation rate constant, [l/mol·sec]

$k_{t1}$ : chain termination rate constant by disproportionation, [l/mol·sec]

$k_{t2}$ : chain termination rate constant by combination, [l/mol·sec]

$k_{tr1}$ : chain transfer rate constant to monomer, [l/mol·sec]

$k_{tr2}$ : chain transfer rate constant to a modifier, [l/mol·sec]

$k_{tr3}(j)$ : chain transfer rate constant to a polymer molecule with  $j$  units, [l/mol·sec]

$k_{tr4}$ : intramolecular chain transfer, [1/sec]

$a, b$ : constants to describe the dependency of rate constant on degree of polymerization

Feucht, P., Tilger, B., and Luft, G., *Chem. Eng. Sci.*, **40**, 1935 (1985).

### Bulk polymerization

Initiator: oxygen and peroxide

Initiation	$I_n \rightarrow 2R_1$	$K_i$
Propagation	$R_1 + M \rightarrow R_2$	$K_p$
	$R_i + M \rightarrow R_{i+1}$	
Monomer transfer	$R_i + M \rightarrow P_i + R_1$	$K_{fin}$
Solvent transfer	$R_i + S_n \rightarrow P_i + R_1$	$K_{fsn}$
Long chain branching termination		
combination	$R_i + R_j \rightarrow R_{i+j}$	$K_{tc}$
disproportionation	$R_i + R_j \rightarrow P_i + P_j$	$K_{td}$
Short chain branching	$R-(CH_2)_5 \rightarrow R-CH-C_4H_9$	$K_{SCB}$

$I_n$ : initiator,  $S_n$ : solvent,  $R_i$ : radical of chain length  $i$ ,  $M$ : monomer,  $P_i$ : polymer of chain length  $i$ .

$$K = k_0 \exp\{-(E_a/1.987 + V_a P/82.06)/T\}$$

## Polymerization rate constants

	Frequency factor	Activation energy [cal/mol]	Activation volume [ml/mol]
Propagation	$5.8 \times 10^7$ [l/mol·sec]	7769	-21.3
Termination by combination	$2.8 \times 10^8$ [l/mol·sec]	298	1.0
Termination by disproportionation	$1.3 \times 10^8$ [l/mol·sec]	0	0
Chain transfer to monomer	- [l/mol·sec]	-	-
Chain transfer to polymer	$7.5 \times 10^6$ [l/mol·sec]	8942	1.6
Short chain branching	$1.3 \times 10^9$ [1/sec]	9935	0

$k_0$ : frequency factor, [-]

$E_a$ : activation energy, [cal/mol]

$V_a$ : activation volume, [ml/mol]

P: pressure, [atm]

T: temperature, [°K]

$K_i$ : initiation rate constant, [1/sec]

$K_p$ : propagation rate constant, [l/mol·sec]

$K_{fm}$ : monomer transfer rate constant, [l/mol·sec]

$K_{fsn}$ : solvent transfer rate constant, [l/mol·sec]

$K_{tc}$ : termination rate constant by combination, [l/mol·sec]

$K_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$K_{SCB}$ : short chain branching rate constant, [1/sec]

Shirodkar, P. P. and Tsien, G. O., *Chem. Eng. Sci.*, **41**, 1031 (1986).

**Bulk polymerization**

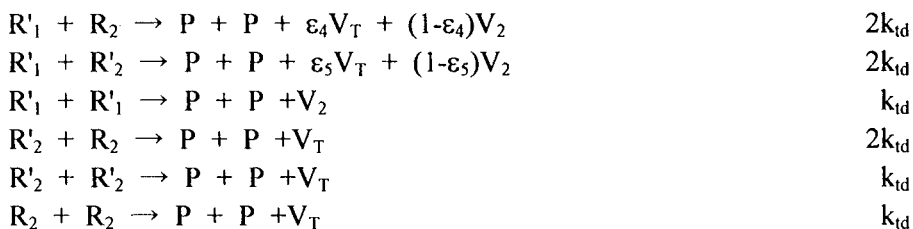
Initiator: di-(2-ethylhexyl)peroxidicarbonate, tert-butyl perneodecanoate, tert-butyl perpivalate, tert-butyl per 2-ethylhexanoate, tert-butyl perbenzoate, and di-tert-butyl peroxide

Temperature: 180–280°C

Pressure: 1300–1950 bar



Decomposition of initiator	$A \rightarrow 2R_1$	$f, k_d$
Linear propagation	$R_1 + M \rightarrow R_1$	$k_p$
	$R'_1 + M \rightarrow R_1$	$k_p$
Transfer to polymer	$R_1 + SC \rightarrow P + R_2$	$k_{tp}$
	$R'_1 + SC \rightarrow P + R_2$	$k_{tp}$
Creation of a long branching point	$R'_2 + M \rightarrow R_1 + LB$	$k_{tp}$
Creation of a secondary short-branched radical by intramolecular transfer (back-biting)	$R_1 \rightarrow R'_2$	$k_{tri}$
Creation of a primary short-branched radical and of a short branching point	$R'_2 + M \rightarrow R'_1 + SB$	$k_p$
$\beta_2$ -scission of secondary radicals and creation of a vinyl double bond	$R_2 \rightarrow R_1 + V_1 + P$	$k_{\beta_2}$
	$R'_2 \rightarrow R_1 + V_1 + P$	$k_{\beta_2}$
$\beta_3$ -scission of a short-branched primary radical and creation of a vinylidene double bond	$R'_1 \rightarrow R_1 + V_2 + P$	$k_{\beta_3}$
Transfer to a tertiary site carried by initiator	$R_1 \text{ or } R'_1 + TA \rightarrow R_1 + P$	$k_{ta}$
Transfer to solvent	$R_1 \text{ or } R'_1 + TS \rightarrow R_1 + P$	$k_{ts}$
Transfer to a transfer agent	$R_1 \text{ or } R'_1 + TAT \rightarrow R_1 + P$	$k_{at}$
Termination by disproportionation of two radicals and creation of a terminal vinyl double bond ( $V_1$ ), a vinylidene double bond ( $V_2$ ) or a trans-vinyl double bond ( $V_T$ )		
	$R_1 \text{ or } R'_1 + Ti \rightarrow R_1 + P$	$k_{ti}$
	$R_1 + R_1 \rightarrow P + P + V_1$	$k_{td}$
	$R_1 + R_2 \rightarrow P + P + \varepsilon_1 V_1 + (1-\varepsilon_1)V_T$	$2k_{td}$
	$R_1 + R'_2 \rightarrow P + P + \varepsilon_2 V_1 + (1-\varepsilon_2)V_T$	$2k_{td}$
	$R'_1 + R_1 \rightarrow P + P + \varepsilon_3 V_1 + (1-\varepsilon_3)V_2$	$2k_{td}$



P: dead macromolecules of any size, M: monomer, A: initiator,  
 R:  $R=R_1+R'_1+R_2+R'_2$  free radical of any size, SB: short branching points,  
 LB: long branching points, SC: secondary carbons,  $V_1$ : vinyl double bonds,  
 $V_2$ : vinylidene double bonds,  $V_T$ : trans-vinyl double bonds.

	$k^0$ [l/mol·sec] or [1/sec]	E [kJ/mol]	$\Delta V$ [ml/mol]
$k_{tp}$	$1.086 \times 10^4$	31.88	49.9
$k_{tri}$	$1.539 \times 10^9$	44.58	5.74
$k_{\beta_2}$	$1.149 \times 10^7$	40.44	-97.2
$k_{\beta_3}$	$5.453 \times 10^{11}$	49.40	179.0
$k_{td}$	$5.719 \times 10^5$	5.083	-14.7
$k_{ta}$	$5.978 \times 10^5$	64.16	-10.0
$k_{tat1}$	$1.247 \times 10^5$	48.83	2.21
$k_{tat2}$	$2.471 \times 10^5$	40.70	46.1
$k_{ts}$	$7.978 \times 10^6$	50.70	7.95

$$k = k^0 \exp\{-(E + P\Delta V)/RT\}$$

E,  $\Delta V$ : activation parameters

$\varepsilon$ : probability for the creation of a vinyl double bond (vs. a trans-vinyl double bond) by disproportionation.

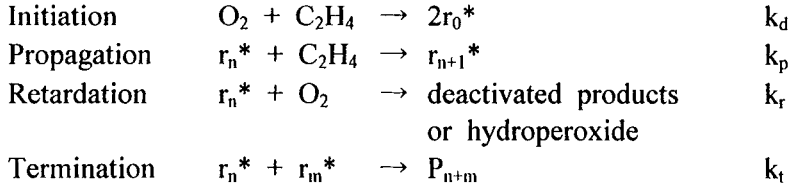
Pons, M., Blavier L., Greffe, J-L., and Villermaux, J., World Congress III of Chem. Eng., Tokyo, p108, 1986.

**Oxygen-initiated bulk polymerization**

Initiator: oxygen and di-tert-butyl peroxide

Temperature: 60–250°C

Pressure: up to 2220 kbar



$r_n^*$ : polymer radical with n units of monomer,  $P_n$ : dead polymer with n units of monomer.

Rate equations

$$d[O_2]/dt = -k_d[O_2][C_2H_4] - k_r[O_2] \sum_{n=0}^{\infty} [r_n^*]$$

$$d[C_2H_4]/dt = -k_p[C_2H_4] \sum_{n=0}^{\infty} [r_n^*]$$

$$d \sum_{n=0}^{\infty} [r_n^*]/dt = k_d[O_2][C_2H_4] - k_r[O_2] \sum_{n=0}^{\infty} [r_n^*] - k_t \left( \sum_{n=0}^{\infty} [r_n^*] \right)^2$$

$$d[O_2]/dt = -k_d[O_2][C_2H_4] - k_r k_d^{1/2} [O_2]^{3/2} [C_2H_4]^{1/2} / k_t^{1/2}$$

$$R_p = -d[C_2H_4]/dt = -k_p k_r [C_2H_4][O_2] / 2k_t + k_p k_d^{1/2} [C_2H_4][O_2]^{1/2} / k_t^{1/2}$$

$$k_d = 3.395 \times 10^{10} \exp(-30000 \text{ cal/RT}), [l/mol \cdot \text{sec}]$$

$$k_r = 3.299 \times 10^9 \exp(-8000 \text{ cal/RT}), [l/mol \cdot \text{sec}]$$

$$f^{1/2} k_p / k_t^{1/2} = 1.23, [l^{1/2}/mol^{1/2} \cdot \text{sec}^{1/2}]$$

$$f = 1$$

$$\Delta E_t = 1000 \text{ [cal/mol]}$$

$$\Delta V_t = 0$$

$k_d$ : initiation rate constant, [l/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_r$ : retardation rate constant by  $O_2$ , [l/mol·sec]

$k_t$ : termination rate constant by combination, [l/mol·sec]

[i]: concentration of species i, [mol/l]

$\Delta E_t$ : activation energy for termination, [cal/mol]

$\Delta V_t$ : volume change for termination, [l/mol]

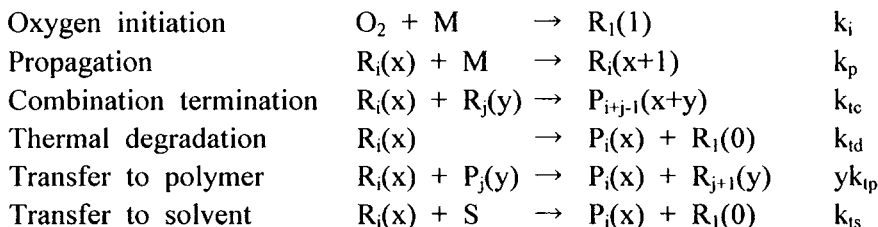
Tatsukami, Y., Takahashi, T., and Yoshioka, H., *Makromol. Chem.*, **181**, 1107 (1980)

### Oxygen-initiated bulk polymerization

Initiator: oxygen

Temperature: 60–320°C

Pressure: 1900–2500 kg/cm<sup>2</sup>



M: monomer,  $R_i(x)$ : radical containing i branches and x total monomer units in its structure,  $P_i(x)$ : dead polymer containing i branches and x total monomer units in its structure, S: solvent.

#### Kinetic constants

Kinetic constant	Frequency factor	Activation energy [cal/mol]
$k_i$	$3.0 \times 10^{10}$ [l <sup>1.1</sup> /mol <sup>1.1</sup> ·sec]	27941
$k_p$	$1.0 \times 10^6$ [l/mol·sec]	5245
$k_{tc}$	$3.0 \times 10^6$ [l/mol·sec]	3950
$k_{td}$	$7.3 \times 10^6$ [1/sec]	11315
$k_{ts}$	$1.7 \times 10^6$ [l/g·sec]	9443
$k_{tp}$	$4.4 \times 10^6$ [l/mol·sec]	9500

$k_i$ : oxygen initiation rate constant, [ $l^{1.1}/mol^{1.1}\cdot sec$ ]

$k_p$ : propagation rate constant, [ $l/mol\cdot sec$ ]

$k_{tc}$ : combination termination rate constant, [ $l/mol\cdot sec$ ]

$k_{td}$ : thermal degradation rate constant, [ $l/sec$ ]

$k_{tp}$ : transfer rate constant to polymer, [ $l/g\cdot sec$ ]

$k_{ts}$ : transfer rate constant to solvent, [ $l/mol\cdot sec$ ]

Brandolin, A., Capiati, N. J., Farber, J. N., and Valles, E. M., *Ind. Eng. Chem. Res.*, **27**, 784 (1988). © 1988 American Chemical Society.

### Photo-induced bulk polymerization

Photo source: high-intensity mercury-xenon arc lamp

Initiator: 1-(tert-butylazo)-1-phenoxy-cyclohexane

Temperature: 130°C

Pressure: 1800 kg/cm<sup>2</sup>

$$k_t = 2.0 \times 10^8$$

$$k_p = 5.4 \times 10^3$$

$k_t$ : termination rate constant, [ $l/mol\cdot sec$ ]

$k_p$ : propagation rate constant, [ $l/mol\cdot sec$ ]

Takahashi, T. and Ehrlich, P., *Macromolecules*, **15**, 714 (1982).  
© 1982 American Chemical Society.

### Photo-induced bulk polymerization

Initiator: diphenyl disulfide

Temperature: 132°C

Pressure: 500–1750 bar

## Rate constant

Pressure [bar]	$k_p$ [ml/mol·sec]	$k_t$ [ml/mol·sec]
500	1.2	17.3
750	1.5	8.8
1000	1.8	5.8
1250	2.2	5.0
1500	2.6	4.8
1750	2.9	4.4

$k_p$ : propagation rate constant, [ml/mol·sec]

$k_t$ : termination rate constant, [ml/mol·sec]

Luft, G., Lim, P.-C., and Yokawa, M., *Makromol. Chem.*, **184**, 207 (1983).

**Photo-induced bulk polymerization**

Initiator: diphenyl disulfide

Temperature: 400–470°C

Pressure: 500–1750 bar

## Rate constant

Rate constant	Activation energy [kJ/mol]	$\Delta v^\ddagger$ [ml/mol]
$k_p$	37	-25.5
$k_t$	9.9	7

$k_p$ : propagation rate constant

$k_t$ : termination rate constant

$\Delta v^\ddagger$ : activation volume, [ml/mol]

Lim, P.-C. and Luft, G., *Makromol. Chem.*, **184**, 849 (1983).

**Photo-induced polymerization**

Photo source: laser

Temperature: 463°C

$$k_p=1.09 \times 10^4$$

$$k_t=1.99 \times 10^8$$

Quantum yield for the production of primary radical species:  $\Phi_s=1$  $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Buback, M., Hippler, H., Schweer, J., and Voge, H.-P., *Makromol. Chem., Rapid Commun.*, 7, 261 (1986).**Photo-induced bulk polymerization**

Photo source: laser

Temperature: 190–230°C

Pressure: up to 3200 bar

$$k_p (220^\circ\text{C}, \text{overall density}=0.54 \text{ g/cm}^3)=30000$$

$$E_p=36 \pm 4$$

 $k_p$ : propagation rate constant, [l/mol·sec] $E_p$ : activation energy for propagation reaction, [kJ/mol]Brackemann, H., Buback, M., and Voge, H.-P., *Makromol. Chem.*, 187, 1977 (1986).

**Solution polymerization**

Solvent: benzene

Initiator: azoisopropane

Temperature: 83°C

Type of reaction	Reaction rate
Termination by disproportionation	$k_{3d}R_2$
Termination by combination	$k_{3c}R_2$
Monoradical termination	$k_5XR$
Transfer with monomer	$k_4MR$
Transfer with solvent	$k_5SR$
Transfer with initiator	$k_KKR$
Initiation	$(k_{3d}+k_{3c})R_2+k_5XR$

Transfer constants:

$$k_4/k_2 \leq 5 \times 10^{-4}, \quad k_5/k_2 \leq 2 \times 10^{-3}, \quad k_K/k_2 = 0.5 \pm 0.1$$

M: concentration of monomer, [mol/l]

S: concentration of solvent, [mol/l]

K: concentration of initiator, [mol/l]

X: concentration of retarder, [mol/l]

R: concentration of growing polymer radical, [mol/l]

 $k_2$ : propagation rate constant, [l/mol·sec] $k_{3c}$ : combination termination rate constant, [l/mol·sec] $k_{3d}$ : disproportionation termination rate constant, [l/mol·sec] $k_5$ : monoradical termination rate constant, [l/mol·sec] $k_4$ : transfer constant with monomer, [l/mol·sec] $k_5$ : transfer constant with solvent, [l/mol·sec] $k_K$ : transfer constant with initiator, [l/mol·sec]

Laita, A., *J. Polym. Sci.*, **38**, 247 (1959). Copyright © 1959 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.



**Solution polymerization**

Solvent: benzene

Initiator: azoisopropane

Temperature: 83°C

## Kinetic constants

Reaction	Value [l/mol·sec]
Propagation $k_2$	$(4.7 \pm 0.3) \times 10^2$
Mutual termination $k_3$	$(1.05 \pm 0.05) \times 10^2$
Monoradical termination $k_5$	$1.85 \times 10^2$
Transfer with monomer $k_4$	0.25
Transfer with benzene $k_s$	1.0

Laita, A. and Machacek, Z., *J. Polym. Sci.*, **38**, 459 (1959).

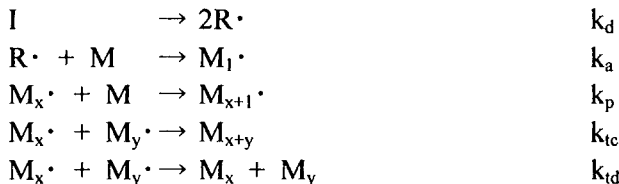
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**Solution polymerization**

Solvent: tert-butylalcohol

Initiator: diethyl peroxy dicarbonate (DEPC)

Temperature: 45–60 °C



I: initiator, M: monomer, R·: primary radical, M<sub>x</sub>·, M<sub>y</sub>·: growing polymer radical with x and y units, respectively, M<sub>x</sub>, M<sub>y</sub>: dead polymer with x and y units, respectively.

$$-d[\text{I}]/dt = k_d[\text{I}]$$

$$k_d = A \exp(-\Delta E_d/RT)$$

$$\log\{[M_0]/([M_0]-[P])\}/[I_0]^{1/2}=B\{1-\exp(-k_d^{1/2})\}$$

$$B=0.869(f/k_d)^{1/2}(k_p/k_t^{1/2})$$

Concentration of DEPC [mol/l]	Temperature [°C]	$k_d \times 10^5$ [1/sec]	A [1/sec]	$\Delta E_d$ [kcal/mol]
1.1	45	1.25		
1.1	55	5.7	$5 \times 10^{17}$	33
1.1	60	13.0		
2.25	45	1.47		
2.25	55	6.2	$1.2 \times 10^{17}$	32
2.25	60	13.6		

$k_d=0.000128$  [1/sec] (for half life of 1.5 hr at 60°C)

$B=1.40$ ,  $f=1$

$k_p^2/k_t=0.00033$  [l/mol·sec]

[M]: concentration of monomer, [mol/l]

[ $M_0$ ]: concentration of monomer at time 0, [mol/l]

[I]: concentration of initiator, [mol/l]

[ $I_0$ ]: concentration of initiator at time 0, [mol/l]

[P]: concentration of polymer, [mol/l]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_a$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$\Delta E_d$ : activation energy of decomposition rate constant of initiator, [kcal/mol]

f: initiator efficiency, [-]

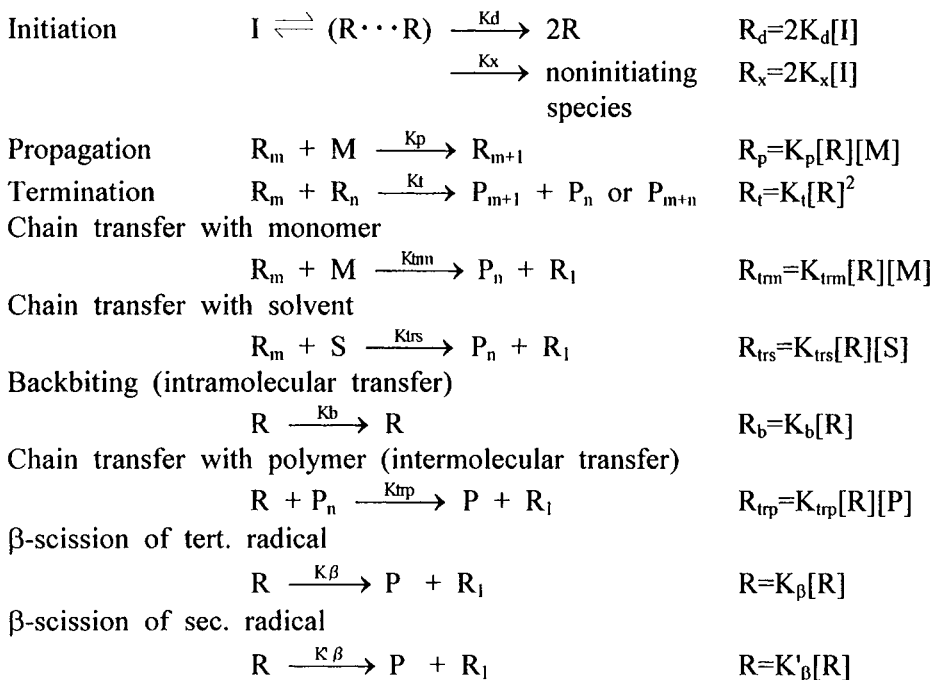
Friedlander, H. N., *J. Polym. Sci.*, **58**, 455 (1962). Copyright © 1962 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Solution polymerization**

Solvent: hydrocarbons, alcohols, and ketones

Initiator: various initiators shown in table

Temperature: 150–300°C

Pressure: 1800–3000 kg/cm<sup>2</sup>

I: initiator, R: primary radical, M: monomer, R<sub>m</sub>: growing polymer radical with m units of monomer, P<sub>m</sub>: dead polymer with m units of monomer, P: total dead polymer with any size.

## Rate constants of initiation

	$K_d$			$K_x$		
	A	$E_a$	$\Delta V^\ddagger$	A	$E_a$	$\Delta V^\ddagger$
TBPV	$5.88 \times 10^{17}$	28300	2.5	$5.99 \times 10^{28}$	51100	0
TBIB	$3.77 \times 10^{18}$	31500	2.5	$1.86 \times 10^{32}$	61500	0
TBPC	$5.12 \times 10^{18}$	33700	2.5	$7.29 \times 10^{30}$	61900	0
DTBP	$2.39 \times 10^{19}$	37300	2.5	$7.36 \times 10^{31}$	68000	0
DCP	$4.03 \times 10^{21}$	40600	2.5	$5.09 \times 10^{33}$	69000	0

TBPV: tert-butyl peroxyvalate, TBIB: tert-butyl perisobutylate,  
 TBPC: tert-butylperisopropylcarbonate, DTBP: di-tert-butyl peroxide,  
 DCP: dicumyl peroxide.

$$K = A \exp(-E_a/RT - P\Delta V^\ddagger/RT)$$

## Rate constants of elementary reactions

	A	$E_a$	$\Delta V^\ddagger$
Propagation $K_p$	$5.63 \times 10^{11}$	10.520	-19.7
Termination $K_t$	$3.00 \times 10^{11}$	3.000	13.0
Chain transfer with solvent (n-hexane) $K_{tm}$	$1.23 \times 10^{11}$	12.820	-19.5
Chain transfer with polymer $K_{tp}$	$1.75 \times 10^{12}$	14.080	4.4
Back biting (overall) $K_b$	$5.63 \times 10^{12}$	13.030	-23.5
$\beta$ -Scission of tert. radical $K_\beta$	$5.82 \times 10^{11}$	15.760	-22.6
$\beta$ -Scission of sec. radical $K'_\beta$	$8.51 \times 10^{11}$	14.530	-19.7

[R]: concentration of total growing radical with ant size

[M]: concentration of monomer

[S]: concentration of solvent

[P]: concentration of total dead polymer of any size

A: frequency factor, [-]

$E_a$ : activation energy, [cal/mol]

$\Delta V^\ddagger$ : activation volume, [cm<sup>3</sup>/mol]

P: pressure, [kg/cm<sup>2</sup>]

Goto, S., Yamamoto, K., Furui, S., and Sugimoto, M., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **36**, 21 (1981).

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## 1.4 Isoprene

### Emulsion polymerization

Ingredients: water, soap, potassium chloride

Emulsifier: soap

Initiator: tetraethylenepentamine (TEPA) and di-isopropylbenzene monohydroperoxide (DIBHP)

Temperature: 5°C and 15°C

Initiator	Temperature [°C]	$k_p$ [l/mol·sec]	Temperature [°C]	Activation energy [kcal/mol]
DIBHP-TEPA	5	2.8	5-15	9.3
			5-15	10.3

$$k_p = 1.2 \times 10^8 \exp(-9800 \text{ cal/RT})$$

$k_p$ : propagation rate constant, [l/mol·sec]

Morton, M., Salatiello, P. P., and Landfield, H., *J. Polym. Sci.*, **8**, 279 (1952).  
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## 1.5 Methyl methacrylate

### Bulk polymerization

Initiator: 2-azobisisobutyronitrile (Azo), benzoyl peroxide ( $Bz_2O_2$ ),  
tert-butyl hydroperoxide (t-BHP) and cumene hydroperoxide (CHP)

Temperature: 60°C

$$1/P_n = c_m + c_i[\text{cat}]/[M] + c_s[S]/[M] + AR_p$$

$$A = (2k_{td} + k_{tc})/k_p^2 [M]^2$$

$$R_p = k_p [c^*][M]$$

$$c_m = k_{trm}/k_p, \quad c_i = k_{tri}/k_p, \quad c_s = k_{trs}/k_p$$

$$R_p^2 = B_I [\text{cat}]$$

$$1/P_n = c_m + c_i R_p^2 / B_I [M] + c_s [S]/[M] + AR_p$$

$$R_i = 2(k_{tc} + k_{td})R_p^2 / k_p^2 [M]^2 = 2AR_p^2 / (1+x)$$

$$x = k_{td} / (k_{td} + k_{tc})$$

$$A = 0.828, \quad c_m = \sim 1.0 \times 10^{-5}$$

Catalyst	$B_I$	$C_i$	$AB_I$	$k_d$	$f(1+x)$
$Bz_2O_2$	$4.00 \times 10^{-6}$	$\sim 0$	$3.31 \times 10^{-6}$	$0.36 \times 10^{-5}$	0.91
Azo	$8.59 \times 10^{-6}$	$\sim 0$	$7.10 \times 10^{-6}$	$9.15 \times 10^{-6}$	0.77
CHP	$2.37 \times 10^{-7}$	0.33	$1.96 \times 10^{-7}$	$7.6 \times 10^{-6}$	0.93
t-BHP	$4.41 \times 10^{-8}$	1.27[cat]	$3.65 \times 10^{-8}$		

[M]: monomer concentration, [mol/l]

[cat]: initiator concentration, [mol/l]

[c\*]: total polymer radical concentration, [mol/l]

[S]: solvent concentration, [mol/l]

$R_i$ : initiation rate, [mol/l·sec]

$R_p$ : propagation rate, [mol/l·sec]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{trm}$ : transfer rate constant to monomer, [l/mol·sec]

$k_{trf}$ : transfer rate constant to catalyst, [l/mol·sec]

$k_{trf_s}$ : transfer rate constant to solvent, [l/mol·sec]

$P_n$ : number-average degree of polymerization, [-]

$f$ : catalyst efficiency, defined as the rate of initiation of polymer chains divided by twice the rate of spontaneous decomposition of catalyst, [-]

Baysal, B. and Tobolsky, A. V., *J. Polym. Sci.*, **8**, 529 (1952).

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### Bulk polymerization

Initiator: 2,2'-azobisisobutyronitrile (AIBN) and dicumyl peroxide (DCP)

Temperature: 30–100 °C

$$\begin{aligned} R_i &= 2k_d f [I] \\ R_p &= k_p [C^*] [M_{av}] \\ R_i &= 2(k_{tc} + k_{td}) [C^*]^2 \\ f' &= f(1+x) \\ x &= k_{td} / (k_{td} + k_{tc}) \\ A' &= (2k_{td} + k_{tc}) / k_p^2 \end{aligned}$$

(1) AIBN, temperature: 30–85 °C

$$k_d f' = 1.26 \times 10^{15} \exp(-30.8 \text{ kcal/RT})$$

$$k_d = 1.58 \times 10^{15} \exp(-30.8 \text{ kcal/RT})$$

$$f' = 0.80$$

$$A' = 3.00 \times 10^{-4} \exp(8.18 \text{ kcal/RT})$$

Temperature [°C]	$k_d f'$ [1/sec]
30.5	$8.82 \times 10^{-8}$
37.0	$2.56 \times 10^{-7}$
45.5	$9.19 \times 10^{-7}$
50.0	$1.83 \times 10^{-6}$
55.0	$4.19 \times 10^{-6}$
67.2	$2.33 \times 10^{-5}$



(2) DCP, temperature: 60–100°C

$$k_{df}' = 1.26 \times 10^6 \exp(-36.4 \text{ kcal/RT})$$

Temperature [°C]	$k_{df}'$ [1/sec]
60.0	$1.68 \times 10^{-8}$
72.0	$1.00 \times 10^{-7}$
84.3	$1.27 \times 10^{-7}$

$R_i$ : initiation rate, [mol/l·sec]

$R_p$ : propagation rate, [mol/l·sec]

$R_t$ : termination rate, [mol/l·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

[I]: concentration of initiator, [mol/l]

$[M_{av}]$ : average monomer concentration, [mol/l]

$[C^*]$ : radical concentration, [mol/l]

$f'$ : initiator efficiency, [-]

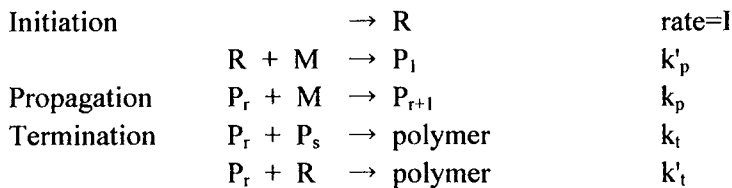
Van Hook, J. P. and Tobolsky, A. V., *J. Polym. Sci.*, **33**, 429 (1958).

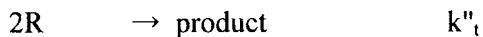
Copyright © 1958 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Bulk polymerization

Initiator: azobis(isobutyronitrile)

Temperature: 60°C





R: primary radical, M: monomer, P<sub>r</sub>: growing polymer radical with x units.

$k_p$ [l/mol·sec]	$k'_p$ [l/mol·sec]	$2k_t \times 10^{-7}$ [l/mol·sec]
700	280	3.6

$$k_2 = 5.55 \times 10^2, \quad k_3 = 2.68 \times 10^7$$

$k'_p$ : rate constant for initiation by primary radical, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k'_t$ : rate constant termination with primary radical, [l/mol·sec]

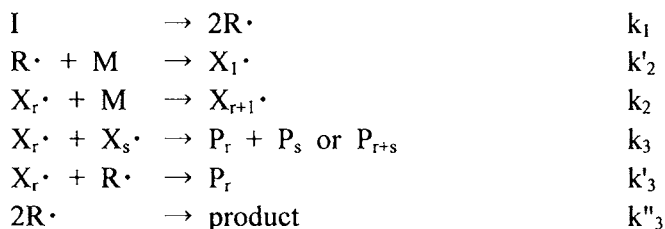
$k''_t$ : rate constant of reaction between primary radicals, [l/mol·sec]

Allen, P. E. and Patrick C. R., *Makromol. Chem.*, **48**, 89 (1961).

### Bulk polymerization

Initiator: 3,3,4,4-tetraphenyl hexane (TPH) and 1,1,2,2-tetraphenyl cyclopentane (TPCP)

Temperature: 60°C



I: initiator, R·: primary radical, X<sub>r</sub>·: growing polymer radical with x units, P<sub>r</sub>: dead polymer with x units.

Initiator	$k_1$ [1/sec]	$k'_3/k'_2$	$k''_3/(k'_2)^2$ [mol·sec/l]
TPH	$2.0 \times 10^{-5}$	$1.5 \times 10^8$	$8.2 \times 10^8$
TPCP	$7.0 \times 10^{-5}$	$2.6 \times 10^8$	$2.6 \times 10^9$

$$k_2 = 5.55 \times 10^2, \quad k_3 = 2.68 \times 10^7$$

$k_1$ : decomposition rate constant of initiator, [1/sec]

$k'_2$ : initiation rate constant, [l/mol·sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : termination rate constant, [l/mol·sec]

$k'_3$ : rate constant termination with primary radical, [l/mol·sec]

$k''_3$ : rate constant of reaction between primary radicals, [l/mol·sec]

Borsig, E., Lazar, M., and Capla, M., *Makromol. Chem.*, **105**, 212 (1967).

### Bulk polymerization

Initiator: 1-methyl-2-(9'-anthryl)-cyclopropyl-carboxylate (ACP) and diphenyldiazomethane (DDM)

Temperature: 60–90°C

Maximum conversion: about 6.0%

$$R_p = k[\text{DDM}]^{0.5}[\text{MMA}]^{1.0} \text{ at } 70^\circ\text{C}$$

$$\text{Overall activation energy} = 13.1 \text{ [kcal/mol]}$$

$$C_m = 2.0 \times 10^{-5}, \quad C_i = 0.0$$

$R_p$ : initial polymerization rate, [mol/l·sec]

$k$ : initial polymerization rate constant, [l<sup>1/2</sup>/mol<sup>1/2</sup>·sec]

[i]: concentration of i, [mol/l]

$C_m$ : chain transfer constant to monomer, [-]

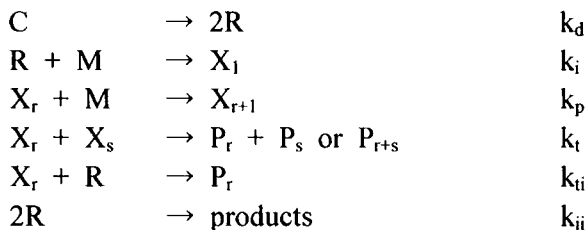
$C_i$ : chain transfer constant to initiator, [-]

Nakaya, T., Ohashi, K., and Imoto, M., *Makromol. Chem.*, **114**, 201 (1968).

**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 60°C



C: initiator, R: primary radical, M: monomer, X<sub>r</sub>: growing polymer radical with r monomer units, P<sub>r</sub>: dead polymer with r monomer units, Y: chain transfer agent.

$$[M][C]^{1/2}/R_p = 1/A + B[C]^{1/2}/A[M]$$

$$A = k_p(2fk_d/k_t)^{1/2}$$

$$B = (k_{ti}/k_i)(2fk_d/k_t)^{1/2}$$

$$A = 3.57 \times 10^{-4}$$

$$B = 1.41 \times 10^{-4}$$

[C]: concentration of initiator, [mol/l]

[M]: concentration of monomer, [mol/l]

k<sub>d</sub>: decomposition rate constant, [1/sec]

k<sub>i</sub>: initiation rate constant, [l/mol·sec]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

k<sub>ti</sub>: primary radical termination rate constant, [l/mol·sec]

k<sub>ii</sub>: rate constant between primary radicals, [l/mol·sec]

R<sub>p</sub>: propagation rate, [mol/l·sec]

Ito, K. and Matsuda, T., *J. Appl. Polym. Sci.*, **14**, 311 (1970).

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**Bulk polymerization**Initiator:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 70–90°C

$$\ln([M_0]/[M]) = k't = k_p(2fk_d/k_t)^{1/2}[I_0]^{1/2}t$$

Initiator concentration:  $5.2 \times 10^{-2}$  [mol/l]

Temperature [°C]	Initial rate constant [1/min]
70	$0.78 \times 10^{-2}$
75	$1.11 \times 10^{-2}$
80	$1.60 \times 10^{-2}$
85	$2.29 \times 10^{-2}$
90	$3.24 \times 10^{-2}$

Overall activation energy=18.4 [kcal/mol]

Temperature: 80°C

Initiator concentration [mol/l]	Initial rate constant $k'$ [1/min]
$2.5 \times 10^{-2}$	$1.13 \times 10^{-2}$
$4.0 \times 10^{-2}$	$1.43 \times 10^{-2}$
$5.2 \times 10^{-2}$	$1.60 \times 10^{-2}$
$6.3 \times 10^{-2}$	$1.85 \times 10^{-2}$
$10.0 \times 10^{-2}$	$2.49 \times 10^{-2}$

[ $I_0$ ], [ $M_0$ ]: initial concentration of initiator and monomer, respectively, [mol/l][ $I$ ], [ $M$ ]: concentration of initiator and monomer, respectively, [mol/l]

f: initiator efficiency, [-]

 $k'$ : overall rate constant, [1/min] $k_p$ : propagation rate constant, [l/mol·min]

$k_d$ : initiator dissociation rate constant, [1/min]

$k_t$ : termination rate constant, [l/mol·min]

Malavasic, T., Vizovisek, I., Lapanje, S., and Moze, A., *Makromol. Chem.*, **175**, 873 (1974).

### Bulk polymerization

Initiator: dibenzoyl peroxide and cyclohexyloxycarbonyl peroxide

Temperature: 45–85°C

$$-d[M]/dt = k_p[M][R\cdot]$$

$$k_t = -d[M]/P[R\cdot]^2 dt$$

$$k_p = 2.5 \times 10^6 \exp(-5400 \pm 600 \text{ cal/RT})$$

$$k_t = 7.2 \times 10^8$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : propagation rate constant, [l/mol·sec]

[M]: concentration of monomer, [mol/l]

[R·]: concentration of macroradicals, [mol/l]

P: degree of polymerization, [-]

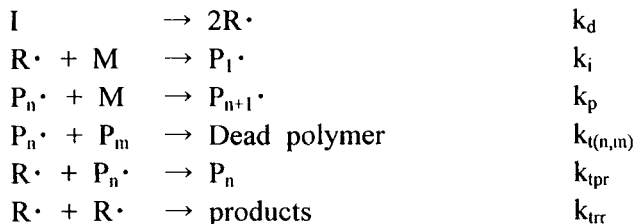
Bresler, S. E., Kazbekov, E. N., and Shadrin, V. N., *Makromol. Chem.*, **175**, 2875 (1974).

### Bulk polymerization

Initiator: 2,2'-azobisisobutyronitrile

Chain transfer agent: 1-butanethiol

Temperature: 50–70°C



I: initiator, M: monomer, R·: primary free radical, P<sub>n</sub>·: growing polymer

radical containing  $r$  units of monomer,  $P_n$ : dead polymer containing  $n$  units of monomer.

$$k_{tpr}/k_p k_i = 7.52 \times 10^{-3} \exp(7791 \text{ cal}/RT)$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tpr}$ : rate constant of termination reaction with primary free radical, [l/mol·sec]

$k_{trr}$ : rate constant of reaction between primary free radicals, [l/mol·sec]

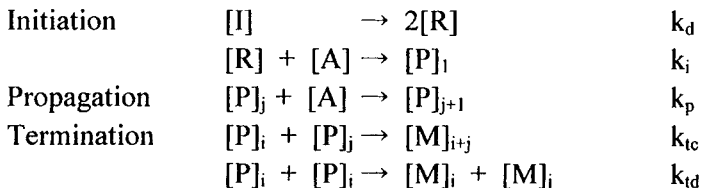
$k_{t(m,n)}$ : termination rate constant, [l/mol·sec]

Mahabadi, H. K. and O 'Driscoll, K. F., *Makromol. Chem.*, **178**, 2629 (1977).

### Bulk polymerization

Initiator: benzoyl peroxide

Temperature: 60°C



[I]: initiator, [R]: primary radical, [A]: monomer,  $[P]_j$ : growing polymer radical containing  $j$  units of monomer,  $[M]_j$ : dead polymer containing  $r$  units of monomer.

$$k_t = k_{tc} + k_{td} = 2.5 \times 10^7$$

$$k_p = 705.6$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

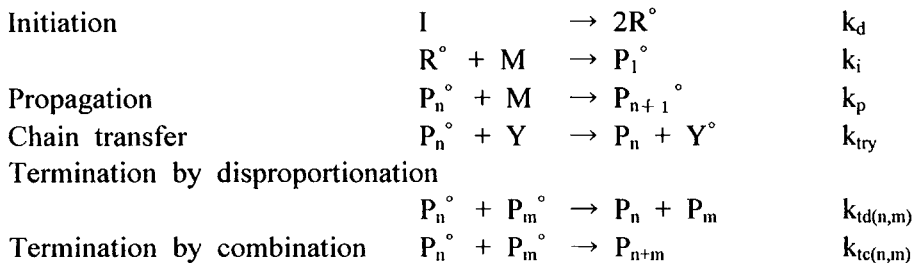
$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

Kuo, J. F. and Chen, C. Y. *Polym. J.*, **13**, 453 (1981).

**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 25°C



I: initiator, M: monomer,  $R^\circ$  : primary free radical,  $P_n^\circ$  : growing polymer radical containing n units of monomer,  $P_n$ : dead polymer containing n units of monomer, Y: chain transfer agent.

$$k_{t(n,m)} = k_{tc(n,m)} + k_{td(n,m)}$$

$$k_{t(n,m)} = k_{tc(n,m)} = 1.22 \times 10^8 (\text{nm})^{-0.075}$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{try}$ : transfer rate constant to Y, [l/mol·sec]

$k_{t(n,m)}$ : termination rate constant, [l/mol·sec]

$k_{tc(n,m)}$ : termination rate constant by combination, [l/mol·sec]

$k_{td(n,m)}$ : termination rate constant by disproportionation, [l/mol·sec]

Mahabadi, H. K., *Macromolecules*, **18**, 1319 (1985).

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**Bulk and solution polymerization**

Solvent: benzene

Initiator:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 50 and 77°C

Temperature [°C]	$k_1$ [1/min]	$k_p/(k_t)^{1/2}$ [(l/mol·min) <sup>1/2</sup> ]
50	$1.2 \times 10^{-4}$	0.67
77	1.09	

 $k_1$ : decomposition rate constant of initiator, [1/min] $k_p$ : propagation rate constant, [l/mol·min] $k_t$ : termination rate constant, [l/mol·min]Arnett, L. M., *J. Am. Chem. Soc.*, **74**, 2027 (1952).

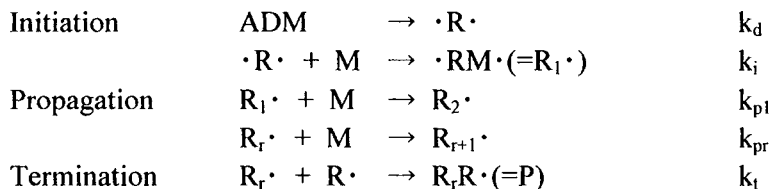
© 1952 American Chemical Society.

**Bulk and solution polymerization**

Solvent: benzene

Initiator: 9-anthryldiazomethane (ADM)

Temperature: 70°C

 $\cdot R \cdot$ : primary radical, M: monomer,  $R_r \cdot$ : polymer radical containing r units.

$$R_p = k[A_{DM}]^{0.05}[MMA]^{1.86}$$

$$k_d = 5.50 \times 10^{12} \exp(-25.2 \text{ kcal/RT}) \text{ for } 34\text{--}60^\circ\text{C}$$

$R_p$ : initial polymerization rate, [mol/l·sec]

[i]: concentration of i, [mol/l]

$k_d$ : decomposition rate constant of ADM, [1/sec]

$k$ : initial polymerization rate constant, [(l/mol)<sup>0.86-0.93</sup>·sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_{pr}$ : propagation rate constant of polymer radical containing r units, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Nakaya, T., Ohashi, K., and Imoto, M., *Makromol. Chem.*, **111**, 115 (1968).

### Bulk and solution polymerization

Solvent: benzene

Initiator: 1-methyl-2-(9'-anthryl)-cyclopropyl-carboxylate (ACPC)  
and  $\alpha,\alpha$ -azobisisobutyronitrile (AIBN)

Temperature: 70°C

Maximum conversion: about 8.0%

For ACPC

$R_p = k[\text{ACPC}]^{0.82}[\text{MMA}]^{1.5}$  for bulk and solution polymerization

$C_M = k_m/k_p = 2.65 \times 10^{-5}$ ,  $C_K = k_K/k_p = 2.0 \times 10^{-3}$  for bulk polymerization

Overall activation energy for initial rate = 18.3 [kcal/mol] for bulk  
polymerization (60–90°C)

$R_p$ : initial polymerization rate, [mol/l·sec]

[i]: concentration of i, [mol/l]

$k$ : initial polymerization rate constant, [l<sup>1.32</sup>/mol<sup>1.32</sup>·sec]

$k_m$ : chain transfer rate constant to monomer, [l/mol·sec]

$k_K$ : chain transfer rate constant to initiator, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

Imoto, M. and Ohashi, K., *Makromol. Chem.*, **117**, 117 (1968).

**Bulk and solution polymerization**

Solvent: benzene

Initiator: p,p'-dimethoxydiphenyldiazomethane (DMDM)

Temperature: 60–90 °C

$$R_p = k[\text{DMDM}]^{0.53}[\text{MMA}]^{0.84}$$

$$1/P_n = Ak_p + C_m + C_i[\text{DMDM}]/[\text{MMA}]$$

$$A = 0.8 \text{ [l}\cdot\text{sec/mol]}, C_m = k_m/k_p = 3.3 \times 10^{-5}, C_i = k_i/k_p = 0.0 \text{ at } 70^\circ\text{C}$$

Overall activation energy = 19.3 [kcal/mol]

 $k_d = 1.0 \times 10^{15} \exp(-29100 \text{ cal/RT})$  for 50–80°C

[i]: concentration of species i, [mol/l]

 $R_p$ : initial rate of polymerization, [mol/l·sec] $P_n$ : number-average degree of polymerization

k: initial rate constant of polymerization, [mol/l·sec]

 $k_d$ : decomposition rate constant of initiator, [1/sec] $k_m$ : chain transfer rate constant to monomer, [l/mol·sec] $k_i$ : chain transfer rate constant to initiator, [l/mol·sec] $k_p$ : propagation rate constant, [l/mol·sec]Nakaya, T., Wada, H., Tanaka, M., and Imoto, M., *J. Macromol. Sci.-Chem.*, **A5**, 1043 (1971).**Emulsion polymerization**

Ingredients: water, polyvinylacetate (PVA), and methylmethacrylate

Initiator: polyvinylacetate

Temperature: 40°C

$$k_p = 140$$

 $k_p$ : rate constant of propagation, [l/mol·sec]Allen, P. E. M., Burnett, G. M., Downer, J. M., and Majer, J. R., *Makromol. Chem.*, **58**, 169 (1962).

**Emulsion polymerization**

Emulsifier: sodium laurylsulfate or + 0.3% of Dowfax 2A1, 46% solution

Initiator: potassium persulfate

Temperature: 40–60°C

$$-d([M]V_p)/dt = k_p[M]/2N_{AV}$$

$$V_p = V_{p\infty}(1-\varepsilon x)/(1-\varepsilon)$$

$$[M]_0(1-x)/(1-\varepsilon x) = [M]$$

$$V_{p\infty}dx/(1-\varepsilon)dt = k_p(1-x)/2N_{AV}(1-\varepsilon x)$$

$$\ln(k_p) = 16.6 - 3500/T$$

$$k_p = 156 \text{ at } 50^\circ\text{C}$$

Temperature [°C]	$k_p$ [l/g·mol·sec]
60	540 <sup>(1)</sup>
50	340 <sup>(2)</sup>
40	171 <sup>(2)</sup>

<sup>(1)</sup> Emulsifier: sodium laurylsulfate.

<sup>(2)</sup> Emulsifier: sodium laurylsulfate + 0.3% of Dowfax 2A1, 46% solution.

[M]: concentration of monomer, [mol/l]

$V_p$ : volume of a latex particle, [cm<sup>3</sup>]

$V_{p\infty}$ : volume of a latex particle at complete conversion, [cm<sup>3</sup>]

$V_{p0}$ : volume of a latex particle at zero conversion, [cm<sup>3</sup>]

$k_p$ : propagation rate constant, [l/mol·sec]

$N_{AV}$ : Avogadro's number, [number/mol]

$\varepsilon$ : volume shrinkage factor  $\varepsilon = (V_{p0} - V_{p\infty})/V_{p0}$ , [-]

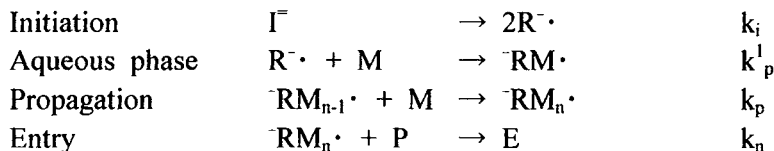
$x$ : fractional conversion, [%]

$k_p$ : propagation rate constant, [l/g·mol·sec]

**Emulsion polymerization**

Initiator: peroxydisulfate anion

Temperature: 50°C



$I^-$ : initiator,  $R^{\cdot}$ : primary radical, M: monomer,  $\overline{RM}_n^{\cdot}$ : polymer radical with n units, P: a latex particle, E: entry into particle.

$$k_i=1.3 \times 10^{-6}, \quad k_p=500, \quad k_t=3 \times 10^7$$

$k_i$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_n$ : entry rate constant of oligomeric free radicals into particles, [l/mol·sec]

Hawkett, B. S., Napper, D. H., and Gilbert, R. G., *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 3173 (1981). Copyright © 1981 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Emulsion polymerization**

Ingredient: methyl methacrylate, water, potassium peroxydisulfate, seed latex, and surfactant

Initiator: potassium peroxydisulfate

Temperature: 50°C

$$\begin{aligned} \ln(k_t) &= 12.1 - 4.94\omega_p & 0.33 \leq \omega_p \leq 0.78 \\ &= 28.9 - 26.6\omega_p & \omega_p > 0.78 \end{aligned}$$

$k_t$ : termination rate constant, [dm<sup>3</sup>/mol·sec]

$\omega_p$ : weight fraction of polymer, [-]

Ballard, M. J., Napper, D. H., and Gilbert, R. G., *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3225 (1984). Copyright © 1984 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Emulsion polymerization**

Ingredient: MMA, DPPH, Aerosol MA 80, seed latex, and water

Initiator: DPPH ( $\alpha, \alpha'$ -diphenyl  $\beta$ -picryl hydrazyl)

Temperature: 50°C

$$k_p = k_p^\circ \quad (0.33 \leq \omega_p \leq 0.84)$$

$$k_p = k_p^\circ \exp\{-29.8(\omega_p - 0.84)\} \quad (0.84 \leq \omega_p \leq 0.99)$$

$$k_p^\circ = 790 \pm 300 \text{ [dm}^3/\text{mol}\cdot\text{sec]}$$

$\omega_p$ : weight fraction of polymer, [-]

$k_p$ : propagation rate constant, [dm<sup>3</sup>/mol·sec]

$k_p^\circ$ : propagation rate constant in the absence of diffusion, [dm<sup>3</sup>/mol·sec]

Ballard, M. J., Gilbert, R. G., Napper, D. H., Pomery, P. J., O'Sullivan, P. W., and O'Donnell, J. H., *Macromolecules*, **19**, 1303 (1986).

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**Photo-induced bulk polymerization**

Temperature: 25°C

$$k_p = 150, \quad k_{tr} = 0.03, \quad k_t = 1.3 \times 10^7$$

$k_p$ : propagation rate constant, [l/mol·sec]

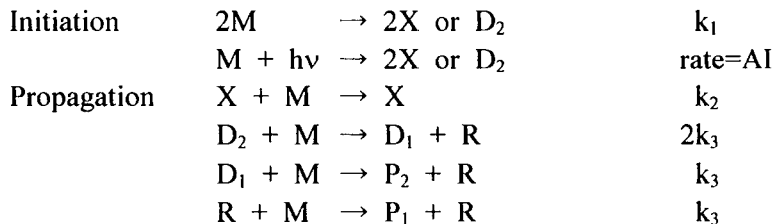
$k_{tr}$ : transfer rate constant, [l/mol·sec]

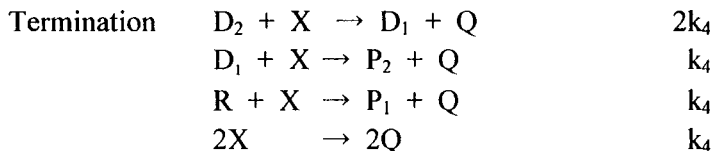
$k_t$ : termination rate constant, [l/mol·sec]

Dewar, M. J. S. and Bamford, C. H., *Nature*, **158**, 380 (1946).

**Photo-induced bulk polymerization**

Temperature: 0°C





M: monomer, X: active center, Q: dead center,  $D_2$ : initial polymer growing at both ends,  $D_1$ : polymer growing at one end, R: growing transfer polymer,  $P_1$ : dead transfer polymer,  $P_2$ : dead initial polymer.

$k_1$ [l/mol·sec]	$k_2$ [l/mol·sec]	$k_3$ [l/mol·sec]	$k_4$ [l/mol·sec]
$6.83 \times 10^{-15}$	41.6	$6.13 \times 10^{-4}$	$2.69 \times 10^6$

$k_1$ : initiation rate constant, [l/mol·sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : transfer rate constant, [l/mol·sec]

$k_4$ : termination rate constant, [l/mol·sec]

AI: rate of initiation, [mol/l·sec]

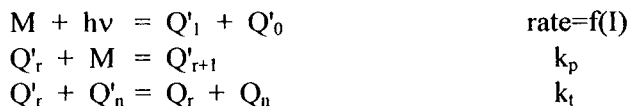
A: constant

I: light intensity

Bamford, C. H. and Dewar, M. J. S., *Faraday Soc. Discussions*, **2**, 310 (1947).

### Photo-induced bulk polymerization

Temperature: 23.6–50.5°C



M: monomer,  $Q'_r$ : an active "half-chain" of length r units,  $Q_r$ : an inactive "half-chain" of length r units.

Temperature [°C]	$k_p \times 10^{-2}$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
23.6	3.1	6.6
35.9	4.05	6.8
50.5	5.8	6.9

$$k_p = 5 \times 10^5 \exp(-4400 \text{ cal/RT})$$

$$k_t = 10^8$$

f(I): rate of initiation, [mol/l·sec]

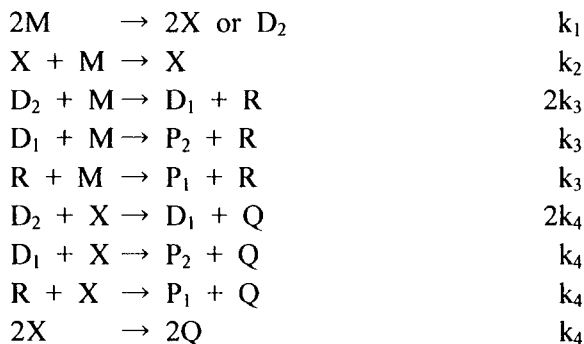
$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : disproportionation termination rate constant, [l/mol·sec]

Mackay, M. H. and Melville, H. W., *Trans. Faraday Soc.*, **45**, 323 (1949).

### Photo-induced bulk polymerization

Temperature: 0°C



M: monomer, X: active center, Q: dead center,  $D_2$ : initial polymer growing at both ends,  $D_1$ : polymer growing at one end, R: growing transfer polymer,  $P_1$ : dead transfer polymer,  $P_2$ : dead initial polymer.



$$P_n = 2k_2(k_1k_4)^{-1/2}/(2\beta + \zeta)$$

$$\beta = k_3(k_1k_4)^{-1/2}, \quad \zeta = (1 + AI/k_1[M]^2)^{1/2}$$

$$k_1 = 6.82 \times 10^{-15}, \quad k_2 = 41.6, \quad k_3 = 6.13 \times 10^{-4}, \quad k_4 = 2.69 \times 10^6,$$

$$\beta = 4.51, \quad A = 32.1$$

$k_1$ : initiation rate constant, [l/mol·sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : transfer rate constant, [l/mol·sec]

$k_4$ : termination rate constant, [l/mol·sec]

$P_n$ : number-average degree of polymerization, [-]

I: light intensity

A: constant

[M]: monomer concentration, [mol/l]

Bamford, C. H. and Dewar, M. J. S., *Proc. Roy. Soc., London*, **A197**, 356 (1949).

### Photo-induced bulk polymerization

Sensitizer: biacetyl

Temperature: 5–70 °C

		Rate
Initiation	$S + h\nu \rightarrow 2R\cdot$	$2qI_a$
	$2R\cdot \rightarrow S$	$2k_r[R\cdot]$
	$R\cdot + M \rightarrow M\cdot$	$2k_a[R\cdot][M]$
Propagation	$M\cdot + M \rightarrow M\cdot$	$k_p[M\cdot][M]$
Transfer with monomer	$M_r\cdot + M \rightarrow M_r + M\cdot$	$k_{tr}[M_r\cdot][M]$
Termination	$M\cdot + M\cdot \rightarrow \text{polymer}$	$2k_t[M\cdot]^2$

S: sensitizer, M: monomer,  $M\cdot$ : monomer radical,  $R\cdot$ : primary radical,  $M_r\cdot$ : polymer radical containing r units of monomer,  $M_r$ : dead polymer containing r units of monomer.

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]	$k_{tr}$ [l/mol·sec]
30	143	$1.22 \times 10^7$	$3.57 \times 10^{-3}$
60	367	$1.87 \times 10^7$	$22.9 \times 10^{-3}$

$$k_p = 5.13 \times 10^6 \exp(-6310 \text{ cal/RT})$$

$$2k_t = 1.36 \times 10^9 \exp(-2840 \text{ cal/RT})$$

$$k_{tr} = 2.75 \times 10^6 \exp(-12280 \text{ cal/RT})$$

h $\nu$ : quantum of frequency  $\nu$

q: quantum yield of dissociation of S

I<sub>a</sub>: absorbed light intensity

k<sub>i</sub>: rate constant of inactive reaction of primary radical, [l/mol·sec]

k<sub>a</sub>: initiation rate constant, [l/mol·sec]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

k<sub>tr</sub>: transfer rate constant to monomer, [l/mol·sec]

Matheson, M. S., Auer, E. E., Bevilacqua, E. B., and Hart, E. J., *J. Am. Chem. Soc.*, **71**, 497 (1949).

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### Photo-induced bulk polymerization

Temperature: 15°C

$$k_p/k_t = 6.75 \times 10^{-6}$$

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

Grassie, N. and Melville, H. W., *Proc. Roy. Soc., London*, **A207**, 285 (1951).

**Photo-induced bulk polymerization**

Temperature: 30–50°C

Maximum conversion: about 72%

Conversion [%]	Temperature [°C]	$k_p/k_t$	$k_{tx}/k_{t0}^{(1)}$
0-1	30	$1.93 \times 10^{-5}$	1
	40	$2.47 \times 10^{-5}$	
47±2	30	$9.20 \times 10^{-3}$	$2.10 \times 10^{-3}$
52±2	30	$9.33 \times 10^{-3}$	$2.07 \times 10^{-3}$
	40	$9.48 \times 10^{-3}$	
	50	$9.86 \times 10^{-3}$	
72±3	30	$2.96 \times 10^{-2}$	$6.52 \times 10^{-4}$

<sup>(1)</sup>The ratio of  $k_t$  at x% conversion to its initial value was estimated at 30°C.

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Fujii, S., *Bull. Chem. Soc. Japan*, **27**, 238 (1954).

**Photo-induced bulk and solution polymerization**

Solvent: benzene

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 25°C

$$k_f/k_p = 3 \times 10^{-5}$$

$$k_t/k_p^2 = 260, \text{ [mol} \cdot \text{sec/l]}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_f$ : transfer rate constant to monomer, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polym. Sci.*, **12**, 449 (1954). Copyright © 1954 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Photo-induced bulk polymerization**

Sensitizer: azobis(cyclohexanecarbonitrile)

Temperature: 15°C

$$k_p/k_t=9.8 \times 10^{-6}$$

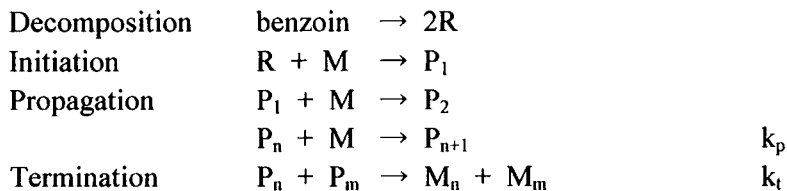
 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]

Bengough, W. I. and Melville, H. W., *Proc. Roy. Soc., London*, **A225**, 330 (1954).

**Photo-induced bulk polymerization**

Sensitizer: benzoin

Temperature: 25°C



R: primary radical, M: monomer, P<sub>n</sub>: growing radical containing n units of monomer, M<sub>n</sub>: dead polymer containing n units of monomer.

$$k_p=512.61$$

$$k_t=4.66 \times 10^7$$

$$\text{Activation energy}=3.6 \text{ [kcal/mol]}$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]

Chinmayanandam, B. R. and Melville, H. W., *Trans. Faraday Soc.*, **50**, 73 (1954).

**Photo-induced bulk polymerization**Sensitizer:  $\alpha$ -azobisisobutyronitrile

Temperature: 30–40°C

$$k_p/k_t = 2.66 \times 10^{-3} \exp(-3540 \text{ cal/RT})$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Miyama, H., *Bull. Chem. Soc. Japan*, **29**, 715 (1956).**Photo-induced bulk polymerization**

Temperature: 20–50°C

Transfer agent: n-butyl mercaptan

Maximum conversion: 35%

Conversion [%]	Temperature [°C]	$k_p/k_t \times 10^5$
(a) n-butyl mercaptan: 0 mol%		
0–2	30	1.4
	50	1.9
6	30	17
26	30	125
35	30	262
(b) n-butyl mercaptan: 0.9 mol%		
3–5	30	0.47
	50	0.53
13	50	0.47
(c) n-butyl mercaptan: 2 mol%		
0–2	20	0.26
	40	0.22
10	20	0.36
	40	0.30
27	20	0.59
	40	0.52

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Fujii, S., Tanaka, S., and Sutani, S., *J. Polym. Sci.*, **20**, 584 (1956).

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### Photo-induced bulk polymerization

Sensitizer: 1,1'-azobiscyclohexanecarbonitrile

Transfer agent: n-butyl mercaptan

Temperature: 20°C

Maximum conversion: 52%

n-Butyl mercaptan	Conversion [%]	$k_p/k_t \times 10^5$
Absence	50	42
Presence	52	1.4

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Fujii, S., Tanaka, S., and Sutani, S., *J. Polym. Sci.*, **20**, 409 (1956).

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**Photo-induced bulk polymerization**

Sensitizer: 1,1'-azobiscyclohexane carbonitrile

Temperature: 30°C

Conversion [%]	$k_p/k_t \times 10^5$
0	0.99
0.6	1.01
1.1	1.12
1.7	1.23
2.0	1.30
2.3	1.38
2.7	1.40
2.8	1.48
3.0	1.54
3.7	1.80
4.4	2.22
5.2	2.60
6.2	3.34
7.2	4.04
8.2	5.22
9.4	7.21
10.8	12.1
12.4	18.1
14.3	32.0
16.6	53.6
19.2	85.5
22.1	121.0

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Miyama, H., *Bull. Chem. Soc. Japan*, **30**, 459 (1957).

**Photo-induced bulk polymerization**

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 22.5°C

Maximum conversion: 80%

Rate of initiation:  $2.83 \times 10^{-8}$ , [mol/l·sec]

Conversion [%]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]
0	384	$4.42 \times 10^7$
10	234	$2.73 \times 10^7$
20	267	$7.26 \times 10^6$
30	303	$1.42 \times 10^6$
40	368	$8.93 \times 10^5$
50	258	$4.03 \times 10^5$
60	74	$4.98 \times 10^4$
70	16	$5.64 \times 10^3$
80	1	$7.6 \times 10^2$

Rate of initiation:  $8.36 \times 10^{-9}$ , [mol/l·sec]

Conversion [%]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]
0	357	$4.10 \times 10^7$
10	234	$2.64 \times 10^7$
20	272	$4.20 \times 10^6$
30	286	$6.26 \times 10^5$
40	364	$4.86 \times 10^5$
50	197	$1.59 \times 10^5$
60	57	$2.72 \times 10^4$
70	16	$7.90 \times 10^3$
80	1.4	$1.51 \times 10^2$



Rate of initiation:  $1.20 \times 10^{-8}$ , [mol/l·sec]

Conversion [%]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]
0	357	$4.18 \times 10^7$
10	234	$3.60 \times 10^7$
20	272	$4.93 \times 10^6$
30	286	$8.84 \times 10^5$

Conversion [%]	$E_t$ [kcal/mol]	$E_{\text{overall}}$ [kcal/mol]	$E_p$ [kcal/mol]
0	0.5	5.6	5.8
5	1.6	5.2	6.0
10	3.8	4.4	6.3
15	6.6	3.3	6.6
2	11.8	1.3	7.2
25	17.5	-0.7	8.0
30	23.8	-3.1	8.8
35	29.2	-4.6	10.0
40	32.4	-4.9	11.3
45	34.8	-4.4	13.0

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$E_p$ : activation energy for propagation reaction, [kcal/mol]

$E_t$ : activation energy for termination reaction, [kcal/mol]

$E_{\text{overall}}$ : overall activation energy, [kcal/mol]

Hayden, P. and Melville, H. W., *J. Polym. Sci.*, **43**, 201 (1960).

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**Photo-induced bulk polymerization**

Sensitizer: benzoin (BZ), benzoin methyl ether (BME), and benzil (BL)

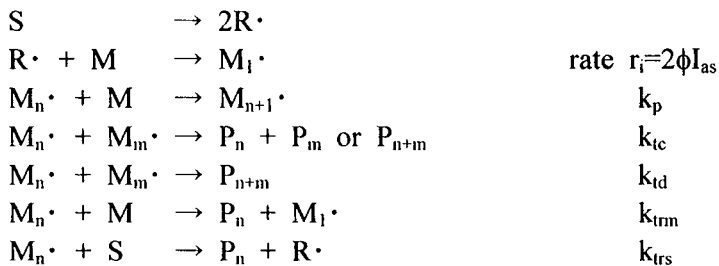
Temperature: 30°C

Sensitizer	$k_p/k_t^{1/2}$ [(l/mol·sec) <sup>1/2</sup> ]
BZ	0.063 ± 0.003
BME	0.059 ± 0.002
BL	0.038 ± 0.004

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Hutchison, J. and Ledwith, A., *Polymer*, **14**, 405 (1973).**Photo-induced bulk polymerization**

Sensitizer: benzoin and benzoin methyl ether

Temperature: 29.8°C



S: sensitizer, M: monomer, R·: primary radical formed from its decomposition,  $M_n\cdot$ : growing radical containing n monomer units,  $P_n$ : polymer molecule containing n monomer units.

Sensitizer	$\phi^{1/2}k_p/k_t^{1/2}$ [(l/mol·sec) <sup>1/2</sup> ]
Benzoin	$1.269 \times 10^{-2}$
Benzoin methyl ether	$4.042 \times 10^{-2}$

$$k_p/k_t^{1/2} = 44.3 \exp(-1934/T)$$

$$k_t = k_{tc} + k_{td}$$

$k_p$ : rate constant of propagation, [l/mol·sec]

$k_{tc}$ : rate constant of termination by combination, [l/mol·sec]

$k_{td}$ : rate constant of termination by disproportionation, [l/mol·sec]

$k_{trm}$ : rate constant of chain transfer to monomer, [l/mol·sec]

$k_{trs}$ : rate constant of chain transfer to sensitizer, [l/mol·sec]

$\phi$ : primary quantum yield

$I_{as}$ : rate of absorption of light by sensitizer

Mendiratta, S. K., Felder, R. M., and Hill, F. B., *AIChE Journal*, **21**, 1115 (1975). Reproduced with permission of the American Institute of Chemical Engineers. Copyright © 1975 AIChE. All rights reserved.

### Photo-induced bulk polymerization

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 25°C

		Rate
Initiation	$C + h\nu \rightarrow 2R\cdot$	$\phi I_{abs}$
	$C \rightarrow 2R\cdot$	$k_d[C]$
	$R\cdot + M \rightarrow P_1\cdot$	$k_i[R\cdot][M]$
Propagation	$P_n\cdot + M \rightarrow P_{n+1}\cdot$	$k_p[P_n\cdot][M]$
Transfer	$P_n\cdot + Y \rightarrow P_n + R\cdot$	$k_{tr,Y}[P_n\cdot][M]$
Termination	$P_n\cdot + P_m\cdot \rightarrow P_{n+m}$	$k_{tc}[P_n\cdot][P_m\cdot]$
	$P_n\cdot + P_m\cdot \rightarrow P_n + P_m$	$k_{td}[P_n\cdot][P_m\cdot]$

C: sensitizer, M: monomer,  $R\cdot$ : primary free radical,  $P_n\cdot$ : growing polymer radical containing n units of monomer,  $P_n$ : dead polymer containing n units of monomer, Y: chain transfer agent.

$$k_p=315, \quad k_t=30 \times 10^6$$

[AIBN]: concentration of AIBN, [mol/l]

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tr,Y}$ : transfer rate constant to Y, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

O'Driscoll, K. F. and Mahabadi, H. K., *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 869 (1976). Copyright © 1976 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Photo-induced bulk polymerization

Sensitizer: 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 15–30°C

Maximum conversion: less than 1%

Temperature [°C]	[AIBN] [mol/l]	$\bar{X}_n \times 10^{-3}$	$k_p$ [l/mol·sec]	$\bar{k}_t$ [l/mol·sec]
15	0.05	14.95	244.1	28.8
20	0.04	13.0	278.5	29.4
25	0.03	13.91	315.0	30.
30	0.025	10.62	356.0	30.6

$$k_p=4.92 \times 10^5 \exp(-4353 \text{ cal/RT})$$

$$\bar{k}_t=9.80 \times 10^7 \exp(-701 \text{ cal/RT})$$

$k_p$ : propagation rate constant, [l/mol·sec]

$\bar{k}_t$ : average rate constant of termination, [l/mol·sec]

$\bar{X}_n$ : number-average degree of polymerization, [-]

Mahabadi, H. K. and O'Driscoll, K. F., *J. Macromol. Sci.-Chem.* **A11**, 967 (1977).

### Photo-induced bulk polymerization

Sensitizer: benzoin

Temperature: 25–40°C

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t \times 10^{-8}$ [l/mol·sec]
25	299	0.45
40	431	0.50

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Ola, O. F., Kremminger, P., and Schnoll-Bitai, I., *Makromol. Chem. Rapid Commun.*, **9**, 771 (1988).

### Photo-induced bulk polymerization

Initiator: azobis(cyclohexanenitrile)

Temperature: 0°C

Maximum conversion: about 75%

$$x=0-0.75: f=0.4-0$$

$$[M]_0-[M]_x=0-6: k_p/k_t=10^{-7}-10^{-2}$$

$$x=0-0.75: k_t=10^4-5 \times 10^7$$

x: conversion, [-]

f: efficiency, the kinetically effective fraction of initiator radicals formed, [-]

$[M]_0$ : monomer concentration at conversion 0, [mol/l]

$[M]_x$ : monomer concentration at conversion x, [mol/l]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Sack, R., Schulz, G. V., and Meyerhoff, G., *Macromolecules*, **21**, 3345 (1988).

### Photo-induced solution polymerization

Solvent: water

Initiator:  $\text{Fe}^{3+}\text{X}^-$  ( $\text{X}^- = \text{OH}^-, \text{Cl}^-, \text{N}_3^-$ )

Temperature: 25°C

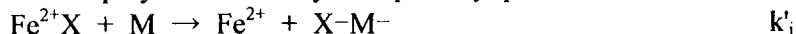
Light absorption



Primary dark back reaction



Initiation of polymerization by the primary product  $\text{Fe}^{2+}\text{X}^-$



Separation of the primary product



Secondary dark back reaction



Free radical initiation of polymerization



Propagation of polymerization

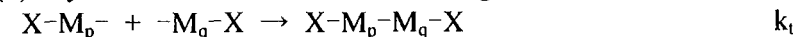


Termination of polymerization

(a) by free radicals



(b) by recombination of active endings



M: monomer,  $\text{M}_p$ : polymer containing p units.

Ion pair	$k_0/k_i$	$k_p/k_t^{1/2}$ [ $(\text{l/mol}\cdot\text{sec})^{1/2}$ ]
$\text{Fe}^{3+}\text{Cl}^-$	—	0.98
$\text{Fe}^{3+}\text{N}_3^-$	46	—

$k_e$ : the fraction of the light absorbed by  $\text{Fe}^{3+}\text{X}^-$ , [1/sec]

$k_d$ : rate constant of primary dark back reaction, [1/sec]

$k'_i$ : rate constant of initiation reaction by the primary product  $\text{Fe}^{2+}\text{X}$ , [ $\text{l/mol}\cdot\text{sec}$ ]

$k_s$ : separation rate constant of the primary product, [1/sec]

$k_0$ : rate constant of secondary dark back reaction, [ $\text{l/mol}\cdot\text{sec}$ ]

$k_i$ : free radical initiation rate constant, [ $\text{l/mol}\cdot\text{sec}$ ]

$k_p$ : propagation rate constant, [ $\text{l/mol}\cdot\text{sec}$ ]

$k'_t$ : termination rate constant by free radical, [ $\text{l/mol}\cdot\text{sec}$ ]

$k_t$ : termination rate constant by recombination of active ending, [ $\text{l/mol}\cdot\text{sec}$ ]

Evans, M. G., Santappa, M., and Uri, N., *J. Polym. Sci.*, 7, 243 (1951).

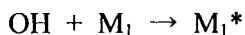
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### Photo-induced solution polymerization

Solvent: water

Initiator: ferric-hydroxide complex

Temperature: 25–35 °C



$\text{M}_1$ : monomer,  $\text{M}_1^*$ : monomer radical,  $\text{M}_j^*$ : radical polymer with  $j$  units,  
 $\text{P}_j$ : dead polymer with  $j$  units.

$$R_i=(k_p/k_t^{1/2})[\text{M}_1](\phi I_a)^{1/2}$$

$$\bar{P}_n = k_t R_i / k_p^2 [M_1]^2 + k_f / k_p$$

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]
25	75	$1.8 \times 10^4$
35	about 100	about $2 \times 10^4$

$R_i$ : rate of polymerization, [mol/l·sec]

$I_a$ : intensity of light absorbed

$h\nu$ : quantum of frequency  $\nu$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_f$ : transfer rate constant to monomer, [l/mol·sec]

$[M_1]$ : monomer concentration, [mol/l]

$\bar{P}_n$ : number-average degree of polymerization, [-]

Atkinson, B. and Cotten, G. R., *Trans. Faraday Soc.*, **54**, 877 (1958).

### Photo-induced solution polymerization

Solvent: viscous or non-viscous media

Sensitizer:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 40°C

Non-viscous media

$$k_p=404, k_t=1.76 \times 10^7, k_f=8.08 \times 10^{-3}$$

Viscous media

$$k_p=360 \pm 100, k_t=(7.7 \pm 2.8) \times 10^4, k_f=(8.0 \pm 2.6) \times 10^{-3}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_f$ : rate constant of combined transfer to monomer and to solvent, [l/mol·sec]

Benson, S. W. and North, A. M., *J. Am. Chem. Soc.*, **81**, 1339 (1959).

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**Photo-induced solution polymerization**

Solvent: ethylacetate

Catalyst:  $\alpha$ -azobisisobutyronitrile

Temperature: -40–-20°C

Temperature [°C]	$(k_{tc}+2k_{td}) \times 10^{-3}/k_p^2$ <sup>(1)</sup> [mol·sec/l]	$k_p$ <sup>(2)</sup> [l/mol·sec]
-20	1.6	24
-30	2.8	13.2
-40	5.8	5.43–11.1

<sup>(1)</sup>From stationary state. <sup>(2)</sup>From non-stationary state. $k_{tc}$ : termination rate constant by combination, [l/mol·sec] $k_{td}$ : termination rate constant by disproportionation, [l/mol·sec] $k_p$ : propagation rate constant, [l/mol·sec]Hughes, J. and North, A. M., *Trans. Faraday Soc.*, **60**, 960 (1964).**Photo-induced solution polymerization**

Solvent: six different solvents (see table)

Sensitizer: azobisisobutyronitrile (AIBN)

Temperature: 25°C

[MMA]: 4.69 [mol/l], [AIBN]:  $6.10 \times 10^{-3}$  [mol/l]

Solvent	$k_p \times 10^{-2}$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
Benzene	2.6	2.1
Fluorobenzene	2.7	2.1
Chlorobenzene	2.8	1.95
Anisole	2.85	1.75
Bromobenzene	3.1	1.7
Benzonitrile	3.3	1.7

[MMA]: concentration of MMA, [mol/l]

[AIBN]: concentration of AIBN, [mol/l]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constants, [l/mol·sec]

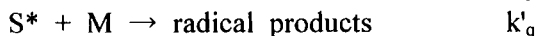
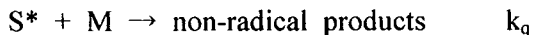
Bamford, C. H. and Brumby, S., *Makromol. Chem.*, **105**, 122 (1967).

### Photo-induced solution polymerization

Solvent: benzene

Sensitizer: benzoin (B), benzoinacetate (BA), and benzoinmethylether (BME)

Temperature: room temperature



$S^*$ : excited sensitizer, M: monomer.

Sensitizer	$k_q/k_1$ [l/mol]	$k_q$ [l/mol·sec]
B	0.4	$4.8 \times 10^8$
BA	15	$8.0 \times 10^8$
BME	0.02	

$k_1$ : decomposition rate constant of sensitizer, [1/sec]

$k_q, k'_q$ : rate constant for reaction of monomers with excited sensitizers which lead to non-radical products and radical products, respectively.

Kuhlmann, R. and Schnabel, W., *Angew. Makromol. Chem.*, **70**, 145 (1978).

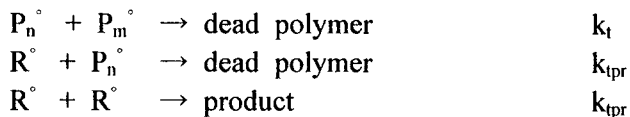
### Photo-induced solution polymerization

Solvent: various solvents

Initiator:  $\alpha, \alpha'$ -azobiscyclohexane carbonitrile (ACN)

Temperature: 0°C





I: initiator,  $R^\circ$ : primary radical, M: monomer,  $P_n^\circ$ : polymer radicals with n units.

$$\begin{aligned}
 k_p &= 163, \quad k_{tpr0}/k_p k_i = 3.45 \times 10^5 \\
 k_{tpr}/k_p k_i &= 3.45 \times 10^5/\eta, \quad k_t = 1.43 \times 10^7/\eta
 \end{aligned}$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{tpr}$ : rate constant for termination by primary radical, [l/mol·sec]

$k_{tpr0}$ : rate constant for termination by primary radical at a viscosity of 1 cP, [l/mol·sec]

$\eta$ : viscosity of solution, [cP]

Mahabadi, H. K. and Meyerhoff, G., *Eur. Polym. J.*, **15**, 607 (1979).

### Photo-induced and thermally-induced solution polymerization

Solvent: benzene

Initiator: 2,2'-azo-bis-isobutyronitrile

Temperature: 0–60°C

Maximum conversion: 7%

Temperature [°C]	0 <sup>(1)</sup>	25 <sup>(1)</sup>	60 <sup>(2)</sup>
$k_{td}/k_{tc}$	1.50	2.13	5.75

<sup>(1)</sup>Photo-induced polymerization.

<sup>(2)</sup>Thermally-induced solution polymerization.

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polym. Sci.*, **14**, 463 (1954). Copyright © 1954 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Photo-induced bulk, thermally-induced bulk, and solution polymerization**

Solvent: four different solvents (see table)

Sensitizer: azobisisobutyronitrile (AZBN) and  
azobiscyclohexane carbonitrile (AZCN)

Temperature: 25–60°C

**(1) Photo-induced bulk and solution polymerization and thermally-induced bulk and solution polymerization**

Sensitizer: AZCN, [AZCN]=1.00 g/l

Temperature: 25°C

Solvent [vol%]	$k_p \times 10^{-2}$ [l/mol·sec]	$k_t \times 10^{-6}$ [l/mol·sec]
–	4.1	42.7
1-Fluoronaphthalene 45	4.5	41.1
1-Chloronaphthalene 25	4.8	48.2
30	4.2	30.4
45	4.4	26.9
60	5.0	30.5
1-Bromonaphthalene 45	4.6	26.1
Toluene 45	3.7	38.9

**(2) Thermally-induced bulk and solution polymerization**

Sensitizer: AZBN and AZCN,

[AZBN] or [AZCN]=1.00 g/l

Temperature: 60°C

Solvent [vol%]	Initiator	$k_p \times 10^{-2}$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
–	AZBN	6.4	2.56
–	AZCN	6.4	2.56
1-Fluoronaphthalene			
40	AZBN	6.6	1.84
40	AZCN	6.3	1.84
60	AZBN	6.4	1.49
1-Chloronaphthalene			
20	AZBN	6.8	2.15
40	AZBN	7.1	1.74
40	AZCN	7.0	1.74
60	AZBN	7.2	1.34
60	AZCN	7.1	1.34
80	AZBN	6.9	0.94
1-Bromonaphthalene			
20	AZBN	7.4	2.13
40	AZBN	8.0	1.70
40	AZCN	8.4	1.70
60	AZBN	8.2	1.28

[AZBN]: concentration of AZBN, [mol/l]

[AZCN]: concentration of AZCN, [mol/l]

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constants, [l/mol·sec]Burnett, G. M., Cameron, G. G., and Zafar, M. M., *Eur. Polym. J.*, **6**, 823 (1970).

**Photo-induced bulk and thermally-induced bulk and solution polymerization**

Solvent: toluene, methanol (MeOH), n-octane, and n-nonane (see table)

Initiator: azobiscyclohexane carbonitrile (AZCN) used in photo-induced polymerization, and azobisisobutyronitrile (AZBN) used in thermally-induced polymerization

Temperature: 25 and 60°C

Reaction medium (parts by vol.)	Temperature [°C]	$k_p^2/k_t \times 10^3$ [l/mol·sec]	$k_p \times 10^{-2}$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
MMA-toluene (50:50)	60 <sup>(1)</sup>	15.3	–	–
MMA-toluene-MeOH (50:15:35)	60 <sup>(1)</sup>	20.7	–	–
Bulk MMA	25 <sup>(2)</sup>	3.50	$3.9 \pm 0.4$	$4.2 \pm 0.4$
MMA-MeOH (50:50)	25 <sup>(2)</sup>	5.92	$4.1 \pm 0.4$	$2.9 \pm 0.3$
MMA/n-octane/n-nonane (75:5:20)	25 <sup>(2)</sup>	6.29	$4.1 \pm 0.4$	$2.6 \pm 0.3$

<sup>(1)</sup>Thermally-induced polymerization<sup>(2)</sup>Photo-induced polymerization $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Cameron, G. G. and Cameron, J., *Polymer*, **14**, 107 (1973).

### Photo-induced bulk and solution polymerization and thermally-induced bulk and solution polymerization

Solvent: thirteen different solvents (see table)

Sensitizer:  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) and  
 $\alpha,\alpha'$ -azobiscyclohexane carbonitrile (ACN)

Temperature: 30–60°C

#### (1) Thermally-induced bulk and solution polymerization

[MMA]: 4.69 [mol/l], [ACN]:  $6.08 \times 10^{-3}$  [mol/l], solvent: 50 vol%

Solvent	$k_d \times 10^5$ [1/sec] 60°C <sup>(1)</sup>	f 60°C	$k_t/k_p^2$ [mol·sec/l] 30°C
MMA	0.84	0.71	300
Benzene	0.86	0.68	280
Toluene	0.98	0.56	320
Ethyl benzene	0.98	0.57	
Anisole	1.01	0.59	190
Benzyl alcohol	1.09		120
Chlorobenzene	0.97	0.55	240
o-Dichlorobenzene	0.99	0.57	180
1,2,4-Trichlorobenzene	1.01	0.55	
Bromobenzene	0.98	0.55	
Benzonitrile	1.07	0.55	160
1,2-Dichloroethane			250
1,1,1-Trichloroethane			340
1,1,2,2-Tetrachloroethane			140

<sup>(1)</sup>The mean value of  $k_d$  in pure MMA monomer and that in pure solvent.

**(2) Photo-induced bulk and solution polymerization**

Temperature: 30°C

[MMA]: 4.69 [mol/l], [ACN]:  $6.08 \times 10^{-4}$  [mol/l], solvent: 50 vol%

Solvent	$k_p$ [l/mol·sec]	$2k_t \times 10^{-7}$ [l/mol·sec]
MMA	260	2.0
Benzene	260	1.8
Toluene	240	1.9
Anisole	270	1.4
Benzyl alcohol	270	0.86
Chlorobenzene	250	1.5
o-Dichlorobenzene	260	1.3
Benzonitrile	300	1.4
1,2-Dichloroethane	260	1.7
1,1,1-Trichloroethane	270	1.0
1,1,2,2-Tetrachloroethane	270	1.0

 $k_d$ : decomposition rate constant, [1/sec]

f: initiator efficiency, [-]

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Yamamoto, T., Yamamoto, T., Yamamoto, T., and Hirota, M., *Nippon Kagaku Kaishi*, 618 (1980).



### Photo-induced bulk and solution polymerization and thermally-induced bulk and solution polymerization

Temperature: 25°C

$$k_p = 295^{(1)} - 299^{(2)} \text{ [l/mol}\cdot\text{sec]}$$

<sup>(1)</sup> bulk or solution polymerization by using  $\alpha, \alpha'$ -azobisisobutyronitrile or benzoin as an initiator.

<sup>(2)</sup> photo-induced bulk polymerization.

$k_p$ : propagation rate constant, [l/mol·sec]

Buback, M., Gilbert, R. G., Russell, G. T., Hill, D. J. T., Moad, G., O'Driscoll, K. F., Shen, J., and Winnik, M. A., *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 851 (1992). Copyright © 1992 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Radiation-induced bulk and solution polymerization and thermally-induced bulk and solution polymerization

Temperature: -78–100°C

-78°C, radiation-induced solution polymerization, solvent: ethyl acetate

0°C, radiation-induced bulk polymerization

50°C, thermally-induced solution polymerization, solvent: Sharples 3B mercaptan (a mixture of tertiary C<sub>12</sub> mercaptans), initiator: benzoyl peroxide

100°C, thermally-induced bulk polymerization, initiator: benzoyl peroxide

$$k_p = (kT/h) \exp(-28.1/R) \{ \exp(-6925 \text{ cal}/RT) + \exp(-6150 \text{ cal}/RT) \}$$

h: Plank's constant

k: Boltzmann's constant

$k_p$ : apparent overall propagation rate constant, [l/mol·sec]

Bovey, F. A., *J. Polym. Sci.*, **56**, 59 (1960). Copyright © 1960 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Radiation-induced bulk polymerization**Radiation source:  $\gamma$ -rayTemperature:  $-25$ – $55^{\circ}\text{C}$ 

Maximum conversion: 80%

$$R_p = k_p [M] R_i^{1/2} / k_t^{1/2}$$

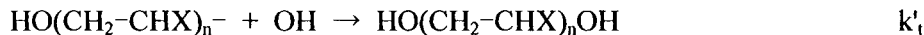
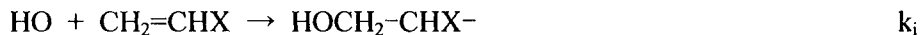
$$k_p = 1.3 \times 10^6 \exp(-5450 \text{ cal/RT})$$

$$k_t = 2.1 \times 10^9 \exp(-3150 \text{ cal/RT})$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec] $R_i$ : initiation rate, [mol/l·sec] $R_p$ : propagation rate, [mol/l·sec] $[M]$ : monomer concentration, [mol/l]Palma, G., Busulini, L., and Lora, S., *Eur. Polym. J.*, **6**, 453 (1970).**Solution polymerization**Solution:  $\text{FeSO}_4$  solution, sulphuric acid

Emulsifier: cetyl trimethyl ammonium bromide

Initiator: ferrous ion + hydrogen peroxide

Temperature:  $25^{\circ}\text{C}$ 

Emulsifying agent concentration [%]	$M_0$ [mol/l]	$a_0 \times 10^4$ [mol/l]	$k_p/(k_1 k_t)^{1/2}$
1.0	0.175	0.241	1.67
1.0	0.175	0.483	1.67
1.0	0.175	0.967	1.70
1.0	0.175	1.934	1.46
3.0	0.175	0.478	1.22
3.0	0.180	0.957	1.22
3.0	0.092	0.971	1.21

$M_0$ =approx. 0.1 [mol/l],  $a_0=10^{-4}$  [mol/l]

Emulsifying agent [%]	0	0.0003	0.003	0.03	0.5	1.0	3.0
$k_p/(k_1 k_t)^{1/2}$	0.153	0.41	0.53	0.83	0.98	1.72	1.22

$k_1$ : rate constant of HO generation reaction, [l/mol·sec]

$k_2$ : rate constant of HO<sup>-</sup> generation reaction, [l/mol·sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t'$ : termination rate constant by free radical, [l/mol·sec]

$k_t$ : termination rate constant by recombination of active endings, [l/mol·sec]

$M_0$ : initial monomer concentration, [mol/l]

$a_0$ : initial initiator concentration, [mol/l]

Baxendale, J. H., Evans, M. G., and Kilham, J. K., *Trans. Faraday Soc.*, **42**, 668 (1946).

### Solution polymerization

Solvent: seven different thiols (see table)

Initiator: 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 60°C

Initiation	$I \rightarrow 2fR\cdot$	$k_d$
Propagation	$R\cdot + M \rightarrow R\cdot$	$k_p$
Monomer transfer	$R\cdot + M \rightarrow P + M\cdot$	$k_m$
Thiol transfer	$R\cdot + S \rightarrow P + S\cdot$	$k_s$
Termination by combination	$R\cdot + R\cdot \rightarrow P$	$k_{tc}$
Termination by disproportionation	$R\cdot + R\cdot \rightarrow P + P$	$k_{td}$

I: initiator,  $R\cdot$ : radical, M: monomer, P: polymer, S: solvent,  $S\cdot$ : radical from solvent.

$$R_p = 3.04 \times 10^{-5} [AIBN]^{1/2}$$

Solvent	$C_s = k_s/k_p$
2-Naphthalenethiol	3.1
Benzenethiol	2.7
1-Butanethiol	0.66
Ethyl mercaptoacetate	0.63
2-Mercaptoethanol	0.62
2-Propanethiol	0.38
2-Methyl-2-propanethiol	0.18

$$k_p = 573, k_{tc} = 0.20 \times 10^7, k_{td} = 1.19 \times 10^7, k_m = 4.0 \times 10^3$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_m$ : transfer rate constant to monomer, [l/mol·sec]

$k_s$ : transfer rate constant to thiol, [l/mol·sec]

$R_p$ : polymerization rate, [mol/l·sec]

[AIBN]: concentration of AIBN, [mol/l]

O'Brien, J. L. and Gornick, F., *J. Am. Chem. Soc.*, **77**, 4757 (1955).

© 1955 American Chemical Society.

**Solution polymerization**

Solvent: seven different solvents (see table)

Initiator: 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 60°C

Solvent	$C_s \times 10^5$	$k_{tr,s} \times 10^5$ [l/mol·sec]
Benzene	0.40	146.8
Toluene	1.70	623.8
Ethyl benzene	7.66	2811.0
Chlorobenzene	0.74	271.6
Chloroform	4.54	1666.0
Carbon tetrachloride	9.25	3384.0
Acetone	1.95	715.7

$$k_p = 367 \text{ [l/mol·sec]}$$

$$C_s = k_{tr,s}/k_p$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tr,s}$ : transfer rate constant to solvent, [l/mol·sec]

Chadha, R. N., Shukla, J. S., and Misra, G. S., *Trans. Faraday Soc.*, **53**, 240 (1957).

**Solution polymerization**

Solvent: ethylacetate, sucrose acetate isobutyrate (SAIB), and butyl phthalate

Initiator:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 30°C

$$R_p = K[M]^{1.1}[I]^{0.51}$$

Solvent mixture	$k_t$ [l/mol·sec]	$k_p$ [l/mol·sec]
Monomer+ethylacetate (1:4)	$1.60 \times 10^7$	229
Monomer+ethylacetate+SAIB (1:1:2)	$2.81 \times 10^6$	210
Monomer+SAIB (1:4)	$4.00 \times 10^5$	235
Monomer+butylphthalate (1:4)	$2.16 \times 10^6$	240

$$k_d = 1.0 \times 10^{25} \exp(-30450 \text{ cal/RT})$$

$$\text{Initiator efficiency} = 0.50$$

[M]: monomer concentration, [mol/l]

[I]: initiator concentration, [mol/l]

$R_p$ : propagation rate, [mol/l·sec]

K: overall polymerization constant, [(l/mol)<sup>0.61</sup>·sec]

$k_d$ : decomposition rate constant of initiator, [l/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

North, A.M. and Reed, G.A., *Trans. Faraday. Soc.*, **57**, 859 (1961).

### Solution polymerization

Solvent: benzene

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 60°C

Monomer concentration: 0.03–1 mol/l



$R\cdot$ : primary radical, M: monomer,  $M_n\cdot$ : growing polymer radical.

$$k_i/k'_t = 3.0 \times 10^{-7}$$

$k_i$ : rate constant for chain initiation by a primary radical, [l/mol·sec]

$k_t$ : rate constant for chain termination by a primary radical, [l/mol·sec]

Baldwin, M. G., *J. Polym. Sci. A1*, 3209 (1963). Copyright © 1963 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Solution polymerization**

Solvent: benzene

Initiator:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 60°C

Maximum conversion: about 15%

$$R_p = k[AIBN]^{0.5}[MMA]^{1.0}$$

$$k = k_p(k_d f / k_t)^{1/2}$$

$$k = 3.15 \times 10^4, \quad k_p/k_t^{1/2} = 0.103, \quad k_d = 1.33 \times 10^{-5}, \quad f = 0.7$$

 $R_p$ : polymerization rate, [mol/l·sec]

[i]: concentration of i, [mol/l]

 $k_d$ : decomposition rate constant of initiator, [1/sec] $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec] $k$ : overall polymerization rate constant, [l<sup>1/2</sup>/mol<sup>1/2</sup>·sec]

f: efficiency of initiator, [-]

Otsu, T., Ito, I., and Imoto, M., *J. Polym. Sci.*, **A2**, 2901 (1964).

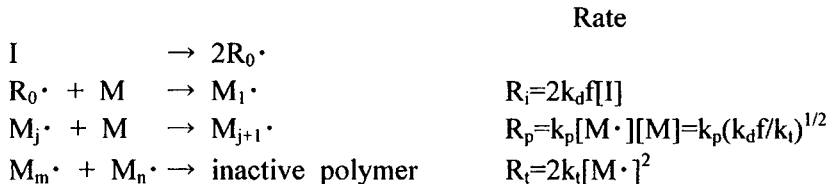
Copyright © 1964 John Wiley &amp; Sons, Inc. Reprinted by permission of John Wiley &amp; Sons, Inc.

**Solution polymerization**

Solvent: benzene

Initiator:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 30°C

I: initiator, M: monomer,  $R_0\cdot$ : primary radical,  $M_j\cdot$ : growing polymer with j units.

$$k_d = 1.31 \times 10^{-7}, \quad f = 0.63, \quad k_p = 141, \quad 2k_t = 11.6 \times 10^6$$

f: initiator efficiency, [-]

[M·]: total polymer radical concentration, [mol/l]

[M]: monomer concentration, [mol/l]

R<sub>i</sub>: initiation rate, [mol/l·sec]

R<sub>p</sub>: propagation rate, [mol/l·sec]

R<sub>t</sub>: termination rate, [mol/l·sec]

k<sub>d</sub>: decomposition rate constant of initiator, [1/sec]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

Yokota, K., Kani, M., and Ishii, Y., *J. Polym. Sci.*, **A-1**, **6**, 1325 (1968).

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### Solution polymerization

Solvent: four different solvents (see table)

Initiator: 2,2'-azobis(2,4-dimethylvaleronitrile)

Temperature: 40–60°C

$$R_p = k_p(2fk_d/k_t)^{1/2}[M][C]^{1/2}$$

Solvent	$k_p(2fk_d/k_t) \times 10^4$ [mol <sup>1/2</sup> /l <sup>1/2</sup> ·sec]	$k_{ti}/k_t k_p \times 10^{-3}$ [mol·sec/l]	Temperature [°C]
EA	4.30	13.5	60
DC	6.23	7.33	60
DEP	9.40	3.44	60
DOP	12.8	1.85	60
EA	1.68	14.3	50
DC	2.47	11.2	50
DEP	3.93	5.25	50
DOP	5.58	5.80	50
EA	0.780	25.0	40
DC	1.012	19.1	40
DEP	1.75	12.3	40



EA: ethyl acetate, DC: dimethyl carbitol,  
DEP: diethyl phthalate, DOP: di-n-octyl phthalate.

[M]: monomer concentration, [mol/l],

[C]: initiator concentration, [mol/l]

f: initiator efficiency, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_{ti}$ : termination rate constant by to primary radical, [l/mol·sec]

Ito, K., *J. Polym. Sci. A-1*, **9**, 2541 (1971). Copyright © 1971 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution polymerization

Solvent: benzene

Initiator: p-methoxy-p'-cyanodiphenyldiazomethane (MCD)  
or diphenyldiazomethane (DDM)

Temperature: 50°C

Maximum conversion: 2.7% (MCD)

For polymerization with MCD

$$R_p = k[MCD]^{0.56}[MMA]^{0.95}$$

$$k_d = 7.42 \times 10^{12} \exp(-25.7 \text{ kcal/RT}) \text{ for } 50\text{--}80^\circ\text{C}$$

$$\text{Overall activation energy} = 15.3 \text{ [kcal/mol] for } 40\text{--}70^\circ\text{C}$$

For polymerization with DDM

$$k_d = 1.32 \times 10^{13} \exp(-27.5 \text{ kcal/RT}) \text{ for } 60\text{--}90^\circ\text{C}$$

$$\text{Overall activation energy} = 18.8 \text{ [kcal/mol] for } 50\text{--}80^\circ\text{C}$$

$R_p$ : initial polymerization rate, [mol/l·sec]

$k$ : initial polymerization rate constant, [l<sup>0.51</sup>/mol<sup>0.51</sup>·sec]

[i]: concentration of i, [mol/l]

$k_d$ : decomposition rate constant of initiator, [1/sec]

Nakaya, T., Wada, H., and Imoto, M., *J. Macromol. Sci.-Chem.*, **A5**, 529 (1971).

**Solution or bulk polymerization**

Solvent: nine different solvents (see table)

Initiator: azobisisobutyronitrile (AIBN)

Temperature: 60°C

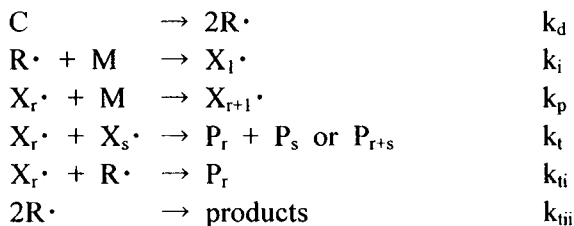
Solvent	[MMA] [mol/l]	$k_t \times 10^{-6}$ [l/mol·sec]	$k_p \times 10^{-2}$ [l/mol·sec]
Diethyl ether (DEE)	5.36	36.2	6.6
MMA	8.94	25.6	6.4
Methylbenzoate (MB)	5.36	18.9	6.4
Phenyl ethyl bromide (PEB)	5.36	17.0	6.5
p,p-Dichloro-diphenyl ether (DCDPE)	4.47	14.8	6.9
Diethyl malonate (DEM)	4.47	13.9	7.4
Phenyl salicylate (PSC)	3.57	10.3	7.0
Diethyl phthalate (DEP)	2.68	8.64	6.9
Dioctyl phthalate (DOP)	1.79	5.96	6.5
Dimethyl glycol phthalate (DMCP)	0.894	3.31	6.0

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constants, [l/mol·sec]Zafar, M. M., *Makromol. Chem.*, **157**, 219 (1972).**Solution polymerization**

Solvent: benzene

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 60°C



C: initiator,  $R\cdot$ : primary radical, M: monomer,  $X_r$ : growing polymer radical with r units,  $P_r$ : dead polymer with r units.

$$k_{ii}/k_i k_p = 3.09 \times 10^3 \text{ [mol}\cdot\text{sec/l]}$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [mol/l·sec]

$k_p$ : propagation rate constant, [mol/l·sec]

$k_t$ : termination rate constant, [mol/l·sec]

$k_{ii}$ : termination rate constant by primary radical, [mol/l·sec]

$k_{iii}$ : termination rate constant, [mol/l·sec]

Ito, K. and Matsuda, T., *Bull. Chem. Soc. Japan*, **42**, 1758 (1973).

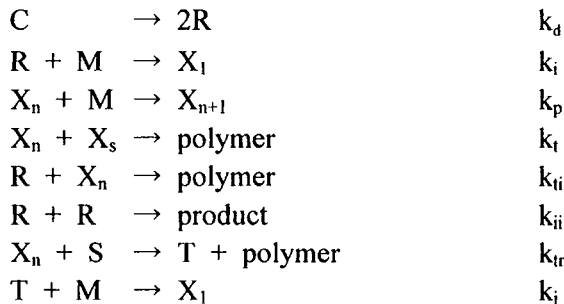
### Solution polymerization

Solvent: diethyl phthalate

Initiator: 2,2'-azobis(2,4-valeronitrile)

Temperature: 50°C

Maximum conversion: 10%



C: initiator, R: primary radical, M: monomer,  $X_n$ : polymer radical with n units, S: solvent, T: solvent radical.

$$k_{ii} = 4 \times 10^9, \quad k_{ii}/k_i k_p = 5250$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

- $k_t$ : termination rate constant, [l/mol·sec]  
 $k_{ti}$ : rate constant for termination by primary radical, [l/mol·sec]  
 $k_{ii}$ : rate constant of reaction between primary radicals, [l/mol·sec]  
 $k_{tr}$ : transfer rate constant to solvent, [l/mol·sec]  
 $k_j$ : reinitiation rate constant by solvent radical, [l/mol·sec]

Ito, K., *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1263 (1974). Copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution polymerization

Solvent: benzene (Bz), ethyl acetate (Ea), isopropyl alcohol (iPA)  
 dimethyl carbitol (DC), diethyl phthalate (DEP)

Initiator: 2,2'-azobis(2,4-dimethylvaleronitrile) (ABVN)

Temperature: 50°C

$$A = k_p(fk_d/k_t)^{1/2}$$

Solvent	$A \times 10^4$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]	$k_t/k_p^2$ [mol·sec/l]	$k_{ti}/10^3 k_i k_p$ [mol·sec/l]
Bz-MMA (3:1)	2.00	154	15.0
Bz-iPA-MMA (1:2:1)	2.12	137	8.9
Bz-iPA-MMA (2:13:5)	2.14	135	5.0
iPA-MMA (3:1)	2.11	138	2.0
Ea-MMA (3:1)	1.68	218	14.3
DC-MMA (3:1)	2.47	101	11.2
DEP-MMA (3:1)	3.93	40	5.25

- $k_p$ : propagation rate constant, [l/mol·sec]  
 $k_t$ : termination rate constant, [l/mol·sec]  
 $k_{ti}$ : termination rate constant by primary radical, [l/mol·sec]  
 $k_i$ : initiation rate constant, [l/mol·sec]  
 $k_d$ : decomposition rate constant of initiator, [l/sec]  
 $f$ : initiator efficiency, [-]

Ito, K., *J. Polym. Sci.*, **12**, 2581 (1974). Copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution polymerization

Solvent: benzene

Initiator: azobisisobutyronitrile

Temperature: 60°C

$$\log(R_p^2/[I][M]) = \log(2f_k k_d k_p^2/k_t) - 0.8684 k_{prt} R_p / k_i k_p [M]^2$$

$$1/P_n = 1/P_{n,0} + (1/P_n - 1/P_{n,0} - k_t R_p / k_p^2 [M]^2) (k_i k_p [M]^2 / k_{prt} R_p)$$

$$k_{prt}/k_i k_p = 1.45 \times 10^4, \quad 2f_k k_d k_p^2/k_t = 11.35 \times 10^{-8}, \quad k_d = 9.4 \times 10^{-6},$$

$$f_k = 0.70, \quad E_p = 4.87, \quad E_t = E_{prt} = 2.5, \quad E_d = 31, \quad E_i = 19$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$f_k$ : initiator efficiency, [-]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{prt}$ : termination rate constant by primary radical, [l/mol·sec]

$R_p$ : propagation rate, [mol/l·sec]

[M]: concentration of monomer, [mol/l]

[I]: concentration of initiator, [mol/l]

$P_n$ : number-average degree of polymerization, [-]

$P_{n,0}$ : number-average degree of polymerization without primary radical termination, [-]

$E_i$ : activation energy for initiation, [kcal/mol]

$E_p$ : activation energy for propagation, [kcal/mol]

$E_t$ : activation energy for termination, [kcal/mol]

$E_{prt}$ : activation energy for termination by primary radical, [kcal/mol]

Deb, P. C. and Kapoor, S. K., *Eur. Polym. J.*, **15**, 477 (1979).

**Solution polymerization**

Solvent: various aromatic solvents (see table)

Initiator: 2,2'-azobisisobutyronitrile (AIBN)  
and 2,2'-azobiscyclohexanecarbonitrile (ACN)

Temperature: 20–40°C

Initiator: AIBN, at 30°C, monomer concentration: 2 [mol/l]

Solvent	$(k_p/k_t) \times 10^3$
C <sub>6</sub> H <sub>5</sub> -OCH <sub>3</sub>	71.19
C <sub>6</sub> H <sub>6</sub>	4.82
C <sub>6</sub> H <sub>5</sub> -F	4.26
C <sub>6</sub> H <sub>5</sub> -Cl	5.78
C <sub>6</sub> H <sub>5</sub> -CN	9.45

Initiator: ACN, at 30°C, monomer concentration: 2 [mol/l]

Solvent	$k_p$	$k_t \times 10^{-7}$
C <sub>6</sub> H <sub>5</sub> -OCH <sub>3</sub>	506 ± 48	3.56 ± 0.39
C <sub>6</sub> H <sub>6</sub>	450 ± 33	4.20 ± 0.30
C <sub>6</sub> H <sub>5</sub> -F	448 ± 47	4.72 ± 0.66
C <sub>6</sub> H <sub>5</sub> -Cl	498 ± 39	4.29 ± 0.47
C <sub>6</sub> H <sub>5</sub> -CN	614 ± 43	3.99 ± 0.33
C <sub>6</sub> D <sub>6</sub>	456 ± 29	4.38 ± 0.20

Effect of monomer concentration on rate constants  
(solvent: benzene, initiator: AIBN, at 30°C)

Monomer concentration [mol/l]	$k_p$	$k_t \times 10^{-7}$
1.0	$427 \pm 38$	$3.09 \pm 0.37$
2.0	$450 \pm 33$	$4.20 \pm 0.30$
3.0	$454 \pm 36$	$4.20 \pm 0.46$

Temperature dependence of rate constants  
(solvent: benzene, initiator: AIBN, monomer concentration: 2 [mol/l])

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
20	$301 \pm 36$	$4.05 \pm 0.54$
30	$450 \pm 33$	$4.20 \pm 0.30$
40	$596 \pm 71$	$4.38 \pm 0.72$

Activation energy of  $k_p = 5.0 \pm 0.8$  [kcal/mol]

Activation energy of  $k_t = 0.38 \pm 0.1$  [kcal/mol]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Kamachi, M., Liaw, D. J., and Nozakura, S., *Polym. J.*, **13**, 41 (1981).

**Solution polymerization**

Solvent: see table

Initiator: 2,2'-azobisisobutyronitrile (AIBN) and benzoin (BZ)

Temperature: 25°C

Initiator	Initiator concentration [mol/l]	Additive	Monomer concentration [mol/l]	$k_p$ [l/mol·sec]
AIBN	$10^{-3}$ , $5 \times 10^{-3}$		9.39	292
BZ	$10^{-2}$ , $5 \times 10^{-3}$		9.39	297
AIBN	$10^{-3}$	EA	1.88–9.39	295
AIBN	$5 \times 10^{-3}$	MEOH	7.51–9.39	292–304
AIBN	$5 \times 10^{-3}$	Polystyrene	9.39	296

EA: ethyl acetate, MEOH: methanol

Average of  $k_p=294 \pm 9$  [l/mol·sec], for bulk polymerizationAverage of  $k_p=295 \pm 12$  [l/mol·sec], for solution polymerization $k_p$ : propagation rate constant, [l/mol·sec]Davis, T. P., O'Driscoll, K. F., Piton, M. C., and Winnik, M. A., *Macromolecules*, **22**, 2785 (1989). © 1989 American Chemical Society.**Solution polymerization**

Solvent: good solvent benzene (BZ), benzene-isopropyl alcohol (BZ-IPA), dimethyl carbitol (DC), and DE

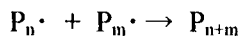
Initiator: AVBN

Temperature: 50°C

Initiation	$I \rightarrow 2R\cdot$	$k_d$
	$R\cdot + M \rightarrow P_1\cdot$	$k_i$
Propagation	$P_n\cdot + M \rightarrow P_{n+1}\cdot$	$k_p$
Chain transfer	$P_n\cdot + Y \rightarrow P_n + Y\cdot$	$k_{tr}$
Termination by disproportionation	$P_n\cdot + P_m\cdot \rightarrow P_n + P_m$	$k_{td(n,m)}$



Termination by combination

 $k_{tc(n,m)}$ 

I: initiator, M: monomer,  $R \cdot$ : primary free radical,  $P_n \cdot$ : growing polymer radical with n units,  $P_n$ : dead polymer with n units, Y: chain transfer agent.

$$k_{t(n,m)} = k_{t0}(nm)^{-a}$$

$$k_{t(n,m)} = k_t^* (\bar{X}_n)^{-2a}/\eta$$

$$R_p = (2fk_d k_p^2 / k_t^*) \eta^{0.5} [M][I]^{0.5} (X_n)^a$$

$$k_{t(n,m)} = k_{tc(n,m)} + k_{td(n,m)}$$

$$2fk_d k_p^2 / k_t^* = 1.70 \times 10^{-4}$$

$$a = 0.0995$$

$R_p$ : polymerization rate, [mol/l·sec]

$\bar{X}_n$ : number-average degree of polymerization, [-]

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tr}$ : transfer rate constant to species Y, [l/mol·sec]

$k_{t(n,m)}$ : termination rate constant, [l/mol·sec]

$k_{tc(n,m)}$ : termination rate constant by combination, [l/mol·sec]

$k_{td(n,m)}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_t^*$ : a constant, [l/mol·sec]

$\eta$ : solvent viscosity

Mahabadi, H. K., *Macromolecules*, **24**, 606 (1991).

© 1991 American Chemical Society.

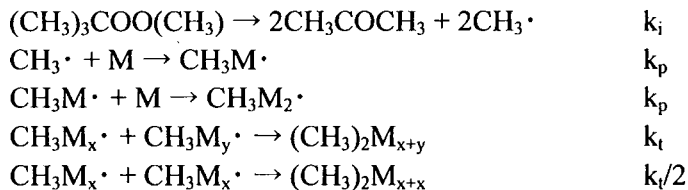
## 1.6 Propylene

### Bulk polymerization

Initiator: tert-butyl peroxide

Temperature: 130–165°C

Phase: gas



M: monomer,  $\text{CH}_3\text{M}_x\cdot$ : growing polymer radical with x units,  $\text{CH}_3\text{M}_x$ : dead polymer with x units.

$$\begin{aligned}
 -d[\text{M}]/dt &= k_p(2k_i/k_t)[\text{M}][\text{C}]^{1/2} \\
 k &= k_p(2k_i/k_t)^{1/2}
 \end{aligned}$$

#### Rate constants

Temperature [°C]	k [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
135.8	0.73
147.9	1.77
160.2	4.07

#### Activation energies

Rate constants	Activation energy [kcal/mol]
k	24.8
k <sub>i</sub>	38.4
k <sub>p</sub>	5.6
k <sub>t</sub>	0

$$k_i = 1.6 \times 10^6 \exp(-38.4/RT)$$

[M]: concentration of monomer, [mol/l]

[C]: concentration of initiator, [mol/l]

k: polymerization rate constant, [ $l^{1/2}/mol^{1/2} \cdot sec$ ]

$k_i$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Landers, L. C. and Volman, D. H., *J. Am. Chem. Soc.*, **79**, 2996 (1957).

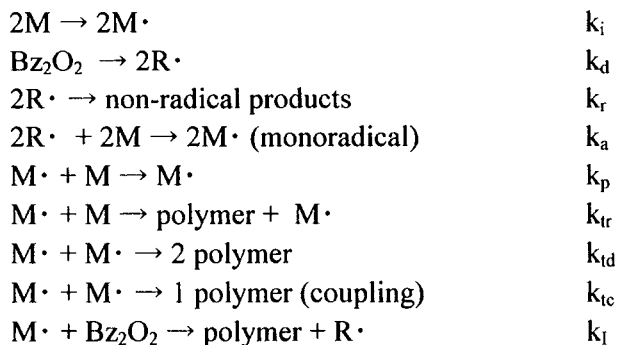
© 1957 American Chemical Society.

## 1.7 Styrene

### Bulk polymerization

Initiator: benzoyl peroxide

Temperature: 60°C



M: monomer,  $R\cdot$ : primary free radical,  $M\cdot$ : growing polymer radical.

$$k_{tr}/k_p = 6 \times 10^{-5}$$

$$k_l/k_p = 0.055$$

$k_i$ : thermally-initiated initiation rate constant, [l/mol·sec]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_r$ : rate constant of reaction between primary radicals, [l/mol·sec]

$k_a$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tr}$ : transfer rate constant of monomer, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_l$ : transfer rate constant of initiator, [l/mol·sec]

Mayo, F. R., Gregg, R. A., and Matheson, M. S., *J. Am. Chem. Sci.*, **73**, 1691 (1951).

© 1951 American Chemical Society.

**Bulk polymerization**

Initiator: dimethylanilinebenzoyl peroxide (DMABP), 2-azobisisobutyronitrile (AZO), benzoyl peroxide (BPO), and di-tert-butyl peroxide (DTBP)

Temperature: 0–90°C

Temperature [°C]	Initiator	$(2k_{td}+k_{tc})/k_p^2$ [mol·sec/l]	$k_{tr,m}/k_p \times 10^5$
0	DMABP	50320	ca.0
30	AZO	5210	2
45	AZO	2190	3
60	BPO and AZO	861	6
70	AZO	494	6
80	DTBP	286	7.5
90	DTBP	183	8.5

$$k_{tr,m}/k_p = 0.22 \exp(-5.6 \text{ kcal}/RT)$$

$$E_{tr,m} = 13-14$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_{tr,m}$ : transfer rate constant to monomer, [l/mol·sec]

$E_{tr,m}$ : activation energy for  $k_{tr,m}$ , [kcal/mol]

Tobolsky, A. V. and Offenbach, J., *J. Polym. Sci.*, **16**, 311 (1955).

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**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile (AIBN) and dicumyl peroxide (DCP)

Temperature: 30.5–85.3°C for AIBN, 59.6–100.0°C for DCP

$$R_i = 2fk_d[I]$$

$$R_p = k_p[C^*][M_{av}]$$

$$R_t = 2(k_{tc} + k_{td})[C^*]^2$$

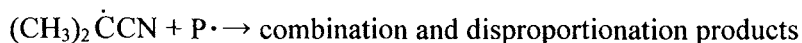
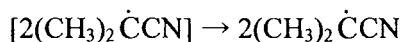
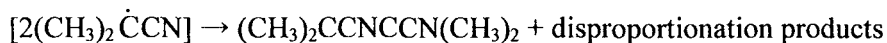
$$f' = f(1+x)$$

$$x = k_{td}/(k_{td} + k_{tc})$$

$$A' = (2k_{td} + k_{tc})/k_p^2$$

## (1) AIBN

Temperature: 30–85 °C



Temperature [°C]	$k_d f'$ [1/sec]
30.5	$6.44 \times 10^{-8}$
37.0	$1.89 \times 10^{-7}$
45.5	$7.08 \times 10^{-7}$
50.0	$1.44 \times 10^{-6}$
55.0	$2.84 \times 10^{-6}$
67.2	$1.84 \times 10^{-5}$
76.2	$5.28 \times 10^{-5}$
85.3	$1.29 \times 10^{-4}$

$$k_d f' = 9.80 \times 10^{14} \exp(-30.8 \text{ kcal/RT})$$

$$k_d = 1.58 \times 10^{15} \exp(-30.8 \text{ kcal/RT})$$

$$f' = 0.62$$

$$A' = 5.68 \times 10^{-4} \exp(12.46 \text{ kcal/RT})$$

## (2) DCP

Temperature: 60–100 °C

Temperature [°C]	$k_{df}'$ [1/sec]	$k_{tr}/k_p$
59.6	$1.04 \times 10^{-8}$	$5.7 \times 10^{-5}$
60.0	–	
68.0	$3.70 \times 10^{-8}$	
72.0	–	
76.5	$1.27 \times 10^{-7}$	
84.3	–	
85.3	$4.86 \times 10^{-7}$	$7.0 \times 10^{-5}$
94.5	$1.35 \times 10^{-6}$	
100.0	$3.62 \times 10^{-6}$	$1.5 \times 10^{-4}$

$$k_{df}' = 1.00 \times 10^6 \exp(-36.4 \text{ kcal/RT})$$

$R_i$ : initiation rate, [mol/l·sec]

$R_p$ : propagation rate, [mol/l·sec]

$R_t$ : termination rate, [mol/l·sec]

$k_d$ : specific decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : specific termination rate constant by combination, [l/mol·sec]

$k_{td}$ : specific termination rate constant by disproportionation, [l/mol·sec]

$k_{tr}$ : transfer rate constant, [l/mol·sec]

[I]: concentration of initiator, [mol/l]

$[M_{av}]$ : average monomer concentration, [mol/l]

[C\*]: radical concentration, [mol/l]

f: initiator efficiency, [-]

Van Hook, J. P. and Tobolsky, A. V., *J. Polym. Sci.*, **33**, 429 (1958).

Copyright © 1958 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Bulk polymerization**

Initiator: 2-azobisisobutyronitrile

Temperature: 100°C

$$-\ln ([M]_{\infty}/[M]_0)=2k_p f^{1/2} [Cat]_0^{1/2} / k_t^{1/2} k_d^{1/2}$$

$$k_d=1.60 \times 10^{-3}$$

$$f=0.60$$

$$k_d/k_t^{1/2}=0.0915$$

$[M]_0, [M]_{\infty}$  : initial concentration of monomer and concentration of monomer when time reaches infinity, respectively, [mol/l]

$[Cat]_0$ : initial concentration of initiator, [mol/l]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination constant, [l/mol·sec]

f: initiator efficiency, [-]

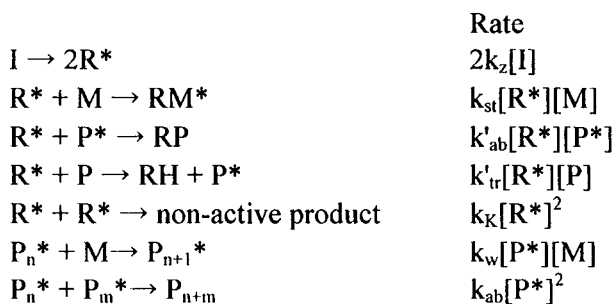
Tobolsky, A. V., *J. Am. Chem. Soc.*, **80**, 5927 (1958).

© 1958 American Chemical Society.

**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 40–70°C



I: initiator, M: monomer,  $R^*$ : primary free radical,  $P_n^*$ : growing polymer radical containing n monomer units,  $P^*$ : growing polymer radical of any size,  $P_n$ : dead polymer containing n monomer units.



$$\log(k_w^2/k_{ab})=4.26-2475/T$$

$$\log(k_w)=6.34-1295/T$$

$$\log(k_{ab})=8.42-115/T$$

$k_z$ : decomposition rate constant, [1/sec]

$k_{st}$ : initiation rate constant, [l/mol·sec]

$k_w$ : propagation rate constant, [l/mol·sec]

$k_K$ : inactive reaction rate constant between primary radicals, [l/mol·sec]

$k'_{tr}$ : transfer rate constant of primary radical to polymer, [l/mol·sec]

$k'_{ab}$ : rate constant of termination by primary radical, [l/mol·sec]

$k_{ab}$ : termination rate constant, [l/mol·sec]

T: temperature, [°K]

Henrici-Olive, G. and Olive, S., *Makromol. Chem.*, **37**, 71 (1960).

### Bulk polymerization

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 60–100°C

Maximum conversion: 97.1%

$$d[M]/dt=k_p k_d^{1/2} f^{1/2} [Cat]^{1/2} [M]/k_t^{1/2}$$

Temperature [°C]	[Cat] <sub>0</sub> <sup>(1)</sup> [mol/l]	$k_p/k_t^{1/2}$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec <sup>1/2</sup> ]	$k_d \times 10^4$ [1/sec]	f
60	0.0216	0.0341	0.12	0.71
70	0.0214	0.0451	0.45	0.71
80	0.0212	0.0592	1.60	0.71
90	0.0210	0.0739	5.08	0.71
100	0.0337	0.0915	18.0	0.76
100	0.0093	0.0915	18.0	0.61

<sup>(1)</sup>Initial concentration of initiator

[M]: concentration of monomer, [mol/l]

[Cat]: concentration of initiator, [mol/l]

[Cat]<sub>0</sub>: initial concentration of initiator, [mol/l]

f: initiator efficiency, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

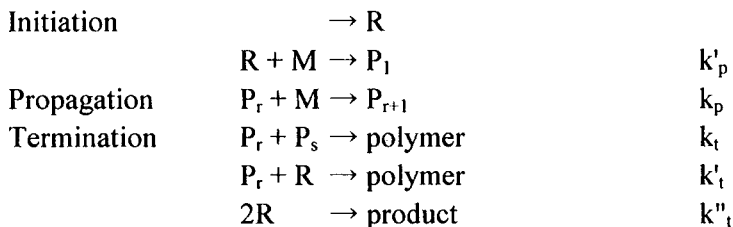
$k_t$ : termination rate constant, [l/mol·sec]

Tobolsky, A. V., Rogers, C. E., and Brickman, R. D., *J. Am. Chem. Soc.*, **82**, 1277 (1960). © 1960 American Chemical Society.

### Bulk polymerization

Initiator: azobisisobutyronitrile

Temperature: 60°C



R: primary radical, M: monomer,  $P_r$ : growing polymer radical containing r monomer units.

$k_p$	$k'_p$	$2k_t \times 10^{-7}$
[l/mol·sec]	[l/mol·sec]	[l/mol·sec]
176	1100	7.0

$k'_p$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k'_t$ : rate constant for termination by primary radical, [l/mol·sec]

$k''_t$ : rate constant for reaction between primary radicals, [l/mol·sec]

Allen, P. E. M. and Patrick, C. R., *Makromol. Chem.*, **48**, 89 (1961).

**Bulk, solution, and radiation-induced solution polymerization**

Formation of primary radicals	$I \rightarrow R_1 \cdot$	$k$
Initiation of polymerization	$R_i \cdot + M \rightarrow M_1 \cdot$	$k'_{pi}$
Propagation	$M_n \cdot + M \rightarrow M_{n+1} \cdot$	$k_p$
Chain transfer	$M_n \cdot + M \rightarrow P_n + R_4 \cdot$	$k_{trM}$
	$M_n \cdot + S \rightarrow P_n + R_5 \cdot$	$k_{trS}$
	$M_n \cdot + I \rightarrow P_n + R_6 \cdot$	$k_{trI}$
Termination	$M_n \cdot + M_m \cdot \rightarrow P_{n+m}$	$k_{tc}$
	$M_n \cdot + M_m \cdot \rightarrow P_n + P_m$	$k_{td}$
	$M_n \cdot + R_i \cdot \rightarrow P_n$	$k'_{ti}$

I: initiator,  $R_i \cdot$ : primary radical, M: monomer,  $M_n \cdot$ : growing polymer radical containing n monomer units,  $P_n$ : dead polymer containing n monomer units, S: solvent.

**(1) Bulk polymerization**

Initiator: azobisisobutyronitrile

Temperature: 60°C

$$k_p^2/(k_{tc}+k_{td})=5.52 \times 10^{-4}, k_{trM}/k_p=6 \times 10^{-5}, k_{trI}/k_p=0, k=1.57 \times 10^{-5}$$

**(2) Solution polymerization**

Initiator: azobisisobutyronitrile

Solvent: carbon tetrachloride

Temperature: 60°C

$$k_p^2/(k_{tc}+k_{td})=5.52 \times 10^{-4}, k_{trM}/k_p=6 \times 10^{-5}, k_{trS}/k_p=1.1 \times 10^{-2}$$

$$k_{trI}/k_p=0, k=1.57 \times 10^{-5}$$

**(3) Radiation-induced solution polymerization**

Sensitizer: azobisisobutyronitrile

Solvent: carbon tetrachloride

Temperature: 60°C

$$k_p^2/(k_{tc}+k_{td})=5.52 \times 10^{-4}, k_{trM}/k_p=6 \times 10^{-5}, k_{trS}/k_p=1.1 \times 10^{-2}$$

$k_{pi}$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

- $k_{tc}$ : termination rate constant by combination, [l/mol·sec]  
 $k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]  
 $k'_{ti}$ : termination rate constant by primary radical, [l/mol·sec]  
 $k_{trM}$ : transfer rate constant to monomer, [l/mol·sec]  
 $k_{trS}$ : transfer rate constant to solvent, [l/mol·sec]  
 $k_{trI}$ : transfer rate constant to initiator, [l/mol·sec]  
 $k$ : decomposition rate constant of initiator, [1/sec]

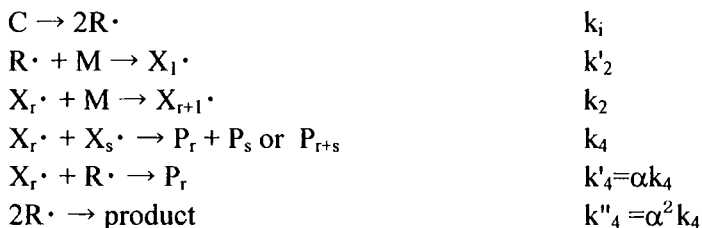
Manabe, T., Utsumi, T., and Okamura, S., *J. Polym. Sci.*, **58**, 121 (1962).

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### Bulk polymerization

Initiator: phenylazotriphenylmethane

Temperature: 50–60°C



C: initiator,  $R\cdot$ : primary radical,  $X_r\cdot$ : polymer radical containing r monomer units,

$P_r$ : polymer molecules containing r monomer units.

$$2k_i k''_4 / k_2'^2 = 4.73 \times 10^4 \text{ at } 50^\circ\text{C}$$

$$2k_i k''_4 / k_2'^2 = 6.8 \times 10^5 \text{ at } 60^\circ\text{C}$$

- $k_i$ : decomposition rate constant, [1/sec]  
 $k'_2$ : initiation rate constant, [l/mol·sec]  
 $k_2$ : propagation rate constant, [l/mol·sec]  
 $k_4$ : termination rate constant, [l/mol·sec]  
 $k'_4$ : rate constant for termination by primary radical, [l/mol·sec]  
 $k''_4$ : rate constant for reaction between primary radicals, [l/mol·sec]

Misra, G. S., Hafeez, A., and Sharma, K. S., *Makromol. Chem.*, **51**, 123 (1962).

**Bulk polymerization**

Initiator: benzoyl peroxide

Temperature: 60°C

$$k_t/k_p^2 = 710 \pm 115$$

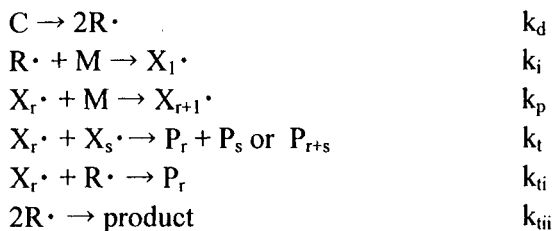
 $k_t$ : termination rate constant, [l/mol·sec] $k_p$ : propagation rate constant, [l/mol·sec]May, J. A. and Smith, W. B., *J. Phys. Chem.*, **72**, 216 (1968).

© 1968 American Chemical Society.

**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO)

Temperature: 60°C



C: initiator,  $R\cdot$ : primary radical, M: monomer,  $X_r\cdot$ : growing polymer radical containing r monomer units,  $P_r$ : dead polymer containing r monomer units.

$$k_{ti}/k_i k_p = 1.36 \times 10^4 \text{ for AIBN}$$

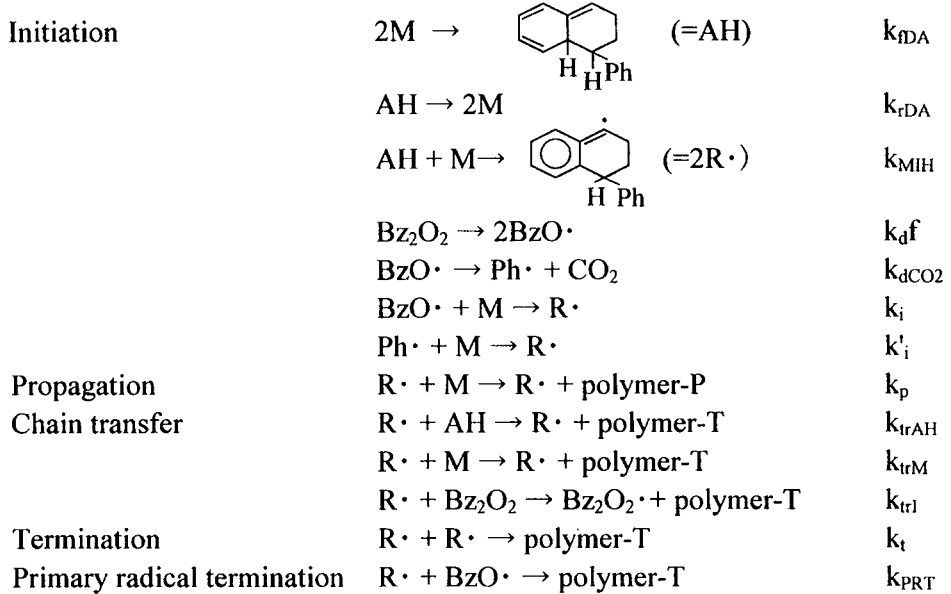
$$k_{tiii}/k_i k_p = 1.23 \times 10^3 \text{ for BPO}$$

 $k_d$ : decomposition rate constant, [1/sec] $k_i$ : initiation rate constant, [l/mol·sec] $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec] $k_{ti}$ : rate constant for termination by primary radical, [l/mol·sec] $k_{tiii}$ : rate constant for reaction between primary radicals, [l/mol·sec]Ito, K. and Matsuda, T., *Bull. Chem. Soc. Japan*, **42**, 1758 (1969).

**Bulk polymerization**

Initiator: benzoyl peroxide

Temperature: 60°C



$$R_{ith} = 2k_{MIH}[AH][M] = 2k_{ith}[M]^3$$

$$R_i = 2k_{df}[I]$$

$$R_p = d[M]/dt = k_p(R_i + R_{ith})^{1/2}[M]/(2k_t)^{1/2}$$

$$1/\bar{P}_n = k_t^{1/2}(k_{df}[I] + k_{MIH}[AH][M])^{1/2}/k_p[M] + k_{trM}/k_p +$$

$$k_{trAH}[AH]/k_p[M] + k_{trI}[I]/k_p[M] + k_{trI}[I\cdot]/k_p[M]$$

$$[AH] = k_{fDA}[M]^2 / \{k_{rDA} + k_{MIH}[M] + k_{trAH}(R_{ith} + R_i)^{1/2}/(2k_t)^{1/2}\}$$

$$k_{fDA} = 1 \times 10^{-9} \text{ [l/mol}\cdot\text{sec]}$$

$$k_{rDA} = 1.3 \times 10^{-4} \text{ [1/sec]}$$

$$k_{MIH} = 1 \times 10^{-8} \text{ [l/mol}\cdot\text{sec]}$$

$$k_{df} = 2 \times 10^{-6} \text{ [1/sec]}$$

$$k_{dCO_2} = 4.8 \times 10^3 \text{ [1/sec]}$$

$$k_i = 1.2 \times 10^4 \text{ [l/mol}\cdot\text{sec]}$$

$$k'_i = 1 \times 10^5 \text{ [l/mol}\cdot\text{sec]}$$

$$k_p = 1.45 \times 10^2 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{trAH} = 1.5 \times 10^2 \text{ [l/mol} \cdot \text{sec]}$$

$$k_{trM} = 1 \times 10^{-3} \text{ [l/mol} \cdot \text{sec]}$$

$$k_{trI} = 8 \text{ [l/mol} \cdot \text{sec]}$$

$$k_i = 1.7 \times 10^7 \text{ [l/mol} \cdot \text{sec]}$$

$$k_{PRT} = 6 \times 10^9 \text{ [l/mol} \cdot \text{sec]}$$

$R_{iTh}$ : rate of thermal initiation, [g-mol/l·sec]

$R_i$  rate of initiation by initiator, [g-mol/l·sec]

$R_p$ : rate of polymerization including both thermal initiation and initiator-initiation, [g-mol/l·sec]

$\bar{P}_n$ : number-average degrees of polymerization, [-]

[M]: monomer concentration, [g-mol/l]

[AH]: concentration of AH, [g-mol/l]

[I]: concentration of initiator, [g-mol/l]

[I·]: concentration of primary radical, [g-mol/l]

Pryor, W. A. and Coco. J. H., *Macromolecules*, **3**, 500 (1970).

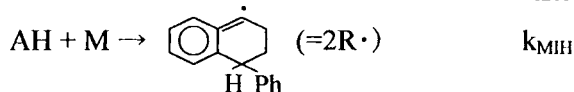
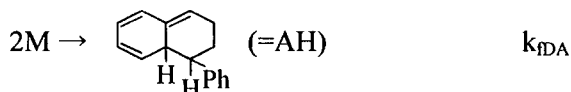
© 1970 American Chemical Society.

### Bulk polymerization

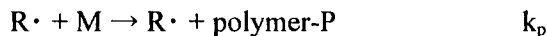
Initiator: azobisisobutyronitrile

Temperature: 60°C

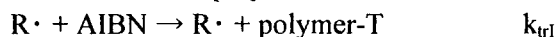
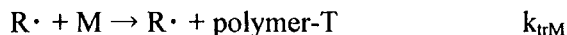
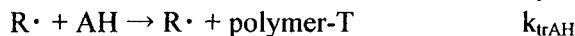
Initiation

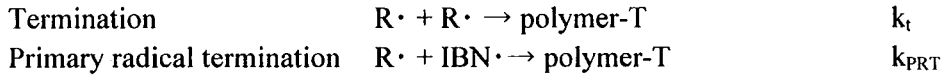


Propagation



Chain transfer





$$R_{\text{ith}}=2k_{\text{MIH}}[\text{AH}][\text{M}]=2k_{\text{ith}}[\text{M}]^3$$

$$R_i=2k_d f [\text{I}]$$

$$R_p=d[\text{M}]/dt=k_p(R_i+R_{\text{ith}})^{1/2}[\text{M}]/(2k_t)^{1/2}$$

$$1/\bar{P}_n=k_t^{1/2}(k_d f [\text{I}]+k_{\text{MIH}}[\text{AH}][\text{M}])^{1/2}/k_p[\text{M}]+k_{\text{trM}}/k_p+$$

$$k_{\text{trAH}}[\text{AH}]/k_p[\text{M}]+k_{\text{trI}}[\text{I}]/k_p[\text{M}]+k_{\text{trI}}[\text{I}\cdot]/k_p[\text{M}]$$

$$[\text{AH}]=k_{\text{fDA}}[\text{M}]^2/\{k_{\text{rDA}}+k_{\text{MIH}}[\text{M}]+k_{\text{trAH}}(R_{\text{ith}}+R_i)^{1/2}/(2k_t)^{1/2}\}$$

$$k_{\text{fDA}}=1 \times 10^{-9} \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{rDA}}=1.3 \times 10^{-4} \text{ [1/sec]}$$

$$k_{\text{MIH}}=1 \times 10^{-8} \text{ [l/mol}\cdot\text{sec]}$$

$$k_d f=6 \times 10^{-6} \text{ [1/sec]}$$

$$k_i=3 \times 10^3 \text{ [l/mol}\cdot\text{sec]}$$

$$k_p=1.45 \times 10^2 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{trAH}}=1.5 \times 10^2 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{trM}}=1 \times 10^{-3} \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{trI}}=5 \text{ [l/mol}\cdot\text{sec]}$$

$$k_t=1.7 \times 10^7 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{PRT}}=8 \times 10^9 \text{ [l/mol}\cdot\text{sec]}$$

$R_{\text{ith}}$ : rate of thermal initiation, [g-mol/l·sec]

$R_i$ : rate of initiation by initiator, [g-mol/l·sec]

$R_p$ : rate of polymerization including both thermal initiation and initiator-initiation, [g-mol/l·sec]

$\bar{P}_n$ : number-average degrees of polymerization, [-]

[M]: monomer concentration, [g-mol/l]

[AH]: concentration of AH, [g-mol/l]

[I]: concentration of initiator, [g-mol/l]

[I·]: concentration of primary radical, [g-mol/l]

Pryor, W. A. and Coco, J. H., *Macromolecules*, **3**, 500 (1970).

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**Bulk polymerization**

Initiator: benzoyl peroxide

Temperature: 50–90°C

$$d[M]/dt = -k_p[M][R^*]$$

$$k_p = 2.4 \times 10^8 \exp\{(-9000 \pm 400 \text{ cal})/RT\}$$

 $k_p$ : propagation rate constant, [l/mol·sec]

[M]: concentration of monomer, [mol/l]

[R\*]: concentration of free radicals, [mol/l]

Bresler, S. E., Kazbekov, E.N., Fomichev, V. N., and Shadrin, V. N., *Makromol. Chem.*, **157**, 167 (1972).

**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 45°C

Maximum conversion: close to 100%

$$[M][C]^{1/2}/R_p = (k_t/fk_dk_p^2)^{1/2} + k_{ti}[C]^{1/2}/k_i k_p [M]$$

x	$k_t/fk_p^2$ [mol·sec/l]	f	$k_{ti}/k_i k_p \times 10^{-4}$ [mol·sec/l]
0	3,730	0.45	0
0.2	2,270	0.45	5
0.3	1,180	0.45	30
0.4	567	0.39	31
0.5	167	0.3	26
0.6	26.8	–	10
0.7	5.18	–	4
0.8	1.5	–	0.9
0.9	0.9	–	0.3

 $R_p$ : polymerization rate, [mol/l·sec]

[M]: monomer concentration, [mol/l]

[C]: initiator concentration, [mol/l]

x: conversion, [-]

f: initiator efficiency, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{t1}$ : rate constant of primary radical termination, [l/mol·sec]

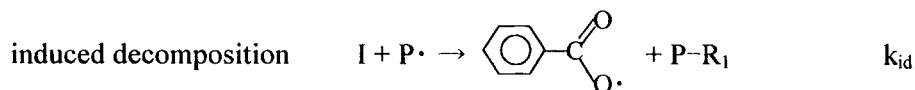
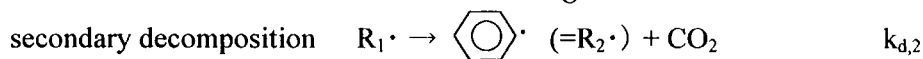
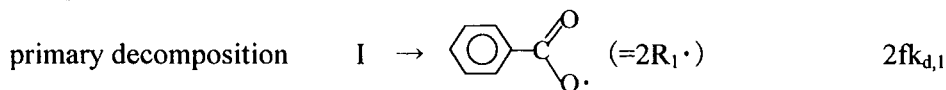
Ito, K., *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 401 (1975). Copyright © 1975 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Bulk polymerization

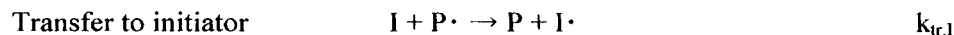
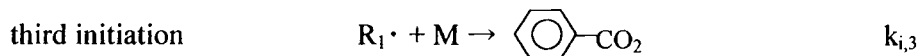
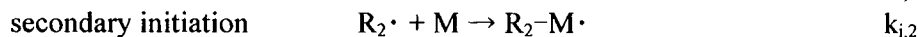
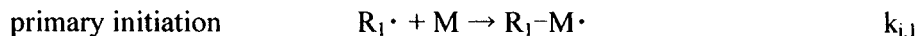
Initiator: benzoyl peroxide

Temperature: 30–80°C

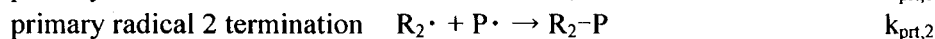
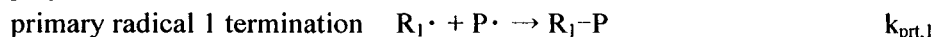
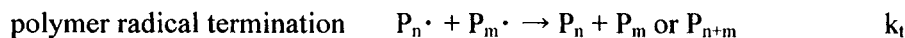
#### Decomposition



#### Initiation



#### Termination



$$\ln(2fk_{d,1})=26.39-107.6 \text{ (kJ/mol)/RT}$$

$$\ln(k_{id}/k_p)=4.11-19.27 \text{ (kJ/mol)/RT}$$

$$\ln(k_{prt,1}/k_{i,1}k_p)=-31.58+88.65 \text{ (kJ/mol)/RT}$$

$$\ln(k_{d,2}/k_{i,1})=-13.30+38.0 \text{ (kJ/mol)/RT}$$

$$\ln(k_{i,3}/k_{i,1})=-18.39+37.78 \text{ (kJ/mol)/RT}$$

$k_{d,1}$ : primary decomposition rate constant, [l/sec]

$k_{d,2}$ : secondary decomposition rate constant, [l/sec]

$k_{id}$ : induced decomposition rate constant, [l/mol·sec]

$k_{i,1}$ : primary initiation rate constant, [l/mol·sec]

$k_{i,2}$ : secondary initiation rate constant, [l/mol·sec]

$k_{i,3}$ : third initiation rate constant, [l/mol·sec]

$k_{tr,1}$ : transfer rate constant to initiator, [l/mol·sec]

$k_t$ : polymer radical termination rate constant, [l/mol·sec]

$k_{prt,1}$ : primary radical 1 termination rate constant, [l/mol·sec]

$k_{prt,2}$ : primary radical 2 termination rate constant, [l/mol·sec]

Berger, K. C., Deb, P. C., and Meyerhoff, G., *Macromolecules*, **10**, 1075 (1977).

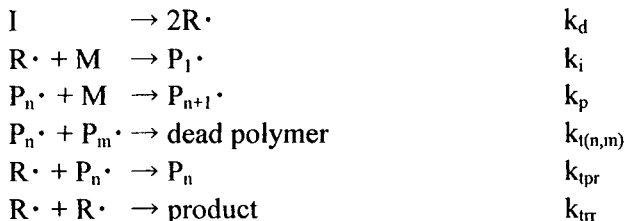
© 1977 American Chemical Society.

### Bulk polymerization

Initiator: 2,2'-azobisisobutyronitrile

Transfer agent: 1-butanethiol

Temperature: 50–70°C



I: initiator, M: monomer,  $R\cdot$ : primary free radical,  $P_n\cdot$ : growing polymer radical containing n monomer units,  $P_n$ : dead polymer containing n monomer units.

$$k_{tpr}/k_p k_i = 5.408 \times 10^{-5} \exp(12915 \text{ cal/RT})$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tpr}$ : rate constant of termination reaction with primary radical, [l/mol·sec]

$k_{trr}$ : rate constant of reaction between primary radicals, [l/mol·sec]

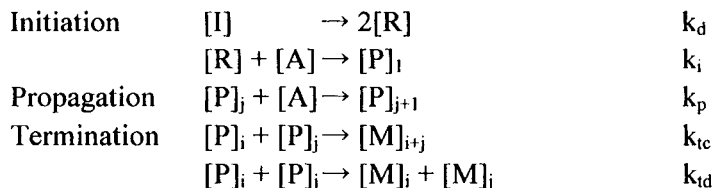
$k_{t(n,m)}$ : termination rate constant, [l/mol·sec]

Mahabadi, H. K. and O'Driscoll, K. F., *Makromol. Chem.*, **178**, 2629 (1977).

### Bulk polymerization

Initiator: benzoyl peroxide

Temperature: 60°C



[I]: initiator, [R]: primary free radical, [A]: monomer, [P]<sub>j</sub>: growing polymer radical with j units, [M]<sub>j</sub>: dead polymer with j units.

$$k_t = k_{tc} + k_{td} = 2.94 \times 10^7$$

$$k_p = 187.1$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : rate constant for termination by combination, [l/mol·sec]

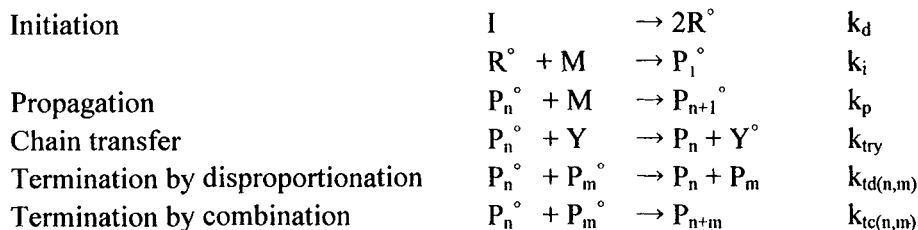
$k_{td}$ : rate constant for termination by disproportionation, [l/mol·sec]

Kuo, J. F. and Chen, C. Y., *Polym. J.*, **13**, 453 (1981).

**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 30°C



I: initiator, M: monomer,  $R^\circ$ : primary free radical,  $P_n^\circ$ : growing polymer radical containing n monomer units,  $P_n$ : dead polymer containing n monomer units, Y: chain transfer agent such as monomer or initiator.

$$k_{t(n,m)} = 1.97 \times 10^8 (nm)^{-0.12}$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{try}$ : transfer rate constant to Y, [l/mol·sec]

$k_{tc(n,m)}$ : rate constant for termination by combination, [l/mol·sec]

$k_{td(n,m)}$ : rate constant for termination by disproportionation, [l/mol·sec]

$k_{t(n,m)}$ : termination rate constant ( $=k_{tc(n,m)}+k_{td(n,m)}$ ), [l/mol·sec]

Mahabadi, H. K., *Macromolecules*, **18**, 1319 (1985).

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**Bulk polymerization**

Initiator: dimethyl 2,2'-azobisisobutyrate

Temperature: 70°C

$$k_p = 480 \pm 10$$

$k_p$ : propagation rate constant, [l/mol·sec]

Yamada, B., Kageoka, M., and Otsu, T., *Polym. Bull.*, **28**, 75 (1992).

**Bulk and photo-induced bulk polymerization**

Initiator: 1,1'-azobis-1-cyanocyclohexane (ACN), 2,2'-azobis-2,4-dimethylvaleronitrile (AVN), methyl 2,2'-azobisisobutyrate (MAIB), or t-butyl peroxide (TBP)

Temperature: 0–130°C

Temperature [°C]	Initiator	[I] [mol/l]	$k_d \times 10^5$ [1/sec]
0	ACN/UV <sup>(1)</sup>	0.05	4.00
50	AVN	0.5	2.05
70	MAIB	0.2	3.20
100	MAIB	0.1	108
130	TBP	0.5	2.92

<sup>(1)</sup>Photo-induced polymerization

Temperature [°C]	Conversion range [%]	$k_p$ [l/mol·sec]
0	0–6	12.3
50	0–35	256
70	0–85	481
100	0–40	1620
130	0–50	3350

$$k_p = 5.50 \times 10^8 \exp(-39.7 \text{ kJ/RT})$$

Temperature [°C]	$k_t \times 10^{-8}$ [l/mol·sec]
0	0.704
50	1.90
70	1.32
100	4.43
130	6.90

$$E_t = 15.6$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$E_t$ : activation energy of termination reaction, [kJ/mol]

[I]: concentration of initiator, [mol/l]

Yamada, B., Kageoka, M., and Otsu, T., *Polym. Bull.*, **29**, 385 (1992).

### Emulsion polymerization

Ingredients: water, potassium persulfate, stearic acid, and styrene

Emulsifier: stearic acid

Initiator: potassium persulfate

Temperature: 40–60°C

$$-d[C_8H_8]/dt = k[cat]^{1/2}$$

Activation energy for  $k = 18500 \pm 500$  [cal/mol]

$[C_8H_8]$ : concentration of monomer, [mol/l]

[cat]: concentration of initiator, [mol/l]

Price, C. C. and Adams, C. E., *J. Am. Chem. Soc.*, **67**, 1674 (1945).

© 1945 American Chemical Society.

**Emulsion polymerization**

Ingredients: water, sodium oleate, potassium persulfate, dodecyl mercaptan, and styrene

Emulsifier: sodium oleate and dodecyl mercaptan

Initiator: potassium persulfate

Temperature: 35–50°C

$$-dC_m/dt = kC_m^{3/2}$$

Temperature [°C]	k [1/sec]
35.0	0.192
42.5	0.304
50.0	0.907

Activation energy of k=22500 [cal/mol]

$C_m$ : concentration of monomer in the polymer, [g/g]

Corrin, M. L., *J. Polym. Sci.*, **2**, 257 (1947). Copyright © 1947 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Emulsion polymerization**

Ingredients: water, soap, potassium persulfate, and styrene

Emulsifier: soap

Initiator: potassium persulfate

Temperature: 30–60°C



M: monomer,  $M_n \cdot$ : growing polymer radical containing n monomer units.

$$k_p = 3.5 \times 10^{10} \exp(-11700 \text{ cal}/RT)$$

$$k_p/k_t = Pr/m = 1.3 \times 10^{-6} \text{ at } 60^\circ\text{C}$$

P: degree of polymerization, [-]

m: number of monomer, [-]

r: number of free radicals present, [-]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Smith, W. V., *J. Am. Chem. Soc.*, **70**, 3695 (1948). © 1948 American Chemical Society.



**Emulsion polymerization**

Ingredients: (1) water, soap, potassium persulfate, sodium sulfate, and styrene  
 (2) water, soap, cumene hydroperoxide, triethylenetetramine, versene, potassium chloride, and styrene

Emulsifier: soap

Initiator: cumene hydroperoxide-triethylenetetramine (CHP-TETA) and potassium persulfate

Temperature: 5°C and 40°C

Maximum conversion: 60%

Initiator	Temperature [°C]	$k_p$ [l/mol·sec]	Temperature [°C]	Activation energy [kcal/mol]
Potassium persulfate	40	139	40-50	6.5
HP-TETA	5	22	5-15 5-15	8.7 7.1

With potassium persulfate:  $k_p=4.1 \times 10^7 \exp(-7400 \text{ cal/RT})$

With CHP-TETA:  $k_p=3.3 \times 10^7 \exp(-8400 \text{ cal/RT})$

$k_p$ : propagation rate constant, [l/mol·sec]

Morton, M., Salatiello, P. P., and Landfield, H., *J. Polym. Sci.*, **8**, 279 (1952).

Copyright © 1952 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Emulsion polymerization**

Ingredients: water, sodium lauryl sulfate, sodium hydrogen phosphate, potassium persulfate, and styrene

Emulsifier: sodium lauryl sulfate

Buffer: sodium hydrogen phosphate

Initiator: potassium persulfate

Temperature: 30.5-70.9°C

$$-dM/dt=k_pM(N/2)$$

Temperature [°C]	$k_p$ [l/mol·sec]
30.5	51.0
40.5	120.5
51.0	311.1
50.2	300.3
50.2	291.0
70.9	357.9

$$k_p = 2.24 \times 10^{14} \exp(-17570 \text{ cal}/RT)$$

M: monomer concentration in polymerization particle, [mol/l]

N: number of latex particles/ml of aqueous phase in the emulsion, [number/ml]

$k_p$ : propagation rate constant, [l/mol·sec]

Paoletti, K. P. and Billmeyer, F. W., *J. Polym. Sci.*, **A2**, 2049 (1964).

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### Emulsion polymerization

Ingredient: potassium persulfate, nonionic octyl phenoxyethyl surfactant, KOH,  
sodium lauryl sulfate

Initiator: potassium persulfate

Temperature: 60°C

Maximum conversion: 91.0%

$$R_{pp} = k_p n [M]$$

$$n = 1 / (2 \times 6.02 \times 10^{23})$$

$$[M] = 905$$

$$k_p = 282$$

$k_p$ : propagation rate constant, [l/mol·sec]

n: number of free radicals per particles, [mol/particle]

[M]: monomer concentration within the particles, [g/l]

$R_{pp}$ : rate of polymerization per particle, [g/particle · sec]

Grancio, M. R. and Williams, D. J., *J. Polym. Sci. A-1*, **8**, 2617 (1970).

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### Emulsion polymerization

Ingredients: water, octylphenoxyethyl surfactant, sodium lauryl sulfate, potassium persulfate, and styrene

Emulsifier: octylphenoxyethyl surfactant and sodium lauryl sulfate

Initiator: potassium persulfate

Temperature: 60°C

Maximum conversion: 70%

$$k_t = (k_t)_0 A_0 \exp\{-(A_1 X + A_2 X^2 + A_3 X^3 + A_4 X^4)\}$$

$$A_0 = 1.203, A_1 = 4.681, A_2 = -33.39, A_3 = 96.56, A_4 = 56.30, (k_t)_0 = 5 \times 10^7$$

$k_t$ : termination rate constant, [l/mol · sec]

$(k_t)_0$ : termination rate constant in pure styrene, [l/mol · sec]

X: conversion of monomer, [-]

Friis, N. and Hamielec, A. E., *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 3321 (1973).

Copyright © 1973 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Emulsion polymerization

Ingredients: water, sodium laurylsulfate, potassium persulfate, and styrene

Emulsifier: sodium laurylsulfate

Initiator: potassium persulfate

Temperature: 40–60°C

$$-d([M]V_p)/dt = k_p[M]/2N_{Av}$$

$$V_p = V_{p\infty}(1-\epsilon x)/(1-\epsilon)$$

$$[M]_0(1-x)/(1-\epsilon x) = [M]$$

$$V_{p\infty} dx/(1-\epsilon) dt = k_p(1-x)/2N_{Av}(1-\epsilon x)$$

$$\ln(k_p) = 16.6 - 3500/T$$

$$k_p = 156 \text{ at } 50^\circ\text{C}$$

[M]: concentration of monomer, [mol/l]

[M]<sub>0</sub>: initial concentration of monomer, [mol/l]

V<sub>p</sub>: volume of a latex particle, [cm<sup>3</sup>]

V<sub>p∞</sub>: volume of a latex particle at complete conversion, [cm<sup>3</sup>]

V<sub>p0</sub>: volume of a latex particle at zero conversion, [cm<sup>3</sup>]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

N<sub>Av</sub>: Avogadro's number

ε: volume shrinkage factor  $\epsilon = (V_{p0} - V_{p\infty}) / V_{p0}$

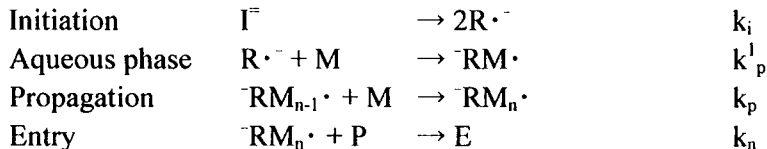
x: fractional conversion, [-]

Soh, S. K., *J. Appl. Polym. Sci.*, **25**, 2993 (1980). Copyright © 1980 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Emulsion polymerization

Initiator: peroxydisulfate anion

Temperature: 50°C



$I^-$ : initiator,  $R^{\cdot-}$ : primary radical, M: monomer,  $\bar{R}M_n^{\cdot}$ : polymer radical with n units, P: a latex particle, E: entry into particle.

$$k_p = 250, \quad k_i = 7 \times 10^7$$

k<sub>i</sub>: decomposition rate constant of initiator, [1/sec]

k<sub>p</sub><sup>1</sup>: initiation rate constant, [dm<sup>3</sup>/mol·sec]

k<sub>p</sub>: propagation rate constant, [dm<sup>3</sup>/mol·sec]

k<sub>t</sub>: termination rate constant, [dm<sup>3</sup>/mol·sec]

k<sub>n</sub>: rate constant for entry of an oligomeric radical ion with n monomer units into a particle, [dm<sup>3</sup>/mol·sec].

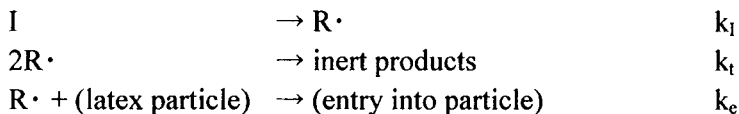
Hawkett, B. S., Napper, D. H., and Gilbert, R. G., *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 3173 (1981). Copyright © 1981 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Emulsion polymerization**

Surfactant: Aerosol MA 80 (sodium dioctyl sulposuccinate)

Initiator: potassium persulphate ( $K_2S_2O_8$ ), hydrogen peroxide and iron (II) sulphate ( $H_2O_2/Fe^{2+}$ ), and 2,2'-azobis(2-amidino-propane)hydrochloride (V-50)

Temperature: 50°C

I: initiator,  $R\cdot$ : radical.

$$\begin{aligned}
 \rho_I &= k_e [R\cdot] \\
 \rho_I &= \gamma \{ (N_c^2/N_A^2 + 4\beta[I])^{1/2} - N_c/N_A \} \\
 \beta &= k_t k_I / k_e^2, \quad \gamma = k_e^2 / 2k_t
 \end{aligned}$$

Initiator	V-50	$k_2S_2O_8$	$H_2O_2/Fe^{2+}$
$k_d$ , [1/sec]	$1 \times 10^{-5}$	$2.4 \times 10^{-6}$	$4 \times 10^{-5}$
$\beta$ , [l/mol]	$0.64 \times 10^{-11}$	$0.20 \times 10^{-10}$	$(0.21 \times 10^{-10})^{(1)}$
$\gamma$ , [l/mol·sec]	$0.10 \times 10^5$	$0.14 \times 10^5$	$0.23 \times 10^5$
$k_I/k_d$	0.013	0.23	$(0.024)^{(1)}$

<sup>(1)</sup>For  $H_2O_2/Fe^{2+}$ ,  $\beta$  value obtained assuming  $[I]=[Fe^{2+}]$ , and thus subject to some uncertainty.

$\rho_I$ : rate of free radicals captured by latex particles, [ml/sec]

$k_d$ : decomposition rate constant per free radical, [1/sec]

$k_I$ : initiation rate constant, [1/sec]

$k_t$ : bimolecular termination rate constant, [l/mol·sec]

$k_e$ : entry rate constant of oligomeric free radicals into the particles, [l/mol·sec]

$N_c$ : the number of particles per unit volume, [number/l]

$N_A$ : Avogadro's constant

[I]: initiator concentration, [mol/l]

Penboss, I. A., Napper, D. H., and Gilbert, R. G., *J. Chem. Soc., Faraday Trans. I*, **79**, 1257 (1983).

**Emulsion polymerization**

Ingredients: water, VERSENEX 80, Aerosol MA, sodium persulfate, and styrene

Initiator: sodium persulfate

Temperature: 70–90°C

		Rate
Persulfate decomposition	$I_2 \rightarrow 2I\cdot$	$\rho_I$
Aqueous-phase initiation and propagation	$I\cdot + M \rightarrow R\cdot$	
Capture of free radicals by latex particles	$R\cdot + L \rightarrow P\cdot$	$\rho$
Aqueous phase termination	$2R\cdot \rightarrow P_{aq}$	$R_t$

$I_2$ : initiator,  $I\cdot$ : primary free radical,  $M$ : styrene dissolved in aqueous phase,  $P\cdot$ : polymer radical,  $L$ : latex,  $P_{aq}$ : aqueous phase.

$$\begin{aligned}\rho_I &= 2k_I C_I V_{aq} \\ \rho &= k_c C_N D_p^J C_R V_{aq} \\ R_t &= k_{wt} C_R^2 V_{aq} \\ \rho_I &= \rho + 2R_t \\ C_N &= N / (N_A V_{aq}) \\ f &= \rho / \rho_I\end{aligned}$$

$$k_I = 4.583 \times 10^{16} \exp(-16708.6 \text{ cal/T})$$

$$k_p = 2.539 \times 10^5 \exp(-4235 \text{ cal/RT})$$

$$k_t = k_{t0} \exp(-2(BX + CX^2 + DX^3))$$

$$k_{t0} = 1.295 \times 10^9 \exp(-2370 \text{ cal/RT})$$

$$J = 2$$

$$k_c / k_{wt}^{1/2} = 2.19 \times 10^{15}$$

$$B = 0.457, C = 3.73, D = -0.1576 \text{ at } 90^\circ\text{C}$$

$R_t$ : aqueous-phase free radical termination rate, [mol/sec]

$\rho_I$ : rate of free radical generation, [mol/sec]

$\rho$ : rate of free radicals captured by latex particles, [mol/sec]

$k_I$ : initiator decomposition rate constant, [1/sec]

$k_p$ : monomer propagation rate constant, [l/mol·sec]

$k_t$ : polymer-phase termination rate constant, [l/mol·sec]

$k_{t0}$ : polymer-phase termination rate constant at low conversion, [l/mol·sec]

$k_c$ : free radical capture rate constant, [ $I^{3-J}/\text{mol} \cdot \text{sec}$ ]

$k_{wt}$ : aqueous-phase termination rate constant, [ $1/\text{mol} \cdot \text{sec}$ ]

$D_p$ : latex diameter, [dm]

$J$ : constant represents the dependence of  $\rho$  on  $D_p$ , [-],  $J=1$  for diffusion;  $J=2$  for collision

$f$ : free radical capture efficiency, [-]

$C_I$ : initiator concentration in aqueous-phase, [mol/l]

$C_R$ : free radical concentration in aqueous-phase, [mol/l]

$C_N$ : latex particle concentration in aqueous-phase, [mol/l]

$V_{aq}$ : volume of aqueous phase, [l]

$N$ : total number of latex particle inside reactor, [-]

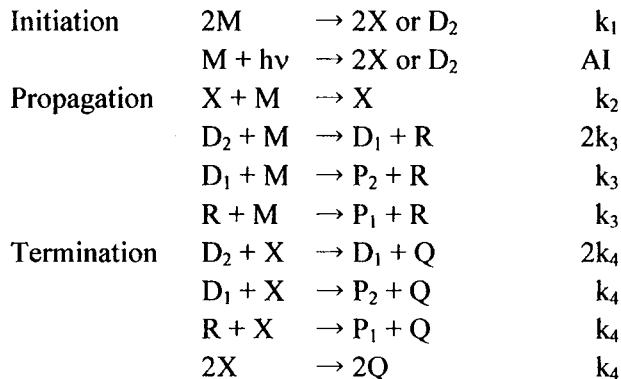
$N_A$ : Avogadro's number,  $6.023 \times 10^{23}$ , [number/mol]

Kao, C. I., Gundlach, D. P., and Nelsen, R. T., *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3499 (1984). Copyright © 1984 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

## Photo-induced bulk and solution polymerization

### (1) Photo-induced bulk polymerization

Temperature: 0–25°C



$X$ : active center,  $Q$ : dead center,  $D_2$ : initial polymer growing at both ends,  $D_1$ : polymer growing at one end,  $R$ : growing transfer polymer,  $P_1$ : dead transfer polymer,  $P_2$ : dead initial polymer.

Temperature [°C]	$k_1$ [l/mol·sec]	$k_2$ [l/mol·sec]	$k_3$ [l/mol·sec]	$k_4$ [l/mol·sec]
0	$4.51 \times 10^{-18}$	6.91	$7.47 \times 10^{-5}$	$1.83 \times 10^6$
25	$1.32 \times 10^{-15}$	18.7	$6.68 \times 10^{-4}$	$2.79 \times 10^6$

$$k_1 = 1.23 \times 10^{12} \exp(-37.0 \pm 2 \text{ kcal/RT})$$

$$k_2 = 1.02 \times 10^6 \exp(-6.5 \pm 1 \text{ kcal/RT})$$

$$k_3 = 1.50 \times 10^7 \exp(-14.2 \pm 1 \text{ kcal/RT})$$

$$k_4 = 3.07 \times 10^8 \exp(-2.8 \pm 1 \text{ kcal/RT})$$

## (2) Photo-induced solution polymerization

Solvent:  $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CH}_2\text{ClCH}_2\text{Cl}$ ,  $\text{C}_2\text{H}_4\text{Br}_2$ , toluene,  
ethylbenzene, benzene, n-heptane, and tetrachloroethane

Temperature: 60–120°C

	$\text{CCl}_4$			$\text{CBr}_4$		$\text{CH}_2\text{ClCH}_2\text{Cl}$	
	60°C	80°C	100°C	60°C	80°C	60°C	80°C
$k'_3$	0.804	1.94	4.54	159	282	$1.904 \times 10^{-3}$	$1.163 \times 10^{-2}$
E		10.7			6.7		21.2
A		$7.60 \times 10^6$			$3.92 \times 10^6$		$1.26 \times 10^{11}$

	$\text{C}_2\text{H}_4\text{Br}_2$		Toluene		
	80°C	100°C	80°C	100°C	120°C
$k'_3$	$5 \times 10^{-2}$	0.1112	$4.15 \times 10^{-3}$	$1.70 \times 10^{-2}$	$5.89 \times 10^{-2}$
E		16.2		18.2	
A		$2.99 \times 10^8$		$6.68 \times 10^8$	



	Ethylbenzene			Benzene	
	80°C	100°C	120°C	80°C	100°C
$k'_3$	$1.43 \times 10^{-2}$	$4.06 \times 10^{-2}$	$1.41 \times 10^{-1}$	$1.57 \times 10^{-3}$	$6.67 \times 10^{-3}$
E		18.2			19.1
A		$1.60 \times 10^9$			$8.79 \times 10^8$

	n-Heptane	Tetrachloroethane
	100°C	100°C
$k'_3$	$3.89 \times 10^{-2}$	0.300

$k_1$ : initiation rate constant, [l/mol·sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : transfer rate constant, [l/mol·sec]

$k_4$ : termination rate constant, [l/mol·sec]

$k'_3$ : chain transfer rate constant to solvent, [l/mol·sec]

E: activation energy for  $k'_3$ , [kcal/mol]

A: frequency factor for  $k'_3$ , [l/mol·sec]

Bamford, C. H. and Dewar, M. J. S., *Faraday Soc. Discussions*, **2**, 310 (1947).

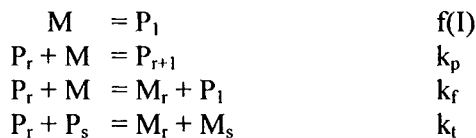
### Photo-induced bulk polymerization

Sensitizer: benzoyl peroxide

Temperature: 25–30°C

Pressure: vacuum

Maximum conversion: about 32%



M: monomer,  $M_i$ : dead polymer containing  $i$  units of monomer,  $P_i$ : polymer radical containing  $i$  units of monomer.

$$-d[M]/dt=R=k_p[M]f(I)^{1/2}/k_t^{1/2}$$

$$1/\bar{P}=k_f/k_p+k_t/(k_p^2[M]^2)$$

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]	$k_f$ [l/mol·sec]
25	$39.5 \pm 5$	$(7.9 \pm 2.0) \times 10^6$	$(1.1 \pm 0.5) \times 10^{-3}$
30	51.9	$1.05 \times 10^7$	$1.66 \times 10^{-3}$

$f(I)$ : rate of initiation, [mol/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_f$ : transfer rate constant to monomer, [l/mol·sec]

$k_t$ : disproportionation termination rate constant, [l/mol·sec]

$[M]$ : concentration of monomer, [mol/l]

$R$ : overall rate of polymerization, [mol/l·sec]

$\bar{P}$ : mean degrees of polymerization, [-]

Melville, H. W. and Valentine, L., *Trans. Faraday Soc.*, **46**, 210 (1950).

### Photo-induced bulk polymerization

Temperature: 0–55°C

Maximum conversion: lower than 1%

		Rate
Initiation	$M = P_1$	I
Propagation	$P_n + M = P_{n+1}$	$k_p[P][M]$
Termination	$P_n + P_m = M_n + M_m$	$k_t[P]^2$
Transfer	$P_n + M = M_n + P_1$	$k_f[P][M]$

M: monomer,  $P_n$ : polymer radical containing  $n$  units of monomer,

$M_n$ : dead polymer containing  $n$  units of monomer.

$$1/\bar{P}=k_f/k_p+k_tR/(k_p^2[M]^2)$$

Temperature [°C]	$k_i$ [l/mol·sec]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]	$k_f$ [l/mol·sec]
15	$1.48 \times 10^{-16}$	29.2	$5.55 \times 10^6$	$5.70 \times 10^{-4}$
25	$1.34 \times 10^{-15}$	39.5	$5.96 \times 10^6$	$1.26 \times 10^{-3}$

$$k_i = 4.15 \times 10^{11} \exp(-36400 \text{ cal/RT})$$

$$k_p = 1.44 \times 10^6 \exp(-6300 \text{ cal/RT})$$

$$k_t = 1.43 \times 10^8 \exp(-1900 \text{ cal/RT})$$

$$k_f = 4.08 \times 10^7 \exp(-14400 \text{ cal/RT})$$

R: rate of monomer conversion, [mol/l·sec]

[M]: concentration of monomer, [mol/l]

$\bar{P}$ : average degree of polymerization, [-]

I: rate of initiation, [mol/l·sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_f$ : transfer rate constant to monomer, [l/mol·sec]

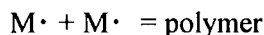
$k_t$ : disproportionation termination rate constant, [l/mol·sec]

Burnett, G. M., *Trans. Faraday Soc.*, **47**, 772 (1950).

### Photo-induced bulk polymerization

Sensitizer:  $\alpha$ -azobisisobutyronitrile and 2-azobispropane

Temperature: 10–60°C



Rate

$$k_p[M \cdot][M]$$

$$2k_t[M \cdot]^2$$

M: monomer,  $M \cdot$ : growing polymer radical.

$$-d[M]/dt = 2k_t[M \cdot]^2$$

$$k_p = 2.16 \times 10^7 \exp(-7700 \text{ cal/RT})$$

$$2k_t = 2.59 \times 10^9 \exp(-2370 \text{ cal/RT})$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

[M]: concentration of monomer, [mol/l]

$[M\cdot]$ : total concentration of growing radicals, [mol/l]

Matheson, M. S., Auer, E. E., Bevilacqua, E. B., and Hart, E. J., *J. Am. Chem. Soc.*, **73**, 1700 (1951). © 1951 American Chemical Society.

### Photo-induced bulk polymerization

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 15°C

$$k_p/k_t=6.8 \times 10^{-7}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Majury, T. G. and Melville, H. W., *Proc. Roy. Soc., London*, **A205**, 496 (1951).

### Photo-induced bulk polymerization

Sensitizer: benzoyl peroxide

Temperature: 15°C

$$k_p/k_t=2.0 \times 10^{-6}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Grassie, N. and Melville, H. W., *Proc. Roy. Soc., London*, **A207**, 285 (1951).

**Photo-induced bulk polymerization**

Sensitizer:  $\alpha$ -azobisisobutyronitrile (A), cumene hydroperoxide (C),  
tert-butylhydroperoxide (TB), and benzoyl peroxide (B)

Temperature: 60°C

$$R_p^2 = B_1 [\text{Cat}]$$

$$1/P_n = C_m + C_1 [\text{Cat}] / [M] + \alpha R_p$$

$$C_m = k_{tr}/k_p, C_1 = k_t/k_p, \alpha = (2k_{td} + k_{tc})/k_p^2 [M]^2$$

Sensitizer	$C_1 = k_t/k_p$	$B_1$ [mol/l·sec <sup>2</sup> ]
A	0	$5.19 \times 10^{-7}$
B	0.048	$1.21 \times 10^{-7}$
C	0.063	$2.49 \times 10^{-8}$
TB	0.035	$4.06 \times 10^{-9}$

$k_t$ : specific rate constant for disappearance of radical pairs by transfer to catalyst,  
[l/mol·sec]

$k_p$ : specific rate constant for propagation, [l/mol·sec]

$k_{tc}$ : specific rate constant for disappearance of radical pairs by combination,  
[l/mol·sec]

$k_{tr}$ : specific rate constant for disappearance of radical pairs by transfer to monomer,  
[l/mol·sec]

$k_{td}$ : specific rate constant for disappearance of radical pairs by disproportionation,  
[l/mol·sec]

$R_p$ : propagation rate, [mol/l·sec]

[Cat]: sensitizer concentration, [mol/l]

$P_n$ : number-average degree of polymerization, [-]

Johnson, D. H. and Tobolsky, A. V., *J. Am. Chem. Soc.*, **74**, 938 (1952).

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**Photo-induced bulk polymerization**

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 25°C

$$k_t/k_p=3 \times 10^{-5}$$

$$k_t/k_p^2=5000$$

$$k_{td}=0$$

$$k_t=k_{tc}+k_{td}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : transfer rate constant to monomer, [l/mol·sec]

$k_{tc}$ : rate constant of termination by combination, [l/mol·sec]

$k_{td}$ : rate constant of termination by disproportionation, [l/mol·sec]

Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polym. Sci.*, **12**, 449 (1954).

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**Photo-induced bulk polymerization**

Sensitizer: with or without 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 20–30°C

Conversion: 0–70%

$$d[M]/dt=k_p[R][M]$$

$$d[R]/dt=qI_{abs}+k_i[M]^2-k_t[R]^n$$

Conversion[%]	Temperature[°C]	n	$k_p/k_t$	$k_{tx}/k_{t0}^{(2)}$
0	20		$0.55 \times 10^{-6(1)}$	
	30	1.9–2.1	$2.36 \times 10^{-6}$	1
38 ± 1	30	1.9–2.1	$6.36 \times 10^{-4}$	$3.75 \times 10^{-3}$
43 ± 2	30		$2.56 \times 10^{-3}$	$9.22 \times 10^{-4}$
60 ± 2	30	1.7–1.8	$1.30 \times 10^{-2}$	$1.81 \times 10^{-4}$
70 ± 2	30	1.4–1.6	$1.37 \times 10^{-2}$	$1.71 \times 10^{-4}$

(1) AIBN was used as a photo-sensitizer in this experiment. No sensitizer was used in the others.

(2) The ratio of  $k_{tx}$  at x% conversion to  $k_{t0}$  at nearly 0% conversion.

$k_i$ : rate constant of thermal initiation, [l/mol·sec]

$k_t$ : rate constant of termination, [l/mol·sec]

$k_p$ : rate constant of propagation, [l/mol·sec]

$I_{\text{abs}}$ : absorbed light intensity

[M]: concentration of monomer, [mol/l]

[R]: concentration of total radical polymers, [mol/l]

Fujii, S., *Bull. Chem. Soc. Japan*, **27**, 216 (1954).

### Photo-induced bulk polymerization

Sensitizer: 2,2'-azobispropane

Temperature: 30°C

$$k_p/k_t = 2.02 \times 10^{-6}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

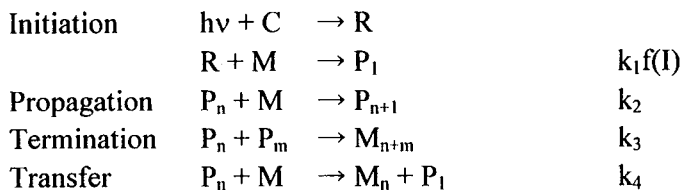
Mikami, H., *Nippon Kagaku Kaishi*, **77**, 196 (1956).

### Photo-induced bulk polymerization

Sensitizer: benzoylperoxide

Temperature: 30°C

Pressure: 1–3000 [kg/cm<sup>2</sup>]



M: monomer, C: sensitizer, R: free radical,  $P_n$ : growing polymer chain containing n units of monomer,  $M_n$ : dead polymer chain containing n units of monomer.

$$1/\bar{P} = k_4/k_2 + k_3 R / (2k_2^2 [M]^2)$$

Pressure [kg/cm <sup>2</sup> ]	k <sub>2</sub> [l/mol·sec]	k <sub>3</sub> [l/mol·sec]	k <sub>1</sub> f(I) [l/mol·sec]
1	72.5	6.65 × 10 <sup>7</sup>	19.2 × 10 <sup>-7</sup>
1000	108	3.25 × 10 <sup>7</sup>	9.9 × 10 <sup>-7</sup>
2000	206	3.05 × 10 <sup>7</sup>	9.8 × 10 <sup>-7</sup>
3000	400	2.54 × 10 <sup>7</sup>	10.5 × 10 <sup>-7</sup>

k<sub>1</sub>f(I): rate constant of initiation, [l/mol·sec]

k<sub>2</sub>: propagation rate constant, [l/mol·sec]

k<sub>3</sub>: termination rate constant of combination, [l/mol·sec]

k<sub>4</sub>: transfer rate constant to monomer, [l/mol·sec]

[M]: monomer concentration, [mol/l]

R: rate of polymerization, [mol/l·sec]

$\bar{P}$ : number-average degree of polymerization, [-]

Nicholson, A. E. and Norrish, R. G. W., *Faraday Soc. Discussions*, **22**, 104 (1956).

### Photo-induced bulk polymerization

Sensitizer: 2,2'-azobispropane

Temperature: 30°C

$$k_p/k_t = 2.02 \times 10^{-6}$$

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

Miyama, H., *Bull. Chem. Soc. Japan*, **29**, 711 (1956).



**Photo-induced bulk polymerization**

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 30–40°C

$$k_p/k_t = 1.09 \times 10^{-3} \exp(-3710 \text{ cal/RT})$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Miyama, H., *Bull. Chem. Soc. Japan*, **29**, 715 (1956).**Photo-induced solution and bulk polymerization**

Sensitizer: 2,2'-azobisisobutyronitrile

Solvent: bromobenzene, diethyl malonate, diethyl phthalate, and dinonyl phthalate

Temperature: 25°C

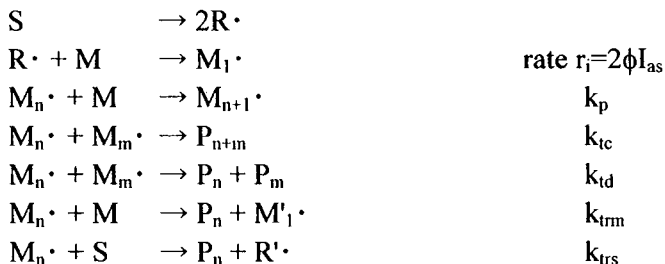
Solvent	vol%	$k_p$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
None		$35 \pm 7$	$1.9 \pm 0.4$
Bromobenzene	20	$35 \pm 5$	$1.9 \pm 0.3$
	50	$29 \pm 8$	$1.6 \pm 0.3$
Diethyl malonate	20	$29 \pm 7$	$1.5 \pm 0.4$
	20	$23 \pm 8$	$1.1 \pm 0.2$
Diethyl phthalate	50	$20 \pm 5$	$0.8 \pm 0.2$
	60	$27 \pm 4$	$0.31 \pm 0.04$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Burnett, G. M., Cameron, G. G., and Joiner, S. N., *Trans. Faraday Soc. I*, **69**, 322 (1973).

**Photo-induced bulk polymerization**

Sensitizer: benzoin and benzoin methyl ether

Temperature: 29.8°C



S: sensitizer, M: monomer,  $R\cdot$ : primary radicals formed from its decomposition,  $M_n\cdot$ : growing radicals containing n monomer units,  $P_n$ : dead polymer molecules containing n monomer units.

Sensitizer	$\phi^{1/2}k_p/k_t^{1/2}$ [(l/mol·sec) <sup>1/2</sup> ]
Benzoin	$1.605 \times 10^{-3}$
Benzoin methyl ether	$4.042 \times 10^{-3}$

$$k_p/k_t^{1/2} = 143 \exp(-2774/T)$$

$k_p$ : rate constant of propagation, [l/mol·sec]

$k_{tc}$ : rate constant of termination by combination, [l/mol·sec]

$k_{td}$ : rate constant of termination by disproportionation, [l/mol·sec]

$k_{trm}$ : rate constant of chain transfer to monomer, [l/mol·sec]

$k_{trs}$ : rate constant of chain transfer to sensitizer, [l/mol·sec]

$k_t = k_{tc} + k_{td}$ , [l/mol·sec]

$\phi$ : primary quantum yield

$I_{as}$ : rate of absorption of light by sensitizer

Mendiratta, S. K., Felder, R. M., and Hill, F. B., *AIChE Journal*, **21**, 1115 (1975).

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**Photo-induced bulk polymerization**

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 25°C

Conversion: 0.01–1.05%

			Rate
Initiator	C	$\xrightarrow{h\nu} 2R\cdot$	$\phi I_{\text{abs}}$
	C	$\rightarrow 2R\cdot$	$k_d[C]$
Propagation	$R\cdot + M$	$\rightarrow P_1\cdot$	$k_i[R\cdot][M]$
	$P_n\cdot + M$	$\rightarrow P_{n+1}\cdot$	$k_p[P_n\cdot][M]$
Transfer	$P_n\cdot + Y$	$\rightarrow P_n + R\cdot$	$k_{tr,Y}[P_n\cdot][Y]$
Termination	$P_n\cdot + P_m\cdot$	$\rightarrow P_{n+m}$	$k_{tc}[P_n\cdot][P_m\cdot]$
	$P_n\cdot + P_m\cdot$	$\rightarrow P_n + P_m$	$k_{td}[P_n\cdot][P_m\cdot]$

C: sensitizer, M: monomer,  $R\cdot$ : primary free radical,  $P_n\cdot$ : growing polymer radical containing n monomer units,  $P_n$ : dead polymer containing n monomer units, Y: chain transfer agent.

$$k_p = 74 \pm 5$$

$$k_t = (37 \pm 0.3) \times 10^6$$

$\phi I_{\text{abs}}$ : rate of photo-induced initiation, [l/mol·sec]

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tr,Y}$ : transfer rate constant to Y, [l/mol·sec]

$k_{tc}$ : rate constant of termination by combination, [l/mol·sec]

$k_{td}$ : rate constant of termination by disproportionation, [l/mol·sec]

[i]: concentration of species i, [mol/l]

O'Driscoll, K. F. and Mahabadi, H. K., *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 869 (1976). Copyright © 1976 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Photo-induced bulk polymerization**

Sensitizer: 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 15–30°C

Temperature [°C]	[AIBN] [mol/l]	$\bar{X}_n$	$k_p$ [l/mol·sec]	$\bar{k}_t \times 10^{-6}$ [l/mol·sec]
15	0.075	2705	48.7	32.4
20	0.045	2686	60.	34.6
25	0.03	2600	73.6	37
30	0.015	2770	89.4	39
30	0.02	2400	89.6	39.4
30	0.03	1650	89.8	44.2
30	0.045	1300	89.6	47
30	0.075	950	89.7	50
30	0.095	780	90.	53

$$k_p = 1.09 \times 10^7 \exp(-7051 \text{ cal/RT})$$

$$\bar{k}_t = 1.703 \times 10^9 \exp(-2268 \text{ cal/RT})$$

[AIBN]: concentration of AIBN, [mol/l]

 $k_p$ : propagation rate constant, [l/mol·sec] $\bar{k}_t$ : average rate constant of termination, [l/mol·sec] $\bar{X}_n$ : number-average degree of polymerization, [-]Mahabadi, H. K. and O'Driscoll, K. F., *J. Macromol. Sci.-Chem.*, **A11**, 967 (1977).

**Photo-induced bulk polymerization**

Sensitizer: benzoin and 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 25°C

Maximum conversion: less than 1.0%

$$R_p = (2f[I]k_d)^{1/2} (k_p/k_t)^{1/2} [M]$$

Sensitizer	[I] [mmol/l]	$k_p/k_t \times 10^{-7}$
Benzoin	0.88	10.4
Benzoin	1.23	11.7
AIBN	2.8	10.0

 $R_p$ : propagation rate, [mol/l·sec]

[M]: concentration of monomer, [mol/l]

[I]: concentration of initiator, [mol/l]

f: sensitizer efficiency, [-]

 $k_d$ : decomposition rate constant, [1/sec] $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Olaj, O. F., Bitai, I., and Gleixner, G., *Makromol. Chem.*, **186**, 2569 (1985).**Photo-induced bulk polymerization**

Sensitizer: benzoin

Temperature: 25°C

$$k_p^2/k_t = 8.9 \times 10^{-5}$$

$$k_p = 80$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Olaj, O. F. and Bitai, I., *Angew. Makromol. Chem.*, **155**, 177 (1987).

**Photo-induced bulk polymerization**

Sensitizer: benzoin

Temperature: 25–40°C

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t \times 10^{-8}$ [l/mol·sec]
25	89	1.32
40	161	1.50

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]

Olaj, O. F., Kremminger, P., and Schnoll-Bitai, I., *Makromol. Chem. Rapid Commun.*, **9**, 771 (1988).

**Photo-induced bulk and solution polymerization**

Photo source: laser

Sensitizer: 2,2'-azobisisobutyronitrile

Solvent: as shown in table

Temperature: 25°C

Initiator concentration [mol/l]	Additive	Monomer concentration [mol/l]	$k_p$ [l/mol·sec]
$10^{-3}, 5 \times 10^{-3}$		8.66	78
$10^{-2}$	EB	1.73–8.66	85
$10^{-3}$	EB	1.73–8.66	80–90
$5 \times 10^{-3}$	MEOH	6.93–8.66	84–91
$5 \times 10^{-3}$	Polystyrene	8.66	84

EB: ethyl benzene, MEOH: methanol.

Average  $k_p = 78 \pm 6$  for bulk polymerization=  $84 \pm 11$  for solution polymerization

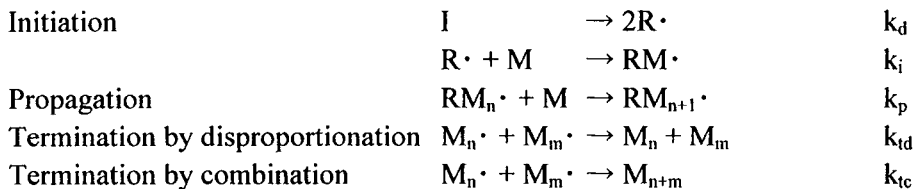
$k_p$ : propagation rate constant, [l/mol·sec]

Davis, T. P., O'Driscoll, K. F., Piton, M. C., and Winnik, M. A., *Macromolecules*, **22**, 2785 (1989). © 1989 American Chemical Society.

### Photo-induced bulk polymerization

Sensitizer: 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO)

Temperature: 30–90°C (AIBN: 30–50°C, BPO: 70–90°C)



I: initiator, M: monomer,  $R\cdot$ : primary radical,  $M_n\cdot$ : growing polymer radical containing n monomer units,  $M_n$ : dead polymer containing n monomer units.

$$k_p = 3.63 \times 10^7 \exp(-31500 \text{ cal}/8.314T)$$

$$k_i = 2.55 \times 10^{10} \exp(-14200 \text{ cal}/8.314T)$$

$$k_t = k_{tc} + k_{td}$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : rate constant for termination by combination, [l/mol·sec]

$k_{td}$ : rate constant for termination by disproportionation, [l/mol·sec]

Clouet, G. and Chaffanjon, P., *J. Macromol. Sci.-Chem.*, **A27**, 193 (1990).

**Photo-induced solution polymerization**

Solvent: dodecane

Sensitizer: azobisisobutyronitrile

Temperature: 25°C

$$k_p = (0.25 \pm 0.03) \times 10^2$$

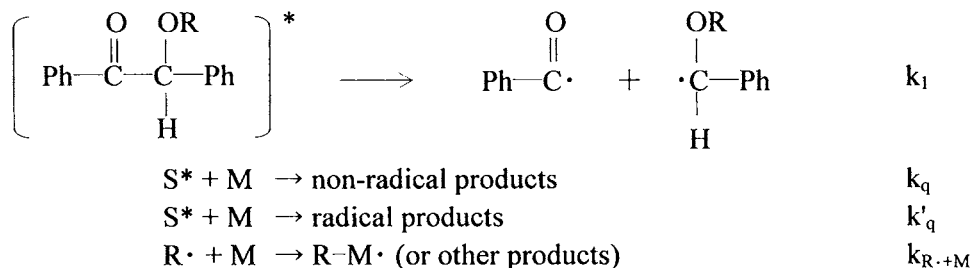
$$k_t = (0.9 \pm 0.15) \times 10^7$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Cameron, G. G. and Cameron, J., *Polymer*, **14**, 107 (1973).**Photo-induced solution polymerization**

Solvent: benzene

Sensitizer: benzoin (B), benzoinacetate (BA), and benzoinmethylether (BME)

Temperature: room temperature



S\*: excited sensitizer, M: monomer, R·: radical.

Sensitizer	$k_q/k_1$	$k_q$ [l/mol]	$k_{\text{R}\cdot+\text{M}}$ [l/mol·sec]
B	6.8	$8.1 \times 10^9$	
BA	90.0	$4.8 \times 10^9$	
BME	0.17		$1.6 \times 10^5$

 $k_1$ : decomposition rate constant, [1/sec]



$k_q, k'_q$ : rate constant for reaction of monomers with excited sensitizers which lead to non-radical products and radical products, respectively, [l/mol·sec]

$k_{R+M}$ : rate constant for reaction of radicals with monomers, [l/mol·sec]

Kuhlmann, R. and Schnabel, W., *Angew. Makromol. Chem.*, **70**, 145 (1978).

### Photo-induced and thermally-induced bulk polymerization

Initiator: dimethyl-2,2'-azobis(isobutyrate) (MAIB) and t-butyl peroxide (TBP)

Temperature: 70°C

$$k_p=350-480$$

Conversion [%]	$k_t$ [dm <sup>3</sup> /mol·sec]
0-20	$1.66 \times 10^7 - 1.70 \times 10^7$
93.8	$7.94 \times 10^3$

$k_p$ : propagation rate constant, [dm<sup>3</sup>/mol·sec]

$k_t$ : termination rate constant, [dm<sup>3</sup>/mol·sec]

Yamada, B., Kageoka, M., and Otsu, T., *Macromolecules*, **24**, 5234 (1991).

**Radiation-induced emulsion polymerization**Radiation source:  $\gamma$ -rayIngredients: seed latexes, potassium persulfate, sodium bicarbonate, water  
and Aerosol MA (100% active dihexyl ester of sodium sulfosuccinate)

Emulsifier: Aerosol MA

Initiator: potassium persulfate or benzoyl peroxide

Temperature: 30–70°C

Conversion range: 97–90%

Temperature	$k_p$ [l/mol·sec]	
	$f_{aq}=1$	$f_{aq}=1/3$
30	88–160	30–57
50	200–380	67–140
70	340–610	120–220

Temperature [°C]	Monomer [%]	$k_t$ [l/mol·sec]	
		$f_{aq}=1$	$f_{aq}=1/3$
30	20	0.37–0.75	–
	40	0.77–3.0	10–170
50	20	1.7–1.9	2.2–6.3
	40	0.28–3.0	1.1–10
70	20	0.10	0.31
	40	0.79	5.3

 $f_{aq}$ : efficiency of radical in the aqueous phase, [-] $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]

Vanderhoff, J. W., Bradford, E. B., and Tarkowski, H. L., *J. Polym. Sci.*, **1**, 265 (1961).  
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**Radiation induced emulsion polymerization**Radiation source:  $\gamma$ -ray

Ingredients: water, polyvinylacetate (PVA), and styrene

Initiator: polyvinylacetate

Temperature: 25–40°C

Initiator	Temperature [°C]	$k_p$ [l/mol·sec]
PVA latex	40	75
PVA latex	25	50

 $k_p$ : rate constant of propagation, [l/mol·sec]Allen, P. E. M., Burnett, G. M., Downer, J. M., and Majer, J. R., *Makromol. Chem.*, **58**, 169 (1962).**Radiation-induced bulk polymerization**Radiation source:  $\gamma$ -ray

Temperature: 0–50°C

Maximum conversion: below 12%

$$k_p^2/k_t = 1.985 \times 10^4 \exp(-11830 \text{ cal/RT})$$

$$k_{tm}/k_t = 4.57 \times 10^{-11} \exp(9490 \text{ cal/RT})$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec] $k_{tm}$ : transfer rate constant to monomer, [l/mol·sec]Huang, R. Y. M., Westlake, J. F., and Sharma, S. C., *J. Polym. Sci.*, **A-1**, **7**, 1729 (1969). Copyright © 1969 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.**Radiation-induced emulsion polymerization**Radiation source:  $\gamma$ -ray

Ingredients: water, sodium dodecylsulfate, and styrene

Emulsifier: sodium dodecylsulfate

Temperature: 25°C

Maximum conversion: 67%

$$-d[M]/dt = k_p[M][R]$$

$$-d[R]/dt = k_t^e[R]^2$$

$$k_t^e = 1 \times 10^3$$

[M]: monomer concentration at the reaction locus, [mol/l]

[R]: radical concentration at the reaction locus, [mol/l]

$k_p$ : propagation rate constant, [mol/l·sec]

$k_t^e$ : apparent termination rate constant in emulsion polymerization, [l/mol·sec]

Ley, G. J. M., Schneider, C., and Hummel, D. O., *J. Polym. Sci.*, **C27**, 119 (1969).  
 Copyright © 1969 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Radiation-induced bulk polymerization

Radiation source:  $\gamma$ -ray

Temperature: 50–109°C

Maximum conversion: 100%

$$R_p = -d[M]/dt = (k_n/k_t^{1/2})(\phi_m[M]I)^m[M]$$

$$1/\bar{P}_n = (k_t R_p / 2k_p^2[M]^2) + (k_{tm}/k_p)$$

$$54\text{--}74^\circ\text{C}: m = 1/2$$

$$74\text{--}109^\circ\text{C}: m = 1/2 - 0$$

$$\text{above } 109^\circ\text{C}: m = 0$$

$$k_p^2/k_t = 2.85 \times 10^4 \exp(-12027 \text{ cal}/RT)$$

$$k_{tm} = 0$$

$R_p$ : rate of polymerization, [mol/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant by combination, [l/mol·sec]

$k_{tm}$ : transfer rate constant to monomer, [l/mol·sec]

[M]: concentration of monomer, [mol/l]

$\phi_m[M]$ : rate of production of free radicals per unit radiation dose

$\bar{P}_n$ : average degree of polymerization, [-]

Sood, S. P. and Hodgins, J. W., *J. Polym. Sci.*, **A-1**, **9**, 3383 (1971). Copyright © 1971 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Radiation-induced emulsion polymerization

Radiation source:  $\gamma$ -ray

Ingredients: water, Aerosol MA80, sodium dodecyl sulphate, polystyrene seed latex, and styrene

Temperature: 30–65°C

$$\log(k)=(3.8 \pm 0.5)-(42 \pm 10 \text{ kJ}/2.303RT)$$

$$\log(\rho_0)=(10.4 \pm 1.0)-(87 \pm 10 \text{ kJ}/2.303RT)$$

$$k_p=10^{7.1 \pm 0.5} \exp\{-(29 \pm 3 \text{ kJ}/RT)\}$$

k: rate constant for the first-order loss of free radicals from the particles, [1/sec]

$\rho_0$ : rate constant for entry of thermally generated free radicals into the particles, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

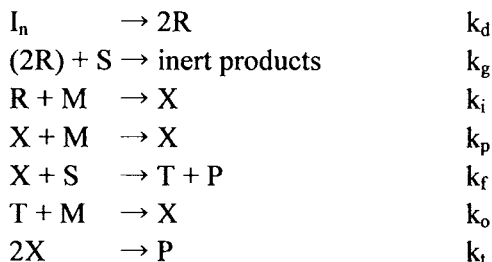
Lansdowne, S. W., Gilbert, R. G., Napper, D. H., and Sangster, D. F., *J. Chem. Soc. Faraday Trans. I*, **76**, 1344 (1980).

### Solution polymerization

Solvent: carbon tetrachloride

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 60°C



$I_n$ : initiator, M: monomer, R: primary radical, S: solvent, T: radical derived from

solvent, X: growing polymer radical, P: dead polymer.

$$R_p = k_p[M][X] + k_o[M][T] = k_p[M][X] + k_f[S][X]$$

$$k_t/2k_p^2 = 765$$

$$k_g/k_i = 0.64$$

$$k_f/k_p = 0.0135$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_g$ : rate constant of reaction between primary radicals, [l/mol·sec]

$k_f$ : transfer rate constant to solvent, [l/mol·sec]

$k_o$ : reinitiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

George, M. H. and Onyon, P. F., *Trans. Faraday Soc.*, **59**, 1390 (1963).

### Solution and bulk polymerization

Solvent: five different hydrocarbons (see table)

Initiator:  $\alpha, \alpha'$ -azobisisobutyronitrile

Temperature: 30–60°C

Solvent	$k_t/k_p^2$ [mol·sec/l]				
	60°C	50°C	40°C	35°C	30°C
Benzene	–	–	7063	7112	
2-Butanone	1737	4417	–	–	
Acetone	–	–	12258	–	
Diethyl oxalate	1585	665			
Cyclohexane	1434	1144			
Bulk styrene	1162	–	–	–	8260
	816	–	3044	–	

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Glass, J. E. and Zutty, N. L., *J. Polym. Sci.*, A-1, 4, 1223 (1966). Copyright © 1966 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution polymerization

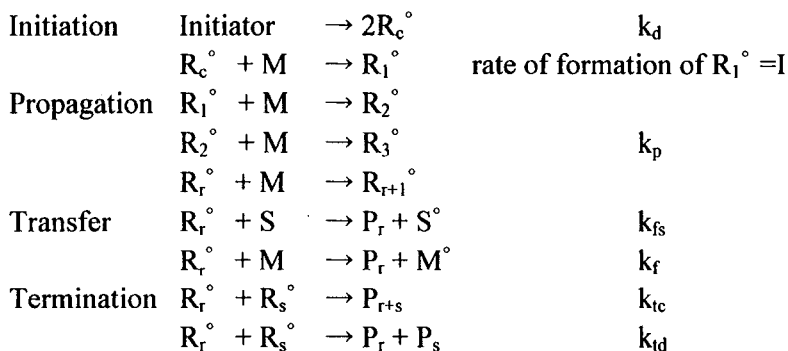
Solvent: benzene

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 50–75°C

Maximum conversion: 42.5%

Reactor: batch



$R_c^\circ$  : primary radical, M: monomer,  $R_r^\circ$  : polymer radical containing r monomer units, S: solvent,  $P_r$ : dead polymer containing r monomer units,  $S^\circ$  : solvent free radical.

$$k_d = 1.58 \times 10^{15} \exp(-15500 \text{ cal/T})$$

$$k_p = 1.051 \times 10^7 \exp(-3557 \text{ cal/T})$$

$$k_{tc} = 1.255 \times 10^9 \exp(-844 \text{ cal/T})$$

$$k_{td} = 0$$

$$k_f = 2.31 \times 10^6 \exp(-6377 \text{ cal/T})$$

$$k_{fs} = 9.55 \times 10^{10} \exp(-11000 \text{ cal/T})$$

The value of  $k_{tc}$  was corrected in the following way:

$$1/(k_{tc})_s^{1/2} = \phi_p / (k_{tc})_{\text{bulk}}^{1/2}$$

$$\phi_p = [M]_{\text{bulk}} / \{ [S](T_s/T_m) + [M] \}$$

$$T_s/T_m = 1.04 \text{ for styrene in benzene}$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [1/g-mol·sec]

$k_{fs}$ : transfer rate constant to solvent, [1/g-mol·sec]

$k_f$ : transfer rate constant to monomer, [1/g-mol·sec]

$k_{tc}$ : rate constant for termination by combination, [1/g-mol·sec]

$(k_{tc})_s$ : rate constant for termination by combination in solvent, [1/g-mol·sec]

$(k_{tc})_{bulk}$ : rate constant for termination by combination in bulk polymerization,  
[1/g-mol·sec]

$k_{td}$ : rate constant for termination by disproportionation, [1/g-mol·sec]

$[M]_{bulk}$ : monomer concentration in bulk polymerization, [g-mol/l]

$[M]$ : monomer concentration in solution polymerization, [g-mol/l]

$[S]$ : solvent concentration, [g-mol/l]

T: temperature, [°K]

Hamielec, A. E., Hodgins, J. W., and Tebbens, K., *AIChE Journal*, **13**, 1087 (1967).

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### Solution polymerization

Solvent: three kinds of solvents as shown in table

Initiator: 2,2'-azobis(2,4-dimethylvaleronitrile)

Temperature: 50 and 70°C

Solvent	$k_p(2fk_d/k_t)^{1/2} \times 10^4$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]	$k_{tr}/k_i k_p \times 10^{-4}$ [mol·sec/l]	Temperature [°C]
DC	0.725	3.6	50
DEP	1.30	3.3	50
DOP	1.72	3.3	50
DC	2.27	3.3	60
DEP	4.00	2.2	60
DOP	5.26	2.2	60
DC	5.26	1.6	70
DEP	7.46	0.70	70
DOP	9.43	1.3	70

DC: dimethyl carbitol, DEP: diethyl phthalate, DOP: di-n-octyl phthalate.



$k_d$ : decomposition rate constant, [1/sec]

$f$ : initiator efficiency, [-]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{ti}$ : termination rate constant by initiator, [l/mol·sec]

Ito, K., *J. Polym. Sci. A-1*, **10**, 931 (1972). Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution and bulk polymerization

Solvent: bromobenzene, diethyl malonate, diethyl phthalate, and benzonitrile

Initiator: 2,2'-azobisisobutyronitrile and benzoyl peroxide

Temperature: 60°C

Solvent	vol%	$k_p$ [l/mol·sec]	$k_t \times 10^{-7}$ [l/mol·sec]
None		186	7.2
None <sup>(1)</sup>		187	7.2
Bromobenzene	20	184	6.7
	20 <sup>(1)</sup>	182	6.7
	40	167	6.2
	50	167	6.0
	50 <sup>(1)</sup>	163	6.0
Diethyl malonate	20	178	6.4
	50	133	5.2
Diethyl phthalate	20	174	5.1
	40	163	3.8
	50	162	3.0
Benzonitrile	20	186	6.6
	40	158	6.1
	50	134	5.8

<sup>(1)</sup> Benzoyl peroxide initiator was used. In other runs, 2,2'-azobisisobutyronitrile was used.

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Burnett, G. M., Cameron, G. G., and Joiner, S. N., *Trans. Faraday Soc. I*, **69**, 322, (1973).

### Solution polymerization

Solvent: benzene, toluene, and dimethyl formamide (DMF)

Initiator: benzoyl peroxide (BPO)

Temperature: 50–60°C

		Rate
Production of primary radicals	$M \rightarrow 2R\cdot$	$2f_k k_d [I]$
Initiation	$R\cdot + M \rightarrow P_1\cdot$	$k_i [R\cdot] [M]$
	$P_1\cdot + M \rightarrow P_2\cdot$	
Propagation	$P_i\cdot + M \rightarrow P_{i+1}\cdot$	$k_p [P\cdot] [M]$
Termination of growing radicals by mutual deactivation	$P_m\cdot + P_n\cdot \rightarrow P_{m+n}$ or $P_m + P_n$	$k_t [P\cdot]^2$
	Primary radical termination	$P_m\cdot + R\cdot \rightarrow \text{polymer}$
Primary radical deactivation	$R\cdot + R\cdot \rightarrow \text{inactive products}$	$k_{rr} [R\cdot]^2$

I: initiator,  $R\cdot$ : primary radical, M: monomer,  $P_m\cdot$ : polymer radical containing m units of monomer,  $P_m$ : dead polymer containing m units of monomer.

$$\ln(R_p^2/[I][M]^2) = \ln(2f_k k_d k_p^2/k_t) - 2k_{prt} R_p/k_i k_p [M]^2$$

System	Temperature [°C]	$k_{prt}/k_i k_p$ [mol·sec/l]	$f_k k_d$ [1/sec]	$k_d$ [1/sec]	$f_k$
Styrene-benzene-BPO	60	$0.97 \times 10^5$	$2.1 \times 10^{-6}$	$2.6 \times 10^{-6}$	0.80
Styrene-toluene-BPO	50	$1.03 \times 10^5$	$1.9 \times 10^{-7}$	$5.5 \times 10^{-7}$	0.35
Styrene-DMF-BPO	60	$2.04 \times 10^4$	$6.75 \times 10^{-6}$	$9.4 \times 10^{-6}$	0.72

$R_p$ : propagation rate, [mol/l·sec]

$f_k$ : catalyst efficiency, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{prt}$ : rate constant of primary radical termination, [l/mol·sec]

$k_{\pi}$ : rate constant of primary radical deactivation, [l/mol·sec]

[M]: concentration of monomer, [mol/l]

[I]: concentration of initiator, [mol/l]

[P·]: total concentration of polymer radical, [mol/l]

Deb, P. C. and Meyerhoff, G., *Eur. Polym. J.*, **10**, 709 (1974).

### Solution polymerization

Solvent: benzene (Bz), ethyl alcohol (EA), and cumene (Cm)

Initiator: 2,2'-azobis(2,4-dimethylvaleronitrile)

Temperature: 50°C

$$A = k_p(fk_d/k_t)^{1/2} \cong R_p/[C]^{1/2}[M]$$

Solvent	$A \times 10^4$ [ $l^{1/2}/mol^{1/2} \cdot sec$ ]	$k_t/k_p^2$ [ $mol \cdot sec/l$ ]	$k_{ti}/10^4 k_i k_p$ [ $mol \cdot sec/l$ ]
St	1.00	833	9.2
St-Bz (1:1)	1.01	850	12.9
St-Bz-EA (3:1:2)	0.840	1204	4.0
St-Bz-EA (6:1:5)	0.746	1530	2.4
St-EA (1:1)	0.746	1530	2.4
St-Cm (1:1)	1.00	850	8.2

$R_p$ : polymerization rate, [mol/l·sec]

[C]: initiator concentration, [mol/l]

[M]: monomer concentration, [mol/l]

$k_p$ : propagation rate constant, [l/mol·sec]

- $k_t$ : termination rate constant, [l/mol·sec]  
 $k_{ti}$ : rate constant for termination by primary radical, [l/mol·sec]  
 $k_i$ : initiation rate constant, [l/mol·sec]  
 $k_d$ : decomposition rate constant of initiator, [1/sec]  
 $f$ : initiator efficiency, [-]

Ito, K., *J. Polym. Sci.*, **12**, 2581 (1974). Copyright © 1974 John Wiley & Sons, Inc.  
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### Solution polymerization

Solvent: toluene

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 75–95°C

Initiation	$I \rightarrow 2A_0$	$k_i$
Propagation	$A_j + M \rightarrow A_{j+1}$	$k_p$
Transfer to monomer	$A_j + M \rightarrow P_j + A_0$	$k_{tm}$
Transfer to solvent	$A_j + S \rightarrow P_j + A_0$	$k_{ts}$
Termination by combination	$A_j + A_k \rightarrow P_{j+k}$	$k_{tc}$
Termination by disproportionation	$A_j + A_k \rightarrow P_j + P_k$	$k_{td}$

I: initiator,  $A_0$ : primary free radical, M: monomer, S: solvent,  $A_j$ : growing polymer radical containing  $j$  monomer units,  $P_j$ : dead polymer containing  $j$  monomer units.

$$f=0.4$$

$$k_i=1.58 \times 10^{15} \exp(-30800 \text{ cal/RT})$$

$$k_{tc}/k_p^2=1.10 \times 10^{-5} \exp(13200 \text{ cal/RT})$$

- $f$ : initiator efficiency, [-]  
 $k_i$ : initiation rate constant, [l/mol·sec]  
 $k_p$ : propagation rate constant, [l/mol·sec]  
 $k_{tm}$ : rate constant of transfer reaction to monomer, [l/mol·sec]  
 $k_{ts}$ : rate constant of transfer reaction to solvent, [l/mol·sec]  
 $k_{tc}$ : rate constant of termination by combination, [l/mol·sec]  
 $k_{td}$ : rate constant of termination by disproportionation, [l/mol·sec]

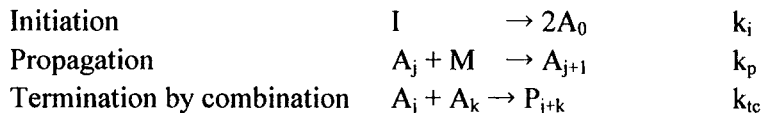
Scamehorn, J. F. and Timm, D. C., *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1241 (1975).  
 Copyright © 1975 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution polymerization

Solvent: toluene

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 75–95°C



I: initiator,  $A_0$ : primary free radical, M: monomer, S: solvent,  $A_j$ : growing polymer radical containing j monomer units,  $P_j$ : dead polymer containing j monomer units.

$$f=0.4$$

$$k_i=1.58 \times 10^{15} \exp(-30800 \text{ cal/RT})$$

$$k_{tc}/k_p^2=1.10 \times 10^{-5} \exp(13200 \text{ cal/RT})$$

f: initiator efficiency, [-]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tc}$ : rate constant of termination by combination, [l/mol·sec]

Timm, D. C. and Scamehorn, J. F., *AIChE Symp. Ser.*, **72**, 43 (1976).

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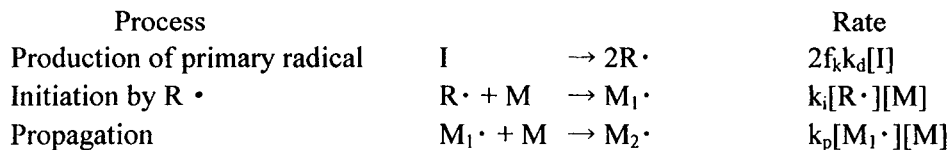
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### Solution polymerization

Solvent: benzene

Initiator: benzoyl peroxide

Temperature: 60°C



Decomposition of primary radical	$R\cdot \rightarrow R_1\cdot + X$	$k'_d[R\cdot]$
Initiation by $R_1\cdot$	$R_1\cdot + M \rightarrow M_1\cdot$	$k'_i[R_1\cdot][M]$
Termination	$P_1\cdot + P_2\cdot \rightarrow \text{polymer}$	$k_t[P\cdot]^2$
Termination with $R\cdot$	$R\cdot + P\cdot \rightarrow \text{polymer}$	$k_{prt}[P\cdot][R\cdot]$
Termination with $R_1\cdot$	$R_1\cdot + P\cdot \rightarrow \text{polymer}$	$k'_{prt}[R_1\cdot][P\cdot]$

I: initiator,  $R\cdot$ : primary radical,  $R_1\cdot$ : radical obtained from decomposition of primary radical, M: monomer,  $M_1\cdot$ : polymer radical with one monomer unit,  $M_2\cdot$ : polymer radical with two monomer units,  $P\cdot$ : polymer radical with any monomer units.

$$\log(R_p^2/[I][M]) = \log(2f_k k_d k_p^2 / k_t) - 0.8684 \{k_{prt}/k_i k_p (1 + k'_d/k_i [M])\} \{R_p/[M]^2\}$$

[M] [mol/l]	$2f_k k_d k_p^2 / k_t$ [l/mol·sec <sup>2</sup> ]	$k_{prt}/k_i k_p$ [mol·sec/l]	$k_d/k_i$ [mol/l]
2.58	$3.0 \times 10^{-9}$		
3.86	$2.9 \times 10^{-9}$		
5.17	$2.9 \times 10^{-9}$	$1.50 \times 10^5$	1.73
6.03	$3.0 \times 10^{-9}$		
6.89	$2.8 \times 10^{-9}$		
7.75	$2.5 \times 10^{-9}$		

$$E_i + E_p + E_{prt} = 96, E_{prt} = 10.5, E_p = 32.6, E_i = 74$$

$R_p$ : propagation rate, [mol/l·sec]

$f_k$ : initiator efficiency, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant by  $R\cdot$ , [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k'_d$ : decomposition rate constant of  $R\cdot$ , [1/sec]

$k'_i$ : initiation rate constant by  $R_1\cdot$ , [l/mol·sec]

$k_t$ : termination rate constant between polymer radicals, [l/mol·sec]

$k_{prt}$ : rate constant for termination by  $R\cdot$ , [l/mol·sec]

$k'_{prt}$ : rate constant for termination by  $R_1\cdot$ , [l/mol·sec]

[I]: concentration of initiator, [mol/l]

[M]: concentration of monomer, [mol/l]

$E_i$ : activation energy for initiation reaction, [kJ/mol]

$E_p$ : activation energy for propagation reaction, [kJ/mol]

$E_{prt}$ : activation energy for termination reaction by  $R\cdot$ , [kJ/mol]

Deb, P. C. and Gaba, I. D., *Makromol. Chem.*, **179**, 1549 (1978).

### Solution polymerization

Solvent: benzene

Initiator: 2,2'-azobisisobutyronitrile (AIBN)

Temperature: 60°C

Process		Rate
Production of primary radical	$I \rightarrow 2R\cdot$	$2f_k k_d [I]$
Initiation by $R\cdot$	$R\cdot + M \rightarrow M_1\cdot$	$k_i [R\cdot] [M]$
Propagation	$M_1\cdot + M \rightarrow M_2\cdot$	$k_p [M_1\cdot] [M]$
Decomposition of primary radical	$R\cdot \rightarrow R_1\cdot + X$	$k'_d [R\cdot]$
Initiation by $R_1\cdot$	$R_1\cdot + M \rightarrow M_1\cdot$	$k'_i [R_1\cdot] [M]$
Termination	$P_1\cdot + P_2\cdot \rightarrow \text{polymer}$	$k_t [P\cdot]^2$
Termination with $R\cdot$	$R\cdot + P\cdot \rightarrow \text{polymer}$	$k_{prt} [P\cdot] [R\cdot]$
Termination with $R_1\cdot$	$R_1\cdot + P\cdot \rightarrow \text{polymer}$	$k'_{prt} [R_1\cdot] [P\cdot]$

I: initiator,  $R\cdot$ : primary radical,  $R_1\cdot$ : radical obtained from decomposition of primary radical, M: monomer,  $M_1\cdot$ : polymer radical with one monomer unit,  $M_2\cdot$ : polymer radical with two monomer units,  $P\cdot$ : polymer radical with any monomer units.

$$\log(R_p^2/[I][M]) = \log(2f_k k_d k_p^2 / k_t) - 0.8684 \{k_{prt} / k_i k_p (1 + k'_d / k_i [M])\} \{R_p / [M]^2\}$$

[M] [mol/l]	$2f_k k_d k_p^2 / k_t$ [l/mol·sec <sup>2</sup> ]	$k_{prt} / k_i k_p$ [mol·sec / l]
1.72	$4.00 \times 10^{-9}$	$3.35 \times 10^4$
2.58	$4.72 \times 10^{-9}$	$3.40 \times 10^4$
3.44	$5.40 \times 10^{-9}$	$3.26 \times 10^4$
5.17	$5.90 \times 10^{-9}$	$3.30 \times 10^4$
6.03	$6.00 \times 10^{-9}$	$3.42 \times 10^4$
6.89	$6.00 \times 10^{-9}$	$3.50 \times 10^4$
7.75	$5.80 \times 10^{-9}$	$2.80 \times 10^4$

$$E_i + E_p + E_{prt} = 88, E_{prt} = 10.5, E_p = 32.6, E_i = 66$$

$R_p$ : propagation rate, [mol/l·sec]

$f_k$ : initiator efficiency, [-]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant by  $R \cdot$ , [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k'_d$ : decomposition rate constant of  $R \cdot$ , [1/sec]

$k'_i$ : initiation rate constant by  $R_1 \cdot$ , [l/mol·sec]

$k_t$ : termination rate constant between polymer radicals, [l/mol·sec]

$k_{prt}$ : rate constant for termination by  $R \cdot$ , [l/mol·sec]

$k'_{prt}$ : rate constant for termination by  $R_1 \cdot$ , [l/mol·sec]

[I]: concentration of initiator, [mol/l]

[M]: concentration of monomer, [mol/l]

$E_i$ : activation energy for initiation reaction, [kJ/mol]

$E_p$ : activation energy for propagation reaction, [kJ/mol]

$E_{prt}$ : activation energy for termination reaction by  $R \cdot$ , [kJ/mol]

Deb, P. C. and Gaba, I. D., *Makromol. Chem.*, **179**, 1559 (1978).

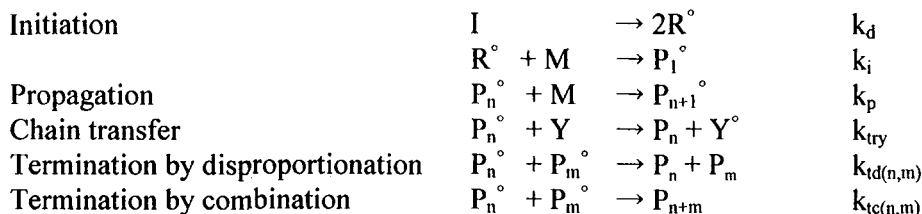


**Solution polymerization**

Solvent: benzene (BZ), benzene-isopropyl alcohol (BZ-IPA), dimethyl carbitol (DC),  
DE, ethyl acetate (EA)

Initiator: 2,2'-azobis(2,4-dimethylvaleronitrile)

Temperature: 50°C



I: initiator, M: monomer,  $R^\circ$ : primary free radical,  $P_n^\circ$ : growing polymer radical containing n monomer units,  $P_n$ : dead polymer containing n monomer units, Y: chain transfer agent.

$$k_{t(n,m)} = k_{tc(n,m)} + k_{td(n,m)} = k_{t_0}(nm)^{-a}$$

$$k_{t(n,m)} = k_t^* (X_n)^{-2a}/\eta$$

$$R_p = (2fk_d k_p^2 / k_t^*) \eta^{0.5} [M][I]^{0.5} (X_n)^a$$

$$k_{t_0} = 10^{-2} CT / rN_0 \eta$$

$$a = 0.1306$$

$$2fk_d k_p^2 / k_t^* = 8.27 \times 10^{-5}$$

$k_d$ : decomposition rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{tr}$ : transfer rate constant, [l/mol·sec]

$k_{t(n,m)}$ : termination rate constant between two radicals of size n and m, [l/mol·sec]

$k_{tc(n,m)}$ : rate constant of termination by combination between two radicals of size n and m, [l/mol·sec]

$k_{td(n,m)}$ : rate constant of termination by disproportionation between two radicals of size n and m, [l/mol·sec]

$R_p$ : polymerization rate, [mol/l·sec]

$X_n$ : number-average degree of polymerization, [-]

$k_t^*$ : a constant

a: a constant

$\eta$ : viscosity of medium

[M]: monomer concentration, [mol/l]

[I]: initiator concentration, [mol/l]

f: initiator efficiency, [-]

C: constant

T: temperature

r: hydrodynamic radius of a monomer unit in a segment

$N_0$ : the number of monomer units in a segment

Mahabadi, H. K., *Macromolecules*, **24**, 606 (1991).

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### Thermally-induced solution polymerization

Solvent: thirteen different hydrocarbons (see table)

Temperature: 60–132°C

Solvent	$k_t/k_p \times 10^5$			$E_t - E_p^{(1)}$ [kcal/mol]	$\ln(A_t/A_p)^{(1)}$
	60°C	100°C	132°C		
Benzene	0.18	1.84	8.9	14.8	9.06
tert-Butylbenzene	0.6	5.5		13.7	8.67
Toluene	1.25	6.45		10.1	4.03
Ethylbenzene	6.7	16.2	29	5.5	-1.27
iso-Propylbenzene	8.2	20.0		5.5	-1.09
Diphenylmethane	23	42		3.7	-2.76
Triphenylmethane	35	80		5.1	0.24
Fluorene	750	1240		3.1	0.19
Pentaphenylethane	200000	–		–	–
Cyclohexane	0.24	1.6	8.7	13.4	7.21
n-Heptane	4.2	9.5		5.0	-2.44
Decalin	4	–		–	–
Carbon tetrachloride	900	1810	3250	4.8	2.53

<sup>(1)</sup>Calculated from the Arrhenius equation,  $k_t/k_p = (A_t/A_p)\exp(-E/RT)$ , where  $E = E_t - E_p$ .

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

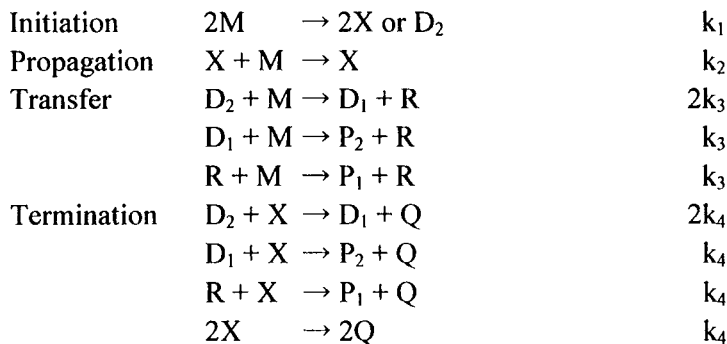
$E_p$ : activation energy for  $k_p$ , [kcal/mol]

$E_i$ : activation energy for  $k_i$ , [kcal/mol]

Gregg, R. A. and Mayo, F. R., *Faraday Soc. Discussions*, **2**, 328 (1947).

### Thermally-induced bulk polymerization

Temperature: 0–25°C



X: active center, Q: dead center, M: monomer,  $D_2$ : initial polymer growing at both ends,  $D_1$ : polymer growing at one end, R: growing transfer polymer,  $P_1$ : dead transfer polymer,  $P_2$ : dead initial polymer.

$$\begin{aligned}
 [X] &= (k_1/k_4)^{1/2} [M] \\
 [D_2] &= k_1 [M] / 4 \{k_3 + (k_1 k_4)^{-1/2}\} \\
 [D_1] &= 2 [D_2] \\
 [R] &= 4 [D_2] k_3 (k_1 k_4)^{-1/2} \\
 \bar{P}_1 &= k_1 / \{k_3 + (k_1 k_4)^{1/2}\} \\
 \bar{P}_2 &= 2 \bar{P}_1 \\
 d[P_1]/dt &= k_3 (k_1/k_4)^{1/2} [M]^2 \\
 d[P_2]/dt &= k_1 [M]^2 / 2 \\
 \bar{P}_n &= 2k_2 (k_1 k_4)^{-1/2} / (2\beta + 1) \\
 \beta &= k_3 (k_1 k_4)^{-1/2}
 \end{aligned}$$

Temperature [°C]	$k_1$ [l/mol·sec]	$k_2$ [l/mol·sec]	$k_3$ [l/mol·sec]	$k_4$ [l/mol·sec]	$\bar{P}_n$	$\beta$
0	$4.51 \times 10^{-16}$	6.91	$7.47 \times 10^{-5}$	$1.83 \times 10^6$	$9.08 \times 10^4$	26
25	$1.32 \times 10^{-15}$	18.7	$6.68 \times 10^{-4}$	$2.79 \times 10^6$	$2.67 \times 10^4$	11

$$k_1 = 1.23 \times 10^{10} \exp(-37.0 \pm 2 \text{ kcal/RT}), \quad k_2 = 1.02 \times 10^6 \exp(-6.5 \pm 1 \text{ kcal/RT}), \\ k_3 = 1.50 \times 10^7 \exp(-14.2 \pm 1 \text{ kcal/RT}), \quad k_4 = 3.07 \times 10^8 \exp(-2.8 \pm 1 \text{ kcal/RT})$$

$k_1$ : initiation rate constant, [l/mol·sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : transfer rate constant, [l/mol·sec]

$k_4$ : termination rate constant, [l/mol·sec]

$\bar{P}_1$  and  $\bar{P}_2$ : number-average degrees of polymerization of the transfer and dead initial polymers, respectively, [-]

$\bar{P}_n$ : number-average degree of polymerization, [-]

Bamford, C. H. and Dewar, M. J. S., *Proc. Roy. Soc., London*, **A192**, 309 (1948).

### Thermally-induced bulk polymerization

Temperature: 25 and 125°C

		25 [°C]	125 [°C]	Activation energy [kcal/mol]
Initiation	$k_i$	$1.3 \times 10^{-15}$	$2.9 \times 10^{-9}$	35.0
Propagation	$k_p$	18.7	170.0	5.5
Transfer	$k_t$	$6.7 \times 10^{-4}$	0.15	13.2
Termination	$k_t$	$2.8 \times 10^6$	$5.2 \times 10^6$	1.8

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

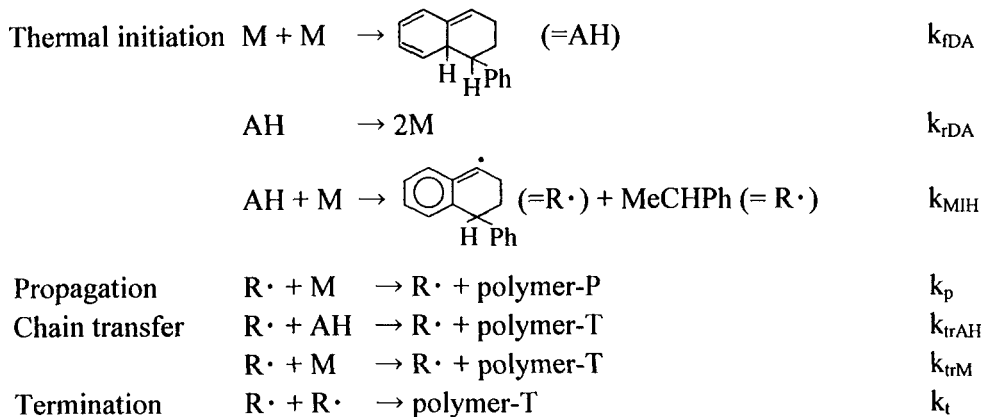
$k_t$ : transfer rate constant to monomer, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Vaughan, M. F., *Trans. Faraday Soc.*, **48**, 576 (1952).

### Thermally-induced bulk polymerization

Temperature: 60°C



$$R_{ith} = 2k_{MIH}[AH][M] = 2k_{ith}[M]^3$$

$$R_{pth} = d[M]/dt = k_p(R_{ith})^{1/2}[M]/(2k_t)^{1/2}$$

$$1/\bar{P}_n = k_t R_{pth} / k_p^2 [M]^2 + k_{trM} / k_p + k_{trAH}[AH] / k_p [M]$$

$$[AH] = k_{fDA}[M]^2 / \{k_{rDA} + k_{MIH}[M] + k_{trAH}(R_{ith}/2k_t)^{1/2}\}$$

$$k_{fDA} = 1 \times 10^{-9} \text{ [l/mol}\cdot\text{sec]}$$

$$k_{rDA} = 1.3 \times 10^{-4} \text{ [1/sec]}$$

$$k_{MIH} = 1 \times 10^{-8} \text{ [l/mol}\cdot\text{sec]}$$

$$k_p = 1.45 \times 10^2 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{trAH} = 1.5 \times 10^2 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{trM} = 1 \times 10^{-3} \text{ [l/mol}\cdot\text{sec]}$$

$$k_t = 1.7 \times 10^7 \text{ [l/mol}\cdot\text{sec]}$$

$R_{ith}$ : rate of thermal initiation, [g-mol/l·sec]

$R_{pth}$ : thermal polymerization rate, [g-mol/l·sec]

$\bar{P}_n$ : number-average degree of polymerization, [-]

[M]: monomer concentration, [g-mol/l]

[AH]: concentration of AH, [g-mol/l]

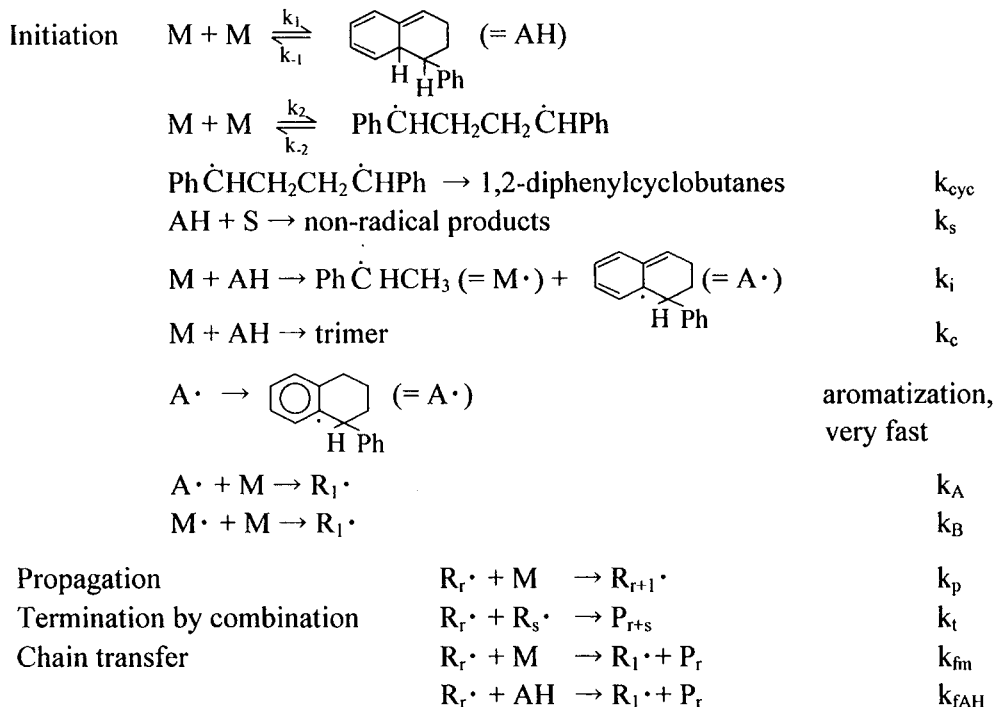
Pryor, W. A. and Coco. J. H., *Macromolecules*, **3**, 500 (1970).

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### Thermally-induced bulk polymerization

Temperature: 100–200°C

Maximum conversion: 100%



M: monomer,  $R_r\cdot$ : polymer radical containing r monomer units,  $P_r$ : dead polymer containing r monomer units.

$$\begin{aligned}
 (Ik_p^2/k_i)^{1/2} &= A_0 \exp(A_1 X + A_2 X^2 + A_3 X^3) \\
 k_{fm}/k_p &= (k_{fm})_0 / (k_p)_0 + B_1 X \\
 I &= 2k_i k_1 [M]^3 / \{k_{-1} + (k_i + k_c)[M] + k_{fAH}(I/k_i)^{1/2}\} \\
 &\cong 2k_i k_1 [M]^3 / k_{-1} = 2k_i [M]^3
 \end{aligned}$$

$$d(MP)_0/dt = R_p(C_m + \beta/2) - (MP)_0 dV/V dt$$

$$d(MP)_1/dt = R_p - (MP)_1 dV/V dt$$

$$d(MP)_2/dt = R_p(2C_m + 3\beta)/(C_m + \beta)^2 - (MP)_2 dV/V dt$$

$$(MP)_0 = \sum_{r=2}^{\infty} [P_r \cdot], \quad (MP)_1 = \sum_{r=2}^{\infty} r [P_r \cdot], \quad (MP)_2 = \sum_{r=2}^{\infty} r^2 [P_r \cdot]$$

$$R_p = d[M]/dt - ([M] \cdot dV)/(V \cdot dt)$$

$$d[P_r]/dt = R_p \{ C_m(C_m + \beta) + \beta(C_m + \beta)^2 r/2 \} \phi^r - ([P_r] \cdot dV)/(V \cdot dt)$$

$$\phi = 1/(1 + C_m + \beta)$$

$$C_m = k_{fm}/k_p$$

$$\beta = k_t R_p / k_p^2 [M]^2$$

$$dV/(V \cdot dt) = - \{ \varepsilon / ([M]_0 + \varepsilon [M]) \} \cdot d[M]/dt$$

$$\varepsilon = (V_{x=1} - V_{x=0}) / V_{x=0}$$

$$(k_p)_0 = 1.051 \times 10^7 \exp(-3557/T)$$

$$(k_{fm})_0 = 2.31 \times 10^6 \exp(-6377/T)$$

$$(k_t)_0 = 1.255 \times 10^9 \exp(-844/T)$$

$$A_0 = 1.964 \times 10^5 \exp(-10040/T)$$

$$A_1 = 2.57 - 5.05 \times 10^{-5} T$$

$$A_2 = 9.56 - 1.76 \times 10^{-2} T$$

$$A_3 = -3.03 + 7.85 \times 10^{-3} T$$

$$B_1 = -1.013 \times 10^{-3} \log_{10} \{ (473.12 - T) / 202.5 \}$$

$$k_i = 2.19 \times 10^5 \exp(-13810/T)$$

r: number of monomer units, [-]

I: rate of initiation, [mol/l·sec]

R<sub>p</sub>: rate of propagation, [mol/l·sec]

[M]: monomer concentration, [mol/l]

[M]<sub>0</sub>: initial concentration of monomer, [mol/l]

V: volume of system, [l]

X: conversion of monomer, [-]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>fm</sub>: transfer rate constant to monomer, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

(k<sub>p</sub>)<sub>0</sub>: propagation rate constant for initial state, [l/mol·sec]

(k<sub>fm</sub>)<sub>0</sub>: transfer rate constant to monomer for initial state, [l/mol·sec]

$(k_t)_0$ : termination rate constant for initial state, [l/mol·sec]

$k_i$ : rate constant of initiation, [l/mol·sec]

$(MP)_n$ : nth moment of dead polymer, [mol/l]

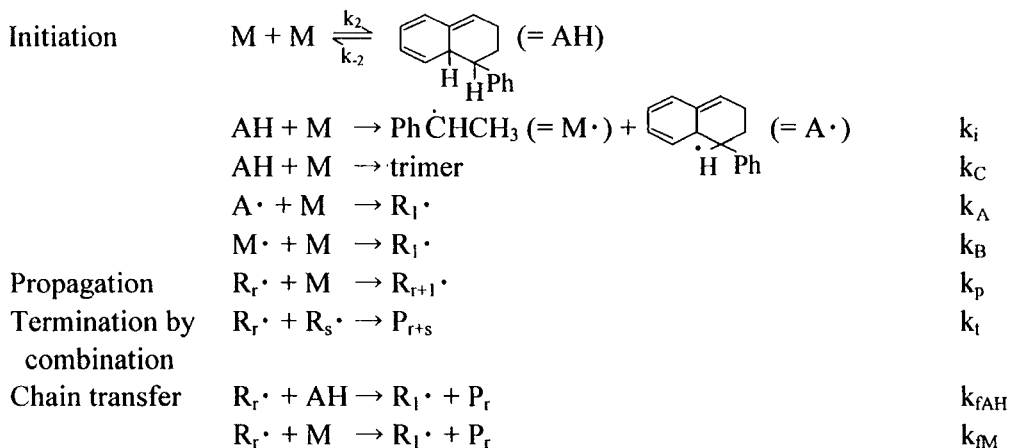
Hui, A. W. and Hamielec, A. E., *J. Appl. Polym. Sci.*, **16**, 749 (1972).

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### Thermally-induced bulk polymerization

Temperature: 200–230°C

Maximum conversion: 98%



M: monomer,  $R_r\cdot$ : polymer radical containing r monomer units,  $P_r$ : dead polymer containing r monomer units.

$$d[M]/dt = -k_p[M](I/k_i)^{1/2} \{([M]_0 + \epsilon[M])/[M]_0\}$$

$$\epsilon = \{(V)_{x=1} - (V)_0\} / (V)_0$$

$$(k_p)_0 = 1.051 \times 10^7 \exp(-3557/T),$$

$$(k_{fM})_0 = 2.31 \times 10^6 \exp(-6377/T)$$

$$(k_t)_0 = 1.255 \times 10^9 \exp(-844/T)$$

$k_p$ : propagation rate constant, [l/g·mol·sec]

$k_t$ : termination rate constant by combination, [l/g·mol·sec]

$k_{fM}$ : transfer rate constant to monomer, [l/g·mol·sec]



$k_p$ : propagation rate constant, [l/g-mol·sec]

$(k_t)_0$ : termination rate constant at the zero conversion, [l/g-mol·sec]

$(k_{fm})_0$ : transfer rate constant to monomer at the zero conversion, [l/g-mol·sec]

I: rate of initiation, [g-mol/l·sec]

$[M]_0$ ,  $[M]$ : monomer concentrations at initial state and time t, respectively, [g-mol/l]

X: conversion, [-]

$(V)_0$ ,  $(V)_{x=1}$ : volumes of system when conversion is 0 and 1, [l]

Husain, A. and Hamielec, A. E., *J. Appl. Polym. Sci.*, **22**, 1207 (1978).

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## 1.8 Vinyl acetate

### Bulk polymerization

Initiator: benzoyl peroxide

Temperature: 45°C



P: initiator, R: primary radical, M: monomer, R-R: dead polymer.

$$\begin{aligned}
 [\text{M}] &= 10.86 \text{ [mol/l]}, \quad [\text{P}] = 8.27 \times 10^{-3} \text{ [mol/l]} \\
 -d[\text{M}]/dt &= 2.3 \times 10^{-4} \text{ [mol/l}\cdot\text{sec]}, \quad k_1 = 1.09 \times 10^{-6} \text{ [1/sec]}
 \end{aligned}$$

% reaction at point of maximum rate	$x_m^{(1)}$	$r^{(2)}$	$k_2$	$k_3$
12.0	0.88	9	0.45	4.0
2.3	0.977	99	4.9	485
0.34	0.9966	999	49.5	$5 \times 10^4$
0.05	0.9995	9999	496	$5 \times 10^6$
0.007	0.99993	99999	4960	$5 \times 10^8$

<sup>(1)</sup> $x_m = (1/(r+1))^{1/2r}$ ,  $x_m$ : the value of  $x$  ( $=[\text{M}]/[\text{M}_0]$ ) at the inflection point.

<sup>(2)</sup> $r = k_3/k_2$

$k_1$ : decomposition rate constant of initiator, [1/sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : termination rate constant, [l/mol·sec]

[M]: initial monomer concentration, [mol/l]

[P]: initiator concentration, [mol/l]

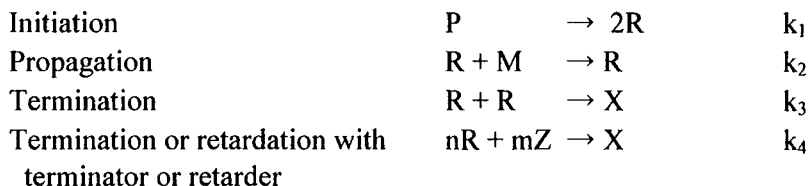
Nozaki, K. and Bartlett, P. D., *J. Am. Chem. Soc.*, **68**, 2377 (1946).

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**Bulk polymerization**

Initiator: benzoyl peroxide

Temperature: 45°C



P: initiator, M: monomer, R: primary radical, Z: terminator or retarder, X: stable product.

$$d[R]/dt = 2k_1[P] - k_4[R]^n[Z]^m \doteq 0$$

$$d[M]/dt = k_2[R][M]$$

$$[R] = (2k_1[P]/k_4[Z]^m)^{1/n}$$

$$[Z] = \{2k_1k_2^n[P]/k_4(-d\ln[M]/dt)^n\}^{1/m}$$

Terminator	k <sub>1</sub> [1/min]	k <sub>4</sub> /k <sub>2</sub>	n	m
2,2-Diphenylpicrylhydrazyl	(1.38-1.46) × 10 <sup>-5</sup>	1	1	
Duroquinone	1.34 × 10 <sup>-5</sup>	90	1	1
Iodine	-	6 × 10 <sup>4</sup>	1	3/2

k<sub>1</sub>: decomposition rate constant of initiator, [1/min]

k<sub>2</sub>: propagation rate constant, [l/mol·min]

k<sub>3</sub>: termination rate constant, [l/mol·min]

k<sub>4</sub>: termination rate constant with terminator or retarder, [l/mol·min]

Bartlett, P. D. and Kwart, H., *J. Am. Chem. Soc.*, **72**, 1051 (1950).

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**Bulk polymerization**

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 55–70°C

Conversion: 90%

---

Temperature [°C]	Initial rate constant [1/min]
55	$0.90 \times 10^{-2}$
60	$1.58 \times 10^{-2}$
65	$2.48 \times 10^{-2}$
70	$3.90 \times 10^{-2}$

---

Overall activation energy: 21.6 [kcal/mol]

Temperature: 60°C

---

Initiator concentration [mol/l]	Initial rate constant [1/min]
$1.0 \times 10^{-2}$	$0.71 \times 10^{-2}$
$2.0 \times 10^{-2}$	$0.97 \times 10^{-2}$
$3.0 \times 10^{-2}$	$1.30 \times 10^{-2}$
$4.0 \times 10^{-2}$	$1.48 \times 10^{-2}$
$5.0 \times 10^{-2}$	$1.58 \times 10^{-2}$
$6.0 \times 10^{-2}$	$1.77 \times 10^{-2}$

---

Moze, A., Vizovisek, I., Malavasic, T., Cernec, F., and Lapanje, S., *Makromol. Chem.*, **175**, 1507 (1974).

**Bulk polymerization**

Initiator: dibenzoyl peroxide and cyclohexyl oxycarbonyl peroxide

Temperature: 43–80°C

Maximum conversion: 20%

$$k_t = 2.75 \times 10^7 \text{ (constant for the temperature range as shown above)}$$

$$k_p = 2.0 \times 10^6 \exp\{(-4700 \pm 700) \text{ cal}/RT\}$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Bresler, S. E., Kazbekov, N. K., and Shadrin, V. N., *Makromol. Chem.*, **175**, 2875 (1974).**Emulsion polymerization**

Emulsifier: potassium peroxide

Temperature: 50–60°C

Propagation	$P_r \cdot + M \rightarrow P_{r+1} \cdot$	$k_p$
Monomer transfer	$P_r \cdot + M \rightarrow P_r + P_1 \cdot$	$k_{fm}$
Polymer transfer	$P_r \cdot + P_s \rightarrow P_r + P_s \cdot$	$k_{fp}$
Terminal double-bond polymerization	$P_r \cdot + P_s \rightarrow P_{r+s} \cdot$	$k_p^*$
Termination by disproportionation	$P_r \cdot + P_s \cdot \rightarrow P_r + P_s$	$k_{td}$
Termination by combination	$P_r \cdot + P_s \cdot \rightarrow P_{r+s}$	$k_{tc}$

M: monomer,  $P_r \cdot$ : growing polymer radical containing r units of monomer, $P_1 \cdot$ : primary radical,  $P_r$ : dead polymer containing r units of monomer.

$$k_{tc} \cong 0$$

$$k_{td} \cong 0$$

$$R_{fm} = k_{fm} n N[M_p] / N_A$$

$$R_i = R_t = 2k_i f[I]$$

Stage 1: monomer/polymer ratio within particles remains constant, volume of the particles increase with time

$$Q_0 \cdot dV_p / V_p \cdot dt = (k_{fm}[M_p] - k_p^* Q_0) Y_0$$

$$Q_1 \cdot dV_p / V_p \cdot dt = (k_p M_p + k_{fm}[M_p]) Y_0$$

$$Q_2 \cdot dV_p/V_p \cdot dt = 2Y_0(k_p[M_p] + k_p^* Q_1)(k_p[M_p] + k_{fm}[M_p] + k_{fp}Q_2 + k_p^* Q_1)/(k_{fm}[M_p] + k_{fp}Q_1) + k_p[M_p]Y_0$$

$$Q_0 B_n \cdot dV_p/V_p \cdot dt = (k_{fp}Q_1 + k_p^* Q_0)Y_0$$

$$Q_0 = \sum_{r=1}^{\infty} [P_r], \quad Q_1 = \sum_{r=1}^{\infty} r[P_r], \quad Q_2 = \sum_{r=1}^{\infty} r^2[P_r], \quad Y_0 = \sum_{r=1}^{\infty} [P_r \cdot]$$

$$M_n = m_0 Q_1/Q_0 = m_0(k_p[M_p] + k_{fm}[M_p] + k_p^* Q_1)/k_{fm}[M_p]$$

$$M_w = m_0 Q_2/Q_1 = m_0 \{ 2(k_p[M_p] + k_p^* Q_1)^2 + k_p[M_p](k_{fm}[M_p] + k_{fp}Q_1) \} / \{ k_p[M_p](k_{fm}[M_p] + k_{fp}Q_1) - 2k_{fp}Q_1(k_p[M_p] + k_p^* Q_1) \}$$

$$B_n = (k_{fp}Q_1^2/Q_0 + k_p^* Q_1) / [M_p](k_p + k_{fm})$$

Stage 2: composition of particles varies with the overall monomer conversion

$$dQ_0/dx = C_m M_0 - K Q_0 M_0 / [M_p]$$

$$dQ_1/dx = M_0$$

$$dQ_2/dx = M_0 + 2(M_0 + K Q_1 M_0 / [M_p]) \{ ( [M_p] + C_p Q_2 + K Q_1) / (C_m [M_p] + C_p Q_1) \}$$

$$d(Q_0 B_n)/dx = (C_p Q_1 + K Q_0) M_0 / [M_p]$$

$$C_m = k_{fm}/k_p, \quad C_p = k_{fp}/k_p, \quad K = k_p^*/k_p$$

$$k_{tc} \approx 0, \quad k_{td} \approx 0$$

$$k_p = 1.89 \times 10^7 \exp(-5650 \text{ cal}/RT), \quad k_{fp} = 1.43 \times 10^6 \exp(-9020 \text{ cal}/RT)$$

$$k_{fm} = 3.55 \times 10^6 \exp(-9950 \text{ cal}/RT), \quad k_p^* = A_0 + A_1 x + A_2 x^2 + A_3 x^3$$

$$A_0 = 1.07 \times 10^7 \exp(-5650 \text{ cal}/RT),$$

$$A_1 = -169.59, \quad A_2 = -479.92, \quad A_3 = -1014.3$$

$k_i$ : initiator decomposition rate constant, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{fm}$ : transfer rate constant to monomer, [l/mol·sec]

$k_{fp}$ : transfer rate constant to polymer, [l/mol·sec]

$k_p^*$ : rate constant of terminal double-bond polymerization, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$R_{fm}$ : transfer rate to monomer, [mol/l·sec]

$R_t$ : termination rate, [mol/l·sec]

$R_i$ : initiation rate, [mol/l·sec]

$N$ : total number of polymer particles, [particles/l]

$n$ : average number of radicals per particles, [-]

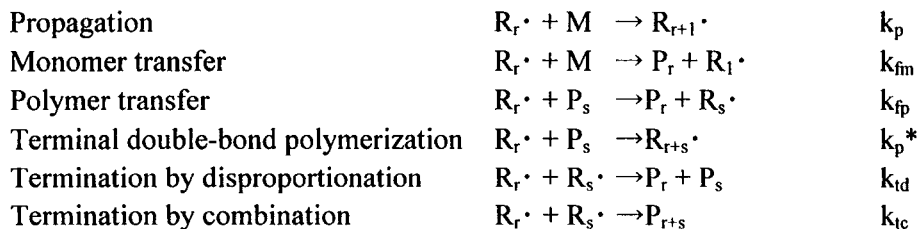
- [P<sub>r</sub>]: concentration of dead polymer with r monomer units, [mol/l]  
 [P<sub>r</sub>·]: concentration of growing radical polymer with r monomer units, [mol/l]  
 [M<sub>p</sub>]: monomer concentration within the polymer particles, [mol/l]  
 M<sub>0</sub>: initial monomer concentration, [mol/l]  
 V<sub>p</sub>: total volume of monomer-swollen polymer particles, [l]  
 N<sub>A</sub>: Avogadro's number, [number/mol]  
 f: initiator efficiency, [-]  
 Q<sub>n</sub>: nth moment of dead polymer, [mol/l]  
 Y<sub>n</sub>: nth moment of polymer radical, [mol/l]  
 B<sub>n</sub>: average number of branch points per molecule, [-]  
 M<sub>n</sub>: number-average molecular weight, [g/mol]  
 M<sub>w</sub>: weight-average molecular weight, [g/mol]  
 m<sub>0</sub>: molecular weight of monomer, [g/mol]  
 x: degree of conversion, [-]

Fris, N., Goosney, D., Wright, J. D., and Hamielec, A. E., *J. Appl. Polym. Sci.*, **18**, 1247 (1974). Copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Emulsion polymerization

Emulsifier: potassium peroxide

Temperature: 50°C



M: monomer, R<sub>r</sub>·: growing polymer radical containing r units of monomer,

R<sub>1</sub>·: primary radical, P<sub>r</sub>: dead polymer containing r units of monomer.

$$R_p = k_p [M_p] / N_A (2fk_i [I])^{1/2} (V_p N_A^2 / k_{tp} + N / 2k_d)^{1/2}$$

$$k_d = k'_d (N / V_p)^{2/3}$$

$$R_p = k_p [M_p] / N_A (2fk_i [I])^{1/2} (V_p N_A^2 / k_{tp} + N^{1/3} V_p^{2/3} / 2k'_d)^{1/2}$$

Stage 1:  $x \leq x_c$

$$d(V_p R_r \cdot) / (V_p \cdot dt) = k_p [M_p] r R_{r-1} \cdot - (k_p [M_p] + k_{fm} [M_p] + k_{fp} Q_1 + k_p^* Q_0) R_r \cdot + k_{fp} r P_r Y_0 + k_p^* \sum_{s=1}^{r-2} P_{r-s} R_s \cdot = 0$$

$$P_r \cdot dV_p / (V_p \cdot dt) = (k_{fm} [M_p] + k_{fp} Q_1) R_r \cdot - (k_{fp} r P_r + k_p^* P_r) Y_0$$

$$Y_0 = \sum_{r=1}^{\infty} [R_r \cdot], \quad Q_0 = \sum_{r=1}^{\infty} [P_r], \quad Q_1 = \sum_{r=1}^{\infty} r [P_r]$$

$$M_n = m Q_1 / Q_0 = m_0 \{ 1 + K x_c / (1 - x_c) \} / C_m$$

$$M_w = m_0 Q_2 / Q_1 = 2 m_0 \{ 1 + K x_c / (1 - x_c) \}^2 / \{ C_m + C_p x_c / (1 - x_c) - (2 C_p x_c / (1 - x_c)) (1 + K x_c / (1 - x_c)) \}$$

$$B_n = C_p M_n x_c / (1 - x_c) m_0 + K x_c / (1 - x_c)$$

$$C_m = k_{fm} / k_p, \quad C_p = k_{fp} / k_p, \quad K = k_p^* / k_p$$

Stage 2:  $x \geq x_c$

$$d[R_r \cdot] / dt = k_p [M_p] [R_{r-1} \cdot] - (k_p [M_p] + k_{fm} [M_p] + k_{fp} Q_1 + k_p^* Q_0) [R_r \cdot] + k_{fp} r [P_r] Y_0 + k_p^* \sum_{s=1}^{r-2} [P_{r-s}] [R_s \cdot]$$

$$d[P_r] / dt = (k_{fm} [M_p] + k_{fp} Q_1) [R_r \cdot] - (k_{fp} r [P_r] + k_p^* [P_r]) Y_0$$

$$dQ_0 / dx = C_m M_0 - K Q_0 M_0 / [M_p]$$

$$dQ_1 / dx = M_0$$

$$dQ_2 / dx = M_0 + 2(M_0 + K Q_1 M_0 / [M_p]) ([M_p] + C_p Q_2 + K Q_1) / (C_m [M_p] + C_p Q_1)$$

$$d(Q_0 B_n) / dx = (C Q_1 + K Q_0) M_0 / [M_p]$$

$$2fk_i = 10^{-6}, \quad k_p = 3000,$$

$$k'_d = 4.55 \times 10^{-15} \{ \{ (1-x)/(1-0.19x) \}^2 + 0.0017x \} / N_A$$

$$k_{ip} = 2 \exp(A + A_1 x + A_2 x^2 + A_3 x^3)$$

$$A = 17.6620, \quad A_1 = -0.4407, \quad A_2 = -6.7530, \quad A_3 = -0.3495$$

$$k_{fp} = 1.25, \quad k_{fm} = 0.75, \quad d_m = 930, \quad d_p = 1150$$

$k_i$ : initiator decomposition rate constant, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_{fm}$ : transfer rate constant to monomer, [l/mol·sec]

$k_{fp}$ : transfer rate constant to polymer, [l/mol·sec]



$k_p^*$ : rate constant of terminal double-bond polymerization, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [l/mol·sec]

$k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{tp}$ : termination rate constant, [l/mol·sec]

$k_d$ : desorption rate constant

$k'_d$ : specific desorption rate constant, [l·mol·dm/sec]

$d_m$ : density of monomer, [g/l]

$d_p$ : density of polymer, [g/l]

$R_{fm}$ : transfer rate to monomer, [mol/l·sec]

$R_t$ : termination rate, [mol/l·sec]

$R_i$ : initiation rate, [mol/l·sec]

$N$ : total number of polymer particles, [particles/l]

$n$ : average number of radicals per particles, [-]

$[M_p]$ : monomer concentration within the polymer particles, [mol/l]

$[R_r \cdot]$ : concentration of radical polymer with  $r$  units, [mol/l]

$[P_r]$ : concentration of dead polymer with  $r$  units, [mol/l]

$M_0$ : initial monomer concentration, [mol/l]

$V_p$ : total volume of monomer-swollen polymer particles, [l]

$N_A$ : Avogadro's number,

$f$ : initiator efficiency, [-]

$Q_n$ :  $n$ th moment of dead polymer, [mol/l]

$Y_n$ :  $n$ th moment of polymer radical, [mol/l]

$B_n$ : average number of branch points per molecule, [-]

$M_n$ : number-average molecular weight, [g/mol]

$M_w$ : weight-average molecular weight, [g/mol]

$m_0$ : molecular weight of monomer, [g/mol]

$x$ : degree of conversion, [-]

$x_c$ : conversion at which the separate monomer phase disappears, [-]

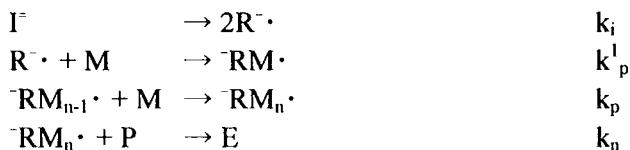
Fris, N. and Hamielec, A. E., *J. Appl. Polym. Sci.*, **19**, 97 (1975).

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**Emulsion polymerization**

Initiator: peroxydisulfate

Temperature: 50°C



$I^-$ : initiator, P: latex particle, M: monomer,  $2R^- \cdot$ : primary radical,  $\bar{R}M_n \cdot$ : growing polymer radical containing n units of monomer, E: entry into particle.

z	$k_i$	$k_p$	$k_t$	[M]	[I]
50	$1.3 \times 10^{-6}$	$3 \times 10^3$	$1 \times 10^8$	0.35	$10^{-2}-10^{-5}$

$k_i$ : decomposition rate constant of initiator, [1/sec]

$k_p^1$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_n$ : entry rate constant of oligomeric free radicals into the particles, [l/mol·sec]

z: critical value of the degree of aqueous phase polymerization, [-]

[M]: monomer concentration, [mol/l]

[I]: initiator concentration, [mol/l]

Hawkett, B. S., Napper, D. H., and Gilbert, R. G., *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 3173 (1981). Copyright © 1981 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Emulsion polymerization**

Initiator: potassium persulfate

Emulsifier: sodium lauryl sulfate

Temperature: 43–45°C

Maximum conversion: 50%

$$R_p = k_p [M]_p (2k_d [I]_w V_w V_p / k_t)^{1/2}$$

$$k_d = 1.95 \times 10^{-7} \text{ [1/sec] at } 43^\circ\text{C}$$

$$k_t = 1.375 \times 10^7 \text{ [l/mol}\cdot\text{sec] in polymer phase}$$

$R_p$ : polymerization rate, [mol/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_t$ : termination rate constant, [l/mol·sec]

$[M]_p$ : concentration of monomer in the polymer phase, [mol/l]

$[I]_w$ : concentration of initiator in aqueous phase, [mol/l]

$V_w$ : volume fraction of the aqueous phase, [-]

$V_p$ : volume fraction of the polymer phase that contains polymer particles and the monomer.

Trivedi, M. K., Rajagopal, K. R., and Joshi, S. N., *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2011 (1983). Copyright © 1983 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Photo-induced, thermally-induced, and peroxide induced bulk polymerization

Temperature: 25°C

$$k_p = 1 \times 10^3$$

$$k_t = 8 \times 10^7$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

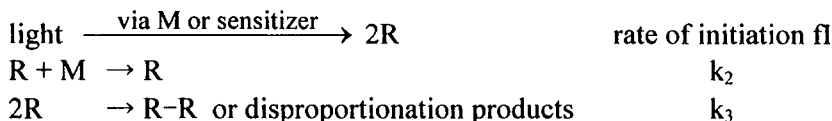
Bartett, P. D. and Swain, C. G., *J. Am. Chem. Soc.*, **67**, 2273 (1945).

© 1945 American Chemical Society.

### Photo-induced bulk polymerization

Sensitizer: benzoyl peroxide

Temperature: 25°C



R: free radical, M: monomer, R-R: dead polymer.

$$k_1 = 3 \times 10^{-8}$$

$$k_2 = 1.1 \times 10^3$$

$$k_3 = 8 \times 10^7$$

$k_1$ : decomposition rate constant of initiator, [1/sec]

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : termination rate constant, [l/mol·sec]

I: intensity of light

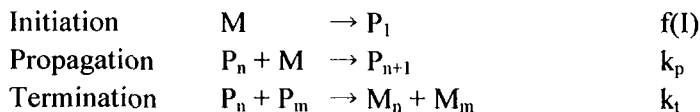
Swain, C. G. and Bartlett, P. D., *J. Am. Chem. Soc.*, **68**, 2381 (1946).

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### Photo-induced bulk polymerization

Sensitizer: benzoquinone

Temperature: 15.9–31.4°C



M: monomer,  $P_r$ : active polymer molecule of  $r$  units,  $M_r$ : deactivated polymer of  $r$  units.

$$\text{at } 15^\circ\text{C} \quad k_t = 3.1 \times 10^9$$

$$k_p = 7.7 \times 10^2$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

I: intensity of light

Burnett, G. M. and Melville, H. W., *Proc. Roy. Soc., London*, **A189**, 456 (1947).

**Photo-induced bulk polymerization**

Temperature: -15-0°C

Initiation	$2M \rightarrow 2X \text{ or } D_2$	$\text{rate}=\alpha I[M]^2$
Propagation	$X + M \rightarrow X$	$k_2$
Transfer	$D_2 + M \rightarrow D_1 + R$	$k_3$
	$D_1 + M \rightarrow P_2 + R$	$k_3$
	$R + M \rightarrow P_1 + R$	$k_3$
Termination	$D_2 + X \rightarrow D_1 + Q$	$2k_4$
	$D_1 + X \rightarrow P_2 + Q$	$k_4$
	$R + X \rightarrow P_1 + Q$	$k_4$
	$2X \rightarrow 2Q$	$k_4$

M: monomer, X: active center, Q: dead center,  $D_2$ : initial polymer growing at both ends,  $D_1$ : polymer growing at one end only, R: growing transfer polymer,  $P_1$ : dead transfer polymer,  $P_2$ : initial polymer.

Temperature [°C]	$k_2$ [l/mol·sec]	$k_3$ [l/mol·sec]	$k_4$ [l/mol·sec]
0	$2.8 \times 10^3$	$1.4 \times 10^{-1}$	$2.2 \times 10^8$
-15	$2.0 \times 10^3$	$7.3 \times 10^{-2}$	$2.2 \times 10^8$

**Activation energies and frequency factors**

Rate constant	E [kcal/mol]	A [l/mol·sec]
$k_2$	3.2	$9.8 \times 10^5$
$k_3$	6.1	$9.9 \times 10^3$
$k_4$	0	$2.2 \times 10^8$

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : transfer rate constant to monomer, [l/mol·sec]

$k_4$ : termination rate constant, [l/mol·sec]

E: activation energy, [kcal/mol]

A: frequency factor, [l/mol·sec]

I: intensity of light

$\alpha$ : constant

[M]: monomer concentration, [mol/l]

Dixon-Lewis, G., *Proc. Roy. Soc., London*, **A195**, 510 (1949).

### Photo-induced bulk polymerization

Sensitizer:  $\alpha$ -azobis(isobutyronitrile)

Temperature: 0–60°C

		Rate
Initiation		$R_i$
Propagation	$M\cdot + M \rightarrow M\cdot$	$k_p[M\cdot][M]$
Termination	$M\cdot + M\cdot \rightarrow \text{polymer}$	$2k_t[M]^2$
Transfer with monomer	$M\cdot + M \rightarrow \text{polymer} + \text{radical from monomer}$	$k_{tr}[M\cdot][M]$

M: monomer,  $M\cdot$ : growing polymer radical.

Temperature [°C]	0	15.9	25	50	60
$k_p$	325	690	1012	2640	3700
$2k_t \times 10^{-7}$	2.7	4.5	5.88	11.68	14.8
$k_{tr}$				0.002	

$$k_p = 2.43 \times 10^8 \exp(-7320 \text{ cal/RT})$$

$$2k_t = 4.16 \times 10^{11} \exp(-5240 \text{ cal/RT})$$

$R_i$ : rate of initiation, [mol/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{tr}$ : transfer rate constant with monomer, [l/mol·sec]

Matheson, M. S., Auer, E. E., Bevilacqua, E. B., and Hart, E. J., *J. Am. Chem. Soc.*, **71**, 2610 (1949).

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### Photo-induced bulk polymerization

Sensitizer: di-tert-butylperoxide

Temperature: 25°C

$$2k_3 \times 10^{-7} = 5.66 - 6.12$$

$$k_2 \times 10^{-3} = 0.944 - 1.01$$

$k_2$ : propagation rate constant, [l/mol·sec]

$k_3$ : termination rate constant, [l/mol·sec]

Kwart, H., Broadbent, H. S., and Bartlett, P. D., *J. Am. Chem. Soc.*, **72**, 1060 (1950).

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### Photo-induced polymerization

Sensitizer: 2,2'-azobisisobutyronitrile

Temperature: 15°C

$$k_p/k_t = 3.5 \times 10^{-6}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Majury, T. G. and Melville, H. W., *Proc. Roy. Soc. London*, **A205**, 496 (1951).

### Photo-induced bulk polymerization

Sensitizer:  $\alpha$ -azobis(isobutyronitrile)

Temperature: 15°C

$$k_p/k_t = 2.0 \times 10^{-5}$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Grassie, N. and Melville, H. W., *Proc. Roy. Soc., London*, **A207**, 285 (1951).

**Photo-induced bulk polymerization**Sensitizer:  $\alpha$ -azobis(cyclohexane)carbonitrile

Temperature: 15°C

$$k_p/k_t=2.5 \times 10^{-5}$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Bengough, W. I. and Melville, H. W., *Proc. Roy. Soc., London*, **A225**, 330 (1954).**Photo-induced bulk polymerization**

Sensitizer: 1,1,1'-azobis(cyclohexane)carbonitrile

Temperature: 16–62°C

Maximum conversion: 65%

Temperature: 25°C

Conversion [%]	$k_p$	$k_t \times 10^{-5}$
4	895	240
23	1290	126
46	1980	90
57	555	6.7
65	87	1.15



Temperature: 15°C (early stage of polymerization)

$$k_p=574, k_t=2.4 \times 10^7$$

Conversion [%]	$E_t$	$E_p$
4	< 1	$\geq 4.2$
6	< 1	$\geq 4.2$
20	–	$\geq 4.0$
23	1.4	4.2
46	3.4	3.6
54	10.8	7.4
57	11.8	8.6
65	> 13.0	> 11.4
73	> 15.4	> 14.4

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$E_p$ : energy of activation for propagation, [kcal/mol]

$E_t$ : energy of activation for termination, [kcal/mol]

Bengough, W. I. and Melville, H. W., *Proc. Roy. Soc., London*, **A230**, 429 (1955).

### Photo-induced bulk polymerization

Sensitizer: azobisisobutyronitrile

Temperature: 30 and 40°C

$$k_p/k_t=2.72 \times 10^{-3} \exp(3250 \text{ cal/RT})$$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Miyama, H., *Bull. Chem. Soc. Japan*, **29**, 715 (1956).

**Photo-induced bulk polymerization**

Sensitizer: 1,1'-azobis(cyclohexane)carbonitrile

Temperature: 20°C

Maximum conversion: 71.10%

Conversion	$k_p/k_t \times 10^5$
0	1.08
28.15	2.02
39.00	2.72
49.80	4.78
59.30	13.1
66.40	16.3
71.10	18.5

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec]Miyama, H., *Bull. Chem. Soc. Japan*, **29**, 720 (1956).**Photo-induced bulk polymerization**

Sensitizer: 1,1'-azobis(cyclohexane)carbonitrile

Temperature: 20°C

Maximum conversion: 71.10%

Conversion	$k_p$	$k_t \times 10^5$
0	559	518
28.15	484	172
39.00	354	85.8
49.80	149	15.6
59.30	29.0	0.90
66.40	9.52	0.20
71.10	2.93	0.05

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Miyama, H., *Bull. Chem. Soc. Japan*, **30**, 10 (1957).

### Photo-induced bulk polymerization

Sensitizer: 1,1'-azobis(cyclohexane)carbonitrile

Temperature: 30°C

Maximum conversion: 68.1%

Conversion	$k_p/k_t \times 10^5$
0	1.20
1.2	1.22
2.4	1.26
3.6	1.31
4.9	1.37
6.2	1.43
7.5	1.49
8.9	1.53
10.3	1.56
10.7	1.64
13.1	1.72
14.6	1.88
16.1	2.10
20.8	2.63
28.8	3.50
37.3	4.89
45.5	6.15
53.2	11.0
60.0	18.2
68.1	35.8

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Miyama, H., *Bull. Chem. Soc. Japan*, **30**, 459 (1957).

**Photo-induced bulk polymerization**

Sensitizer: 1,1'-azo-bis-(cyclohexane)carbonitrile

Temperature: 15°C

$$k_p=795$$

$$k_t=4.6 \times 10^7$$

$$\text{Overall energy of activation}=4.6 \text{ [kcal/mol]}$$

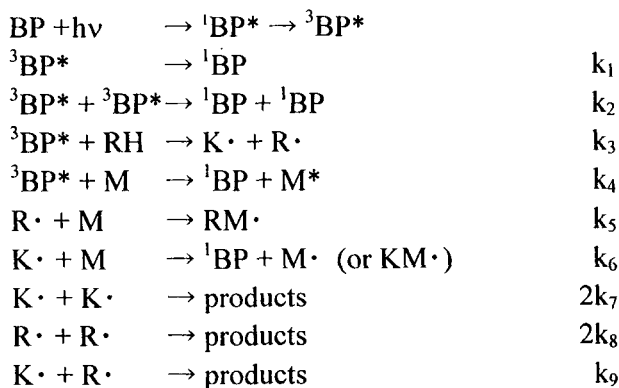
$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Bengough, W. I., *Trans. Faraday Soc.*, **54**, 868 (1958).

**Photo-induced bulk polymerization**

Sensitizer: benzophenone



BP: benzophenone, <sup>3</sup>BP\*: triplet excited benzophenone molecules, M: monomer, RM·: growing polymer radical.

$$k_4=(5.4 \pm 0.5) \times 10^8 \text{ [l/mol·sec]}$$

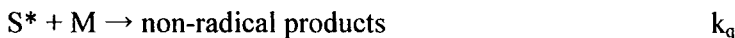
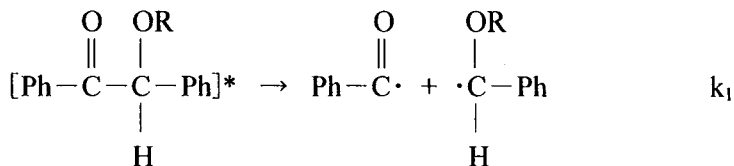
$$k_6=(5.5 \pm 1.5) \times 10^3 \text{ [l/mol·sec]} \quad \text{at [M] = 0.4 [mol/l]}$$

Kuhlmann, R. and Schnabel, W., *Polymer*, **17**, 419 (1976).

**Photo-induced solution polymerization**

Sensitizer: benzoin (B), benzoinacetate (BA), Benzoinmethylether (BME), and benzoinisopropylether (BIPE)

Solvent: benzene



S\*: excited sensitizer, M: monomer.

Sensitizer	B		BA		BME	
	$k_1$ [1/sec]	$k_q/k_1$ [l/mol]	$k_1$ [1/sec]	$k_q/k_1$ [l/mol]	$k_q$ [l/mol]	$k_q/k_1$ [l/mol]
	$1.2 \times 10^9$	$< 10^{-2}$	$5.3 \times 10^7$	1.1	$6 \times 10^7$	$< 10^{-2}$

$k_1$ : decomposition rate constant, [1/sec]

$k_q$ : rate constant for reaction of monomers with excited sensitizers which lead to non-radical products, [l/mol·sec]

$k_{qr}$ : rate constant for reaction of monomers with excited sensitizers which lead to radical products, [l/mol·sec]

Kuhlmann, R. and Schnabel, W., *Angew. Makromol. Chem.*, **70**, 145 (1978).

**Photo-induced solution polymerization**

Sensitizer: azobiscyclohexane carbonitrile (ACN)

Solvent: see table (50 vol%)

Temperature: 30°C

Solvent	$\tau$ [sec]	$k_p$ [l/mol·sec]	$2k_t \times 10^{-7}$ [l/mol·sec]
None <sup>(1)</sup>	0.42	3550	2.8
Benzene	0.49	290	2.3
Toluene	0.43	250	3.0
Ethylbenzene	0.48	80	2.6
Chlorobenzene	0.50	110	2.1
o-Dichlorobenzene	0.40	170	3.4
Cyclohexane	0.39	2350	3.1
1,2-Dichloroethane	0.50	2730	1.9
1,1,2,2-Tetrachloroethane	0.42	1130	3.2

<sup>(1)</sup>No solvent case, [VAc]=10.72 [mol/l] and [ACN]= $1.50 \times 10^{-3}$  [mol/l]

In the other cases, [VAc]=5.36 [mol/l]

 $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec] $\tau$ : radical life time, [sec]

[VAc]: concentration of vinyl acetate, [mol/l]

[ACN]: concentration of ACN, [mol/l]

Yamamoto, T., Yamamoto, T., Mito, A., and Hirota, M., *Nippon Kagaku Kaishi*, **3**, 408 (1979).

**Radiation-induced emulsion polymerization**Radiation source:  $\gamma$ -ray

Ingredients: water, polyvinylacetate, and vinylacetate

Initiator: polyvinylacetate

Temperature: 14–28°C

Initiator	Temperature [°C]	$k_p$ [l/mol·sec]
$\gamma$ -ray	15	230
$\gamma$ -ray	14	230
$\gamma$ -ray	28	220
PVA latex and $\gamma$ -ray	25	310–470

 $k_p$ : propagation rate constant, [l/mol·sec]Allen, P. E. M., Burnett, G. M., Downer, J. M., and Majer, J. R., *Makromol. Chem.*, **58**, 169 (1962).**Solution and bulk polymerization**

Solvent: ethylacetate and n-hexane

Temperature: 31–63°C

Solvent	Activation energy [kcal/mol]
Ethylacetate	4.42
n-Hexane	-1.30

	Bulk	Normal solution	Abnormal (after 5% polymerization)
$k_p$	$6.7 \times 10^2$	$7.0 \times 10^2$	$6.8 \times 10^2$
$k_t$	$2.5 \times 10^9$	$2.6 \times 10^9$	$5.0 \times 10^8$

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Burnett, G. M. and Melville, H. W., *Proc. Roy. Soc., London*, **A189**, 494 (1947).

### Solution polymerization

Solvent: see table

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 60°C

Solvent	$C_S \times 10^5$	$k_{tr,S} \times 10^2$ [l/mol·sec]
Benzene	29.60	109.5
Toluene	208.90	772.7
Ethyl benzene	551.50	2040.0
Chlorobenzene	83.50	308.9
Chloroform	1251.80	4633.0
Carbon tetrachloride	–	–
Acetone	117.00	432.9

$$k_p = 3700$$

$$C_S = k_{tr,S} / k_p$$

$k_{tr,S}$ : transfer rate constant to solvent, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

Chadha, R. N., Shukla, J. S., and Misra, G. S., *Trans. Faraday Soc.*, **53**, 240 (1957).



**Solution polymerization**

Solvent: benzene

Initiator: 2,2'-azobis(isobutyronitrile)

Temperature: 60°C

		Rate
Initiation	$\rightarrow R$	I
Propagation	$R + M \rightarrow P_1$	$k'_p[R][M]$
	$P_r + M \rightarrow P_{r+1}$	$k_p[P][M]$
Chain termination	$P_r + P_s \rightarrow \text{polymer}$	$k_t[P]^2$
	$P_r + R \rightarrow \text{polymer}$	$k'_t[R][P]$
	$2R \rightarrow \text{products}$	$2k''_t[R]^2$

R: primary radical, M: monomer,  $P_r$ : growing radical with r units of monomer.

$k_p$	$k'_p$	$2k_t \times 10^{-7}$
2300	9	6.0

I: decomposition rate of initiator, [mol/l·sec]

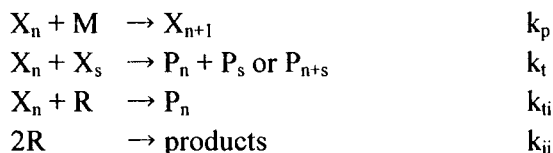
 $k'_p$ : initiation rate constant, [l/mol·sec] $k_p$ : propagation rate constant, [l/mol·sec] $k_t$ : termination rate constant, [l/mol·sec] $k'_t$ : rate constant for termination by primary radical, [l/mol·sec] $k''_t$ : rate constant for reaction between primary radicals, [l/mol·sec]Allen, P. E. M. and Patrick, C. R., *Makromol. Chem.*, **48**, 89 (1961).**Solution polymerization**

Solvent: ethyl acetate (EA) and dimethyl carbitol (DC)

Initiator: 2,2'-azobis(2,4-dimethylvaleronitrile)

Temperature: 50°C

C	$\rightarrow 2R$	$k_d$
R + M	$\rightarrow X_1$	$k_i$



C: initiator, R: primary radical, M: monomer,  $X_n$ : growing radical with  $n$  units of monomer,  $P_n$ : dead polymer with  $n$  units of monomer.

Solvent	Solvent/monomer [volume/volume]	$k_t/k_p^2$	$k_{ii}/k_i k_p \times 10^{-4}$
EA	1	29.0	6.8
DC	3	18.4	5.4
DC	7	16.2	7.0

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{ti}$ : rate constant for termination by primary radical, [l/mol·sec]

$k_{ii}$ : rate constant for reaction between primary radicals, [l/mol·sec]

Ito, K., *J. Polym. Sci.*, A-1, 10, 1481 (1972). Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Thermally-induced and photo-induced solution polymerization

Initiator: 2,2'-azobis(isobutyronitrile) (AZBN)

Sensitizer: 2,2'-azobis(cyclohexane-1-carbonitrile)

Solvent: shown in table

Temperature: 30°C

## Thermally-induced polymerization

Solvent	$k_p^2/k_t \times 10^5$ [l/mol·sec]
C <sub>6</sub> H <sub>5</sub> -OCH <sub>3</sub>	0.974
C <sub>6</sub> H <sub>6</sub>	4.30
C <sub>6</sub> H <sub>5</sub> -F	3.02
C <sub>6</sub> H <sub>5</sub> -Cl	1.39
C <sub>6</sub> H <sub>5</sub> -COOC <sub>2</sub> H <sub>5</sub>	0.334
C <sub>6</sub> H <sub>5</sub> -CN	0.0235
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	430.8
C <sub>6</sub> D <sub>6</sub>	3.64

Initiator [2,2'-azobis(isobutyronitrile)]=0.10 [mol/l]  
[monomer]=2.00 [mol/l], Inhibitor=p-benzoquinone

## Photo-induced polymerization

Solvent	$k_p \times 10^{-2}$ [l/mol·sec]	$k_t \times 10^{-8}$ [l/mol·sec]
C <sub>6</sub> H <sub>5</sub> -OCH <sub>3</sub>	0.48 ± 0.05	2.39 ± 0.45
C <sub>6</sub> H <sub>6</sub>	1.17 ± 0.12	3.19 ± 0.61
C <sub>6</sub> H <sub>5</sub> -F	0.97 ± 0.10	3.11 ± 0.59
C <sub>6</sub> H <sub>5</sub> -Cl	0.61 ± 0.09	2.66 ± 0.75
C <sub>6</sub> H <sub>5</sub> -COOC <sub>2</sub> H <sub>5</sub>	0.37 ± 0.05	4.12 ± 1.04
C <sub>6</sub> H <sub>5</sub> -CN	0.08 ± 0.10	2.58 ± 0.76
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	6.37 ± 1.01	0.942 ± 0.237
C <sub>6</sub> D <sub>6</sub>	1.13 ± 0.10	3.51 ± 0.54

Sensitizer [2,2'-azobis(cyclohexane-1-carbonitrile)]=  
 $3.00 \times 10^{-3}$  [mol/l], [monomer]=2.00 [mol/l]

## Photo-induced polymerization

Solvent		$k_p \times 10^{-2}$ [l/mol·sec]
EtAc:EtBz Molar ratio	EtAc:EtBz Volume ratio	
8.22:0	1:0	637
5.48:1.88	2:1	104
4.11:2.82	1:1	78
2.74:3.76	1:2	48
0:5.64	0:1	37

[Monomer]=2.0 [mol/l]

EtAc: ethyl acetate, EtBz: ethyl benzoate

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Kamachi, M., Liaw, D. J., and Nozakura, S., *Polym. J.*, **11**, 921 (1979).

## 1.9 Vinyl chloride

### Bulk polymerization

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 30, 50, and 70°C

$$R = k_p(fk_d[I]/k_t)^{1/2} = k[I]^{1/2}$$

$$R_i = k_i[I]^{1/2}$$

Temperature [°C]	$(k_p^2/k_t) \times 10^{-2}$ [1/hr·mol%]	$k_i$ [1/hr·(mol%) <sup>1/2</sup> ]
30	1.89	0.23
50	2.41	1.25
70	3.61	6.21

$$C_M = k_{fm}/k_p = 5.78 \exp(-2768.1/T)$$

$$k_i = 3.54 \times 10^{11} \exp(-8505.5/T)$$

$$k_d = 3.79 \times 10^{18} \exp(-15460/T)$$

[I]: initiator concentration, [mol%]

R: overall rate of polymerization, [1/hr]

k: overall rate constant of polymerization, [1/hr·(mol%)<sup>1/2</sup>]

R<sub>i</sub>: initiation rate, [1/hr]

k<sub>i</sub>: initiation rate constant, [1/hr·(mol%)<sup>1/2</sup>]

k<sub>fm</sub>: transfer rate constant to monomer, [1/hr·mol%]

k<sub>d</sub>: initiator decomposition rate constant, [1/hr]

k<sub>p</sub>: propagation rate constant, [1/hr·mol%]

k<sub>t</sub>: termination rate constant, [1/hr·mol%]

f: initiator efficiency, [-]

Abdel-Alim, A. H. and Hamielec, A. E., *J. Appl. Polym. Sci.*, **16**, 783 (1972).

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**Bulk polymerization**

Initiator: lauroyl peroxide

Temperature: 50°C

$$dC/dt = (k_i[I]_0/k_{tp})^{1/2} 0.45 k_p C^{1/2}$$

$$k_{tp} = 1.3 \times 10^8, \quad k_p = 1.1 \times 10^4, \quad k_i = 1.15 \times 10^{-6}$$

C: conversion, [-]

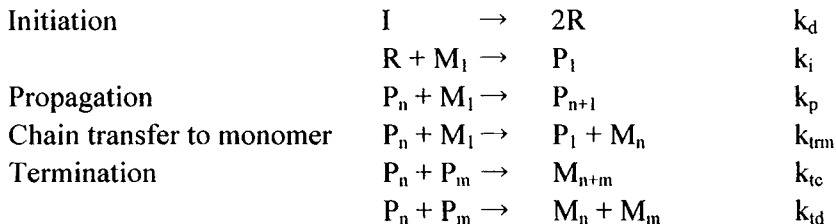
 $k_{tp}$ : termination rate constant in the polymer phase, [l/mol·sec] $k_p$ : propagation rate constant, [l/mol·sec] $k_i$ : rate constant for the decomposition of initiator, [1/sec] $[I]_0$ : initial concentration of initiator, [mol/l]

Ugelstad, J., Fløgstad, H., Hertzberg, T., and Sund, E., *Makromol. Chem.*, **164**, 171 (1973).

**Bulk polymerization**

Initiator: lauroyl peroxide

Temperature: 50°C



I: initiator, R: primary radical,  $M_1$ : monomer,  $P_n$ : growing polymer radical with n units of monomer,  $M_n$ : dead polymer with n units of monomer.

$$k_p = 1.013 \times 10^4, \quad k_i = 1.8702 \times 10^9$$

$$k_{trm} = 10.02, \quad k_d = 1.15 \times 10^{-6}$$

 $k_p$ : propagation rate constant, [l/mol·sec] $k_i$ : initiation rate constant, [l/mol·sec] $k_{trm}$ : chain transfer rate constant to monomer, [l/mol·sec] $k_{tc}$ : termination rate constant by combination, [l/mol·sec]

$k_{td}$ : termination rate constant by disproportionation, [1/mol·sec]

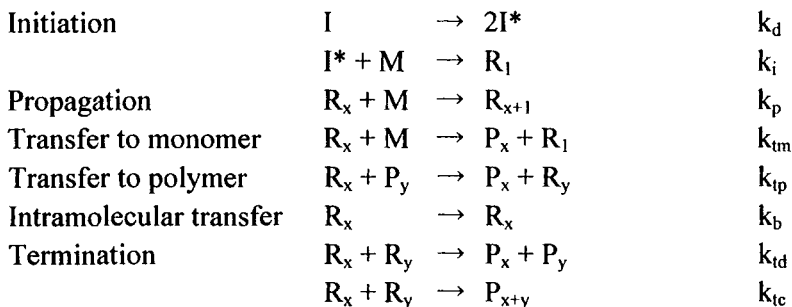
$k_d$ : decomposition rate constant, [1/sec]

Ray, W. H., Jain, S. K., and Salovey, R., *J. Appl. Polym. Sci.*, **19**, 1297 (1975).

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### Bulk and suspension polymerization

Temperature: 50 °C



M: monomer, I: initiator,  $I^*$ : primary radical,  $R_x$ : growing polymer radical with n units of monomer,  $P_x$ : dead polymer with n units of monomer.

$$\begin{aligned}
 k_b &= 0.0115k_{tm} \\
 k_d &= 6.32 \times 10^{16} \exp(-15460/T) \\
 k_{p0} &= 3 \times 10^9 \exp(-3320/T) \\
 k_p &= k_{p0} \exp\{0.2(1/V_f - 1/V_{fer})\} \\
 k_{tm} &= 5.78k_p \exp(-2768/T) \\
 k_{tp} &= 0.32k_{tm} \\
 k_{t1} &= 7.8 \times 10^{13} \exp(-2190/T) \\
 V_0 &= 5 [I] \\
 V_{fer} &= V_f \text{ at } x_f \\
 V_f &= \alpha x + \beta \\
 \alpha &= -0.41591 \\
 \beta &= 0.42642
 \end{aligned}$$

$k_b$ : rate constant for short-chain branching, [1/min]

$k_d$ : rate constant for decomposition of initiator, [1/min]

$k_i$ : rate constant for chain initiation, [1/mol·min]

$k_p$ : rate constant for chain propagation, [l/mol·min]

$k_{tc}$ : rate constant for termination by combination, [l/mol·min]

$k_{td}$ : rate constant for termination by disproportionation, [l/mol·min]

$k_{tm}$ : rate constant for chain transfer to monomer, [l/mol·min]

$k_{tp}$ : rate constant for chain transfer to polymer, [l/mol·min]

$k_t = k_{tc} + k_{td}$

$k_{t1}$ : termination rate constant in monomer rich phase, [l/mol·min]

$V_f$ : free volume fraction of reacting mixture in polymer-rich phase

$V_{fcr}$ : critical value of  $V_f$  beyond the propagation rate becomes diffusion-controlled

Sidiropoulou, E. and Kiparissides, C., *J. Macromol. Sci.-Chem.*, **A27**, 257 (1990).

### Emulsion polymerization

Initiator:  $K_2S_2O_8$

Emulsifier: Empicol-8043 (sodium laurylsulfate) and  
Aerosol DBM (di-n-butylsulfosuccinate)

Temperature: 50°C

$$r_p = k_p C_M^p n N^w / N_A$$

$$C_M^p = 6 \text{ [mol/l]}$$

$$k_p = 3.6 \times 10^7 \text{ [l/mol·hr]}$$

$$n = 10^{-5} - 5 \times 10^{-4}$$

$r_p$ : polymerization rate, [mol VC/l  $H_2O$ ·hr].

VC: vinyl chloride.

$k_p$ : propagation rate constant, [l/mol·hr]

$C_M^p$ : monomer concentration in latex particles [mol/l]

$N_A$ : Avogadro's number, [number/mol]

$n$ : average number of radicals per latex particle, [-]

$N^w$ : number of latex particles per liter  $H_2O$ . [1/l]

Ugelstad, J., Mork, P. C., Dahl, P., and Rangnes, P., *J. Polym. Sci.*, **C27**, 49 (1969).

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**Photo-induced solution polymerization**

Sensitizer: 1,1-azo-1-cyclohexanenitrile

Solvent: tetrahydrofuran (THF)

Retarder: 2,2'-diphenyl-1-picryl hydrazyl

Temperature: 25–55°C

Initiation	$A + h\nu \rightarrow R$	Rate
	$R + M \rightarrow P$	$R_i$
Propagation	$P + M \rightarrow P$	$k_p[P][M]$
Monomer termination	$P + M \rightarrow \text{inactive products}$	$k_x[P][M]$
Mutual termination	$P + P \rightarrow \text{inactive products}$	$k_t[P]^2$

A: photosensitizer, R: primary radical from sensitizer, M: monomer, P: growing polymer radical.

$$k_x = 1.9 \times 10^5 \exp(-7800 \text{ cal/RT})$$

$$k_t = 1.3 \times 10^{12} \exp(-4200 \text{ cal/RT})$$

$$k_p = 3.3 \times 10^6 \exp(-3700 \text{ cal/RT})$$

$$R_i = 2.07 \times 10^{-8} \text{ [mol/l} \cdot \text{sec] at } 25^\circ\text{C}$$

$$R_i = 3.39 \times 10^{-8} \text{ [mol/l} \cdot \text{sec] at } 55^\circ\text{C}$$

$$\text{Activation energy of initiation} = 3200 \text{ [cal/mol]}$$

$k_x$ : monomer termination rate constant, [l/mol·sec]

$k_t$ : mutual termination rate constant, [l/mol·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$R_i$ : initiation rate, [mol/l·sec]

Burnett, G. M. and Wright, W. W., *Proc. Roy. Soc., London*, **A221**, 41 (1954).

**Solution polymerization**

Solvent: tetrahydrofuran

Initiator: 2,2'-azobisisobutyronitrile

Temperature: 40°C

$$I=2fk_d[C]$$

$$k_d=2 \times 10^{-2}, f=0.75$$

$$C_M=k_f/k_p=5 \times 10^{-3}$$

$$C_S=k_{ts}/k_p=3 \times 10^{-3}$$

I: initiation rate, [mol/l·hr]

f: initiator efficiency, [-]

 $k_d$ : initiator decomposition rate constant, [1/hr] $k_f$ : monomer transfer rate constant, [l/mol·hr] $k_p$ : propagation rate constant, [l/mol·hr] $k_{ts}$ : solvent transfer rate constant, [l/mol·hr]

[C]: initiator concentration, [mol/l]

Mickley, H. S., Michaels, A. S., and Moore, A. L., *J. Polym. Sci.*, **60**, 121 (1962).

Copyright © 1962 John Wiley &amp; Sons, Inc. Reprinted by permission of John Wiley &amp; Sons, Inc.

**Solution polymerization**

Solvent: diethyl oxalate and 2,4-dichloropentane

Initiator: 2,2'-azobis(2,4-dimethyl-4-methoxy) valeronitrile

Transfer agent: tetrabromomethane

Temperature: 25°C

$$k_p^2/k_t=4.1 \times 10^{-2}$$

 $k_p$ : propagation rate constant $k_t$ : transfer rate constantRyska, M., Kolinsky, M., and Lim, D., *J. Polym. Sci.*, **C16**, 621 (1967).

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**Solution polymerization**

Solvent: 1,2-dichloroethane

Initiator: lauroyl peroxide

Temperature: 50°C

$$1/P_n = (1/P_n)_0 + C_S[S]/[M]$$

$$(1/P_n)_0 = C_M + (fk_d k_t)^{1/2} [I]^{1/2} / k_p [M]$$

$$C_M = k_{tm} / k_p = 1.1 \times 10^{-3}$$

$$C_S = k_{ts} / k_p = 4.5 \times 10^{-4}$$

$$k_t^{1/2} / k_p = 1.69 [\text{min}^{1/2} \cdot \text{mol}^{1/2} / \text{l}^{1/2}]$$

 $P_n$ : number-average polymerization degree, [-] $(P_n)_0$ : number-average polymerization degree in absence of solvent, [-]

[S]: concentration of solvent, [mol/l]

[M]: concentration of monomer, [mol/l]

[I]: concentration of initiator, [mol/l]

 $k_d$ : decomposition rate constant of initiator, [1/min] $k_p$ : propagation rate constant, [l/mol·min] $k_t$ : termination rate constant, [l/mol·min] $k_{ts}$ : transfer rate constant to solvent, [l/mol·min] $k_{tm}$ : transfer rate constant to monomer, [l/mol·min]

f: initiator efficiency, [-]

Vidotto, G., Crosato-Arnaldi, A., and Talamini, G., *Makromol. Chem.*, **114**, 217 (1968).

**Suspension polymerization**

Medium: water

Suspending agent: vinylacetate/maleic anhydride copolymer

Initiator: lauroyl peroxide (LPO), benzoyl peroxide (BPO), and  
2,2'-azo-bis-isobutyronitrile (AIBN)

Temperature: 50°C

Maximum conversion: 90%

Rate constant	LPO	AIBN
$k_t^{1/2}/k_p$	1.45	1.85

 $k_p$ : propagation rate constant $k_t$ : transfer rate constantCrosato-Arnaldi, A., Gasparini, P., and Talamini, G., *Makromol. Chem.*, **117**, 140 (1968).**Suspension polymerization**

$$dx/dt=r(T(t), t)$$

$$d[I]/dt=-k_d[I]+([I]/\rho)(dx/\rho)(dx/dt)$$

$$r=k[I]^{0.5}R$$

$$R=(1+qx), \quad x \leq \omega_s$$

$$R=p(1-x)g, \quad x > \omega_s$$

$$q=\{p(1-\omega_s)-1\}/\omega_s$$

$$k_d=3.79 \times 10^{18} \exp(-15460/T) \quad [1/\text{hr}]$$

$$k=2.79 \times 10^{13} \exp(-19806/RT) \quad [1/\text{mol}\%^{1/2} \cdot \text{hr}]$$

$$p=5.98 \times 10^{-3} \exp(4828.6/RT)$$

$$1/\rho=(x/\rho_p)+((1-x)/\rho_m) \quad [\text{g}/\text{cm}^3]$$

$$\rho_m=0.85 \quad [\text{g}/\text{cm}^3]$$

$$\rho_p=1.40 \quad [\text{g}/\text{cm}^3]$$

$$g^2=(1-\omega_s)(1-x)$$

[I]: concentration of initiator, [mol%]

x: monomer conversion., [-]

- r: overall polymerization rate, [mol%/hr]  
R: rate defined as above equation, [-]  
T: reaction temperature, [ $^{\circ}$  K]  
 $k_d$ : initiator decomposition rate constant, [1/hr]  
k: overall polymerization rate constant, [1/mol%<sup>1/2</sup>·hr]  
q: kinetic constant defined as above, [-]  
 $\omega_s$ : critical conversion defined as above, [-]  
p: kinetic constant defined as above, [-]  
g: gel effect correlation defined as above, [-]  
 $\rho$ : density of system, [g/cm<sup>3</sup>]  
 $\rho_m$ : density of monomer, [g/cm<sup>3</sup>]  
 $\rho_p$ : density of polymer, [g/cm<sup>3</sup>]

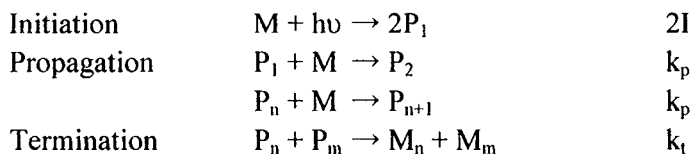
Pinto, J. C., *Polym. Eng. Sci.*, **30**, 925 (1990).

## 1.10 Vinylidene chloride

### Photo-induced bulk polymerization

Temperature: 15–35°C

Maximum conversion: 5.26%



M: monomer,  $P_1$ : primary radical,  $P_n$ : growing radical containing n units of monomer,  $M_n$ : dead polymer containing n units of monomer.

$$d[M]/dt = [M](2I)^{1/2}k_p/k_t^{1/2}$$

Temperature [°C]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]
15	2.3	$0.23 \times 10^5$
25	8.6	$1.75 \times 10^5$
35	36.8	$18.0 \times 10^5$

Activation energy of  $k_p=25$  [kcal/mol]

Activation energy of  $k_t=40$  [kcal/mol]

Frequency factor of  $k_p=A_p$ =the order of  $10^{16}$

Frequency factor of  $k_t=A_t$ =the order of  $10^{30}$

[M]: monomer concentration, [mol/l]

I: light density, [mol radical/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : mutual termination rate constant, [l/mol·sec]

Burnett, J. D. and Melville, H. W., *Trans. Faraday Soc.*, **46**, 976 (1950).

**Thermally-induced and photo-induced solution polymerization**

Solvent: N-methylpyrrolidone

Temperature: 25–75°C

		Rate
Initiation	$I \rightarrow 2R\cdot \rightarrow 2M\cdot$	$2fk_d[I]$
Propagation	$M\cdot + M \rightarrow M\cdot$	$k_p[M][M\cdot]$
Monomer transfer	$M\cdot + M \rightarrow P + M''\cdot$	$k_{tm}[M][M\cdot]$
Solvent transfer	$M\cdot + S \rightarrow P + S\cdot$	$k_{trs}[S][M\cdot]$
Regeneration	$M'\cdot + M \rightarrow M\cdot$	very fast
Termination	$S\cdot + M \rightarrow M\cdot$	$k_r[M][S\cdot]$
	$M\cdot + M\cdot \rightarrow P \text{ or } 2P$	$k_t[M\cdot]^2$
	$M\cdot + S\cdot \rightarrow P$	$\sigma k_t[M\cdot][S\cdot]$
	$S\cdot + S\cdot \rightarrow X$	$\sigma^2 k_t[S\cdot]^2$

I: initiator,  $R\cdot$ : primary radical, M: monomer,  $M'\cdot$ : growing radical,  
S: solvent, P: polymer.

$$\log(k_p)=9.0-1970/T, \log(k_t)=12.0-1160/T$$

$$E_p=9 \pm 1.4, E_t=5 \pm 2.5, A_p=10^9, A_t=10^{12}$$

$k_d$ : decomposition rate constant of initiator, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

$k_{tm}$ : transfer rate constant to monomer, [l/mol·sec]

$k_{trs}$ : transfer rate constant to solvent, [l/mol·sec]

$k_r$ : regeneration rate constant, [l/mol·sec]

$E_p$ : activation energy for propagation reaction, [kcal/mol]

$E_t$ : activation energy for termination reaction, [kcal/mol]

$A_p$ : frequency factor for propagation reaction, [l/mol·sec]

$A_t$ : frequency factor for termination reaction, [l/mol·sec]

Matsuo, K., Nelb, G. W., Nelb, R. G., and Stockmayer, W. H., *Macromolecules*, **10**, 654 (1977). © 1977 American Chemical Society.

## 2. Ionic polymerization

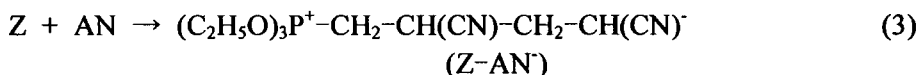
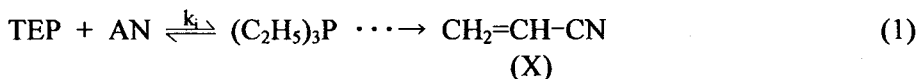
### 2.1 Acrylonitrile

#### Anionic solution polymerization

Solvent: benzene and acetonitrile

Catalyst: triethyl phosphite (TEP)

Temperature: -10–50°C



AN: acrylonitrile, Z: zwitterion.

$$R_p = k_p[\text{AN}^-][\text{AN}]$$

At the low temperature such as below 0°C:

$$k_z < k_i$$

$$k_z[\text{X}] = k_i[\text{AN}^-]$$

$$R_p = (k_z k_p K / k_i) [\text{AN}]^2 [\text{TEP}]$$

At the high temperature such as about room temperature:

$$k_z > k_i$$

$$k_i[\text{Z}] = k_i[\text{AN}^-]$$

$$R_p = (k_i k_p K / k_i) [\text{AN}]^3 [\text{TEP}]$$

Overall activation energy for the polymerization = 6.8 [kcal/mol]

[i]: concentration of species i

R<sub>p</sub>: polymerization rate

k<sub>p</sub>: propagation rate constant

k<sub>t</sub>: termination rate constant



$k_2$ : rate constant for reaction (2)

$k_i$ : initiation rate constant for reaction (3)

$K$ : equilibrium constant for reaction (1)

Ogawa, T. and Quintana, P., *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 2517 (1975).  
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## 2.2 Butadiene

### Anionic solution polymerization

Solvent: n-hexane and tetrahydrofuran (THF)

Catalyst: butyllithium

Temperature: 0–50°C

Maximum conversion: 90%

Solvent	Activation energy of propagation [kcal/mol]
n-hexane	21.5 ± 0.3
THF	6.1 ± 0.05

$$k_p = 4.3 \times 10^4 \exp(-6100 \text{ cal/RT}) \text{ for THF}$$

$k_p$ : propagation rate constant, [l/mol·sec]

Morton, M., Bostick, E. E., Livigni, R. A., and Fetters, L. J., *J. Polym. Sci.*, **A1**, 1735 (1963). Copyright © 1963 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Solvent: cyclohexane, n-hexane, and toluene

Catalyst: n-butyllithium (n-BuLi)

Temperature: 5–50°C

Maximum conversion: 100%

$$R = K[M]^2$$

Polymerization rate constant K [l/mol·min]

Cyclohexane 30°C	Cyclohexane 5°C	Hexane 50°C	Toluene 50°C
0.0012 <sup>(1)</sup>	0.0114 <sup>(1)</sup>	0.0076 <sup>(1)</sup>	0.0443 <sup>(2)</sup>

<sup>(1)</sup>[n-BuLi] > 0.004 [mol/l]. <sup>(2)</sup>[n-BuLi] > 0.010 [mol/l].

R: polymerization rate, [mol/l·min]

K: polymerization rate constant, [l/mol·min]

[M]: monomer concentration, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 153 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Solvent: cyclohexane, n-hexane, and toluene

Catalyst: n-butyllithium(n-BuLi), sec-BuLi, tert-BuLi, and i-BuLi

Temperature: 50°C

$$R_i = k_i [\text{BuLi}] [\text{M}]$$

Initiation rate constant  $k_i$  [l/mol·min]

$k_i$ (n-BuLi)			$k_i$ (Cyclohexane)		
Cyclohexane	n-Hexane	Toluene	n-BuLi	sec-BuLi	tert-BuLi
0.015 ± 0.002	0.024 ± 0.003	0.51 ± 0.03	0.015	0.90	0.16

$R_i$ : initiation rate, [mol/l·min]

$k_i$ : initiation rate constant, [l/mol·min]

[BuLi]: concentration of butyllithium, [mol/l]

[M]: concentration of monomer, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 163 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Solvent: cyclohexane and toluene

Catalyst: sec-butyllithium (sec-BuLi)

Temperature: 5–30°C

$$R_p = k_p [\text{BuLi}]^{1/2} [\text{M}] \quad \text{for } [\text{BuLi}] > 10^{-2} \text{ [mol/l]}$$

$$R_p = k'_p [\text{BuLi}]^{1/3} [\text{M}] \quad \text{for } 10^{-4} < [\text{BuLi}] < 10^{-2} \text{ [mol/l]}$$

Propagation rate constant  $k_p$  and  $k'_p$

Solvent	Temperature [°C]	$k_p$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·min]	$k'_p$ [l <sup>1/3</sup> /mol <sup>1/3</sup> ·min]
Cyclohexane	30	0.033	0.020

$k_p$ : propagation rate constant, [l<sup>1/2</sup>/mol<sup>1/2</sup>·min]

$k'_p$ : propagation rate constant, [l<sup>1/3</sup>/mol<sup>1/3</sup>·min]

$R_p$ : propagation rate, [mol/l·min]

[BuLi]: concentration of sec-butyllithium, [mol/l]

[M]: concentration of monomer, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 173 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

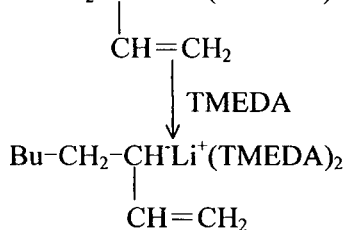
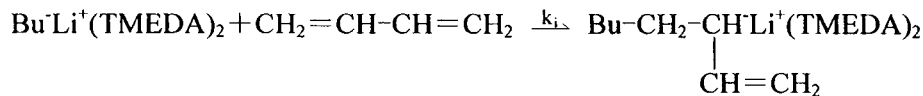
Modifier: N,N,N',N'-tetramethyl ethylene diamine (TMEDA)

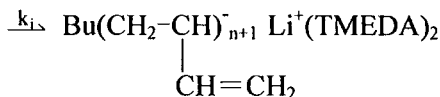
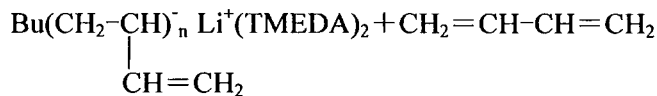
Catalyst: n-butyllithium (n-BuLi)

Solvent: n-hexane

Maximum conversion: 30%

Temperature: -4-7°C





$$\text{Initial polymerization rate} = k_p k_i [\text{B}]^2 [\text{A}]$$

	Activation energy [kJ/mol]	Pre-exponential factor logA	Rate constant $\times 10^3$ at 240°K
Initiation	$15.8 \pm 2.0$	9.5	397.0
Propagation	$14.5 \pm 1.0$	4.8	0.12

$k_i$ : initiation rate constant, [ $\text{dm}^3/\text{mol}\cdot\text{sec}$ ]

$k_p$ : propagation rate constant, [ $\text{dm}^3/\text{mol}\cdot\text{sec}$ ]

[A]: ratio of BuLi/TMEDA

[B]: concentration of butadiene, [ $\text{mol}/\text{dm}^3$ ]

Hay, J. N., McCabe, J. F., and Robb, J. C., *J. Chem. Soc., Faraday, Trans., I*, **68**, 1 (1972).

### Anionic solution polymerization

Solvent: hexane

Catalyst: n-butyllithium (n-BuLi)

Modifier: tetramethyl ethylene diamine (TMEDA)

Temperature: 50–70°C

Maximum conversion: 100% for 60 and 70°C, 90% for 50°C



I: initiator, M: monomer,  $\text{P}_1$ : growing polymer with one unit of monomer,

$\text{P}_x$ : growing polymer with x units of monomer.

For fully modified (excess TMEDA at TMEDA/Li=2.5)

$$K_p[I]_0 = 7.024 \times 10^8 [I]_0 \exp(-10332 \text{ cal/RT})$$

For unmodified polymerization (no TMEDA)

$$K_p[I]_0 = 1.994 \times 10^{12} [I]_0^{0.3338} \exp(-19306 \text{ cal/RT})$$

$K_p$ : propagation rate constant

$K_i$ : initiation rate constant

$[I]_0$ : effective initiator concentration

Chang, C. C., Miller, J. W. Jr., and Schorr, G. R., *J. Appl. Polym. Sci.*, **39**, 2395 (1990). Copyright © 1990 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

## 2.3 $\epsilon$ -Caprolactam

### Anionic polymerization

Catalyst: sodium caprolactam

Cocatalyst (accelerator): hexamethylene-1,6-bis(carbamidocaprolactam)

Initial temperature: 122–156°C

$$v_{Br} = 2.5 \times 10^{18} \exp(-36.6 \text{ kcal/RT}) [\text{catalyst}] [\text{cocatalyst}] [\text{monomer}]$$

$v_{Br}$ : polymerization rate, [mol/l·sec]

[i]: concentration of species i, [mol/l]

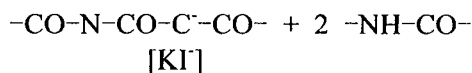
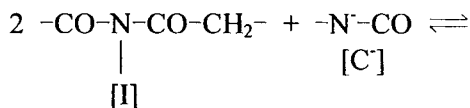
Wittmer, V. P. and Gerrens, H., *Makromol. Chem.*, **89**, 27 (1965)

### Anionic polymerization

Catalyst: a mixture of sodium caprolactam and tetraacetylhexamethylene diamine

Temperature: 140–170°C

Maximum conversion: 9.2 mol%



At 150°C

$$-d[\text{CH}]/dt = k \cdot K^{0.5} [\text{I}] [\text{C}]^{0.5}$$

$$[\text{I}] = (0.44 - 1.77) \times 10^{-2} \text{ [mol/kg]}, \quad [\text{C}] = (0.44 - 0.88) \times 10^{-2} \text{ [mol/kg]}$$

$$kK^{0.5} = 1.62 - 1.79 \text{ [kg}^{1/2}\text{/mol}^{1/2}\text{·sec]}$$

$$\text{Overall activation energy } E = 17.5 \text{ [kcal/mol]}$$

[CH]: concentration of caprolactam, [mol/kg]

[I]: concentration of imide groups in the form of acyllactam and, at more advanced stages of the reaction, in the form of diacylamino groups in the polymeric chain. [mol/kg]

[C]: concentration of sodium caprolactam added, [mol/kg]

K: dissociation constant, [mol/kg]

k: polymerization rate constant, [kg/mol·sec]

Sittler, E. and Sebenda, J., *Collection Czechoslov. Chem. Commun.*, **33**, 270 (1968).

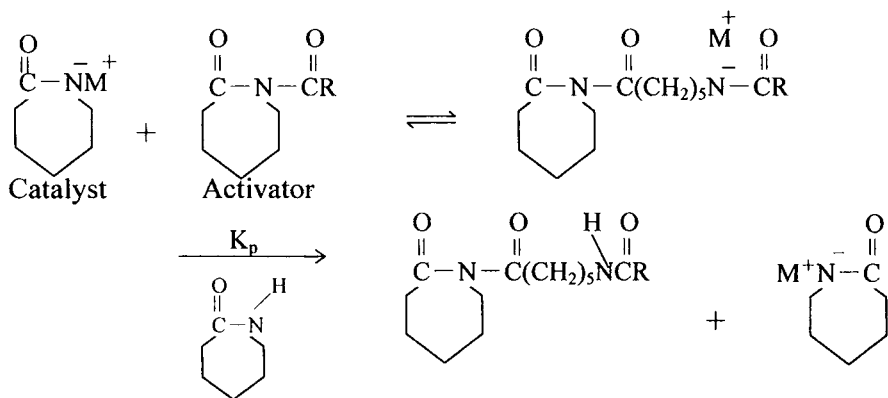
### Anionic polymerization

Catalyst: sodium caprolactam

Activator: N-carbanilinocaprolactam

Temperature: 85–135°C

Maximum conversion: 30%



Temperature [°C]	Activator [equiv]	Catalyst [mol]	$K_p$ [ $l^{3/2}/\text{mol}^{3/2}\cdot\text{min}$ ]
85	0.014	0.009	2.9
100	–	–	15.5
115	0.014	0.009	61.4
135	0.014	0.009	223
150	0.002	0.002	804

$K_p$ : propagation rate constant, [ $l^{3/2}/\text{mol}^{3/2}\cdot\text{min}$ ]

Greenley, R. Z., Stauffer, J. C., and Kurz, J. E., *Macromolecules*, **2**, 561 (1969).

© 1969 American Chemical Society.



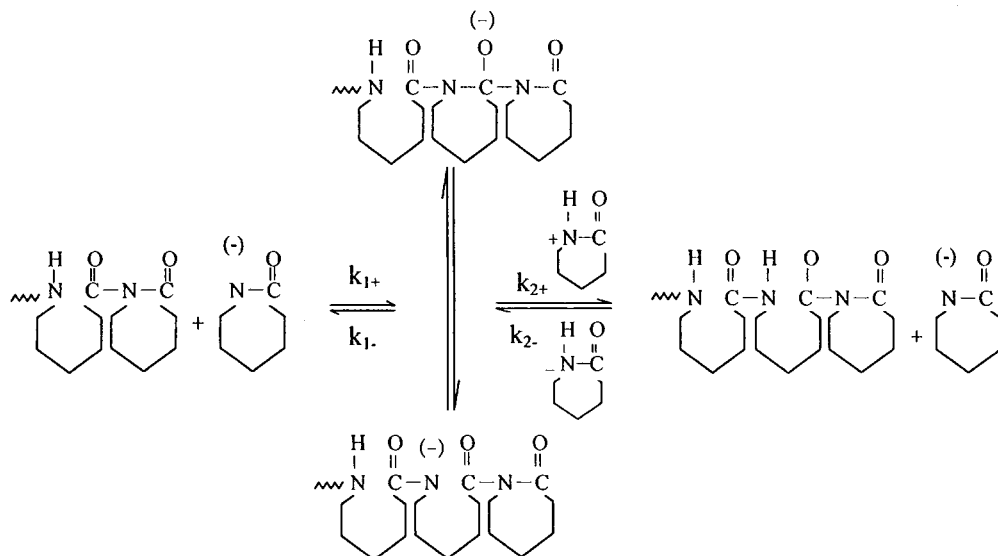
**Anionic polymerization**

Catalyst: sodium lactam (NaL)

Promoter: hexamethylenediisocyanate (HMDI)

Temperature: 180–201°C

Maximum conversion: 60%



Temperature [°C]	[NaL] [mol/l] × 10 <sup>2</sup>	2[HMDI] <sub>0</sub> [mol/l] × 10 <sup>2</sup>	k' × 10 <sup>3</sup> [1/sec]	k <sub>1+</sub> k <sub>2+</sub> /k <sub>1-</sub> <sup>(1)</sup> [l <sup>2</sup> /mol <sup>2</sup> ·sec]	k <sub>2-</sub> <sup>(2)</sup> [l/mol·sec]
180	0.99	0.99	3.98	93.5	37.4
185	2.0	2.0	20.6	118	50.1
185	1.80	2.50	21.3	109	46.4
187	0.99	0.99	5.58	132	57.0
187	1.58	1.58	14.15	130	56.5
194	1.58	1.58	17.30	159	74.8
201	0.99	0.99	9.27	217	108.5
201	1.58	1.58	22.3	205	102.5

(1)  $k_{1+}k_{2+}/k_{1-} = 2.3k'/2[\text{HMDI}]_0[\text{NaL}]_0$ (2)  $k_{2-} = k_{1+}k_{2+}/k_{1-}$

$k_{1+}$ ,  $k_{2+}$ ,  $k_{1-}$ ,  $k_{2-}$ : rate constants defined in reaction schemes, [mol<sup>2</sup>/l<sup>2</sup>/sec]

Rigo, A., Fabbri, G., and Talamini, G., *Polym. Lett. Ed.*, **13**, 469 (1975).

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### Anionic polymerization

Catalyst: sodium metal or sodium caprolactam

Activator: shown in table

Initial temperature: 160 and 190°C

$$d\beta/dt = (k[A]^2/[M]_0)(1-\beta)(1+m\beta/[A])\exp(-U/RT)$$

Activator	$k \times 10^{-10}$ [l/mol·min]	m [mol/l]
AcCl	0.77	0.93
PhCCl	2.22	0.36
2,4-TCCl	2.70	0.70
DPhMCCl	6.70	0.16
HMCCl	10.0	0.033

AcCl: n-acetylcaprolactam, PhCCl: phenylcarbamoyl caprolactam,  
2,4-TCCl: 2,4-tolulene-bis-carbamoyl caprolactam,  
DPhMCCl: 4,4-diphenylmethane-bis-carbamoyl caprolactam,  
HMCCl: hexamethylene-bis-carbamoyl caprolactam.

k: polymerization rate constant, [l/mol·min]

$[M]_0$ : initial monomer concentration, [mol/l]

m: describes the intensity of self-acceleration effect during chain growth,  
[mol/l]

U: activation energy for polymerization, [kcal/mol]

$\beta$ : degree of conversion, [-]

[A]: concentration of activator = [C]/N, [mol/l]

N: the functionality of the activator, [-]

[C]: concentration of catalyst, [mol/l]

Malkin, A. Y., Ivanova, S. L., Frolov, V. G., Ivanova, A. N., and Andrianova, Z. S., *Polymer*, **23**, 1791 (1982).

### Anionic polymerization

Catalyst: sodium metal

Initiator: phenyl isocyanate

Temperature: 140–145°C

Autocatalytic type rate equation

$$dX/dt = A_0(1-X)^n(1+B_0X)\exp(-E_a/RT)$$

$A_0$ [1/sec]	n	$B_0$	$E_a$ [kcal/mol]
$2.42 \times 10^{12}$	1.2	6.0	2494

X: monomer conversion, [-]

$A_0$ : pre-exponential constant, [1/sec]

$B_0$ : autocatalytic parameter, [-]

$E_a$ : apparent activation energy, [kcal/mol]

n: the order of dependence on monomer concentration, [-]

t: reaction time, [sec]

Lin, D. J., Ottino, J. M., and Thomas, E. L., *Polym. Eng. Sci.*, **25**, 1155 (1985).

**Anionic polymerization**

Catalyst: sodium metal

Initiator: phenyl isocyanate (PhNCO) and hexamethylene diisocyanate (HDI)

Initial temperature: 130–160°C

Maximum conversion: 100%

Reaction	System	Pre-exponential factor [l <sup>3/2</sup> /mol <sup>3/2</sup> ·sec]	Activation energy [kcal/mol]
Polymerization	Na/PhNCO	1.83 × 10 <sup>7</sup>	16.36 <sup>(1)</sup>
Degradation	Na/PhNCO	1.50 × 10 <sup>7</sup>	20.00 <sup>(1)</sup>
Polymerization	Na/HDI	1.83 × 10 <sup>7</sup>	15.42
Degradation	Na/HDI	1.50 × 10 <sup>7</sup>	19.00

<sup>(1)</sup> Published values of reference: Sibal, P. W. et al, "Designing Nylon-6 polymerization systems for RIM". Presented at the Second International Conference on Reactive Polymer Processing, Pittsburgh, PA (Nov. 1982).

Cimini, R. A. and Sundberg, D. C., *Polym. Eng. Sci.*, **26**, 560 (1986).

**Anionic polymerization**

Catalyst: sodium hydride

Activator: bis- $\epsilon$ -caprolactam bis-diphenyl methane diisocyanate polypropylene glycol 1000

Maximum conversion: 95.8 %

Initial reaction temperature: 153–157°C

Temperature rise during the reaction: 32–37°C

$$dX/dt = A_0(1-X)(1+BX)\exp(-E_a/RT)$$

## Kinetic Parameters of Malkin's Equation

$[A]_0$ [mol%]	$X_e$ [%]	$A_0 \times 10^{-10}$ [1/sec]	B	$E_a$ [kcal/mol]	$A \times 10^{-10}$
1.140	94.0	$2.46 \pm 0.01$	$0.88 \pm 0.03$	$25.16 \pm 0.05$	2.10
0.758	93.9	$2.38 \pm 0.03$	$0.36 \pm 0.04$	$25.43 \pm 0.02$	4.60
0.568	95.0	$2.20 \pm 0.01$	$0.42 \pm 0.02$	$25.43 \pm 0.03$	7.58
0.376	95.8	$2.01 \pm 0.05$	$1.59 \pm 0.15$	$26.01 \pm 0.02$	15.87

$$dX/dt = A'_0(1-X)^n(1+B'X)\exp(-E'_a/RT)$$

## Kinetic Parameters

$[A]_0$ [mol%]	$A'_0 \times 10^{-10}$ [1/sec]	n	B'	$E_a$ [kcal/mol]
1.140	$2.30 \pm 0.04$	$1.50 \pm 0.05$	$4.50 \pm 0.20$	$25.15 \pm 0.08$
0.758	$2.20 \pm 0.05$	$1.40 \pm 0.04$	$1.50 \pm 0.08$	$25.20 \pm 0.05$
0.568	$1.89 \pm 0.04$	$1.60 \pm 0.02$	$2.15 \pm 0.14$	$25.33 \pm 0.04$
0.376	$1.77 \pm 0.03$	$1.20 \pm 0.05$	$3.02 \pm 0.08$	$26.00 \pm 0.05$

$$dX/dt = (K_1[A]_0^2/[M]_0 - K_2[A]_0^3/[M]_0^2)(1-X)(1+BX)\exp\{-E_a/R(1/T-1/T_0)\}$$

$$K_1 = 13 \text{ [l/mol]}, K_2 = 962 \text{ [l/mol]}, T_0 = 155 \text{ [}^\circ\text{C]}, E_a = 25.5 \text{ [kcal/mol]}$$

$[A]_0$ : initial activator concentration, [mol/l]

$[M]_0$ : initial monomer concentration, [mol/l]

X: monomer conversion, [-]

$A_0, A'_0$ : pre-exponential constant, [1/sec]

B, B': autocatalytic parameter, [-]

$E_a$ : apparent activation energy, [kcal/mol]

n: the order of dependence on monomer concentration, [-]

t: reaction time, [sec]

A:  $A = A_0([M]_0/[A]_0^2)$

$X_e$ : equilibrium conversion, [%]

$K_1, K_2$ : constant, [l/mol]

$T_0$ : initial temperature, [°C]

Yeh, J. L., Kuo, J. F., and Chen, C. Y., *J. Appl. Polym. Sci.*, **50**, 1671 (1993).  
Copyright © 1993 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

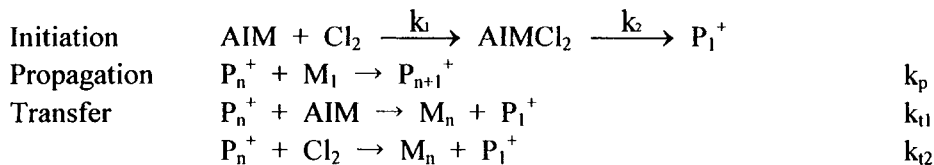
## 2.4 Isobutylene

### Cationic solution polymerization

Solvent: CH<sub>3</sub>Cl

Initiator: AlEt<sub>2</sub>Cl+Cl<sub>2</sub>

Temperature: -45°C



AIM: Et<sub>2</sub>AlCl, M<sub>1</sub>: monomer, P<sub>n</sub><sup>+</sup>: propagating species, M<sub>n</sub>: dead polymer chain.

$$k_p=7500, k_1=100, k_2=0.05, k_{t1}=100, k_{t2}=500$$

k<sub>1</sub>: initiation rate constant, [l/mol·sec]

k<sub>2</sub>: initiation rate constant, [1/sec]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t1</sub>, k<sub>t2</sub>: transfer rate constants, [l/mol·sec]

Maschio, G., Artigiani, F., Dimaina, M., and Giusti, P., *J. Appl. Polym. Sci.*, **29**, 1215 (1984). Copyright © 1984 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

## 2.5 Isoprene

### Anionic solution polymerization

Solvent: n-hexane or tetrahydrofuran (THF)

Initiator: butyllithium

Temperature: 0–29°C

Maximum conversion: about 50% for 0°C, 53% for 29°C

For THF

$$k_p = 1.0 \times 10^4 \exp(-6800 \text{ cal/RT})$$

### Solvent effect on apparent activation energy for propagation

Solvent	Activation energy [kcal/mol]
n-Hexane	22.6 ± 0.3
THF	6.8 ± 0.1

$k_p$ : propagation rate constant, [l/mol·sec]

Morton, M., Bostick, E. E., Livigni, R. A., and Fetters, L. J., *J. Polym. Sci.*, **A1**, 1735 (1963). Copyright © 1963 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Solvent: n-hexane or tetrahydrofuran (THF)

Initiator: polyisoprenyl lithium

Temperature: 30–60°C

Maximum conversion: about 90% for 0°C, 70% for 50°C



Solvent	Rate constant	
	THF	Hexane
$k_p$ at 30°C, [l/mol·sec]	0.14	4.7
$E_p$ , [kcal/mol]	6.8	4.1
A, [l/mol·sec]	$1.5 \times 10^4$	$3.4 \times 10^3$
$k_p$ at 60°C, [l/mol·sec]	0.40	8.9

$k_p$ : propagation rate constant, [l/mol·sec]

$E_p$ : activation energy for propagation, [kcal/mol]

A: frequency factor, [l/mol·sec]

Morton, M. and Fetters, L. J., *J. Polym. Sci.*, **A2**, 3311 (1964).

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### Anionic solution polymerization

Solvent: cyclohexane, n-hexane, and toluene

Initiator: n-butyllithium (n-BuLi)

Temperature: 5–50°C

Maximum conversion: 100%

$$R = K[M]^2$$

Polymerization rate constant K, [l/mol·min]

Cyclohexane 30°C	Cyclohexane 50°C	Hexane 50°C	Toluene 50°C
0.0022 <sup>(1)</sup>	0.0189 <sup>(1)</sup>	0.0148 <sup>(1)</sup>	0.118 <sup>(2)</sup>

<sup>(1)</sup>[n-BuLi] > 0.001 [mol/l]. <sup>(2)</sup>[n-BuLi] = 0.002–0.04 [mol/l].

R: polymerization rate, [mol/l·min]

K: polymerization rate constant, [l/mol·min]

[M]: monomer concentration, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 153 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Solvent: cyclohexane, n-hexane, and toluene

Initiator: n-butyllithium (n-BuLi), sec-BuLi, tert-BuLi, and i-BuLi

Temperature: 50°C

$$R_i = k_i [\text{BuLi}] [\text{M}]$$

Initiation rate constant  $k_i$ , [l/mol·min]

$k_i$ (n-BuLi)			$k_i$ (Cyclohexane)			
Cyclohexane	n-Hexane	Toluene	n-BuLi	sec-BuLi	tert-BuLi	i-BuLi
0.012 ± 0.002	0.018 ± 0.003	0.43 ± 0.03	0.012	0.44	0.27	0.035

$R_i$ : initiation rate, [mol/l·min]

$k_i$ : initiation rate constant, [l/mol·min]

[BuLi]: concentration of butyllithium, [mol/l]

[M]: concentration of monomer, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 163 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Solvent: cyclohexane, and toluene

Initiator: sec-butyllithium (sec-BuLi)

Temperature: 5–30°C

$$R_p = k_p [\text{BuLi}]^{1/2} [\text{M}] \quad \text{for } [\text{BuLi}] > 10^{-2} \text{ [mol/l]}$$

$$R_p = k'_p [\text{BuLi}]^{1/3} [\text{M}] \quad \text{for } 10^{-4} < [\text{BuLi}] < 10^{-2} \text{ [mol/l]}$$

Propagation rate constant  $k_p$  and  $k'_p$  [l/mol·min]

Solvent	Temperature[°C]	$k_p$	$k'_p$
Cyclohexane	30	0.155	0.096
Toluene	5	0.012	0.0067

$k_p$ : propagation rate constant, [ $l^{1/2}/mol^{1/2}\cdot min$ ]

$k'_p$ : propagation rate constant, [ $l^{1/3}/mol^{1/3}\cdot min$ ]

$R_p$ : propagation rate, [mol/l·min]

[BuLi]: concentration of sec-butyllithium, [mol/l]

[M]: concentration of monomer, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 173 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic Solution polymerization

Solvent: hexane

Catalyst: n-butyllithium

Temperature: 30–50°C

$$R_i = (k_a[I] + k_b[I][P_T])[M]/(1 + K_1[I]^2)$$

Initiation rate constants and equilibrium constants

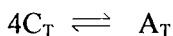
Constant	Definition	Value			Unit
		30°C	40°C	50°C	
$k_a$	$4.39 \times 10^7 \exp(-6930/T)$	0.00514	0.0107	0.0212	l/mol·min
$k_b$	$1.14 \times 10^{23} \exp(-16700/T)$	0.133	0.775	4.04	l <sup>2</sup> /mol <sup>2</sup> ·min
$K_1$	$6.58 \times 10^5 \exp(-1340/T)$	7920	9130	10400	l <sup>2</sup> /mol <sup>2</sup>

Propagation reaction



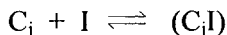
$k_p$  rate controlling

Association of active polymer



$K_p = [A_T]/[C_T]^4$  at equilibrium

Association of active polymer with initiator



$k_2$

$C_j$ : active polymer of length  $j$ ,  $C_T$ : total active polymer,  $= \sum C_j$ ,  $A_T$ : total associated polymer.

$$[C_T] = [P_T](1 + K_2[I]^a + K_3[P_T]^b)$$

$$a = 3/4, b = 3$$

### Propagation rate constants and equilibrium constants

Constant	Definition	Value			Unit
		30°C	40°C	50°C	
$k_p$	$2.68 \times 10^5 \exp(-3140/T)$	8.47	11.8	16.1	$l/mol \cdot min$
$K_2$	$1.03 \times 10^{-11} \exp(9180/T)$	148	56.2	22.7	$l^{3/4}/mol^{3/4}$
$K_3$	$4.08 \times 10^{-2} \exp(5660/T)$	$5.28 \times 10^6$	$2.91 \times 10^6$	$1.66 \times 10^6$	$l^3/mol^3$

$[P_T]$ : total polymer concentration ( $= \sum [P_j]$ ), [mol/l]

$[I]$ : initiator concentration, [mol/l]

$[M]$ : monomer concentration, [mol/l]

$R_i$ : initiation rate, [mol/l·min]

$k_a$ : initiation rate constant, [l/mol·min]

$k_b$ : initiation rate constant, [l<sup>2</sup>/mol<sup>2</sup>·min]

$K_1$ : equilibrium constant of initiation reaction, [l<sup>2</sup>/mol<sup>2</sup>]

$k_p$ : propagation rate constant, [l/mol·min]

$K_2$ : equilibrium constant for association of active polymer with initiator, [l<sup>3/4</sup>/mol<sup>3/4</sup>]

$K_3$ : equilibrium constant related with  $K_p$  [l<sup>3</sup>/mol<sup>3</sup>]

$K_p$ : equilibrium constant for association of active polymers, [l<sup>3</sup>/mol<sup>3</sup>]

Porter, R. E., Ahmad, A., and Anthony, R. G., *J. Appl. Polym. Sci.*, **18**, 1805 (1974). Copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Anionic solution polymerization**

Solvent: benzene

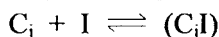
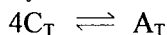
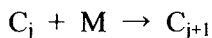
Catalyst: n-butyllithium

Temperature: 20–40°C

$$R_i = k_i[I]/(1 + K_1[I]^2 + K_2[P_T])$$

## Initiation rate constants and equilibrium constants

Constant	Definition	Value			Unit
		20°C	30°C	40°C	
$k_i$	$\exp(19.51)\exp(-6960/T)$	$1.43 \times 10^{-2}$	$3.14 \times 10^{-2}$	$6.54 \times 10^{-2}$	l/mol·min
$K_1$	$\exp(128.4)\exp(-37905/T)$	$4.17 \times 10^{-1}$	$2.98 \times 10$	$1.62 \times 10^3$	l <sup>2</sup> /mol <sup>2</sup>
$K_2$	$\exp(-5.206)\exp(3220/T)$	$3.24 \times 10^2$	$2.26 \times 10^2$	$1.61 \times 10^2$	l/mol



$C_j$ : active polymer of length  $j$ ,  $C_T$ : total active polymer,  $=\sum C_j$ ,  $A_T$ : total associated polymer,  $I$ : initiator,  $M$ : monomer.

$$R_p = k_p[P_T][M]/\{1 + (1 + k_p[P_T]^3)^{1/4} + K_1[I]^2\}$$

$$K'_p C_T^3 = (1 + K_p P_T^3)^{1/4}$$

## Propagation rate constants and equilibrium constants

Constant	Definition	Value			Unit
		20°C	30°C	40°C	
$k_p$	$\exp(23.78)\exp(-6320/T)$	9.12	$1.86 \times 10$	$3.62 \times 10$	l/mol·min
$K_p$	$\exp(-41.38)\exp(18600/T)$	$3.97 \times 10^9$	$4.89 \times 10^8$	$6.87 \times 10^7$	l <sup>3</sup> /mol <sup>3</sup>
$K_1$	$\exp(-28.3)\exp(14800/T)$	$2.01 \times 10^5$	$3.70 \times 10^4$	$7.98 \times 10^3$	l <sup>2</sup> /mol <sup>2</sup>

$[P_T]$ : total polymer concentration,  $= \sum [P_j]$ , [mol/l]

$[M]$ : monomer concentration, [mol/l]

$[I]$ : initiator concentration, [mol/l]

$R_i$ : initiation rate, [mol/l·min]

$k_i$ : initiation rate constant, [mol/l·min]

$K_1$ : equilibrium constant of initiation reaction, [l<sup>2</sup>/mol<sup>2</sup>]

$K_2$ : equilibrium constant of initiation reaction, [l/mol]

$k_p$ : propagation rate constant, [l/mol·min]

$K_p$ : equilibrium constant for association of active polymers, [l<sup>3</sup>/mol<sup>3</sup>]

$K_I$ : equilibrium constant for association of active polymer with initiator, [l<sup>2</sup>/mol<sup>2</sup>]

Magott, R. J., Ahmad, A., and Anthony, R. G., *J. Appl. Polym. Sci.*, **19**, 165 (1975). Copyright © 1975 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

## 2.6 $\alpha$ -Methylstyrene

### Anionic solution polymerization

Solvent: tetrahydrofuran (THF)

Catalyst: sodium naphthalene

Temperature: -77- -10°C

$$-d[\text{monomer}]/dt = k[\text{initiator}]\{[\text{monomer}]-[\text{monomer}]_e\}$$

Temperature [°C]	Catalyst concentration $\times 10^4$ [mol/l]	k [l/mol·min]
-10	11.8	84.5
-10	12.2	96.3
-10	13.9	85.3
-10	16.8	82.2
-10	23.6	74.1
-10	24.8	69.1
-77	16.4	20.6
-77	26.5	16.4
-77	28.2	11.2
-77	31.2	12.7
-77	50.2	14.1

k: polymerization rate constant, [l/mol·min]

[initiator]: concentration of initiator, [mol/l].

[monomer]: concentration of monomer, [mol/l].

[monomer]<sub>e</sub>: equilibrium concentration of monomer, [mol/l].

Worsfold, D. J. and Bywater, S., *Can. J. Chem.*, **36**, 1141 (1958).

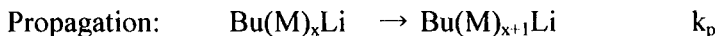
## 2.7 Styrene

### Anionic solution polymerization

Solvent: benzene and toluene

Catalyst: n-butyllithium (BuLi)

Temperature: 20–50°C



M: monomer.

$$R_p = k_p[M][\text{BuLi}] \quad \text{for } [\text{BuLi}] < 0.020 \text{ [mol/l]}$$

$$R_p = k[M] \quad \text{for } [\text{BuLi}] > 0.020 \text{ [mol/l]}$$

$$\text{Activation energy for propagation} = 17 \text{ [kcal/mol]}$$

[M]: concentration of monomer, [mol/l]

[BuLi]: concentration of n-butyllithium, [mol/l]

$R_p$ : propagation rate, [mol/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

k: propagation rate constant, [1/sec]

$k_i$ : initiation rate constant, [l/mol·sec]

Welch, F. J., *J. Am. Chem. Soc.*, **81**, 1345 (1959).

© 1959 American Chemical Society.

### Anionic solution polymerization

Solvent: benzene

Catalyst: butyllithium

Temperature: 10–30°C

$$d[C]/dt = -k_1[C]^{1/6}[M]$$

$$d[M]/dt = -k_2[C]^{1/2}[M]$$

C: butyllithium, M: styrene monomer.



---

Temperature [°C]	$k_1 \times 10^4$ [l <sup>1/6</sup> /mol <sup>1/6</sup> ·min]	$k_2$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·min]
30.3	14.0	0.929
25.0		0.563
20.0	4.68	0.387
15.0		0.265
10.0	1.45	0.155

---

Apparent activation for initiation=18000 [cal/mol]

Apparent activation for propagation=14300 [cal/mol]

$k_1$ : initiation rate constant, [l/mol·sec]

$k_2$ : propagation rate constant, [l/mol·sec]

[M]: monomer concentration, [mol/l]

[C]: catalyst concentration, [mol/l]

Worsfold, D. J. and Bywater S., *Can. J. Chem.* **38**, 1891 (1960).

**Anionic solution polymerization**

Solvent: cyclohexane

Initiator: n-butyllithium (n-BuLi)

Temperature: 5–50°C

Maximum conversion: 100%

$$R=K[M]^2$$

Solvent	Temperature [°C]	Polymerization rate constant K [l/mol·min]
Cyclohexane	30	0.0131 <sup>(1)</sup>

<sup>(1)</sup>[n-BuLi] > 0.007 [mol/l]

R: polymerization rate, [mol/l·min]

K: polymerization rate constant, [l/mol·min]

[M]: monomer concentration, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 153 (1965).

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**Anionic solution polymerization**

Initiator: n-butyllithium (BuLi), sec-BuLi, tert-BuLi, and i-BuLi

Solvent: cyclohexane, n-hexane, and toluene

Temperature: 50°C

$$R_i=k_i[\text{BuLi}][M]$$

Initiation rate constant  $k_i$  [l/mol·min]

$k_i$ (n-BuLi)			$k_i$ (cyclohexane)			
Cyclohexane	n-Hexane	Toluene	n-BuLi	sec-BuLi	tert-BuLi	tert-BuLi
0.028 ± 0.002	0.042 ± 0.008	0.85 ± 0.03	0.028	2.0	0.015	0.061

$R_i$ : initiation rate, [mol/l·min]

$k_i$ : initiation rate constant, [l/mol·min]

[BuLi]: concentration of butyllithium, [mol/l]

[M]: concentration of monomer, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 163 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Anionic solution polymerization

Initiator: sec-butyllithium (sec-BuLi)

Solvent: cyclohexane and toluene

Temperature: 5–30°C

$$R_p = k_p [\text{BuLi}]^{1/2} [\text{M}] \quad \text{for } [\text{BuLi}] > 10^{-4} \text{ [mol/l]}$$

Propagation rate constant  $k_p$  [l<sup>1/2</sup>/mol<sup>1/2</sup>·min]

Solvent	Temperature [°C]	$k_p$
Cyclohexane	30	0.494
Toluene	5	0.080

$k_p$ : propagation rate constant, [l<sup>1/2</sup>/mol<sup>1/2</sup>·min]

$R_p$ : propagation rate, [mol/l·min]

[BuLi]: concentration of sec-butyllithium, [mol/l]

[M]: concentration of monomer, [mol/l]

Hsieh, H. L., *J. Polym. Sci.*, **A3**, 173 (1965). Copyright © 1965 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Anionic solution polymerization**

Solvent: benzene, dioxane, and tetrahydrofuran

Catalyst: polystyryllithium, polystyrylpotassium, polystyrylsodium, polystyrylrubidium, and polystyrylcaesium

Temperature: 25°C

Absolute values of  $k_p$  for propagation via ion-pairs

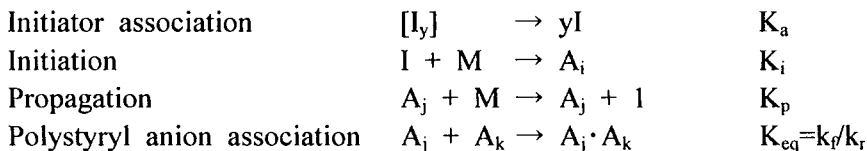
Counter-ion	Benzene	Dioxane <sup>(1)</sup>	Tetrahydrofuran <sup>(2)</sup>
Li	17 <sup>(3)</sup> , >30 <sup>(4)</sup>	0.94	160
Na	–	3.4	80
K	47	19.8	60–80
Rb	24	21.5	50–80
Cs	18	24.5	22

<sup>(1)</sup>Bhattacharyya et al., *J. Phys. Chem.*, **69**, 624 (1965).<sup>(2)</sup>Bhattacharyya et al., *J. Phys. Chem.*, **69**, 612 (1965).<sup>(3)</sup>Morton, *A. C. S., Div. Polymer Chem. Polym. Prep.*, **5**, 1092 (1964).<sup>(4)</sup>at 30°C. Bywater, *Fortschr. Hochpolym.-Forsch.*, **4**, 66 (1965). $k_p$ : propagation rate constant, [l/mol·sec]Roovers, J. E. L. and Bywater, S., *Trans. Faraday Soc.*, **62**, 701 (1966).**Anionic solution polymerization**

Solvent: benzene

Initiator: n-butyllithium (n-BuLi)

Temperature: 10–25°C

I: unassociated n-BuLi,  $[I_y]$ : associated n-BuLi, M: monomer,  $A_j$ : activated intermediate  $BuM_jLi^+$  an activator,  $A_j \cdot A_k$ : activated polystyryl anion complex.

	Activation energy [cal/mol]	Frequency factor
Initiation	10500	$1.1 \times 10^5$
Propagation	2000	$3.1 \times 10^2$
Association	-312001	$1.0 \times 10^5$

$K_i$ : initiation rate constant, [l/mol·min]

$K_p$ : propagation rate constant, [l/mol·sec]

$K_{eq}$ : polystyryl anion association equilibrium constant

Timm, D. C. and Kubicek, L. F., *Chem. Eng. Sci.*, **29**, 2145 (1974).

### Anionic solution polymerization

Solvent: tetrahydrofuran in the presence of pyridine

Initiator:  $\alpha$ -methylstyrene tetramer disodium



$$K = [\text{Complex}]/[\text{LE}][\text{Py}] = [\text{LE}]_0/[\text{LE}]\{[\text{Py}]_0 - [\text{LE}]_0\}$$

$$-d[\text{M}]/dt = k_p[\text{LE}]_0[\text{M}]$$

$$= k_p^0[\text{LE}][\text{M}] + k'_p[\text{Complex}][\text{M}]$$

$$= k_p^0[\text{LE}][\text{M}] + k'_p[\text{LE}]_0[\text{M}]$$

$$k_p = k_p^0/K([\text{Py}]_0 - [\text{LE}]_0) + k'_p$$

$$K = 4 \times 10^5 \text{ [l/mol]}$$

$$k_p^0 = 2900 \text{ [l/mol·sec]}$$

$K$ : equilibrium constant of complex formation, [l/mol]

$k_p$ : apparent rate constant of polymerization, [l/mol·sec]

$k_p^0$ : rate constant for polymerization by uncomplexed living ends, [l/mol·sec]

$k'_p$ : rate constant for polymerization by complex, [l/mol·sec]

$[\text{M}]$ : concentration of monomer, [mol/l]

$[\text{LE}]_0$ : initial concentration of total living ends, [mol/l]

$[\text{LE}]$ : total living ends concentration, [mol/l]

[Py]: concentration of pyridine, [mol/l]

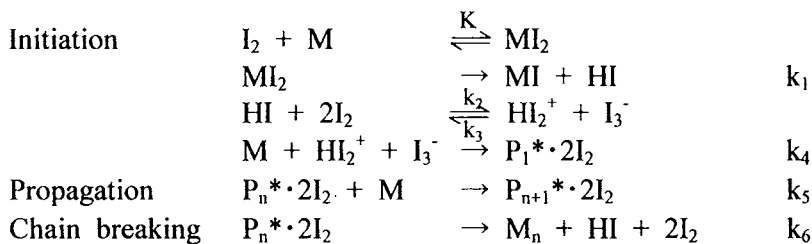
[Py]<sub>0</sub>: initial concentration of pyridine, [mol/l]

Yagi, K., Tsuyama, S., Toda, F., and Iwakura, Y., *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 1097 (1976). Copyright © 1976 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Pseudocationic solution polymerization

Solvent: ethylene dichloride

Initiator: iodine



M: styrene,  $I_2$ : iodine,  $MI_2$ : styrene diiodide, MI: unsaturated side product,  $P_n^*$ : growing polymer chain,  $M_n$ : dead polymer chain.

$$k_1 = 0.7 \text{ [l/min]}$$

$$k_2 = 4.0 \text{ [l}^2\text{/mol}^2\text{·min]}$$

$$k_3 = 0.1 \text{ [l/mol·min]}$$

$$k_4 = 0.6 \text{ [l}^2\text{/mol}^2\text{·min]}$$

$$k_5 = 10.0 \text{ [l/mol·min]}$$

$$k_6 = 0.1 \text{ [l/min]}$$

$$K = 0.5$$

$k_1, k_2, k_3, k_4$ : initiation rate constants, units are [l/min], [l<sup>2</sup>/mol<sup>2</sup>·min], [l/mol·min], and [l<sup>2</sup>/mol<sup>2</sup>·min], respectively.

$k_5$ : propagation rate constant, [l/mol·min]

$k_6$ : chain breaking rate constant, [l/min]

K: equilibrium constant

Maschio, G., Cerrai, P., and Giusti, P., *Polym. Bull.*, **8**, 147 (1982).

### 3. Ziegler-Natta polymerization

#### 3.1 Butadiene

##### Homogeneous polymerization

Catalyst:  $\text{TiI}_2\text{Cl}_2/\text{Al}(\text{iso-C}_4\text{H}_9)_3$

Temperature: 20–30°C

Monomer concentration: 0.5 mol/l (constant)

$$c_0 = Q(t)/M_n(t)$$

$$w_0 = k_p[\text{TiI}_2\text{Cl}_2][\text{M}]$$

$$c_0 = \alpha[\text{TiI}_2\text{Cl}_2][\text{M}]$$

$$w_0 = k'_p c_0$$

Assumption:

1. The initiation is instantaneous.
2. At the beginning of polymerization, all the macromolecules are growing.
3. A reversible bimolecular deactivation of active sites occurs in the course of polymerization, the stationary rate conforming to the established equilibrium.

$$\text{At time } t \quad w(t) = k'_p c(t)$$

Two kinds of deactivation/reactivation processes:



$c_{\text{act}}$ : concentration of active sites, [mol/l],

$c_{\text{inact}}$ : concentration of inactive sites, [mol/l]

$$\text{case I:} \quad k_1 = \frac{1}{2At} \log \frac{K/2 - A - c_0 c (c_0 - c)^{-1}}{K/2 + A - c_0 c (c_0 - c)^{-1}}$$

$$c = c_0 \frac{K/2 + A \operatorname{cth}(Ak_1 t)}{K/2 + c_0 + A \operatorname{cth}(Ak_1 t)}$$

$$K = k_2 / 2k_1 = c_{\text{st}}^2 (c_0 - c_{\text{st}})^{-1}$$

$$M_n(t) = \frac{54k'_p}{c_0} \left\{ c_{st}t + \frac{1}{k_1} \log \frac{\exp\{-c_{st}(2c_0 - c_{st})/(c_0 - c_{st})\} - c_0^2/(c_0 - c_{st})^2}{1 - c_0^2/(c_0 - c_{st})^2} \right\}$$

case II:  $k_1 = \frac{1}{2c_0t\sqrt{K}} \log \frac{1 - c_0^{-1}(c_0 - c)(1 - \sqrt{K})}{1 - c_0^{-1}(c_0 - c)(1 + \sqrt{K})}$

$$c = c_0 \frac{\sqrt{K} \operatorname{cth}(c_0 k_1 t \sqrt{K})}{1 + \sqrt{K} \operatorname{cth}(c_0 k_1 t \sqrt{K})}$$

$$K = k_2/k_1 = c_{st}^2 (c_0 - c_{st})^{-2}$$

$$M_n(t) = \frac{54k'_p}{c_0(\sqrt{K} + 1)} \left\{ c_0 t \sqrt{K} + \frac{1}{k_1(1 - \sqrt{K})} \log \frac{\sqrt{K} + 1 - (1 - \sqrt{K}) \exp(-2c_0 k_1 t \sqrt{K})}{2\sqrt{K}} \right\}$$

Temperature [°C]	$k'_p$ [1/sec]	case I			case II		
		$k_1$ [l/mol·sec]	$k_2 \times 10^5$ [1/sec]	$K \times 10^7$ [mol/l]	$k_1$ [l/mol·sec]	$k_2 \times 10^2$ [l/mol·sec]	$K \times 10^3$
10	1.86	9.96	4.89	24.60	13.1	5.59	4.80
20	3.98	17.8	2.52	6.92	23.2	3.73	1.63
30	8.31	31.2	1.35	2.15	39.4	2.57	0.75
40	15.7	52.6	0.75	0.72	65.1	1.82	0.32
$E_{act}$ [kcal/mol]	$12.5 \pm 0.4$	$9.8 \pm 0.6$	$-11.0 \pm 0.5$		$9.5 \pm 0.5$	$-6.8 \pm 0.5$	

$c_0$ : initial concentration of active sites, [mol/l]

$c, c(t)$ : concentration of active sites at time  $t$ , [mol/l]

$c_{st}$ : concentration of active sites at stationary state, [mol/l]

$Q(t)$ : polymer yield at time  $t$ , [g/l]

$[M]$ : molar concentration of monomer, [mol/l]

$[TiCl_2]$ : molar concentration of titanium halide, [mol/l]

$M_n(t)$ : number-average molecular weight at time  $t$ , [g/mol]

$w_0$ : initial propagation rate, [mol/l·sec]



$w(t)$ : propagation rate at time  $t$ , [mol/l·sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k'_p$ : rate constant defined in above equation, [1/sec]

$k_1$ : rate constant of deactivation, [l/mol·sec]

$k_2$ : rate constant of reactivation, [l/mol·sec]

$K$ : equilibrium constant, [mol/l] or [-]

$E_{act}$ : activation energy, [kcal/mol]

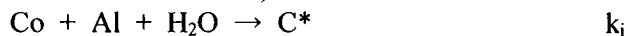
Bresler, L. S., Grechanovsky, V. A., Muzsay, A., and Poddubnyi, I. Ya., *Makromol. Chem.*, **133**, 111 (1970)

### Homogeneous polymerization

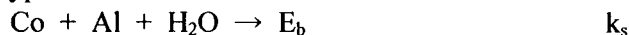
Catalyst: cobalt octoate/diethylaluminium chloride/water

Temperature: 15°C

Initiation (formation of active sites)



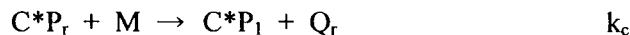
Formation of byproducts



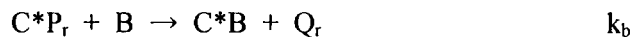
Propagation



Transfer to monomer



Transfer to but-1-ene



Regeneration of active sites



Cobalt deactivation



Co: cobalt octoate, Al: diethylaluminium chloride, C\*: active catalyst site, E<sub>b</sub>: catalyst byproduct, M: butadiene monomer, C\*P<sub>1</sub>: growing chain of unit length, C\*P<sub>r</sub>: growing chain of chain length r, C\*B: short-lived but-1-ene/catalyst complex, Q<sub>r</sub>: dead polymer chain of chain length r, B: but-1-ene, C: deactivated catalyst site.

$$d[M]/Vdt = -k_p[C^*][M]$$

$$d[Co]/Vdt = -k_i[Co]^m - k_s[Co]$$

$$d[C^*P]/Vdt = k_i[Co]^m - k_t[C^*P]$$

$$dY_0/dt = k_p[C^*][M] - k_t Y_0$$

$$dY_1/dt = k_p[M]Y_0 + k_p[C^*][M] + k_c[M](Y_0 - Y_1) + k_b[B](Y_0 - Y_1) + k_t Y_1$$

$$dY_2/dt = k_p[M](Y_0 - 2Y_1) + k_p[C^*][M] - k_c[M](Y_0 - Y_2) + k_b[B](Y_0 - Y_2) - k_t Y_2$$

$$dX_0/dt = k_p[C^*][M] + k_c[M]Y_0 + k_b[B]Y_0 - k_c[M][C^*P_1] - k_b[B][C^*P_1] - k_t[C^*P_1]$$

$$dX_1/dt = dX_0/dt + k_p[M]Y_0$$

$$dX_2/dt = dX_0/dt + k_p[M](Y_0 + 2Y_1)$$

$$M_N = M_m X_1 / X_0$$

$$M_W = M_m X_2 / X_1$$

$$f = (k_t - k_s) / k_i$$

$$k_s = k_i(1 - f)$$

$$k_i = 1.0 \times 10^9, [1/\text{min}][\text{mol/l}]^{1-m}$$

$$k_p = 1.95 \times 10^9 \exp(-4570.6 \text{ cal/T}) [1/\text{mol} \cdot \text{min}]$$

$$k_c = 2.82 \times 10^6 \exp(-5117.1 \text{ cal/T}) [1/\text{mol} \cdot \text{min}]$$

$$k_b = 1.0 \times 10^{-4} [1/\text{mol} \cdot \text{min}] \text{ (at } 15^\circ\text{C)}$$

$$k_t = 0.002 [1/\text{min}] \text{ (at } 15^\circ\text{C)}$$

$$m = 1.4$$

V: volume of reaction mixture, [l]

[C\*P]: total moles of growing chains, [mol/l]

[i]: concentration of species i, [mol/l]

k<sub>i</sub>: rate constant of initiation, [1/min][mol/l]<sup>1-m</sup>, m: constant

k<sub>p</sub>: rate constant of propagation, [l/mol·min]

k<sub>c</sub>: rate constant of transfer to cobalt, [l/mol·min]

k<sub>b</sub>: rate constant of transfer to but-1-ene, [l/mol·min]

k<sub>t</sub>: rate constant of catalyst deactivation, [1/min]

k<sub>z</sub>: rate constant of regeneration of active sites, [l/mol·min]

k<sub>s</sub>: rate constant of formation of byproduct, [l/mol·min]

$Y_i$ :  $i$ -th moment of the growing chain distribution, [mol/l]

$X_i$ :  $i$ -th moment of the total chain distribution, [mol/l]

$M_N$ : number average molecular weight, [g/mol]

$M_W$ : weight average molecular weight, [g/mol]

$M_m$ : molecular weight of monomer, [g/mol]

$T$ : temperature, [ $^{\circ}$  K]

$f$ : catalyst formation efficiency, [-]

Honig, J. A. J., Gloor, P. E., MacGregor, J. F., and Hamielec, A. E., *J. Appl. Polym. Sci.*, **34**, 829 (1987). Copyright © 1987 John Wiley & Sons, Inc.  
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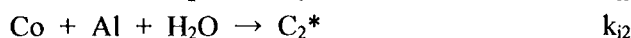
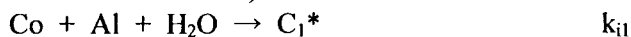
### Homogeneous polymerization

Catalyst: cobalt octoate/diethyl aluminium chloride/water

Temperature: 15 $^{\circ}$ C

Maximum conversion: 80%

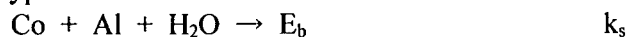
Initiation (formation of active site)



Initiation



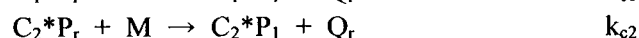
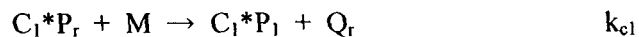
Formation of byproducts



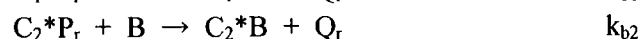
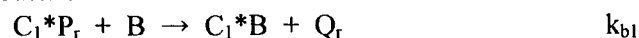
Propagation



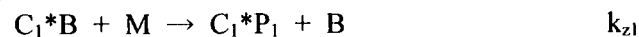
Transfer to monomer

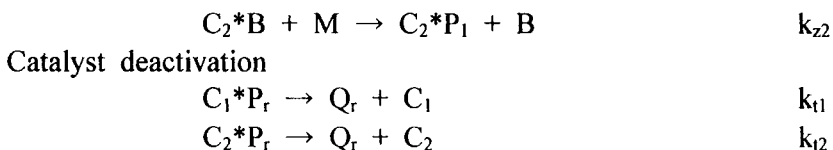


Transfer to 1-butene



Regeneration of active sites





Co: cobalt octoate, Al: diethylaluminium chloride,  $\text{C}_1^*$ : active catalyst site 1,  $\text{C}_2^*$ : active catalyst site 2, M: butadiene monomer,  $\text{C}_1^*\text{P}_r$ : growing chain of length  $r$  with site 1,  $\text{C}_2^*\text{P}_r$ : growing chain of length  $r$  with site 2,  $\text{E}_b$ : catalyst byproduct,  $\text{C}_1^*\text{B}$ : short-lived 1-butene/catalyst complex with active site 1,  $\text{C}_2^*\text{B}$ : short-lived 1-butene/catalyst complex with active site 2, B: 1-butene,  $\text{Q}_r$ : dead polymer chain of chain length  $r$ ,  $\text{C}_1$ : deactivated catalyst site with active site 1,  $\text{C}_2$ : deactivated catalyst site with active site 2.

$$K_p = (1.95 \times 10^9) \exp(-4570.6 \text{ cal/T}) \text{ [l/mol}\cdot\text{min]}$$

$$k_c = (2.82 \times 10^6) \exp(-5117.1 \text{ cal/T}) \text{ [l/mol}\cdot\text{min]}$$

$$k_b = 10^{-4} \text{ [l/mol}\cdot\text{min]} \text{ (at } 15^\circ\text{C)}$$

$$k_t = 0.002 \text{ [1/min]} \text{ (at } 15^\circ\text{C)}$$

$k_{ji}$ : rate constant of initiation with site  $i$ ,  $[1/\text{min}][\text{mol/l}]^{1-m}$ ,  $m$ : constant

$k_{pi}$ : rate constant of propagation with site  $i$ ,  $[1/\text{mol}\cdot\text{min}]$

$k_{ci}$ : rate constant of transfer to cobalt with site  $i$ ,  $[1/\text{mol}\cdot\text{min}]$

$k_{bi}$ : rate constant of transfer to 1-butene with site  $i$ ,  $[1/\text{mol}\cdot\text{min}]$

$k_{ti}$ : rate constant of catalyst deactivation with site  $i$ ,  $[1/\text{min}]$

$k_{zi}$ : rate constant of regeneration of active sites with site  $i$ ,  $[1/\text{mol}\cdot\text{min}]$

$k_s$ : rate constant of formation of byproduct,  $[1/\text{min}][\text{mol/l}]^{1-r}$ ,  $r$ : constant.

Nitirahardjo, S., Lee, S., and Miller, J. W. Jr., *J. Appl. Polym. Sci.*, **44**, 837 (1992). Copyright © 1992 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Solution polymerization**Solvent: toluene/water (water:  $2 \times 10^{-3}$  mol/l)

Catalyst: cobalt acetyl acetonate and aluminium diethyl chloride

Temperature:  $-2-40^{\circ}\text{C}$ 

$$R_p = k_p' [\text{Butadiene}] [\text{Co}(\text{acac})_3]$$

$$E_p = 11.86 \text{ [kcal/mol]}$$

 $R_p$ : polymerization rate, [mol/l·sec] $k_p'$ : polymerization rate constant, [l/mol·sec] $E_p$ : activation energy of polymerization, [kcal/mol]

[Butadiene]: concentration of butadiene, [mol/l]

[Co(acac)<sub>3</sub>]: concentration of cobalt acetyl acetonate, [mol/l]Bawn, C. E. H., *Rubber and Plastic Age*, 510 (1965).**Solution polymerization**

Solvent: benzene

Catalyst: nickel carboxylate/boron trifluoride etherate/triethylaluminium

Monomer concentration: 1.18 [mol/l], nickel carboxylate:  $2.56 \times 10^{-3}$  [mol/l],boron trifluoride etherate:  $18.6 \times 10^{-3}$  [mol/l],triethylaluminium:  $16.6 \times 10^{-3}$  [mol/l]Temperature:  $20-40^{\circ}\text{C}$ 

Maximum conversion: 100%

$$-d[M]/dt = \alpha k_p [C]_0 [M]$$

$$1/\bar{P} = k_{tm}/k_p + \alpha [C]_0/x[M]_0$$

Temperature [ $^{\circ}\text{C}$ ]	$\alpha 10^2$	$k_{tm} \times 10^4/k_p$	$k \times 10^4$ [1/sec]	$k_p$ [l/mol·sec]	$k_{tm} \times 10^4$ [l/mol·sec]
40	1.8	1.3	2.7	6	8
30	1.9	1.8	1.6	3	5
40	6.8	1.2	5.7	3	4
40	5.4	1.0	2.5	2	2

$$k_t=0$$

[M]: monomer concentration, [mol/l]

[M]<sub>0</sub>: monomer concentration at initial time, [mol/l]

[C]<sub>0</sub>: catalyst concentration at initial time, [mol/l]

x: conversion, [-]

α: constant, [-]

$\bar{p}$ : number-average degree of polymerization, [-]

k<sub>tm</sub>: transfer rate constant to monomer, [l/mol·sec]

k<sub>p</sub>: propagation rate constant, [l/mol·sec]

k<sub>t</sub>: termination rate constant, [l/mol·sec]

k: first-order rate constant, [l/sec]

Yoshimoto, T., Komatsu, K., Sakata, R., Yamamoto, K., Takeuchi, Y., Onishi, A., and Ueda, K., *Makromol. Chem.*, **139**, 61 (1970).

### Solution polymerization

Solvent: benzene

Catalyst: CoCl<sub>2</sub>·4C<sub>5</sub>H<sub>5</sub>N-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlCl-Et<sub>2</sub>AlCl·H<sub>2</sub>O

[Al]=5.0-24.7 [mmol/l], [Co]=0.029-10.0 [mmol/l],

[H<sub>2</sub>O]=1.4-4.1 [mmol/l]

Temperature: 25°C

$$d[M]/dt=k_p[M][P]$$

$$[P_T]=\frac{k_c[Co]_i}{k_c-k_t} \{ \exp(-k_t t) - \exp(-k_c t) \}$$

$$[Co]=[Co]_i \exp(-k_c t)$$

$$\ln \frac{[M_0]}{[M]} = \frac{k_p k_c [Co]_i}{k_c - k_t} \left\{ \frac{1 - \exp(-k_t t)}{k_t} - \frac{1 - \exp(-k_c t)}{k_c} \right\}$$

$$k_c = (8.88 \pm 3.81) \times 10^{-3}, [1/\text{sec}]$$

$$k_p \sim [H_2O]/[Al]^{1/2}$$

$$k_t = (3.29 \pm 0.94) \times 10^{-4}, [1/\text{sec}]$$

[Co]: concentration of free  $\text{CoCl}_2 \cdot 4\text{Py}$ , [mol/l]

[Co]<sub>i</sub>: initial concentration of  $\text{CoCl}_2 \cdot 4\text{Py}$ , [mol/l]

[P<sub>T</sub>]: concentration of total active polymer, [mol/l]

[M<sub>0</sub>]: initial monomer concentration, [mol/l]

[M]: concentration of monomer at any reaction time, [mol/l]

k<sub>c</sub>: rate constant of initiation, [1/sec]

k<sub>p</sub>: rate constant of propagation, [l/mol·sec]

k<sub>t</sub>: rate constant of termination, [1/sec]

Hsu, C. C. and Ng, L., *AIChE Journal*, **22**, 66 (1976).

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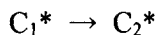
Copyright © 1976 AIChE. All rights reserved.

### Solution polymerization

Solvent: toluene

Catalyst: nickel(II) stearate-diethyl aluminium chloride

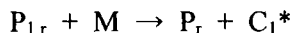
Temperature: 20°C



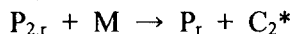
k<sub>r</sub>



k<sub>pi</sub>



k<sub>fm1</sub>



k<sub>fm2</sub>

M: monomer, DEAC: diethyl aluminium chloride, C<sub>1</sub>\*: Complex of type I, C<sub>2</sub>\*: Complex of type II, P<sub>1,1</sub>: the living polymer of chain length one of type I species, P<sub>i,r</sub>: the living polymer of chain length r of type i, P<sub>r</sub>: dead polymer with chain length r.

$$\ln[M_0]/[M]=k_{p2}[C^*]t+[C^*](k_{p1}-k_{p2})\{1-\exp(-k_{tr})\}/k_r$$

Parameter	Activation energy [kJ/mol]
$k_r$	21
$k_{p1}C^*$	6.8
$k_{p2}C^*$	17
$k_{p1}/k_{p2}$	-2.6

$[M_0]$ : initial monomer concentration, [mol/l]

$[M]$ : monomer concentration at any time  $t$ , [mol/l]

$[C^*]$ : total concentration of active species, the sum of  $[C_1^*]$  and  $[C_2^*]$ , [mol/l]

$k_r$ : rate constant of type I converted to type II, [1/sec]

$k_{pi}$ : propagation rate constant of type  $i$  complex, [l/mol·sec]

$k_{p1}$ : propagation rate constant of type I complex, [l/mol·sec]

$k_{p2}$ : propagation rate constant of type II complex, [l/mol·sec]

$k_p$ : overall propagation rate constant, [l/mol·sec]

$k_{fm1}$ : transfer rate constant of chain to monomer with respect to active species I, [l/mol·sec]

$k_{fm2}$ : transfer rate constant of chain to monomer with respect to active species II, [l/mol·sec]

Lee, D-H. and Hsu, C. C., *J. Appl. Polym. Sci.*, **26**, 653 (1981).

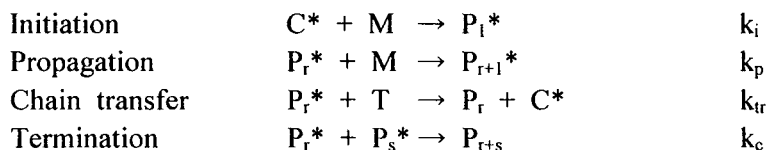
Copyright © 1981 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Solution polymerization

Solvent: toluene

Catalyst:  $\text{Co}(\text{acac})_3\text{-(i-Bu)}_3\text{Al-H}_2\text{O}$

Temperature: 20°C





C\*: active complex formed from the reduction of Co(III) + Co(II) with (i-Bu)<sub>3</sub>Al and water, P<sub>r</sub>\*: living polymers with chain length of r, P<sub>i</sub>: inactive polymers with chain length of r, T: transfer agent.

$$\begin{aligned}
 -d[P^*]/dt &= k_c [P^*]^2 \\
 -d[M]/dt &= k_p [P^*][M] \\
 [P^*] &= -[C^*]_0 / (k_c [C^*]_0 t + 1) \\
 \ln \frac{[M]_0}{[M]} &= \frac{k_p [C^*]_0}{k_c [C^*]_0} \ln(1 + k_c [C^*]_0 t)
 \end{aligned}$$

[M] <sub>0</sub> [mol/l]	[Co] [mmol/l]	[Al] [mmol/l]	$\frac{[Al]}{[H_2O]}$	k <sub>p</sub> [C*] <sub>0</sub> [1/min]	k <sub>p</sub> [C*] <sub>0</sub> /[Co] [l/mol·min]	k <sub>c</sub> [C*] <sub>0</sub> [1/min]	k <sub>c</sub> [C*] <sub>0</sub> /[Co] [l/mol·min]	k <sub>c</sub> /k <sub>p</sub>
1.4	0.42	14.5	0.94	2.0	4760	0.047	112	0.024
0.94	1.26	16.4	1.06	0.97	770	0.024	19.2	0.025
1.4	0.42	13.3	0.86	0.41	976	0.011	26.2	0.027

k<sub>i</sub>: rate constant of initiation, [l/mol·min]

k<sub>p</sub>: rate constant of propagation, [l/mol·min]

k<sub>c</sub>: rate constant of termination by combination, [l/mol·min]

k<sub>t</sub>: rate constant of transfer, [l/mol·min]

[P\*]: total concentration of living polymers, [mol/l]

[C\*]: concentration of active complex, [mol/l]

[C\*]<sub>0</sub>: initial concentration of active complex, [mol/l]

[M]: monomer concentration, [mol/l]

[M]<sub>0</sub>: initial monomer concentration, [mol/l]

[i]: concentration of species i, [mol/l]

Yang, W. L. and Hsu, C. C., *J. Appl. Polym. Sci.*, **28**, 145 (1983).

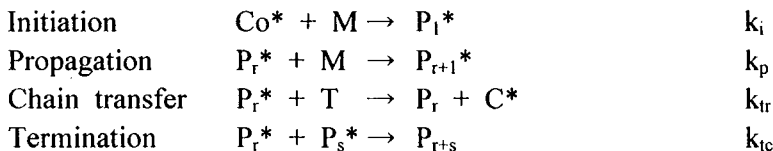
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**Solution Polymerization**

Solvent: toluene

Catalyst:  $\text{CoCl}_2 \cdot 4\text{Py}/\text{Et}_2 \cdot \text{AlCl}/\text{H}_2\text{O}$ 

Temperature: 11.6–25°C



$\text{Co}^*$ : active complex; M: monomer,  $\text{P}_r^*$ : living polymers with chain length of r,  $\text{P}_r$ : inactive polymers with chain length of r, T: transfer agent.

$$\ln[\text{M}]_i/[\text{M}] = (k_p[\text{Co}^*]_i/k_{tc}[\text{Co}^*]_i) \ln(1 + k_{tc}[\text{Co}^*]_i t)$$

$$k_p[\text{Co}^*]_i = 5.46 \times 10^{-4} + \text{B}_1 \text{T} + \text{B}_2 [\text{H}_2\text{O}] + \text{B}_5 [\text{H}_2\text{O}]^2 + \text{B}_7 \text{T} [\text{H}_2\text{O}] + \text{B}_9 [\text{H}_2\text{O}] [\text{DEAC}]$$

$$k_{tc}[\text{Co}^*]_i = -1.44 \times 10^{-3} + \text{B}_3 [\text{DEAC}] + \text{B}_4 \text{T}^2 + \text{B}_7 \text{T} [\text{H}_2\text{O}] + \text{B}_8 \text{T} [\text{DEAC}] + \text{B}_9 [\text{H}_2\text{O}] [\text{DEAC}]$$

Rate constant	Parameter estimate	Rate constant	Parameter estimate
$k_p[\text{Co}^*]_i$	$\text{B}_1 \quad 4.50 \times 10^{-5}$	$k_{tc}[\text{Co}^*]_i$	$\text{B}_3 \quad 1.55 \times 10^{-4}$
	$\text{B}_2 \quad -2.42 \times 10^{-4}$		$\text{B}_4 \quad 1.62 \times 10^{-6}$
	$\text{B}_5 \quad 7.71 \times 10^{-6}$		$\text{B}_7 \quad -8.78 \times 10^{-6}$
	$\text{B}_7 \quad -1.67 \times 10^{-6}$		$\text{B}_8 \quad -5.46 \times 10^{-6}$
	$\text{B}_9 \quad 4.97 \times 10^{-6}$		$\text{B}_9 \quad -8.64 \times 10^{-6}$

$$\text{M}_w = -1.39 \times 10^6 + \text{B}_1 \text{T} + \text{B}_2 [\text{H}_2\text{O}] + \text{B}_3 [\text{DEAC}] + \text{B}_4 \text{T}^2 + \text{B}_5 [\text{H}_2\text{O}]^2 + \text{B}_6 [\text{DEAC}]^2$$

$$\text{M}_n = -1.11 \times 10^6 + \text{B}_1 \text{T} + \text{B}_2 [\text{H}_2\text{O}] + \text{B}_3 [\text{DEAC}] + \text{B}_4 \text{T}^2 + \text{B}_5 [\text{H}_2\text{O}]^2 + \text{B}_6 [\text{DEAC}]^2$$

$$\text{PD} = -13.99 + \text{B}_2 [\text{H}_2\text{O}] + \text{B}_3 [\text{DEAC}] + \text{B}_5 [\text{H}_2\text{O}]^2 + \text{B}_6 [\text{DEAC}]^2$$

Parameter estimate			Parameter estimate			Parameter estimate		
M <sub>w</sub>	B <sub>1</sub>	6.18 × 10 <sup>4</sup>	M <sub>n</sub>	B <sub>1</sub>	8.09 × 10 <sup>3</sup>	PD	B <sub>2</sub>	1.76
	B <sub>2</sub>	1.16 × 10 <sup>5</sup>		B <sub>2</sub>	1.34 × 10 <sup>4</sup>		B <sub>3</sub>	1.34
	B <sub>3</sub>	6.30 × 10 <sup>4</sup>		B <sub>3</sub>	4.22 × 10 <sup>3</sup>		B <sub>5</sub>	-1.28 × 10 <sup>-1</sup>
	B <sub>4</sub>	-1.39 × 10 <sup>3</sup>		B <sub>4</sub>	-1.89 × 10 <sup>2</sup>		B <sub>6</sub>	-3.30 × 10 <sup>-2</sup>
	B <sub>5</sub>	-9.58 × 10 <sup>3</sup>		B <sub>5</sub>	-1.33 × 10 <sup>3</sup>			
	B <sub>6</sub>	-1.58 × 10 <sup>3</sup>		B <sub>6</sub>	-1.01 × 10 <sup>2</sup>			

k<sub>i</sub>: rate constant of initiation, [l/mol·sec]

k<sub>p</sub>: rate constant of propagation, [l/mol·sec]

k<sub>tc</sub>: rate constant of termination by combination, [l/mol·sec]

k<sub>tr</sub>: rate constant of chain transfer, [l/mol·min]

[Co\*]: concentration of active complex, [mol/l]

[Co\*]<sub>i</sub>: initial concentration of active complex, [mol/l]

[M]: concentration of monomer, [mol/l]

[M]<sub>i</sub>: initial concentration of monomer, [mol/l]

[H<sub>2</sub>O]: concentration of water, [mol/l]

[DEAC]: concentration of diethylaluminium chloride, [mol/l]

T: temperature, [°C]

t: polymerization time, [sec]

M<sub>w</sub>: weight-average molecular weight, [g/mol]

M<sub>n</sub>: number-average molecular weight, [g/mol]

PD: polydispersity, PD=M<sub>w</sub>/M<sub>n</sub>

Ho, F. K. W., Hsu, C. C., and Bacon, D. W., *J. Appl. Polym. Sci.*, **32**, 5287 (1986). Copyright © 1986 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### 3.2 Ethylene

#### Solution polymerization

Solvent: hexane

Catalyst:  $\text{Ti}(\text{OC}_4\text{H}_9)_4\text{-Al}(\text{C}_2\text{H}_5)_3$

Temperature: 25–50°C

Ethylene pressure: 25–95 mmHg

Activation energy=13 [kcal/mol] for

$[\text{AlEt}_3]=0.213$  [mol/l]

$[\text{Ti}(\text{OC}_4\text{H}_9)_4]=0.07$  [mol/l]

$\text{C}_2\text{H}_4$  pressure=56 mmHg and 90 mmHg.

Bawn, C. E. H. and Symcox, R., *J. Polym. Sci.*, **34**, 139 (1959).

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#### Solution polymerization

Solvent: toluene

Catalyst: bis-(cyclopentadienyl)-titanium dichloride/dimethylaluminium chloride

Temperature: 0–60°C



Chain propagation

$$d[\text{P}]/dt = k_p[\text{C}][\text{m}]$$

Activation energy=12.2 [kcal/mol]

Chain termination

$$-d[\text{C}]/dt = k_t[\text{C}]^2$$

Activation energy=16.4 [kcal/mol]

Temperature [°C]	$k_i \times 10^3$ [1/sec]	$k_p$ [l/mol·sec]	$k_t$ [l/mol·sec]
0	$0.282 \pm 0.26$	$1.50 \pm 0.15$	$0.49 \pm 0.05$
15	$1.12 \pm 0.13$	$5.19 \pm 0.57$	$2.19 \pm 0.43$
30	$4.99 \pm 0.71$	$13.6 \pm 1.4$	$9.07 \pm 0.58$
40		39.0	

[AT]: propagating metal alkyl complex

[P]: concentration of polymer formed, [mol/l]

[C]: concentration of propagating metal alkyl complex, [mol/l]

[m]: concentration of monomer, [mol/l]

$k_i$ : initiation rate constant, [1/sec]

$k_p$ : propagation rate constant, [l/mol·sec]

$k_t$ : termination rate constant, [l/mol·sec]

Chien, J. C. W., *J. Am. Chem. Soc.*, **81**, 86 (1959).

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### Solution polymerization

Solvent: hexane and heptane

Catalyst:  $TiCl_4$ -alkylaluminium

Temperature: 39–67°C

Ethylene pressure: 760mmHg

$$R_p = k_p MN$$

Propagation rate constant as a function of temperature

Temperature [°C]	$N \times 10^5$ [mol/l]	$k_p$ [l/mol·sec] 90% confidence limits
39.4 <sup>(1)</sup>	10.9	$52 \pm 2.7$
54.5 <sup>(1)</sup>	2.30	$127 \pm 16$
67.0 <sup>(2)</sup>	50.0	$175 \pm 35$

<sup>(1)</sup>[Ti]=2.14 [mmol/l], Al/Ti=2.0

<sup>(2)</sup>[Ti]=16.7 [mmol/l], Al/Ti=0.5

$R_p$ : polymerization rate, [mol/l·sec]  
 $k_p$ : propagation rate constant, [l/mol·sec]  
 M: solubility of ethylene in solvent, [mol/l]  
 N: active center concentration, [mol/l]

Feldman, C. F. and Perry, E., *J. Polym. Sci.*, **56**, 217 (1960).

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### Solution polymerization

Solvent: n-heptane  
 Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$   
 Pressure: 43 kg/cm<sup>2</sup>

Activation energy of polymerization in the liquid phase=2.7 [kcal/mol]

Fukui, K., Kagiya, T., Machi, S., Shimidzu, T., and Yuasa, S., *Bull. Chem. Soc., Japan*, **35**, 303 (1962).

### Solution polymerization

Solvent: cyclohexane  
 Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}/\gamma\text{-TiCl}_3$   
 Temperature: 30–60°C

$$\text{Rate} = k[\text{TiCl}_3]^1[\text{C}_2\text{H}_4][\text{Al}]^0$$

$$k = 6.1 \times 10^{15} \exp(-17300 \text{ cal}/RT)$$

Rate: polymerization rate, [mol/l·h]  
 $k$ : polymerization rate constant, [l/mol·h]  
 $[\text{TiCl}_3]$ : concentration of  $\gamma\text{-TiCl}_3$ , [mol/l]  
 $[\text{C}_2\text{H}_4]$ : concentration of ethylene, [mol/l]  
 $[\text{Al}]$ : concentration of  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}$ , [mol/l]

Berger, M. N. and Grievson, B. M., *Makromol. Chem.*, **83**, 80 (1965).

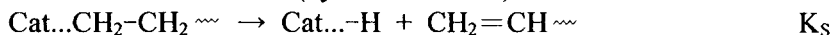
**Solution polymerization**

Solvent: cyclohexane

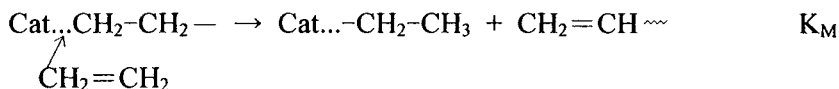
Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}/\gamma\text{-TiCl}_3$ 

Temperature: 30–60°C

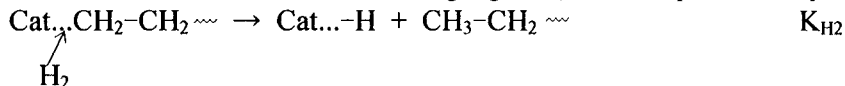
Spontaneous termination (hydride transfer)



Chain transfer with monomer



Chain transfer with added terminating agent (for example with hydrogen)



$$\text{Propagation rate} = K_p[\text{M}][\text{C}^*]$$

$$\text{Termination rate} = K_S[\text{C}^*] + K_M[\text{M}][\text{C}^*] + K_{\text{H}_2}[\text{H}_2][\text{C}^*]$$

$$K_p \sim 80.1 \text{ [l/mol}\cdot\text{sec]}$$

$$K_S/K_p = 3.4 \times 10^{-6}, \quad K_S \sim 3 \times 10^{-4} \text{ [l/mol}\cdot\text{sec]}$$

$$K_M/K_p = 1.8 \times 10^{-4}, \quad K_M \sim 10^{-2} \text{ [l/mol}\cdot\text{sec]}$$

$$K_{\text{H}_2}/K_p = 3.7 \times 10^{-2}, \quad K_{\text{H}_2} \sim 3 \text{ [l/mol}\cdot\text{sec]}$$

[M]: monomer concentration, [mol/l]

[C\*]: concentration of active polymerization sites, [mol/l]

[H<sub>2</sub>]: concentration of hydrogen, [mol/l]K<sub>p</sub>: propagation rate constant, [l/mol·sec]K<sub>S</sub>: solvent transfer rate constant, [l/mol·sec]K<sub>M</sub>: monomer transfer rate constant, [l/mol·sec]K<sub>H<sub>2</sub></sub>: hydrogen transfer rate constant, [l/mol·sec]Grieverson, B. M., *Makromol. Chem.*, **84**, 93 (1965).

**Solution polymerization**

Solvent: toluene

Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{TiCl}_3$ 

Temperature: 0–60°C

$$r = A \exp(-k\tau) + B$$

$$A = k'_1 P_E^2 / (1 + k'_2 P_E^2)$$

$$B = k_B P_E$$

$$k = k_1 P_E + k_2$$

Temperature [°C]	0	20	30	40
$k'_1$ [ $\text{g} \cdot \text{C}_2\text{H}_4 / \text{g} \cdot \text{TiCl}_3 \cdot \text{h}(\text{cmHg})^2$ ]	–	$2.8 \times 10^{-2}$	$3.04 \times 10^{-2}$	$4.64 \times 10^{-2}$
$k'_2$ [1/cmHg]	–	$11.9 \times 10^{-2}$	$8.67 \times 10^{-2}$	$8.36 \times 10^{-2}$
$k_B$ [ $\text{g} \cdot \text{C}_2\text{H}_4 / \text{g} \cdot \text{TiCl}_3 \cdot \text{h}(\text{cmHg})^2$ ]	0.3	0.59	0.75	1.01
$k_1$ [1/h·cmHg]	–	$1.2 \times 10^{-2}$	$1.63 \times 10^{-2}$	$3.5 \times 10^{-2}$
$k_2$ [1/h]	–	0.35	0.5	0.6

Activation energy of  $k_1 = 10.5$  [kcal/mol]Activation energy of  $k_2 = 4.6$  [kcal/mol]Activation energy of  $k_B = 6-7$  [kcal/mol] $k'_1, k'_2, k_1, k_2$ : constants $r$ : polymerization rate, [ $\text{g} \cdot \text{C}_2\text{H}_4 / \text{g} \cdot \text{TiCl}_3 \cdot \text{h}(\text{cmHg})^2$ ] $\tau$ : reaction time, [hr] $P_E$ : ethylene pressure, [cmHg]Matsuda, T., Keii, T., Kojima, A., and Ishida, T., *Kogyo Kagaku Zashi*, **71**, 1124 (1968).



**Solution polymerization**

Solvent: hexane

Catalyst:  $\delta$ -TiCl<sub>3</sub>, 0.3AlCl<sub>3</sub>+Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

Temperature: 75°C

$$V=K_p C_p C_m$$
$$K_p=(1.2 \pm 0.3) \times 10^4$$

K<sub>p</sub>: propagation rate constant, [l/mol·sec]

V: polymerization rate, [mol/l·sec]

C<sub>p</sub>: number of active centers, [mol/l]C<sub>m</sub>: monomer concentration, [mol/l]

Chumaevskii, N. B., Zakharov, V. A., Bukatov, G. D., Kuznetzova, G. I., and Yermakov Y. I., *Makromol. Chem.*, **177**, 747 (1976).

**Solution polymerization**

Solvent: hexane

Catalyst:  $\delta$ -TiCl<sub>3</sub>, 0.3AlCl<sub>3</sub>+Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

Temperature: 20–80°C

$$V=K_p C_p C_m$$
$$K_p=8.0 \times 10^5 \exp(-13 \text{ kJ/RT})$$

K<sub>p</sub>: propagation rate constant, [l/mol·sec]

V: polymerization rate, [mol/l·sec]

C<sub>p</sub>: number of active centers, [mol/l]C<sub>m</sub>: monomer concentration, [mol/l]

Zakharov, V. A., Chumaevskii, N. B., Bukatov, G. D., and Yermakov Y. I., *Makromol. Chem.*, **177**, 763 (1976).

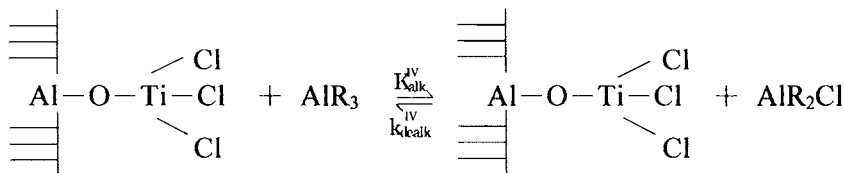
**Solution polymerization**

Solvent: cyclohexane

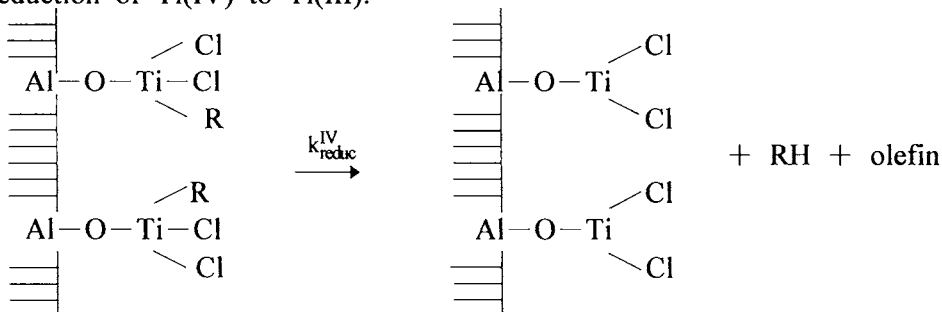
Catalyst:  $\text{TiCl}_3/\text{Al}/\text{Al}(\text{CH}_2\text{CH}(\text{CH}_3)_2)_3$ Temperature:  $68^\circ\text{C}$ 

Polymerization scheme:

Alkylation and dealkylation of supported Ti(IV):



Reduction of Ti(IV) to Ti(III):



The alkylation, dealkylation and reduction of Ti(III) to Ti(II) may occur in the same way.

Coordination of ethylene:  $\text{P}_n\text{-cat} + \text{E} \xrightleftharpoons[k_2]{k_1} \text{P}_n\text{-cat}\cdots\text{E}$

Insertion of ethylene:  $\text{P}_n\text{-cat}\cdots\text{E} \xrightarrow{k_i} \text{P}_{n+1}\text{-cat}$

$\text{P}_n$ : polymer chain, cat: catalyst, E: ethylene

$$R_p = \sum_i R_p(i) = \sum_i (k_p(i)\theta_{\text{active}}(i) \cdot c)$$

$$d\theta(-\text{TiCl}_2\text{R})/dt = k_{\text{alk}}^{\text{IV}} c(\text{AlR}_3)\theta(-\text{TiCl}_3) - k_{\text{dealk}}^{\text{IV}} c(\text{AlR}_2\text{Cl})\theta(-\text{TiCl}_2\text{R}) - k_{\text{reduc}}^{\text{IV}} \theta(-\text{TiCl}_2\text{R})^2$$

$$d\theta(-\text{TiClR})/dt = k_{\text{alk}}^{\text{III}} c(\text{AlR}_3) \theta(-\text{TiCl}_2) - k_{\text{dealk}}^{\text{III}} c(\text{AlR}_2\text{Cl}) \theta(-\text{TiClR}) - k_{\text{reduc}}^{\text{III}} \theta(-\text{TiClR})^2$$

$$d\theta(-\text{TiR})/dt = k_{\text{alk}}^{\text{II}} c(\text{AlR}_3) \theta(-\text{TiCl}) - k_{\text{dealk}}^{\text{II}} c(\text{AlR}_2\text{Cl}) \theta(-\text{TiR}) - k_{\text{reduc}}^{\text{II}} \theta(-\text{TiR})^2$$

$$d\theta(-\text{TiCl}_3)/dt = k_{\text{dealk}}^{\text{IV}} c(\text{AlR}_2\text{Cl}) \theta(-\text{TiCl}_2\text{R}) - k_{\text{alk}}^{\text{IV}} c(\text{AlR}_3) \theta(-\text{TiCl}_3)$$

$$d\theta(-\text{TiCl}_2)/dt = k_{\text{dealk}}^{\text{III}} c(\text{AlR}_2\text{Cl}) \theta(-\text{TiClR}) - k_{\text{alk}}^{\text{III}} c(\text{AlR}_3) \theta(-\text{TiCl}_2)$$

$$d\theta(-\text{TiCl})/dt = k_{\text{dealk}}^{\text{II}} c(\text{AlR}_2\text{Cl}) \theta(-\text{TiR}) - k_{\text{alk}}^{\text{II}} c(\text{AlR}_3) \theta(-\text{TiCl})$$

$$k_p(-\text{TiCl}_2\text{R}) = 1.16 \text{ [1/sec]}$$

$$k_p(-\text{TiClR}) = 3.41 \times 10^{-1} \text{ [1/sec]}$$

$$k_p(-\text{TiR}) = 7.50 \times 10^{-2} \text{ [1/sec]}$$

$$k_{\text{alk}}^{\text{IV}} = k_{\text{alk}}^{\text{III}} = k_{\text{alk}}^{\text{II}} = 10 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{dealk}}^{\text{IV}} = k_{\text{dealk}}^{\text{III}} = k_{\text{dealk}}^{\text{II}} = 1 \text{ [l/mol}\cdot\text{sec]}$$

$$k_{\text{reduc}}^{\text{IV}} = 5.46 \times 10^{-1} \text{ [1/sec]}$$

$$k_{\text{reduc}}^{\text{III}} = 2.52 \times 10^{-2} \text{ [1/sec]}$$

$$k_{\text{reduc}}^{\text{II}} = 8.18 \times 10^{-4} \text{ [1/sec]}$$

If concentration are used instead of surface coverages:

$$k_p(-\text{TiCl}_2\text{R}) = 17 \text{ [l/mol}\cdot\text{sec]}$$

$$k_p(-\text{TiClR}) = 5 \text{ [l/mol}\cdot\text{sec]}$$

$$k_p(-\text{TiR}) = 1.1 \text{ [l/mol}\cdot\text{sec]}$$

$R_p(i)$ : propagation rate of active center (i), [mol/l·sec]

c: concentration of ethylene, [mol/l]

$k_p$ : propagation rate constant of active center (i), [1/sec] or [l/mol·sec] .

$k_{\text{alk}}^{\text{IV}}$ ,  $k_{\text{alk}}^{\text{III}}$ ,  $k_{\text{alk}}^{\text{II}}$ : alkylation rate constants of supported titanium(IV), (III) and (II), respectively, [l/mol·sec].

$k_{\text{dealk}}^{\text{IV}}$ ,  $k_{\text{dealk}}^{\text{III}}$ ,  $k_{\text{dealk}}^{\text{II}}$ : dealkylation rate constants of supported titanium(IV), (III) and (II), respectively, [l/mol·sec]

$k_{\text{reduc}}^{\text{IV}}$ ,  $k_{\text{reduc}}^{\text{III}}$ ,  $k_{\text{reduc}}^{\text{II}}$ : reduction rate constants of Ti(IV) to Ti(III), Ti(III) to Ti(II) and Ti(II) to Ti(I), respectively, [1/sec]

$\theta_{\text{active}}(i)$ : the degree of coverage of active sites (i) on the surface, [mol/l]

$c(\text{AlR}_3)$ ,  $c(\text{AlR}_2\text{Cl})$ : concentration of  $\text{AlR}_3$  and  $\text{AlR}_2\text{Cl}$ , respectively, [mol/l]

Active center:  $-\text{TiCl}_2\text{R}$ ,  $-\text{TiClR}$ ,  $-\text{TiR}$ .

**Solution polymerization**

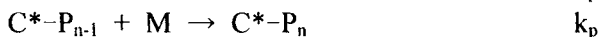
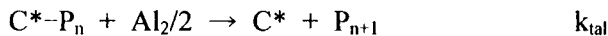
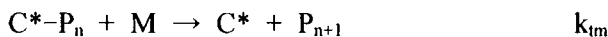
Solvent: tetrahydrofuran(THF)

Catalyst: silica-supported  $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$  activated by  $\text{Al}(\text{C}_2\text{H}_5)_3$ 

Temperature: 50–80°C

Ethylene concentration: 128–428 [mmol/l]

Initiation (formation of active sites)

Propagation  $\text{C}^* + \text{M} \rightarrow \text{C}^*-\text{P}_1$   $k_p$ Termination  $\text{C}^*-\text{P}_n + \text{H}_2/2 \rightarrow \text{C}^* + \text{P}_n$   $k_{th}$ Deactivation  $\text{C}^*-\text{P} \rightarrow \text{C}_1$   $k_d$ 

S: surface site,  $\text{C}_1$ : deactivated site,  $\text{C}^*$ : active center,  $\text{C}^*-\text{P}_n$ : living polymer with n units, M: monomer,  $\text{P}_n$ : dead polymer chain,  $\text{Al}_2$ : aluminium alkyl dimer.

$$(1/V)(d[\text{M}]/dt) = k_p[\text{C}^*-\text{P}][\text{M}]$$

$$d[\text{P}]/dt = k_{th}[\text{C}^*-\text{P}][\text{H}_2]^{1/2} + k_{tm}[\text{C}^*-\text{P}][\text{M}] + k_{tal}[\text{C}^*-\text{P}][\text{Al}_2]^{1/2} + k_{tB}[\text{C}^*-\text{P}]$$

$$d[\text{S}]/dt = -k_i[\text{S}][\text{Al}_2]^{1/2}$$

$$d[\text{C}^*-\text{P}]/dt = k_i[\text{S}][\text{Al}_2]^{1/2} - k_d[\text{C}^*-\text{P}]$$

$$d[\text{C}_1]/dt = -k_d[\text{C}^*-\text{P}]$$

$$d[\text{H}_2]/dt = -(1/2)k_{th}[\text{C}^*-\text{P}][\text{H}_2]^{1/2}$$

$$d[\text{Al}_2]/dt = -(1/2)(k_i[\text{S}][\text{Al}_2]^{1/2} + k_{tal}[\text{C}^*-\text{P}][\text{Al}_2]^{1/2})$$

k	Value at 80°C	Unit
$k_p$	16680	[l/mol·sec]
$k_i$	0.103	[l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
$k_{tm}$	12.8	[l/mol·sec]
$k_{th}$	175	[l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
$k_{tal}$	0.989	[l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]
$k_d$	$1.01 \times 10^{-4}$	[1/sec]

$[C^*-P] = \sum [C^*-P_n]$ : total concentration of living polymer, [mol/l]

[M]: monomer concentration, [mol/l]

[H]: concentration of hydrogen, [mol/l]

$[P] = \sum P_n$ : total concentration of dead polymer, [mol/l]

[S]: concentration of surface site, [mol/l]

[Al]: concentration of aluminium alkyl dimer, [mol/l]

$[C_i]$ : concentration of deactivated site, [mol/l]

V: volume of reactor, [l]

$k_i$ : rate constant of active site formation, [l<sup>1/2</sup>/mol<sup>1/2</sup>·sec]

$k_p$ : rate constant of propagation, [l/mol·sec]

$k_{th}$ : hydrogen transfer reaction constant, [l<sup>1/2</sup>/mol<sup>1/2</sup>·sec]

$k_{tm}$ : monomer transfer reaction constant, [l/mol·sec]

$k_{tal}$ : alkylaluminium transfer reaction constant, [l<sup>1/2</sup>/mol<sup>1/2</sup>·sec]

$k_{tB}$ : spontaneous transfer reaction constant, [1/sec]

$k_d$ : rate constant of deactivation, [1/sec]

Kim, J. H., Kim, I., and Woo, S. I., *Ind. Eng. Chem. Res.*, **30**, 2074 (1991).  
 © 1991 American Chemical Society.

### 3.3 Isoprene

#### Solution polymerization

Solvent: heptane and pentane

Catalyst: aluminium triisobutyl-TiCl<sub>4</sub>, Al/Ti molar ratio=1.20

Temperature: 0-20°C

Polymerization rate=0.760[M][Al alkyl][TiCl<sub>4</sub>] at 10 °C

Activation energy=14400 [cal/mol]

[M]: monomer concentration of monomer, [mol/l]

[Al alkyl]: concentration of aluminium triisobutyl, [mol/l]

[Ti]: concentration of TiCl<sub>4</sub>, [mol/l]

Saltman, W. M., Gibbs W. E., and Lal, J., *J. Am. Chem. Soc.*, **80**, 5615 (1958).  
© 1958 American Chemical Society.

### 3.4 Propylene

#### Gas phase polymerization

Catalyst:  $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$   $[\text{TiCl}_3]=2$  [g/l],  $[\text{Al}]/[\text{Ti}]=0.4\text{-}3.0$

Temperature: 30–70°C

Pressure: 100–700 [mmHg]

Stage I: initial polymerization stage (polymerization rate  $R$  increases rapidly)

(1) Propylene is introduced after the addition of  $\text{Al}(\text{C}_2\text{H}_5)_3$

$$R = k_1 P^2 K[A]t / (1 + K[A])$$

Temperature [°C]	Initial rate [mol/l·sec]	Stationary rate [mol/l·sec]
57	0.07–0.08	0.06
44	0.17	0.12
32	0.28	0.22

(2) Propylene is introduced before the addition of  $\text{Al}(\text{C}_2\text{H}_5)_3$

$$R = k_2 P[A]t$$

Stage II: kinetic behaviors are almost independent of the addition of propylene and  $\text{Al}(\text{C}_2\text{H}_5)_3$ .

$$\frac{R - R_\infty}{R_0 - R_\infty} = \exp\{-(k'_3 + k''_3 P)t\}$$

$$k_3 = k'_3 + k''_3 P$$

$$k_3 = k_3^0 \exp(-6.5 \text{ kcal/RT})$$

$$R_\infty = k_p^0 \exp(-10 \text{ kcal/RT})$$

## Values of activation energies

Rate constant	Activation energy [kcal/mol]
$k_1$	15
$k_2$	17
$k'_3$	2-3
$k''_3$	12
$k_p^0$	10

K: constant, [l/mol]

$k_1$ : rate constant, [l/mol·sec]

$k_2$ : rate constant, [l/mol·sec]

$k_3$ : rate constant, [l/sec]

$k'_3$ : rate constant, [l/sec]

$k''_3$ : rate constant, [l/sec]

$k_p^0$ : rate constant, [l/atm·sec]

P: propylene pressure, [cmHg]

[A]: concentration at  $Al(C_2H_5)_3$ , [mmol/l]

t: polymerization time, [sec]

R: polymerization rate at time t, [g-C<sub>3</sub>H<sub>6</sub>/g-TiCl<sub>3</sub>·hr]

$R_\infty$ : polymerization rate at stationary state, [g-C<sub>3</sub>H<sub>6</sub>/g-TiCl<sub>3</sub>·hr]

$R_0$ : initial polymerization rate, [g-C<sub>3</sub>H<sub>6</sub>/g-TiCl<sub>3</sub>·hr]

Keii, T., Soga, K., and Saiki, N., *J. Polym. Sci.*, **C16**, 1507 (1967).

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**Gas phase polymerization**Catalyst: MgCl<sub>2</sub>-supported TiCl<sub>4</sub>/C<sub>6</sub>H<sub>5</sub>COOC<sub>2</sub>H<sub>5</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

Temperature: 38–41°C

$$R_t = k_p[M][C^*]_t$$

$$-d[C^*]_t/dt = k'_d[C^*]_t^2$$

$$k_d = k'_d/k_p[M]$$

$$1/R_t = 1/R_0 + k_d t$$

$$1/[C^*]_t = 1/[C^*]_0 + k'_d t$$

Catalyst-system	Temperature [°C]	Time [min]	k <sub>p</sub> [l/mol·sec]
A-1/Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	41	10	300 ± 15
	41	60	320 ± 25
B-1/Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	38	10	320 ± 40
	38	30	320 ± 30
	38	60	360 ± 60
δ-TiCl <sub>3</sub> /Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl	41	80	32 ± 3
δ-TiCl <sub>3</sub> /Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	40	60	31 ± 10

A-1: Ti content 0.48%, B-1: Ti content 1.02%

[M]: monomer concentration, [mol/l]

[C\*]<sub>t</sub>: catalyst concentration at time t, [mol/l][C\*]<sub>0</sub>: initial concentration of catalyst, [mol/l]R<sub>t</sub>: polymerization rate at time t, [mol/l·sec]R<sub>0</sub>: initial polymerization rate, [mol/l·sec]k<sub>p</sub>: mean propagation rate constant, [l/mol·sec]k<sub>d</sub>: constant, [l/mol]k'<sub>d</sub>: constant, [l/mol·sec]Doi, Y., Murata, M., Yano, K., and Keii, T., *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 580 (1982). © 1982 American Chemical Society.

**Solution polymerization**

Solvent: n-heptane

Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)_3/\alpha\text{-TiCl}_3$ 

$$r = A \exp(-10000 \text{ cal}/RT) G_{\text{Ti}} P_{\text{C}_3\text{H}_6}$$

r: polymerization rate under steady-state conditions,  $[\text{g} \cdot \text{C}_3\text{H}_6/\text{hr}]$  $P_{\text{C}_3\text{H}_6}$ : partial pressure of propylene, [atm] $G_{\text{Ti}}$ : weight of  $\alpha\text{-TiCl}_3$  in the catalyst system, [g]Natta, G. and Pasquon, I., *Advances in Catalysis*, **XI**, 1 (1959).**Solution polymerization**

Solvent: n-heptane

Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$ 

Temperature: 2–149°C

Pressure: 3.7–37.0  $[\text{kg}/\text{cm}^2]$ 

Maximum conversion: 100%

Apparent activation energy = 5.7 [kcal/mol] for 2–40°C

Kodama, S., Kagiya, T., Machi, S., Shimidzu, T., Yuasa, S., and Fukui, K., *J. Appl. Polym. Sci.*, **3**, 20 (1960). Copyright © 1960 John Wiley & Sons, Inc.  
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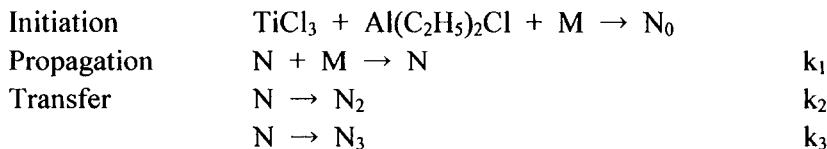
**Solution polymerization**

Solvent: hexane

Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-TiCl}_3$ 

Temperature: 50–90°C

Pressure: 1.36–6.80 [atm]



M: monomer,  $\text{N}_0$ : initiated active complex, N: active site,  $\text{N}_2$ : inactive complex,  $\text{N}_3$ : exchanged active complex.

## Rate constants

Temperature [°C]	$k_1$ [1/min·atm]	$k_2 \times 10^3$ [1/min]	$k_3 \times 10^3$ [1/min]
50	109	3.6	9.0
70	124	7.1	31
90	126	11.5	110

$k_1$ : propagation rate constant, [1/min·atm]

$k_2, k_3$ : transfer rate constant, [1/min]

Kohn, E., Schuurmans, H. J. L., and Cavender, J. V., *J. Polym. Sci.*, **58**, 681 (1962). Copyright © 1962 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Solution polymerization**

Solvent: n-heptane

Catalyst:  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{TiCl}_3$

Temperature: 16–57°C

$$r_\tau = r_\infty [f \cdot \exp(-k\tau + 1)]$$

$$k = k_0 \exp(-6.5 \text{ kcal}/RT)$$

$r_\tau$ : polymerization rate at  $\tau$  hours after the polymerization starts.

$r_\infty$ : polymerization rate at steady state.

$k_0$ : constant

$k$ : constant

$f$ : constant

Keii, T., Takagi, T., Taira, M., Soga, K., Saiki, N., and Murayama, Y., *Shokubai*, **5**, 243 (1963).

**Solution polymerization**

Solvent: heptane

Catalyst:  $\alpha$ -TiCl<sub>3</sub>-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlCl

Temperature: 30–90°C

$$R_p = k_p [C][m]$$

$$R_{tr} = k_{tr1} [C] [(C_2H_5)_2AlCl]^{1/2} + k_{tr2} [C] [\alpha-TiCl_3]$$

Temperature [°C]	$k_p$ [l/mol·sec]	$k_{tr1}$ [l <sup>1/2</sup> /mol <sup>1/2</sup> ·sec]	$k_{tr2}$ [l/mol·sec]
30	0.100 ± 0.20	–	–
50	0.426 ± 0.018	6.54 × 10 <sup>-5</sup>	9.54 × 10 <sup>-4</sup>
70	1.15 ± 0.20	3.50 × 10 <sup>-4</sup>	1.90 × 10 <sup>-3</sup>
90	3.50 ± 0.12	1.58 × 10 <sup>-3</sup>	3.60 × 10 <sup>-3</sup>

$$E_p = 13.0 \text{ [kcal/mol]}, E_{tr1} = 18.6 \text{ [kcal/mol]}, E_{tr2} = 7.6 \text{ [kcal/mol]}$$

$R_p$ : polymerization rate, [mol/l·sec]

[C]: concentration of catalyst, [mol/l]

[m]: concentration of monomer, [mol/l]

$k_p$ : polymerization rate constant, [l/mol·sec]

$R_{tr}$ : rate of increase of C<sup>14</sup> activity, [mol/l·sec]

$k_{tr1}$ : rate constant of chain transfer reaction, [l<sup>1/2</sup>/mol<sup>1/2</sup>·sec].

$k_{tr2}$ : rate constant of chain transfer reaction, [l/mol·sec].

$E_p$ : activation energy for  $k_p$ , [kcal/mol]

$E_{tr1}$ ,  $E_{tr2}$ : activation energy for  $k_{tr1}$ ,  $k_{tr2}$ , [kcal/mol]

Chien, J. C. W., *J. Polym. Sci.* **A1**, 425 (1963). Copyright © 1963 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

**Solution polymerization**

Solvent: n-heptane

Catalyst:  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{TiCl}_3$ 

Temperature: 25–56°C

$$r = BP[1 + f \cdot \exp(-kt)]$$

$$B = B_0 \exp(-2.7 \text{ kcal}/RT)$$

$$k = k_0 \exp(-3.8 \text{ kcal}/RT)$$

$\text{Zn}(\text{C}_2\text{H}_5)_2$ [mmol/l]	$B_0$ [g(C <sub>2</sub> H <sub>5</sub> )/g(TiCl <sub>3</sub> )·hr·atm]			
	48.5 [°C]	43.5 [°C]	37.5 [°C]	30.5 [°C]
80	200	286	298	300
40	–	261	–	–
28	–	214	–	–
16	133	142	157	171
8	110	118	118	–
4	37	53	43	–

r: polymerization rate, [g(C<sub>2</sub>H<sub>5</sub>)/g(TiCl<sub>3</sub>)·hr]

P: propylene pressure, [atm]

B: constant, [g(C<sub>2</sub>H<sub>5</sub>)/g(TiCl<sub>3</sub>)·hr·atm]

f: constant, [1/hr]

k: constant, [-]

Soga, K. and Keii, T., *J. Polym. Sci.*, A1, 4, 2429 (1966).

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**Solution polymerization**

Solvent: hexane

Catalyst:  $\delta$ -TiCl<sub>3</sub>, 0.3AlCl<sub>3</sub>+Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl

Temperature: 70°C

$$V=K_p C_p C_m$$

$$K_p=90 \pm 20$$

K<sub>p</sub>: propagation rate constant, [l/mol·sec]

V: polymerization rate, [mol/l·sec]

C<sub>p</sub>: number of active centers, [mol/l],C<sub>m</sub>: monomer concentration, [mol/l]

Chumaevskii, N. B., Zakharov, V. A., Bukatov, G. D., Kuznetzova, G. I., and Yermakov Y. I., *Makromol. Chem.*, **177**, 747 (1976).

**Solution polymerization**

Solvent: hexane

Catalyst:  $\delta$ -TiCl<sub>3</sub>, 0.3AlCl<sub>3</sub> + Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Al

Temperature: 30–70°C

$$V=K_p C_p C_m$$

$$K_p=3.0 \times 10^5 \exp(-23 \text{ kJ/RT})$$

K<sub>p</sub>: propagation rate constant, [l/mol·sec]

V: polymerization rate, [mol/l·sec]

C<sub>p</sub>: number of active centers, [mol/l]C<sub>m</sub>: monomer concentration, [mol/l]

Zakharov, V. A., Chumaevskii, N. B., Bukatov, G. D., and Yermakov Y. I., *Makromol. Chem.*, **177**, 763 (1976).

**Solution polymerization**

Solvent: heptane

Catalyst:  $\text{TiCl}_4/\text{MgCl}_2/\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5/\text{Al}(\text{C}_2\text{H}_5)_3$ Temperature:  $41^\circ\text{C}$ 

Pressure: 660 Torr

$$P_n = k_p[M]t$$

With  $0.45 \text{ mol/dm}^3$  and 5 seconds

$$k_p > 4.4 \times 10^2 \text{ [dm}^3/\text{mol}\cdot\text{sec]}$$

 $k_p$ : overall polymerization rate constant,  $[\text{dm}^3/\text{mol}\cdot\text{sec}]$  $[M]$ : monomer concentration in the solvent,  $[\text{mol/dm}^3]$  $P_n$ : number-average degree of polymerization, [units/mol]

t: polymerization time, [sec]

Suzuki, E., Tamura, M., Doi, Y., and Keii, T., *Makromol. Chem.*, **180**, 2235 (1979).

**Solution polymerization**

Solvent: hexane

Catalyst:  $\text{TiCl}_m(\text{Mg})$ Temperature:  $70^\circ\text{C}$ 

$$v = k_p C_p C_M$$

$$k_p = 500\text{--}1000 \text{ [l/mol}\cdot\text{sec]}$$

v: polymerization rate,  $[\text{mol}/(\text{mol of Ti})\cdot\text{sec}]$  $k_p$ : propagation rate constant,  $[\text{l/mol}\cdot\text{sec}]$  $C_p$ : number of active centers,  $[\text{mol/mol of Ti}]$  $C_M$ : monomer concentrations,  $[\text{mol/l}]$ 

Bukatov, G. D., Shepelev, S. H., Zakharov, V. A., Sergeev, S. A., and Yermakov, Y. I., *Makromol. Chem.*, **183**, 2657 (1982).

## 4. Polycondensation reactions

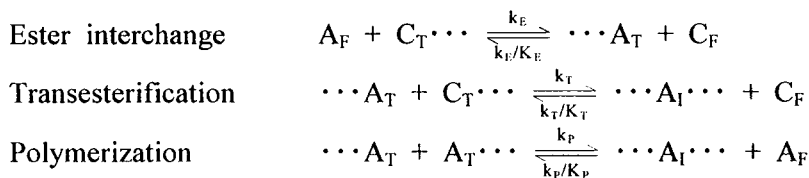
### 4.1 Transesterification of dimethyl terephthalate with ethylene glycol

Zero functional species: dimethyl terephthalate and its oligomer

Monofunctional species: methanol, singly substituted mixed ester,  
and its higher oligomer

Bifunctional species: ethylene glycol, monomer, and its high oligomer

Temperature: 180–262°C



$A_F$ : free ethylene glycol species (HOCH<sub>2</sub>CH<sub>2</sub>OH),

$A_T$ : end-group ethylene glycol ester unit (HOCH<sub>2</sub>CH<sub>2</sub>O-),

$A_I$ : an internal ethylene glycol ester unit (-OCH<sub>2</sub>CH<sub>2</sub>O-),

$C_F$ : free methanol (CH<sub>3</sub>OH),  $C_T$ : the end methanol ester group(CH<sub>3</sub>O-).

Second-order rate constants from the literature

Reaction	Catalyst	Rate constant [l/mol·min]	Energy [kcal/mol]	Reference
Ester interchange DMT <sup>(1)</sup> with EG <sup>(1)</sup>	zinc acetate	$k_E=3.0 \times 10^{-3}$ at 180°C <sup>(2)</sup> $k_T/k_E=0.5$	15	(3)
Polymerization BHET <sup>(1)</sup>	no catalyst	$k_P=3.2 \times 10^{-3}$ at 262°C	23	(4)
BHET	antimony trioxide	$k_P=2.5 \times 10^{-3}$ at 231°C	29	(5)

<sup>(1)</sup>DMT: dimethyl terephthalate, EG: ethylene glycol.

BHET: bis(2-hydroxyethyl)terephthalate



(2) Fontana's original rate constants were based on a third order rate expression (one order with respect to catalyst concentration). Here the catalyst concentration was included in  $k_E$ .

(3) Fontana, C. M., *J. Polym. Sci.*, A-1, 6, 2343 (1968).

(4) Challa, G., *Makromol. Chem.*, 38, 125 (1960).

(5) Stevenson, R. W. and Nettleton, H. R., *J. Polym. Sci.*, A-1, 6, 889 (1968).

At 220°C

$$K_P = K_E = K_T = 1$$

$$k_E/k_P = 4, \quad k_T/k_P = 8, \quad k_T/k_E = 4$$

$K_E$ : ester interchange reaction equilibrium constant, [-]

$K_P$ : polymerization reaction equilibrium constant, [-]

$K_T$ : transesterification reaction equilibrium constant, [-]

$k_E$ : second- or third-order forward ester interchange rate constant, [l/mol·min]

$k_P$ : second-order forward polymerization rate constant, [l/mol·min]

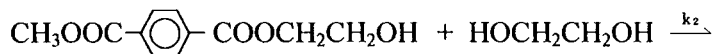
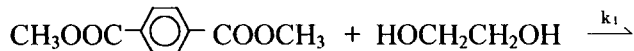
$k_T$ : second- or third-order forward transesterification rate constant, [l/mol·min]

Ault, J. W. and Mellichamp, D. A., *Chem. Eng. Sci.*, 27, 2219 (1972).

Catalyst: zinc acetate

Temperature: 180–197°C

Molecular species model:



$$d(N_E)/dt = 2k_1(N_C/V)(N_E/V)(N_B/V)$$

$$d(N_m)/dt = k'_a N_B(N_A + KN_R)/V^2$$

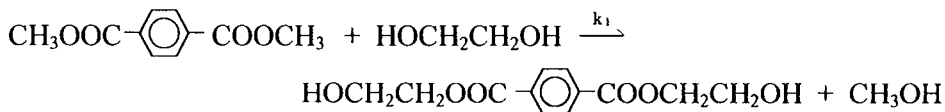
$$k'_a = 4N_C k_1, \quad K = k_2/2k_1$$

## Rate constants for the molecular species model

Data	Catalyst		Reaction temperature [°C]	Apparent rate constant $k'_a \times 10^3$	True rate constant $k_1$ [l <sup>2</sup> /mol <sup>2</sup> ·min]
	Compound	Mass, [mol] $\times 10^4$			
Fontana <sup>(1)</sup>	zinc acetate	1.81	180	2.5535	3.527
Tomita and Ida <sup>(2)</sup>	zinc acetate	1.00	197	2.0370	5.093
Tomita and Ida <sup>(2)</sup>	zinc acetate	0.70	197	1.4187	5.067
Tomita and Ida <sup>(2)</sup>	zinc acetate	0.50	197	0.98768	4.938
Tomita and Ida <sup>(2)</sup>	zinc acetate	1.00	180	1.4372	3.593
Peebles and Wagner <sup>(3)</sup>	zinc acetyl- acetate	5.51	175	3.1787	1.442

$$\ln k_1 = 4335.5/T + 10.840$$

Methyl ester group model:



## Rate constants for the methyl ester group model

Data	Catalyst		Reaction temperature [°C]	Apparent rate constant $k'_a \times 10^3$	True rate constant $k_1$ [l <sup>2</sup> /mol <sup>2</sup> ·min]
	Compound	Mass $\times 10^4$ [mol]			
Fontana <sup>(1)</sup>	zinc acetate	1.81	180	7.7373	3.527
Tomita and Ida <sup>(2)</sup>	zinc acetate	1.00	197	6.0264	5.092
Tomita and Ida <sup>(2)</sup>	zinc acetate	0.70	197	4.1646	5.027
Tomita and Ida <sup>(2)</sup>	zinc acetate	0.50	197	2.9248	4.943
Tomita and Ida <sup>(2)</sup>	zinc acetate	1.00	180	4.3551	3.593
Peebles and Wagner <sup>(3)</sup>	zinc acetyl- acetate	5.51	175	3.5508	1.350

(1) Fontana, C. M., *J. Polym. Sci.*, **A-1**, **6**, 2343 (1968).

(2) Tomita, K. and Ida, H., *Polymer*, **14**, 55 (1973).

(3) Peebles, L. H. and Wagner, W. S., *J. Phys. Chem.*, **63**, 1206 (1959).

$$\ln k_1 = -4306.8/T + 10.777$$

$k'_a$ : apparent rate constant, [-]

$k_1$ : true rate constant, [ $l^2/mol^2 \cdot min$ ]

$N_X$ : the number of moles of species X

A: DMT, B: ethylene glycol, C: catalyst, E: methyl ester, m: methanol,

R: methyl 2-hydroxyethyl terephthalate (MHET), V: reaction volume.

Yamanis, J. and Adelman, M., *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 1961 (1976).

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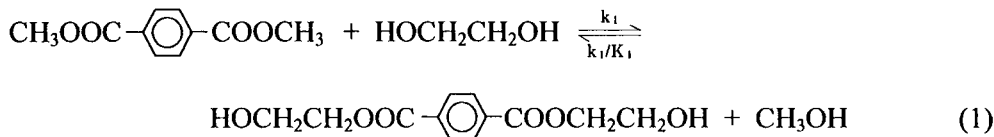
Catalyst: zinc acetate

Temperature: the first stage: prepolymer (monomer for polycondensation stage) containing mainly bis(2-hydroxyethyl) terephthalate (and its linear oligomers) is prepared by dimethyl terephthalate and ethylene glycol. 140–220°C

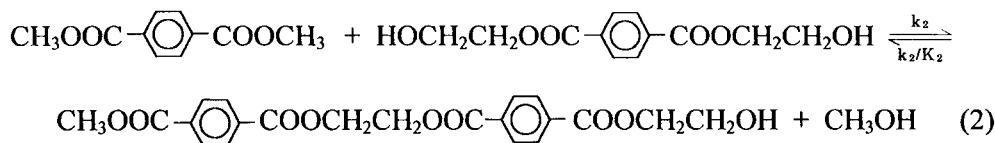
the second stage: polycondensation stage, prepolymer produced in the first stage is polycondensed. 260–290°C.

The first stage:

Ester interchange reaction

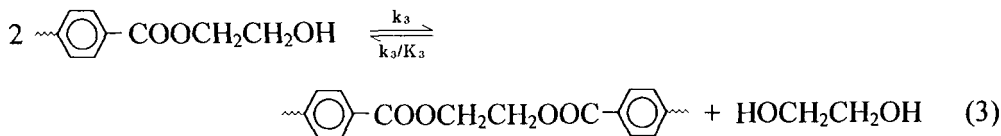


Transesterification reaction

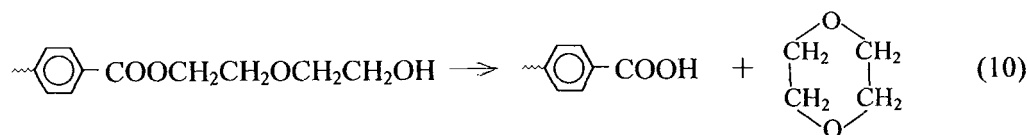
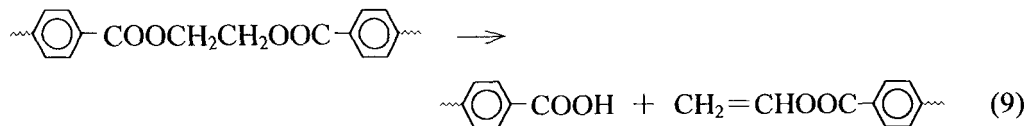
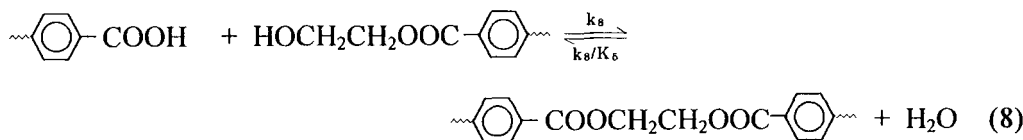
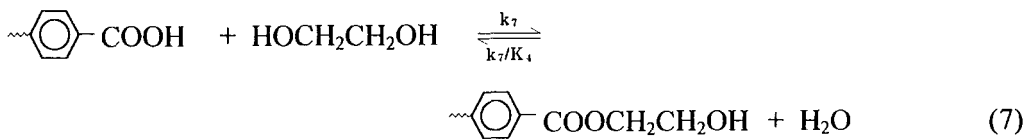
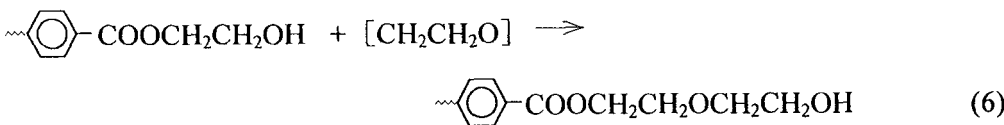
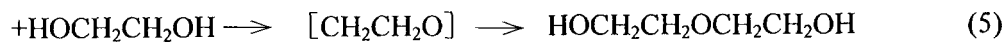


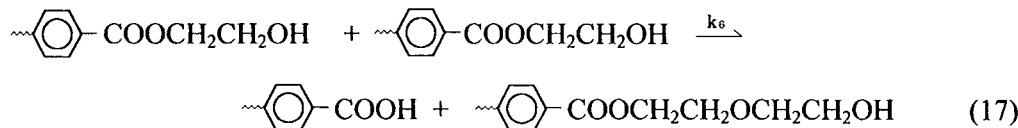
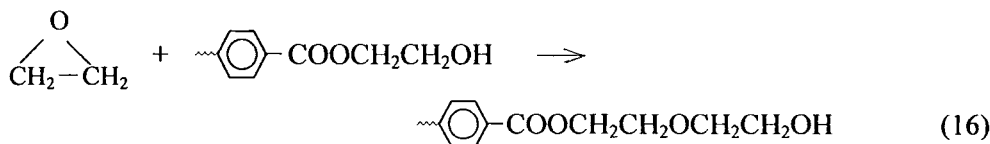
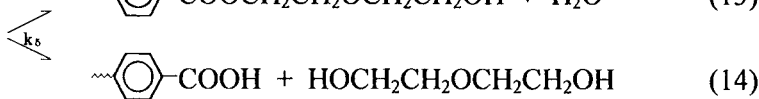
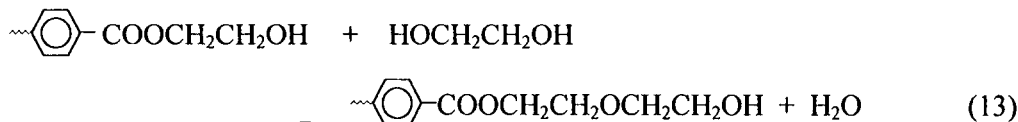
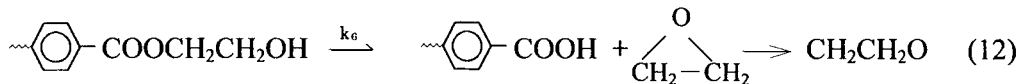
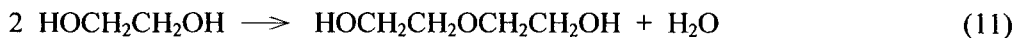
The second stage:

Polycondensation



Side reactions





## Kinetic parameters used in the present work

Reaction	Activation energy [kcal/mol]	Frequency factor [l/mol·min]	Equilibrium constant
Ester interchange eq.(1)	15.0	$6.0 \times 10^4$ $4.0 \times 10^4$ $2.0 \times 10^4$	0.3
Transesterification eq.(2)	15.0	$3.0 \times 10^4$ $2.0 \times 10^4$ $1.0 \times 10^4$	0.15
Polycondensation eq.(3)	18.5	$6.8 \times 10^5$	0.5
Acetaldehyde formation eq.(4)	29.8	$2.17 \times 10^9$ <sup>(1)</sup>	–
Free DEG <sup>(2)</sup> formation eq.(14)	29.8	$2.17 \times 10^9$	–
Incorporated DEG formation eq.(17)	29.8	$2.17 \times 10^9$	–
Esterification reaction eq.(7)	17.6	$1.0 \times 10^6$	2.5
Esterification reaction eq.(8)	17.6	$1.0 \times 10^6$	1.25

<sup>(1)</sup>Units are 1/min. <sup>(2)</sup>DEG: diethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH)

$k_1$ - $k_3$ ,  $k_5$ - $k_8$ : second-order rate constants, [l/mol·min]

$k_4$ : first-order rate constant, [1/min]

$K_1$ - $K_5$ : equilibrium constants, [-]

Ravindranath, K. and Mashelkar, R. A., *J. Appl. Polym. Sci.*, **26**, 3179 (1981).  
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## 4.2 Esterification of terephthalic acid with ethylene glycol

Catalyst: no catalyst

Temperature: 180–196.7°C



A: terephthalic acid, B: ethylene glycol, C: 2-(hydroxyethyl)terephthalate, D: bis(2-hydroxyethyl)terephthalate, E: water.

$$[A'] = [A']_0 / (1 + k_{11}[A']_0 t) \quad (3)$$

$$d[C]/dt = k_{21}[C] + k_{22}[C]^2 \quad (4)$$

$$d[C]/dt = k_2[C]_0 \quad (5)$$

$$d[D]/dt = k_3[C] \quad (6)$$

$$k_3 = k_{31} + k_{32}[A'] \quad (7)$$

Effect of initial concentration of 2-hydroxyethyl terephthalate [C] and bis(2-hydroxyethyl)terephthalate [D] on the rate of esterification of terephthalic acid [A'] at 196.7°C

[A'] <sub>0</sub> [mol/kg]	[C] <sub>0</sub> [mol/kg]	[D] <sub>0</sub> [mol/kg]	k <sub>11</sub> × 10 <sup>2</sup> [kg/mol·min]
0.1913	–	–	5.74
0.1952	–	–	5.67
0.153	0.210	–	6.25
0.1046	0.1886	–	5.84
0.0427	0.1913	–	6.25
0.183	–	0.42	3.70

Estimates of rate constants at 196.7°C

$$k_{21} = 7.5 \times 10^{-4} \text{ [1/min]}$$

$$k_{22} = 4.0 \times 10^{-3} \text{ [kg/mol·min]}$$

$$k_{31} = (7.1 \pm 1.53) \times 10^{-4} \text{ [1/min]}$$

$$k_{32} = (2.38 \pm 0.081) \times 10^{-2} \text{ [kg/mol·min]}$$

[A']: instantaneous concentration of terephthalic acid, [mol/kg]

[A']<sub>0</sub>: instantaneous concentration of terephthalic acid at time zero, [mol/kg]

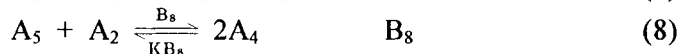
[C]<sub>0</sub>: instantaneous concentration of 2-(hydroxyethyl)terephthalate at time 0, [mol/kg]

k<sub>11</sub>, k<sub>21</sub>, k<sub>22</sub>, k<sub>31</sub>, k<sub>32</sub>, k<sub>2</sub>, k<sub>3</sub>: defined in equations (3)–(7)

Mareš, F., Bazant, V., and Krupička, J., *Collection Czechoslov. Chem. Commun.*, **34**, 2208 (1969).

Catalyst: cobalt acetate, manganese acetate, or no catalyst

Temperature: 240°C (at the boiling point of the reaction mixture)



List of symbol and chemical formulas of compounds

Symbol	Compound	Chemical formula
A <sub>1</sub>	Terephthalic acid	HOOC <sub>6</sub> H <sub>4</sub> COOH
A <sub>2</sub>	Ethylene glycol	HOC <sub>2</sub> H <sub>4</sub> OH
A <sub>3</sub>	2-Hydroxyethyl hydrogen terephthalate	HOC <sub>2</sub> H <sub>4</sub> OOCC <sub>6</sub> H <sub>4</sub> COOH
A <sub>4</sub>	Bis(2-hydroxyethyl) terephthalate	HOC <sub>2</sub> H <sub>4</sub> OOCC <sub>6</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OH
A <sub>5</sub>	Dimer	HO(C <sub>2</sub> H <sub>4</sub> OOCC <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub> C <sub>2</sub> H <sub>4</sub> OH
A <sub>6</sub>	Trimer	HO(C <sub>2</sub> H <sub>4</sub> OOCC <sub>6</sub> H <sub>4</sub> COO) <sub>3</sub> C <sub>2</sub> H <sub>4</sub> OH
A <sub>7</sub>	Tetramer	HO(C <sub>2</sub> H <sub>4</sub> OOCC <sub>6</sub> H <sub>4</sub> COO) <sub>4</sub> C <sub>2</sub> H <sub>4</sub> OH
A <sub>8</sub>	Acidic dimer	HO(C <sub>2</sub> H <sub>4</sub> OOCC <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub> H
A <sub>13</sub>	Diethylene glycol	HOC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OH
A <sub>14</sub>	Water	H <sub>2</sub> O



## Parameter Values

Parameter [l/mol·hr]	Series I <sup>(1)</sup>	Series II <sup>(2)</sup>
B <sub>1</sub>	1.670	0.764
B <sub>2</sub>	0.193	0.134
B <sub>4</sub> (=B <sub>3</sub> )	2.28	2.52
B <sub>5</sub>	3.03	1.26
B <sub>6</sub>	1.39	0.35
B <sub>7</sub> (=B <sub>10</sub> )	0.57	0.71
B <sub>8</sub>	1.52	0.19
KB <sub>8</sub>	0.96	0.12
B <sub>9</sub>	1.26	2.48
K	0.63	

<sup>(1)</sup> Catalyst concentration 0.3% based on the total batch weight:  
potassium chloride concentration 0.3% based on the total  
batch weight.

<sup>(2)</sup> No catalyst, no potassium chloride was present.

Effect of reaction mixture composition on parameter B<sub>8</sub> [l/mol·hr]

Catalyst [%]	0.3	0.03	–	–
KCl [%]	0.3	0.3	0.3	–
B <sub>8</sub> [l/mol·hr]	1.524	0.762	0.389	0.19

B<sub>1</sub>–B<sub>8</sub>: reaction rate constant, defined in equations (1)–(9), [l/mol·hr]

K: equilibrium constant of equation (8), [-]

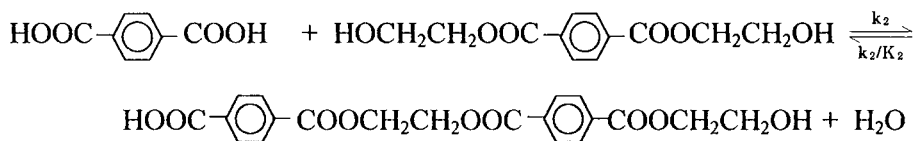
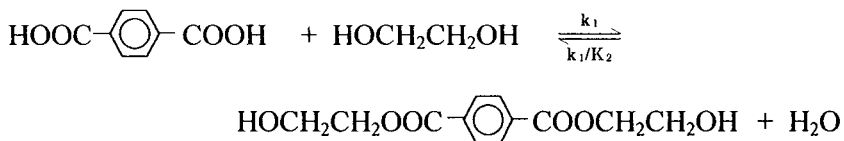
Rod, V., Eldiwani, G., Minárik, M., and Šir, Z. *Collection Czechoslov. Chem. Commun.* **41**, 2339 (1976).

Catalyst: no catalyst

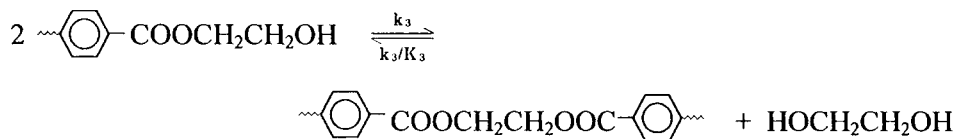
Temperature: 240–260°C

Pressure: 3–6 atm.

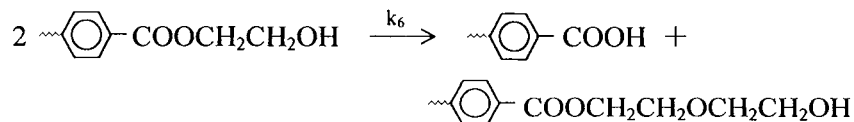
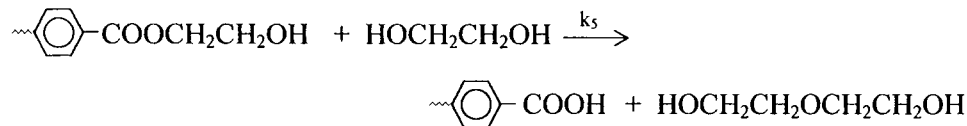
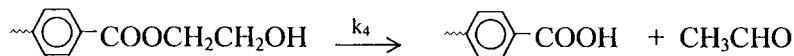
Esterification reactions



Polycondensation reaction



Side reactions



Rate equations:

$$R_1 = k_1(2e_c g - e_g w / K_1)$$

$$R_2 = k_2(e_c e_g - 2zw / K_2)$$

$$R_3 = k_3(e_g^2 - 4zg / K_3)$$

$$R_4 = k_4 e_g$$

$$R_5 = 2k_5 e_g g$$

$$R_6 = k_6 e_g^2$$

$$k_i = k_i^0 + k_i^c e^c \quad i=1, 2, 3$$

$$k_i = A_i \exp(-E_i / RT)$$

$$K_i = \exp(\Delta S_i / R - \Delta H_i / RT) \quad i=2, 3$$

$$K_1 = K_2 / K_3$$

Kinetic and thermodynamic parameters

	A	$E \times 10^{-3}$ [cal/mol]	$\Delta S$ [cal/mol·°K]	$\Delta H$ [cal/mol]
$k_1^0$ [kg/mol·min]	$2.55 \times 10^{-5}$	0.00		
$k_1^c$ [kg <sup>2</sup> /mol <sup>2</sup> ·min]	$8.672 \times 10^5$	20.63		
$k_2^0$ [kg/mol·min]	$8.462 \times 10^8$	29.71		
$k_2^c$ [kg <sup>2</sup> /mol <sup>2</sup> ·min]	$7.564 \times 10$	10.31		
$k_3^0$ [kg/mol·min]	$5.038 \times 10^{17}$	49.16		
$k_3^c$ [kg <sup>2</sup> /mol <sup>2</sup> ·min]	$3.325 \times 10^6$	21.86		
$k_4$ [1/min]	$1.04 \times 10^8$	29.80		
$k_5, k_6$ [kg/mol·min]	$1.04 \times 10^8$	29.80		
$K_2$			-10.80	-5666
$K_3$			-19.21	-9122

$e_c, e_g$ : concentration of acid end groups and hydroxyl end groups in the liquid phase, [equiv/kg]

$g$ : concentration of ethylene glycol in the liquid phase, [mol/kg]

$z$ : concentration of diester group in the liquid phase, [mol/kg]

$w$ : concentration of water in the liquid phase, [mol/kg]

$E_i$ : activation energy of  $i$ -th reaction, [cal/mol]

$\Delta S_i$ : entropy change of  $i$ -th reaction, [cal/mol·°K]

$\Delta H_i$ : enthalpy change of  $i$ -th reaction, [cal/mol]

$k_1, k_2, k_3, k_5, k_6$ : second order rate constant, [kg/mol·min]

$k_4$ : first order rate constant, [1/min]

$K_1, K_2, K_3$ : equilibrium constants, [-]

$R_1, R_2, R_3, R_4, R_5, R_6$ : reaction rates, [mol/kg·min]

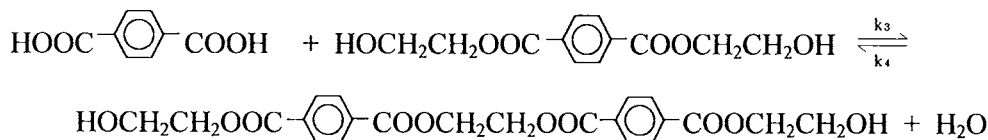
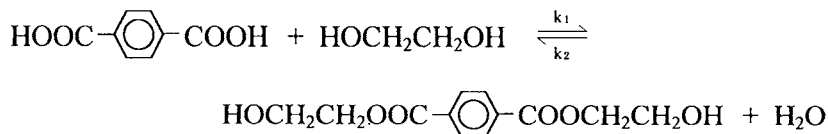
Ravindranath, K. and Mashelkar, R. A., *Polym. Eng. Sci.*, **22**, 610 (1982).

Catalyst: not specified

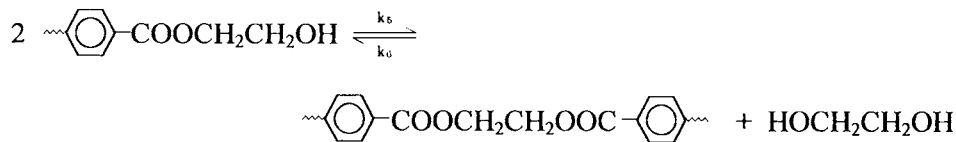
Temperature: 240–265°C

Pressure: atmospheric – 1.0 kg/cm<sup>2</sup>

Esterifications

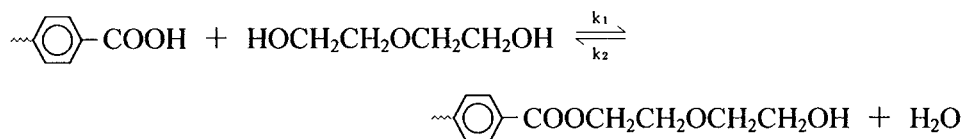
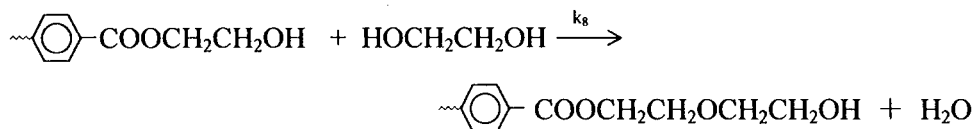


Polycondensation reaction



Side reactions





Kinetic constants:  $k_i = A_i \exp(-E_i/RT)$

	A	E [cal/mol]
$k_1$	$1.8006 \times 10^9$	19640
$k_2$	$1.8463 \times 10^8$	18140
$k_3$	$4.5716 \times 10^9$	22310
$k_4$	$7.9816 \times 10^7$	18380
$k_5$	9.0941	2810
$k_6$	$6.8229 \times 10^6$	14960
$k_7$	$2.4905 \times 10^{15}$	42520

$k_1$ – $k_7$ : rate constants, [kg/mol·hr]

E: activation energy, [cal/mol]

A: frequency factor, [kg/mol·hr]

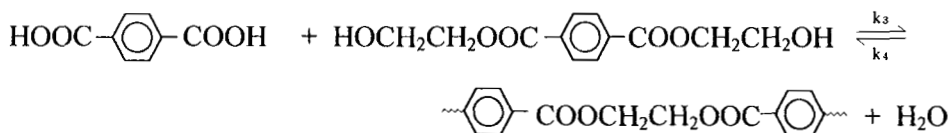
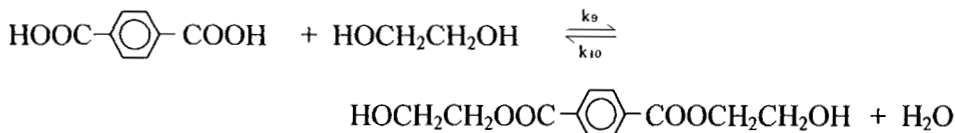
Yamada, T., Imamura, Y., and Makimura, O., *Polym. Eng. Sci.*, **26**, 708 (1986).

Catalyst: potassium titanium oxyoxalate

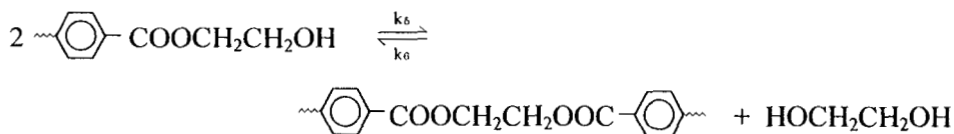
Temperature: 250°C

Pressure: atmospheric

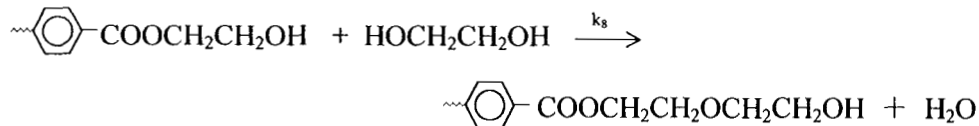
Esterification reactions

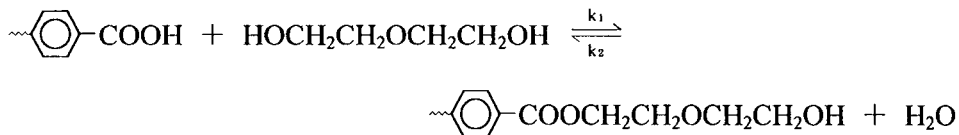


Polycondensation reaction



Side reactions





### Rate constants

$$k_1 = (0.015T_i + 1) \times 1.5657 \times 10^9 \exp(-19640 \text{ cal/RT})$$

$$k_2 = (9.1667 \times 10^{-3}T_i + 1) \times 1.5515 \times 10^8 \exp(-18140 \text{ cal/RT})$$

$$k_3 = (0.01916T_i + 1) \times 3.5165 \times 10^9 \exp(-22310 \text{ cal/RT})$$

$$k_4 = (1.6667 \times 10^{-3}T_i + 1) \times 6.7640 \times 10^7 \exp(-18380 \text{ cal/RT})$$

$$k_5 = (0.015833T_i + 1) \times 7.7069 \exp(-2810 \text{ cal/RT})$$

$$k_6 = (3.3333 \times 10^{-3}T_i + 1) \times 6.2595 \times 10^6 \exp(-14960 \text{ cal/RT})$$

$$k_7 = (0.0125T_i + 1) \times 2.0583 \times 10^{15} \exp(-42520 \text{ cal/RT})$$

$$k_8 = 2k_7$$

$$k_9 = 4k_7$$

$T_i$ : mole number of potassium titanium oxyoxalate supplied for  $10^6$  moles of TPA.

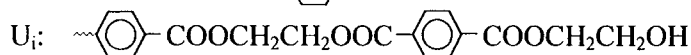
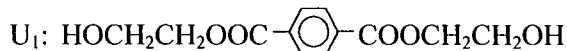
$k_1$ – $k_7$ : rate constants, [kg/mol·hr]

Yamada, T. and Imamura, Y., *Polym. Eng. Sci.*, **28**, 385 (1988).

### 4.3 Polycondensation of bis(2-hydroxyethyl)terephthalate

Catalyst: no catalyst

Temperature: 195.0–282.0°C



$$dg/dt = ke^2 - 4k'zg$$

Rate constants  $k$  and  $k'$  of reversible polycondensation

Temperature [°C]	$k \times 10^2$ [l/mol·hr]	$k' \times 10^2$ [l/mol·hr]
195.0	0.23	0.54
223.0	1.4	2.7
254.0	4.7	10.0
282.0	11.4	30.0
223.0	2.1	2.9
254.0	8.2	11.2
262.0	17.4	15.8

$$E_a = 24 \text{ [kcal/mol]}, E'_a = 23 \text{ [kcal/mol]}$$

Energies and entropy changes of activation at 262.0°C

Rate constant [l/mol·h]	$E_a$ [kcal/mol]	$\Delta S^\ddagger$ [cal/mol·°K]
$k_1 = 3.0 \times 10^{-5}$	22	-41.4
$k_0 = 5.3 \times 10^{-5}$	23	-38.6
$k' = 4.4 \times 10^{-5}$	23.5	-37.8

$$k_{11}/k_1/k_0 = 1/1.8/1.8^2$$



- g: concentration of free ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH), [mol/l]  
 e: concentration of 2-hydroxyethyl ester end-groups (-COOCH<sub>2</sub>CH<sub>2</sub>OH), [mol/l]  
 z: concentration of ethylene diester groups (-COOCH<sub>2</sub>CH<sub>2</sub>OOC-), [mol/l]  
 k: rate constant for polycondensation to PET, [l/mol·hr]  
 k': rate constant for glycolysis of PET, [l/mol·hr]  
 k<sub>0</sub>: rate constant of polycondensation reaction between polymer molecules, [l/mol·hr]  
 k<sub>1</sub>: rate constant of polycondensation reaction between monomer and polymer molecules, [l/mol·hr]  
 k<sub>11</sub>: rate constant of polycondensation reaction between monomer molecules, [l/mol·hr]  
 ΔS<sup>‡</sup>: entropy of activation, [cal/mol·°K]  
 E<sub>a</sub>: activation energy for k, [kcal/mol]  
 E'<sub>a</sub>: activation energy for k', [kcal/mol]

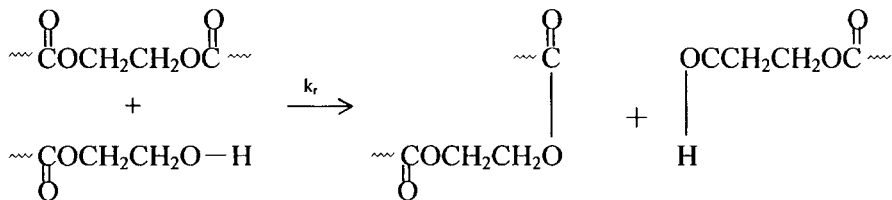
Challa, G., *Makromol. Chem.*, **38**, 123 (1960).

Catalyst: no catalyst

Temperature: 223–254°C

Redistribution reaction:

Ester interchange between the alcoholic hydroxyl group of a 2-hydroxyethyl ester end-group and an ester linkage of an ethylene diester group:



Temperature [°C]	$k_r$ [l/mol·h]
223	$1.9 \times 10^{-2}$
254	$1.2 \times 10^{-2}$

Activation energy:  $E_a=31$  [kcal/mol]

$k_r$ : rate constant of redistribution reaction, [l/mol·sec]

$E_a$ : activation energy for redistribution reaction, [kcal/mol]

Challa, G. *Makromol. Chem.* **38**, 138 (1960).

Temperature: 221–251°C

Catalyst: antimony trioxide ( $Sb_2O_3$ )



at 231°C

$k_p=0.151$  [l/mol·hr],  $k'=0.33$  [l/mol·hr],  $k_R=0.11$  [l/mol·hr]

$E_p=29$  [kcal/mol],  $E_R=24$  [kcal/mol]

$k_p$ ,  $k'$ : rate constants defined in reaction scheme, [l/mol·hr]

$k_R$ : redistribution rate constant, [l/mol·hr]

$E_p$ : activation energy for polymerization reaction, [kcal/mol]

$E_R$ : activation energy for redistribution reaction, [kcal/mol]

Stevenson, R. W. and Nettleton, H. R., *J. Polym. Sci.*, A-1, **6**, 889 (1968).

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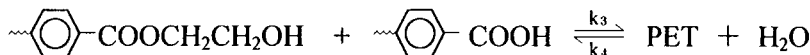
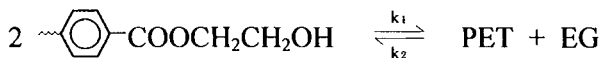
Catalyst:  $Sb_2O_3$

Stabilizer:  $(C_6H_5O)_3PO$  (0.06% w/w BHET)

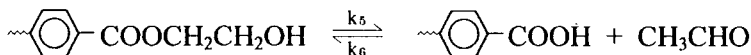
Temperature: 275–285°C

Pressure: 0.6 Torr

## Main reactions



## Side reactions



$$-dC_{\text{OH}}/dt = k_1 C_{\text{OH}}^2 - k_2 C_{\text{EG}} C_{\text{DES}} - dC_{\text{COOH}}/dt + k_5 C_{\text{OH}} - k_7 C_{\text{DES}}$$

$$k_1 = 84.5 \times 10^8 C_x \exp(-18500 \text{ cal}/RT)$$

$$k_1 = k_2, \quad k_1 = 0.25k_3, \quad k_3 = 4.0k_4, \quad k_5 \gg k_6, \quad k_7 \gg k_8, \quad k_5 = 180k_7$$

OH: hydroxyethyl-ester end-group, COOH: carboxyl end-group,

DES: diester radical in polymer, EG: ethylene glycol

$C_x$ : weight percent of catalyst in BHET (%)

$C_i$ : concentration of  $i$  component in reaction mixture, [mol/⟨C<sub>6</sub>H<sub>4</sub>⟩]

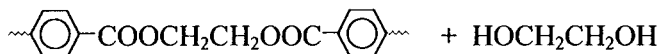
$k_1, k_2, k_3, \dots, k_9, k_{10}$ : polycondensation reaction rate constant, [⟨C<sub>6</sub>H<sub>4</sub>⟩/mol·hr]

Yokoyama, H., Sano, T., Chijiwa, T., and Kajira, R., *J. Japan Petrol. Inst.*, **21**, 58 (1978).

Catalyst: Sb<sub>2</sub>O<sub>3</sub>

Stabilizer: (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>PO

Temperature: 275–285°C



$$k_1 = \{2.29 \times 10^{10} \exp(-16.8C_x)\} C_x \exp(-18500 \text{ cal/RT}) + 4.0 \times 10^{16} \exp(-40000 \text{ cal/RT})$$

$$0.01 \ll (C_x, C_z) \ll 0.09$$

$C_x$ : weight percent of catalyst in monomer, [-]

$C_z$ : weight percent of stabilizer in monomer [-]

$k_1$ : polycondensation reaction rate constant, [ $\text{C}_6\text{H}_4$  / mol·hr]

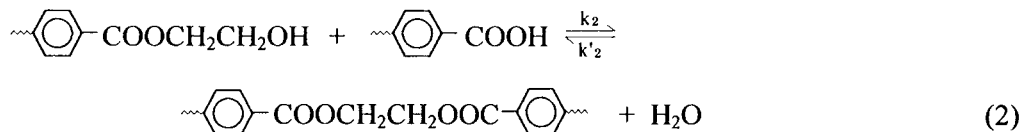
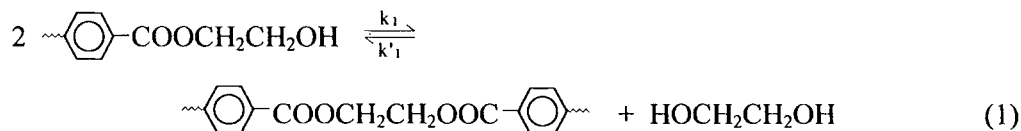
Yokoyama, H., Sano, T., Chijiwa, T., and Kajira, R., *J. Japan Petrol. Inst.*, **21**, 208 (1978).

Catalyst:  $\text{Sb}_2\text{O}_3$

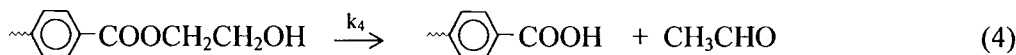
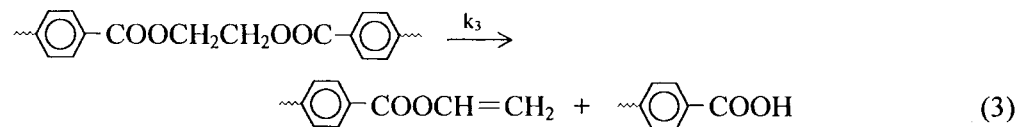
Stabilizer:  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$

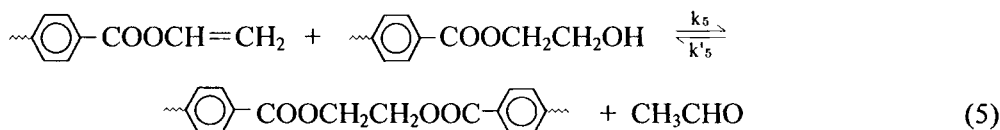
Temperature: 275–285°C

Main reactions



Side reactions





$$\begin{aligned} -dC_{\text{OH}}/dt &= k_1 C_{\text{OH}}^2 - k'_1 C_{\text{EG}} C_{\text{DES}} - dC_{\text{COOH}}/dt + k_4 C_{\text{OH}} - k_3 C_{\text{DES}} \\ -dC_{\text{COOH}}/dt &= k_2 C_{\text{OH}} C_{\text{COOH}} - k'_2 C_{\text{H}_2\text{O}} C_{\text{DES}} - k_4 C_{\text{OH}} - k_3 C_{\text{DES}} \\ dC_{\text{EG}}/dt &= -(dC_{\text{OH}}/dt - dC_{\text{COOH}}/dt - k_3 C_{\text{DES}} + k_4 C_{\text{OH}})/2 \\ dC_{\text{H}_2\text{O}}/dt &= -(dC_{\text{COOH}} - k_3 C_{\text{DES}} - k_4 C_{\text{OH}}) \end{aligned}$$

$$k_1 = 8.5C_x \times 10^9 C_x \exp(-18500 \text{ cal/RT}) + 4.0 \times 10^{16} \exp(-40000 \text{ cal/RT})$$

$$k_2 = 1.3C_x \times 10^{10} C_x \exp(-17400 \text{ cal/RT}) + 8.1 \times 10^{10} \exp(-24200 \text{ cal/RT})$$

$$k_3 = 4.5C_x \times 10^{13} C_x \exp(-37800 \text{ cal/RT})$$

$$k_4 = 5.2C_x \times 10^{12} C_x \exp(-29800 \text{ cal/RT})$$

OH: hydroxyethyl-ester end-group, COOH: carboxyl end-group, DES: diester radical in polymer, EG: ethylene glycol, H<sub>2</sub>O: water

C<sub>x</sub>: weight percent of catalyst in polymer [%]

C<sub>i</sub>: concentration of component i in a reaction mixture, [mol/⊞ ]

k<sub>1</sub>, k'<sub>1</sub>, k<sub>2</sub>, k'<sub>2</sub>, k<sub>3</sub>, k<sub>4</sub>, k<sub>5</sub>, k'<sub>5</sub>: reaction rate constants, [⊞ /mol·hr]

Yokoyama, H., Sano, T., Chijiiwa, T., and Kajira, R., *J. Japan Petrol. Inst.*, **21**, 271 (1978).

Yokoyama, H., Sano, T., Chijiiwa, T., and Kajira, R., *Kagaku kogaku Ronbunshu.*, **5**, 236 (1979).

Catalyst:  $\text{Sb}_2\text{O}_3$ 

Temperature: 240–290°C

Ester interchange reaction



Transesterification reaction



Polycondensation reaction



Side reactions forming acetaldehyde, DEG, and acid end groups

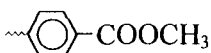


Esterification reactions



Degradation reactions of diester groups

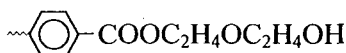


$E_m$   Methyl ester end group

$E_g$   Hydroxyethyl ester end group

$Z$   Diester group

$E_c$   Acid end group

$E_{\text{DEG}}$   DEG ester end group

$E_v$   Vinyl ester end group

EG	HOC <sub>2</sub> H <sub>4</sub> OH	Ethylene glycol
M	CH <sub>3</sub> OH	Methanol
W	H <sub>2</sub> O	Water
DEG	HOC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OH	Diethylene glycol
A	CH <sub>3</sub> CHO	Acetaldehyde

## Kinetic parameters

	Activation energy [kcal/mol]	Frequency factor [l/mol·min]	Equilibrium constant
k <sub>1</sub>	15.0	4.0 × 10 <sup>4</sup>	0.3
k <sub>2</sub>	15.0	2.0 × 10 <sup>4</sup>	0.15
k <sub>3</sub>	18.5	6.8 × 10 <sup>5</sup>	0.5
k <sub>4</sub>	29.8	4.16 × 10 <sup>7(1)</sup>	–
k <sub>5</sub> , k <sub>6</sub>	29.8	4.16 × 10 <sup>7</sup>	–
k <sub>7</sub>	17.6	1.04 × 10 <sup>6</sup>	2.5
k <sub>8</sub>	17.6	1.04 × 10 <sup>6</sup>	1.25
k <sub>9</sub>	37.8	3.6 × 10 <sup>9(1)</sup>	–

<sup>(1)</sup>Units are [1/min]

k<sub>1</sub>–k<sub>3</sub>, k<sub>5</sub>–k<sub>8</sub> : the second rate constants, [l/mol·min]

k<sub>4</sub>, k<sub>9</sub>: first-rate constants, [1/min]

K<sub>1</sub>–K<sub>5</sub>: equilibrium constants

Ravindranath, K. and Mashelkar, R. A., *Polym. Eng. Sci.*, **22** 619 (1982).

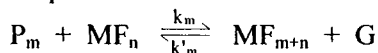
Ravindranath, K. and Mashelkar, R. A., *J. Appl. Polym. Sci.*, **27**, 2625 (1982).

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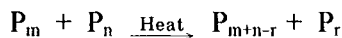
Temperature: 254–300°C



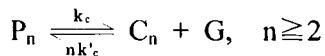
Reaction with monofunctional compounds



Redistribution



Cyclization

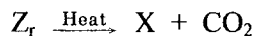
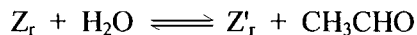
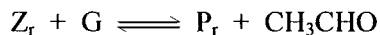
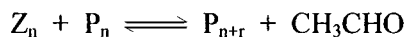


Degradation reactions

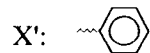
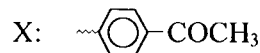
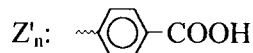
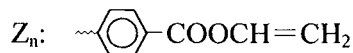
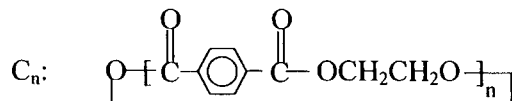
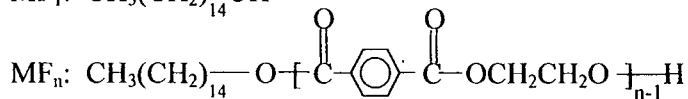
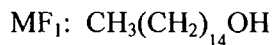
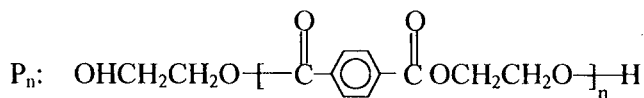
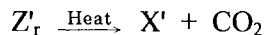
Thermal chain scission



Vinyl end reactions



Carbonyl end reaction



$$R_1 = k'_p/k_p, \quad R_2 = k_m/k_p, \quad R_3 = k'_m/k_p, \quad R_4 = k_c[P_1]_0/k_p, \quad R_5 = k'_c/k_p, \quad R_6 = k_r/k_p$$



## Various rate parameters

Temperature [°C]	$k_p$ [l/mol·hr]	$R_1$	$R_2$	$R_3$	$R_4$	$R_5$	$R_6$
254	0.047 (exptl) <sup>(1)</sup>	2.13 (exptl)	1.00	2.13	0.1	0.21	2.55 (exptl)
260	0.054 (exptl)	2.37 (exptl)	1.00	2.37	0.1	0.24	3.17 (exptl)
282	0.114 (exptl)	2.63 (exptl)	1.00	2.63	0.1	0.26	4.78 (exptl)
300	0.229	2.71	1.00	2.71	0.1	0.27	5.75

<sup>(1)</sup>exptl: experimental data.

$$\ln(k_p) = -22.00/1.987T \times 10^3 + 17.85 \quad [\text{l/mol} \cdot \text{hr}]$$

$$\ln(k'_p) = -23.00/1.987T \times 10^3 + 19.724 \quad [\text{l/mol} \cdot \text{hr}]$$

$$\ln(k_r) = -30.88/1.987T \times 10^3 + 27.397 \quad [\text{l/mol} \cdot \text{hr}]$$

$[P_1]_0$ : initial concentration of BHET, [mol/l]

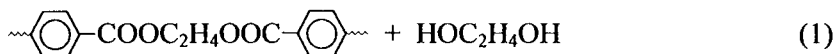
Kumar, A., Gupta, S. K., Gupta, B., and Somu, N., *Polym. Eng. Sci.*, **22**, 314 (1982).

Kumar, A., Gupta, S. K., Gupta, B., and Kunzru, D., *J. Appl. Polym. Sci.*, **27**, 4421 (1982). Copyright © 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

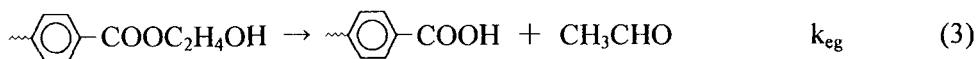
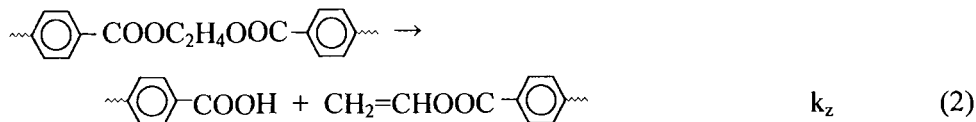
Catalyst:  $\text{Sb}_2\text{O}_3$

Temperature: 280°C

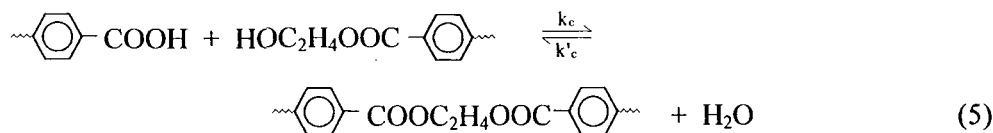
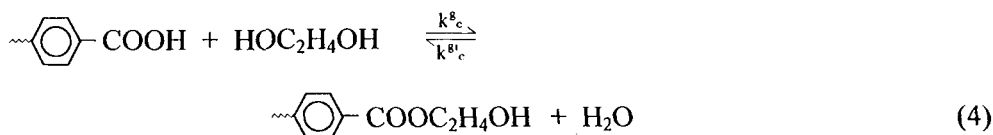
Polycondensation reactions



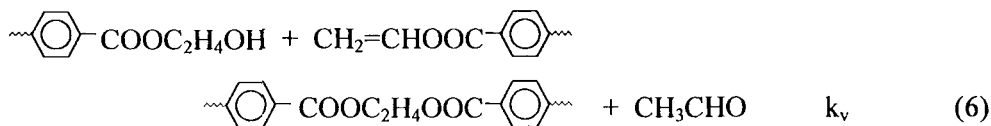
Polymer chain and hydroxyl end group degradations



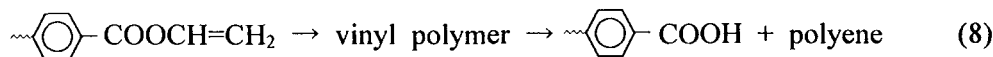
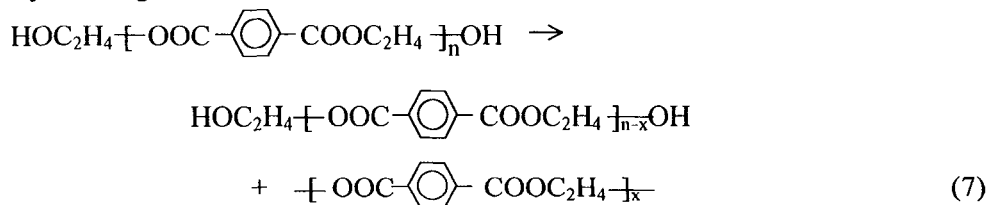
Esterification reactions



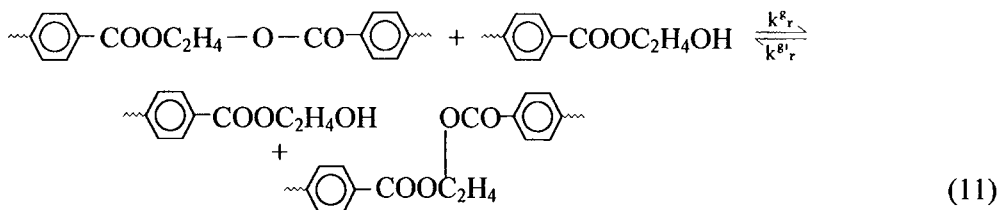
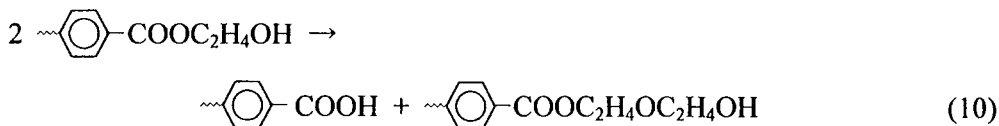
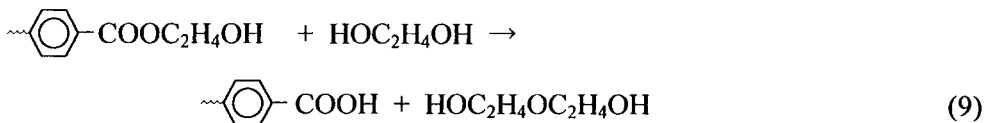
Polycondensation involving vinyl end group



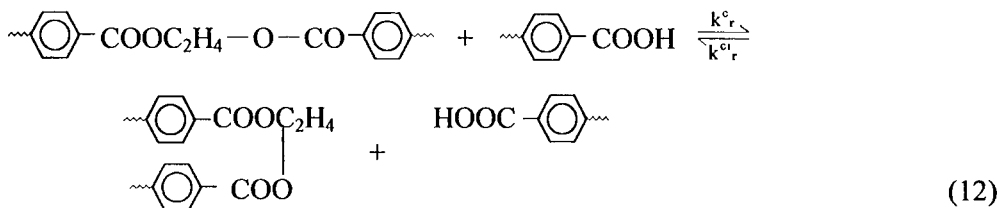
Cyclic oligomer formations



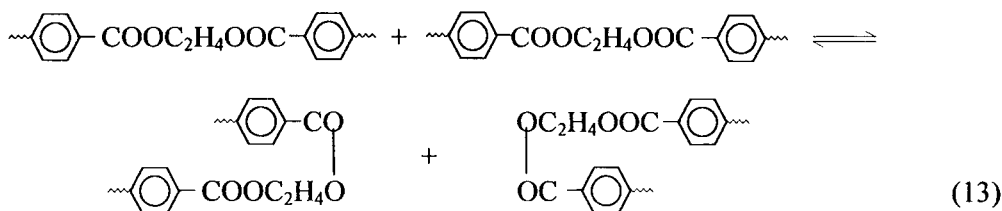
## Diethylene glycol formations



## Intermolecular acidolysis



## Transesterification:



## Kinetic parameters

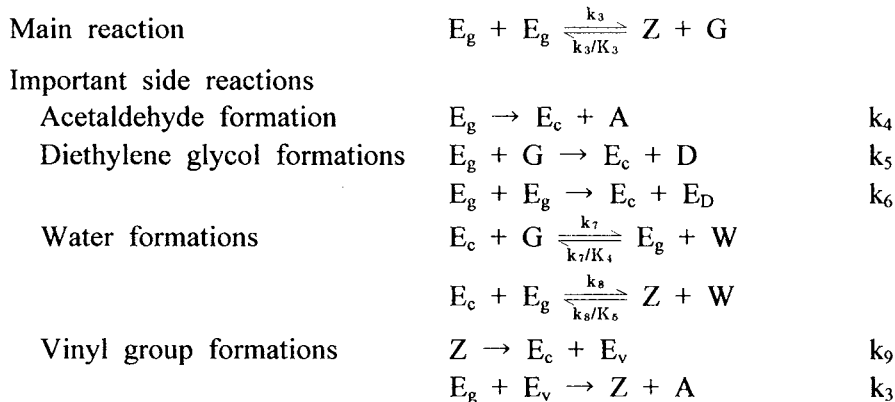
	Activation energy [kcal/mol]	Frequency factor [l/mol·min]	Equilibrium constant
Eq(1)	18.5	$1.36 \times 10^6$	0.5
Eq(3)	29.8	$8.32 \times 10^{7(1)}$	—
Eq(4)	17.6	$2.08 \times 10^6$	2.5
Eq(5)	17.6	$2.08 \times 10^6$	1.25
Eq(2)	37.8	$7.2 \times 10^9$	—
Eq(11)	18.5	$1.36 \times 10^5$	—
Eq(12)	18.5	$1.36 \times 10^5$	—

<sup>(1)</sup>Units are [l/min].

$k_c, k'_c, k_g, k'_g, k_{eg}, k_z, k^g_c, k^g'_c, k_v, k^g_r, k^c_r$ : forward and reverse rate constants of reactions (1)–(6), (11), (12).

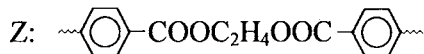
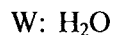
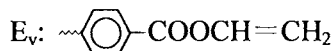
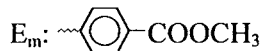
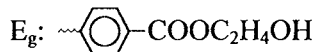
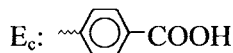
Ravindranath, K. and Mashelkar, R. A., *Polym. Eng. Sci.*, **24**, 30 (1984).

Temperature: 217–277°C



A:  $\text{CH}_3\text{CHO}$

D:  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$



Temperature dependence of various rate and equilibrium constants

	Activation energy [kcal/mol]	Frequency factor [l/mol·min]	Equilibrium constant
$k_3$	18.5	$6.8 \times 10^5$	$K_3=0.5$
$k_4$	29.8	$4.16 \times 10^{7(1)}$	—
$k_5$	29.8	$4.16 \times 10^7$	—
$k_6$	29.8	$4.16 \times 10^7$	—
$k_7$	17.6	$1.04 \times 10^6$	$K_4=2.5$
$k_8$	17.6	$1.04 \times 10^6$	$K_5=1.25$
$k_9$	37.8	$3.6 \times 10^9$	—

<sup>(1)</sup>Units are [1/min]

$k_3, k_5-k_9$ : the second rate constants, [l/mol·min]

$k_4$ : first-order rate constants, [1/min]

$K_3-K_5$ : equilibrium constants, [-]

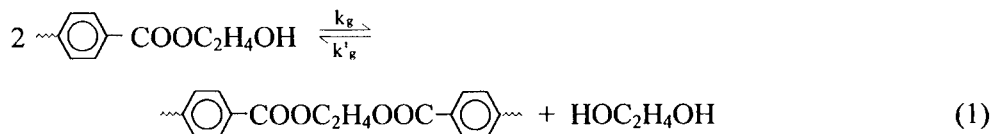
Kumar, A., Sharma, S. N., and Gupta, S. K., *J. Appl. Polym. Sci.*, **29**, 1045 (1984). Copyright © 1984 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

#### 4.4 Polycondensation of molten-state poly(ethylene terephthalate)

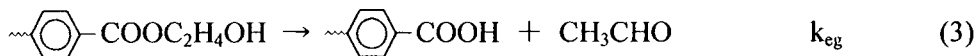
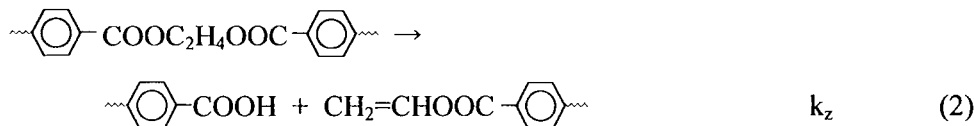
Catalyst:  $\text{Sb}_2\text{O}_3$

Temperature:  $280^\circ\text{C}$

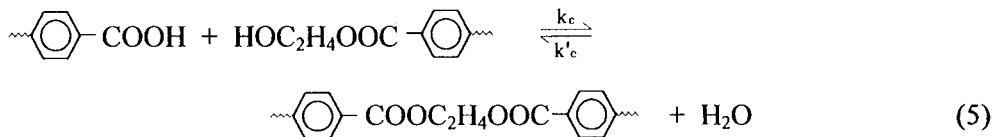
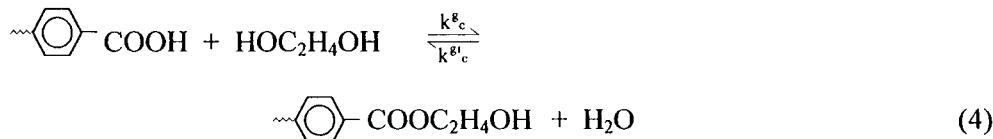
Polycondensation reaction



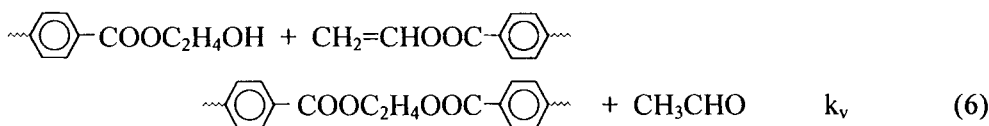
Polymer chain and hydroxyl end group degradations



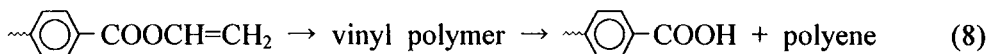
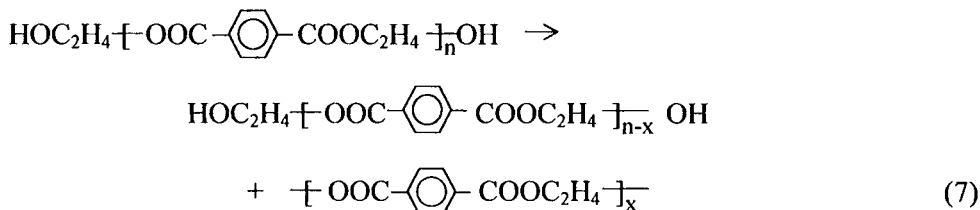
Esterification reactions



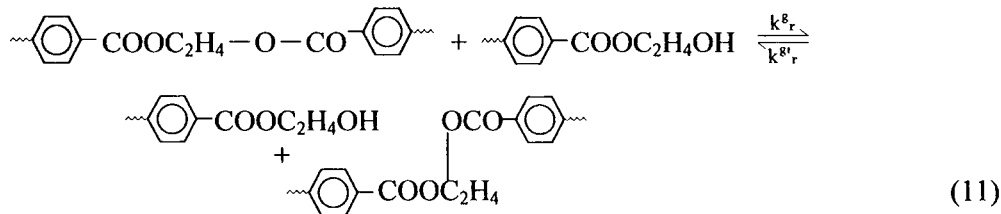
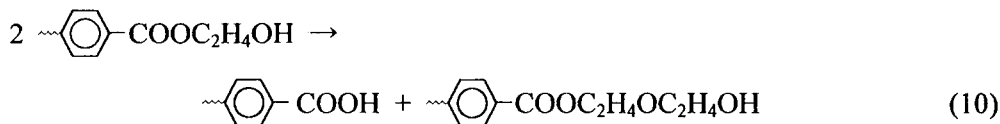
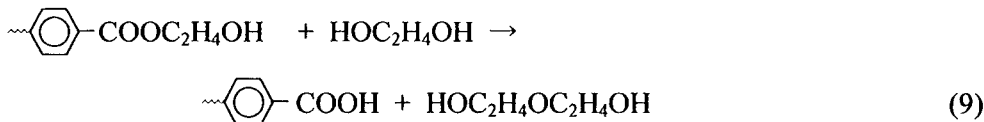
Polycondensation involving vinyl end group



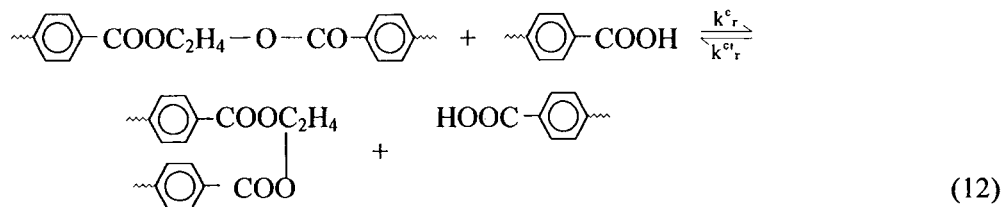
Cyclic oligomer formation



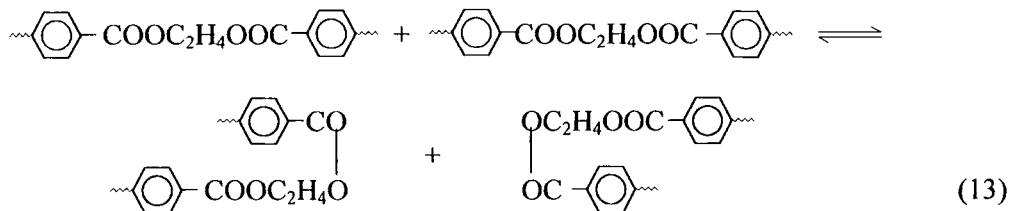
Diethylene glycol formations



Intermolecular acidolysis



## Transesterification



## Kinetic parameters

	Activation energy [kcal/mol]	Frequency factor [l/mol·min]	Equilibrium constants
Eq(1)	18.5	$1.36 \times 10^6$	0.5
Eq(3)	29.8	$8.32 \times 10^{7(1)}$	–
Eq(4)	17.6	$2.08 \times 10^6$	2.5
Eq(5)	17.6	$2.08 \times 10^6$	1.25
Eq(2)	37.8	$7.2 \times 10^9$	–
Eq(11)	18.5	$1.36 \times 10^5$	–
Eq(12)	18.5	$1.36 \times 10^5$	–

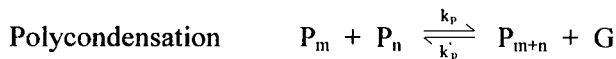
<sup>(1)</sup>Units are [1/min]

$k_c, k'_c, k_g, k'_g, k_{eg}, k_z, k_c^g, k'_c^g, k_v, k_r^g, k_r^c$ : forward and reverse rate constants of reactions (1)–(6), (11), (12).

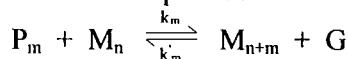
Ravindranath, K. and Mashelkar, R. A., *Polym. Eng. Sci.*, **24**, 30 (1984).



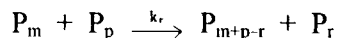
Temperature: 280–360°C



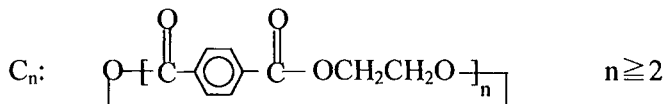
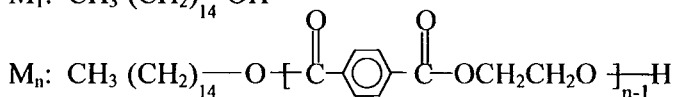
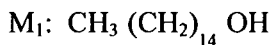
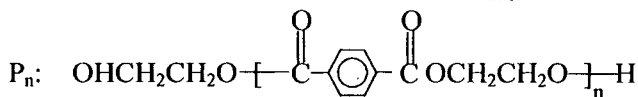
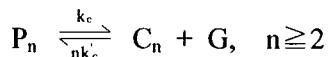
Reaction with monofunctional compounds



Redistribution



Cyclization



$$R_1 = k_p'/k_p, \quad R_2 = k_m/k_p, \quad R_3 = k_m'/k_p, \quad R_4 = k_c/k_p, \quad R_5 = k_c'/k_p, \quad R_6 = k_r/k_p$$

Rate parameters  $R_1$  to  $R_6$  at various temperatures

Temperature[°C]	$R_1$	$R_2$	$R_3$	$R_4$	$R_5$	$R_6$
280	2.0	1.0	2.0	0.01/0.001	0.02/0.002	0.248
290	2.0	1.0	2.0	0.01/0.001	0.02/0.002	0.303
300	2.0	1.0	2.0	0.01/0.001	0.02/0.002	0.368
320	2.0	1.0	2.0	0.01/0.001	0.02/0.002	0.531
340	2.0	1.0	2.0	0.01/0.001	0.02/0.002	0.747
360	2.0	1.0	2.0	0.01/0.001	0.02/0.002	1.03

$$\ln(k_p) = -18.5 \times 10^3 / 1.987T + 13.4298$$

$$\ln(k_r) = -30.88 \times 10^3 / 1.987T + 27.397$$

$k_p$ : polycondensation rate constant, [l/mol·min]

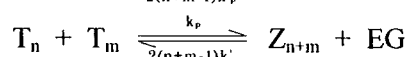
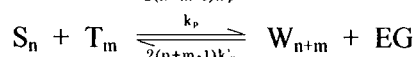
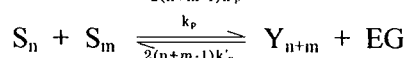
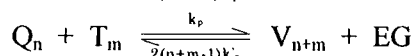
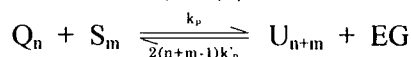
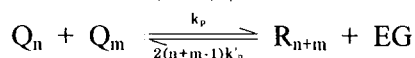
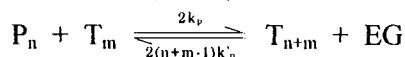
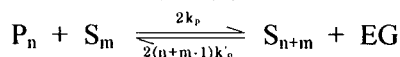
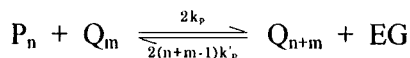
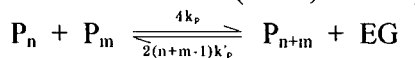
$k_r$ : redistribution rate constant, [l/mol·hr]

Kumar, A., Madan, S., Shah, N. G., and Gupta, S. K., *Polym. Eng. Sci.*, **24**, 194 (1984).

Catalyst:  $Sb_2O_3$

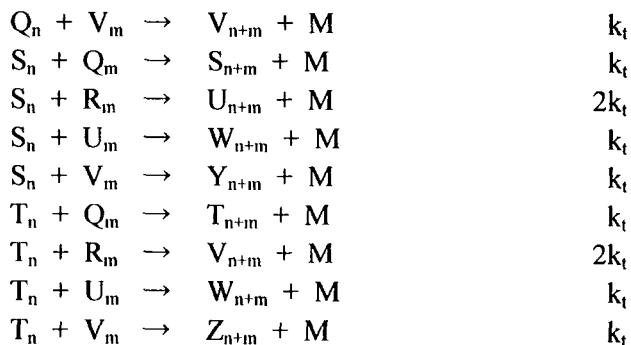
Temperature: 260–300°C

Polycondensation reactions (for  $n, m \geq 10$ )

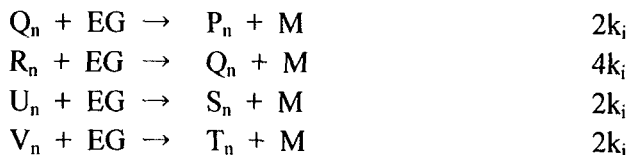


Transesterification reactions (for  $n, m \geq 1$ )

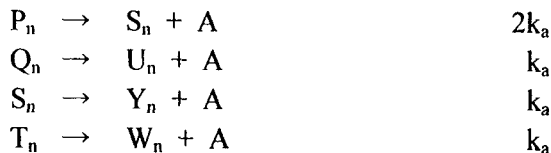




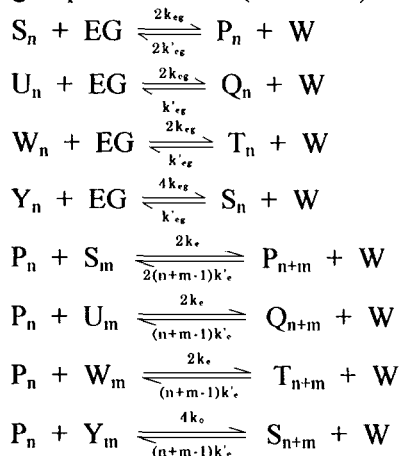
Ester interchange reactions (for  $n \geq 1$ )

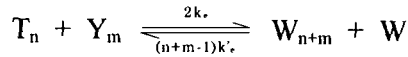
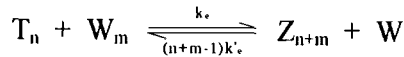
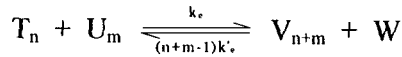
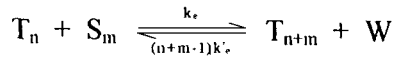
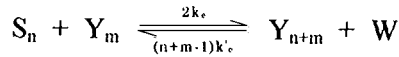
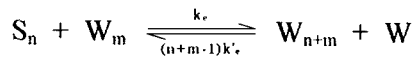
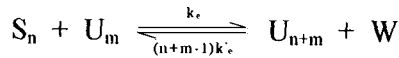
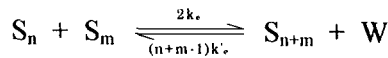
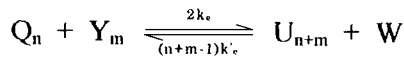
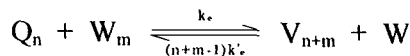
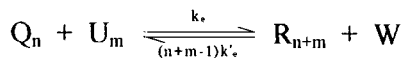
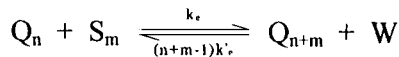


Esterifications (for  $n \geq 1$ )



Acid end group formations (for  $n \geq 1$ )

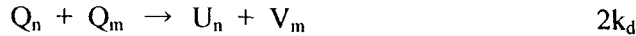
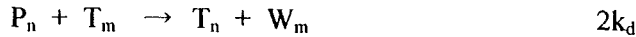


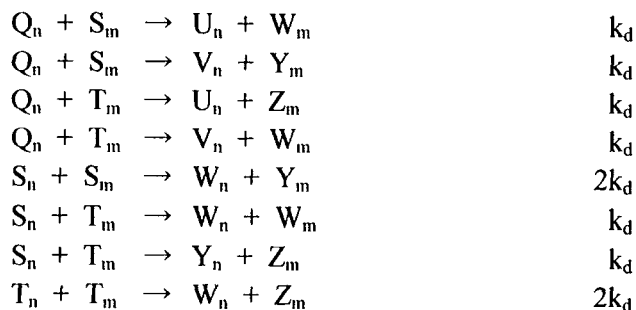


Free diethylene glycol formations (for  $n \geq 1$ )

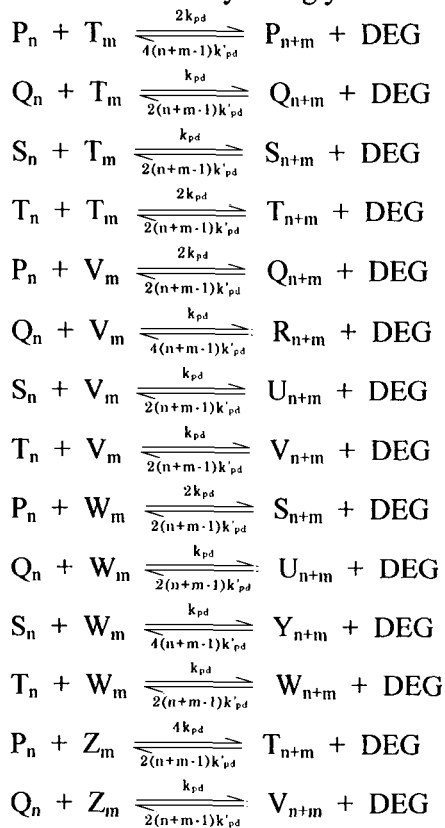


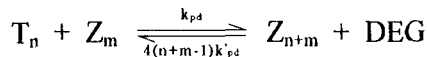
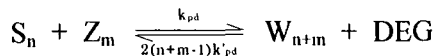
Diethylene glycol end group formations (for  $n, m \geq 1$ )



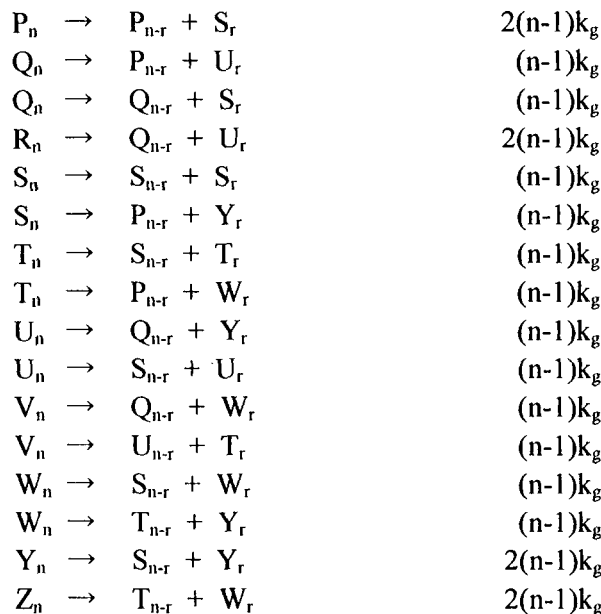


Polycondensations of diethylene glycol end groups (for  $n, m \geq 1$ )

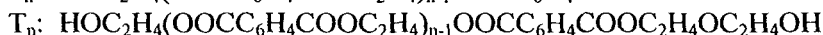
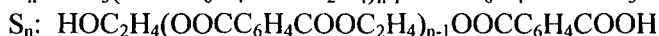
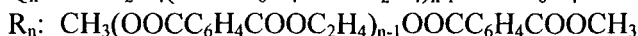
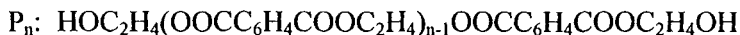
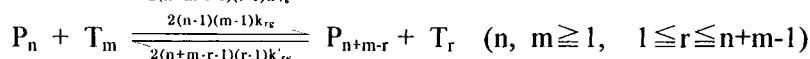
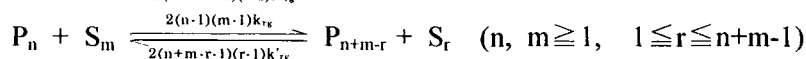
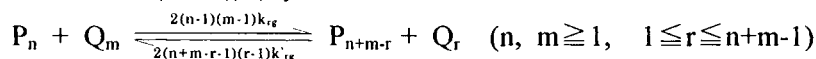
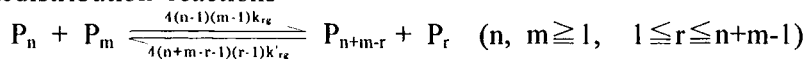


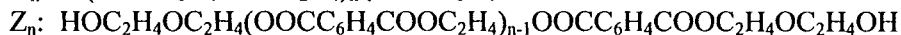
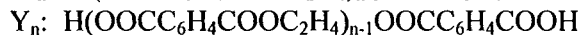
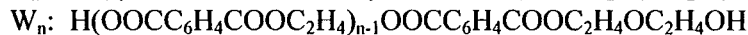
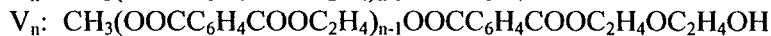


Degradations of diester groups (for  $n \geq 2$ ,  $1 < r \leq n-1$ )



Redistribution reactions





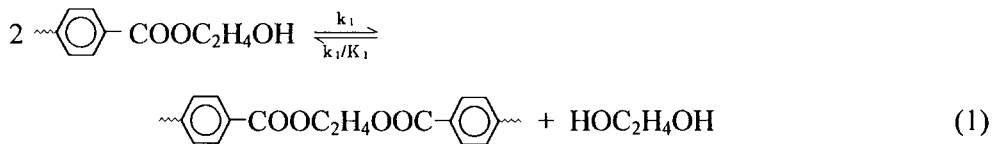
Rate constant		Unit
$k_p$	$7.9286 \times 10^8 \exp(-18500/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k'_p$	$3.1714 \times 10^9 \exp(-18500/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_t$	$2.3320 \times 10^7 \exp(-15000/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_i$	$4.6640 \times 10^7 \exp(-15000/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_a$	$4.8505 \times 10^{10} \exp(-29800/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_{eg}$	$1.2126 \times 10^9 \exp(-17600/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k'_{eg}$	$4.8504 \times 10^8 \exp(-17600/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_e$	$1.2126 \times 10^9 \exp(-17600/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k'_e$	$9.7008 \times 10^8 \exp(-17600/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_f$	$4.8505 \times 10^{10} \exp(-29800/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_d$	$4.8505 \times 10^{10} \exp(-29800/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_{pd}$	$7.9286 \times 10^8 \exp(-18500/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k'_{pd}$	$1.5857 \times 10^9 \exp(-18500/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$
$k_g$	$4.1975 \times 10^{12} \exp(-37800/RT)$	$l/\text{mol} \cdot \text{min}$
$k_{rg}$	$7.9286 \times 10^8 \exp(-18500/RT)$	$l^2/\text{mol}^2 \cdot \text{min}$

Lei, G. D. and Choi, K. Y., *J. Appl. Polym. Sci.*, **41**, 2987 (1990).

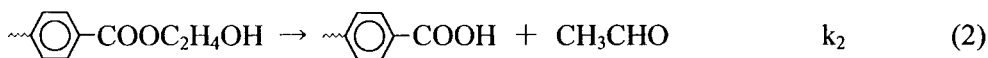
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Temperature: 280°C

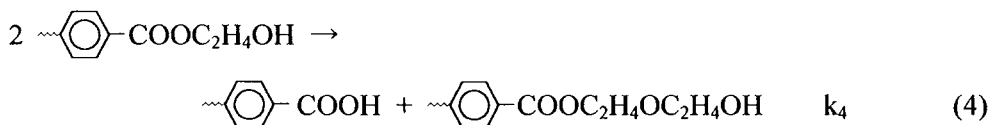
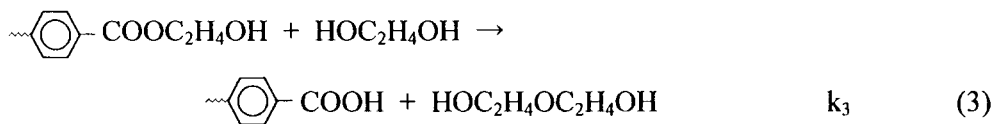
Polycondensation reactions through ester interchange



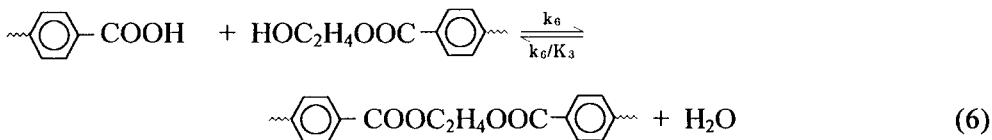
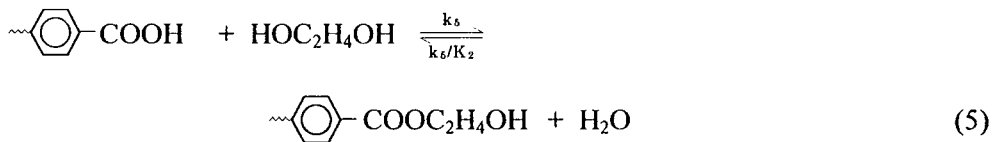
Acetaldehyde formation



Diethyleneglycol (DEG) formations

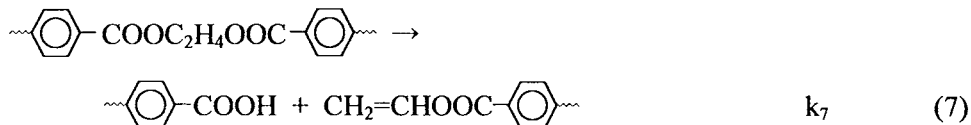


Water formations

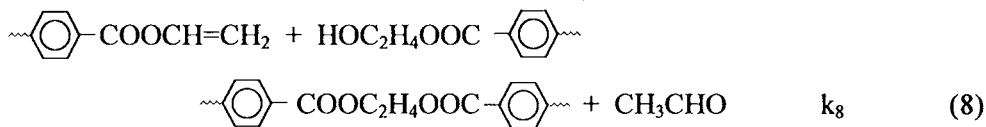




Degradation of diester end group



Polycondensation reaction of vinyl end group



Kinetic parameters

	Activation energy [kcal/mol]	Frequency factor [l/mol·min]	Equilibrium constant
Eq(1)	18.5	$1.36 \times 10^6$	0.5
Eq(2)	29.8	$8.32 \times 10^{7(1)}$	–
Eq(3), (4)	29.8	$8.32 \times 10^7$	–
Eq(5)	17.6	$2.08 \times 10^6$	2.5
Eq(6)	17.6	$2.08 \times 10^6$	1.25
Eq(7)	37.8	$7.2 \times 10^{9(1)}$	–
Eq(8)	18.5	$1.36 \times 10^6$	–

<sup>(1)</sup>Units are [1/min]

$k_1, k_3-k_6, k_8$ : second order rate constants, [l/mol·min]

$k_2, k_7$ : first-order rate constants, [1/min]

$K_1-K_3$ : equilibrium constants, [-]

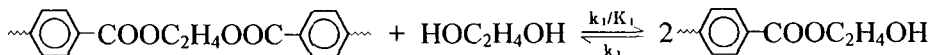
Ravindranath, K. and Mashelkar, R. A., *AIChE Journal*, **30**, 415 (1984).

Reproduced with permission of the American Institute of Chemical Engineers.

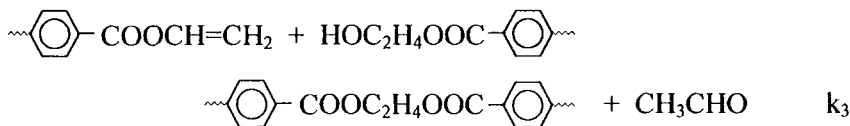
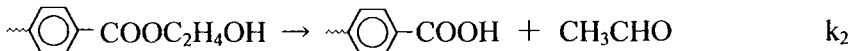
Copyright © 1984 AIChE. All rights reserved.

Temperature: 265–275°C

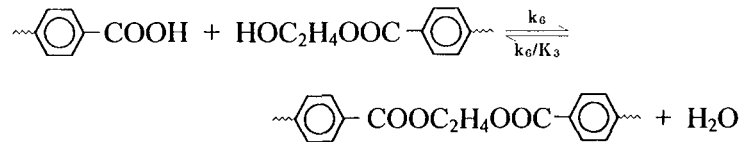
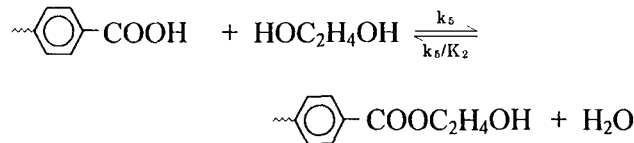
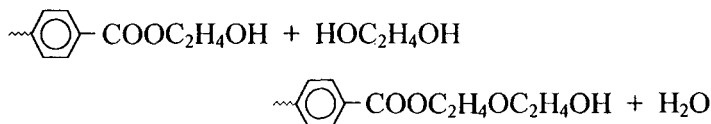
Depolymerization reactions



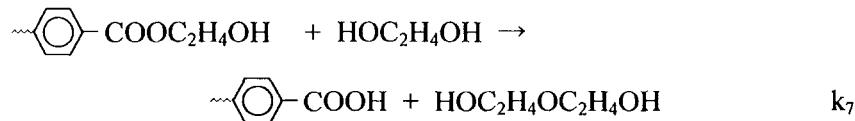
Acetaldehyde formation reactions



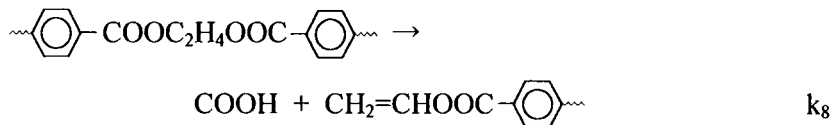
Water formation reactions



Diethyleneglycol (DEG) formation reaction



Diester group degradation reaction



Kinetic parameters

Reaction	Activation energy [kcal/mol]	Frequency factor $\times 10^{-9}$ [ml/mol·min]
$k_1$	18.5	0.584
$k_2$	29.8	390 <sup>(1)</sup>
$k_3$	18.5	13.6
$k_4$	29.8	83.2
$k_5$	17.6	2.08
$k_6$	17.6	2.08
$k_7$	29.8	83.2
$k_8$	37.8	7.2 <sup>(1)</sup>

<sup>(1)</sup>Unit is [1/min]

$$D_e = 2.58 \times 10^{-7} \text{ [cm}^2\text{/s] at } 265^\circ\text{C}$$

$$\text{Activation energy for } D_e = 38.4 \text{ [kal/g}\cdot\text{mol]}$$

$D_e$ : diffusion coefficient of ethylene glycol in poly(ethylene terephthalate) melts, [cm<sup>2</sup>/s]

$k_1, k_3$ – $k_7$ : second order rate constants, [ml/mol·min]

$k_2, k_8$ : first order rate constants, [ml/mol·min]

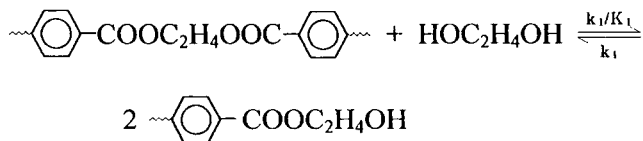
Lee, K. J., Moon, D. Y., Park, O. O., and Kang, Y. S., *J. Polym. Sci., B Polym. Phys.*, **30**, 707 (1992).

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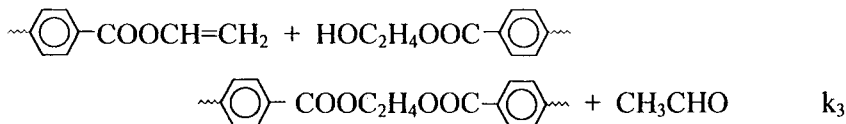
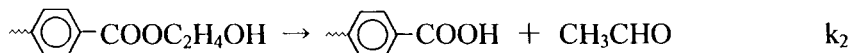
#### 4.5 Polycondensation of solid state poly(ethylene terephthalate)

Temperature: 230–245°C

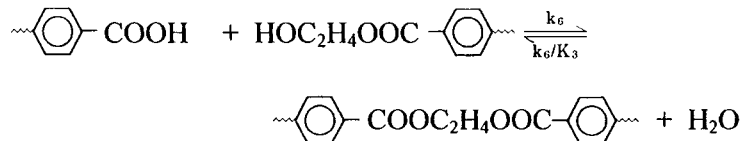
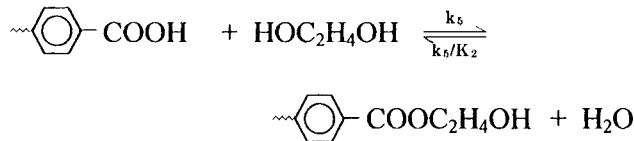
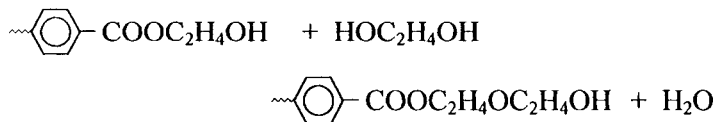
Depolymerization reaction



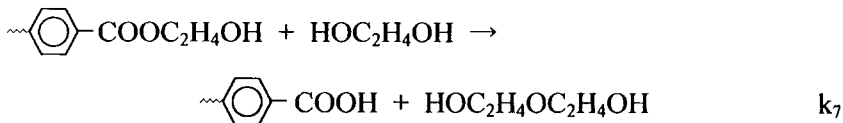
Acetaldehyde formation reactions



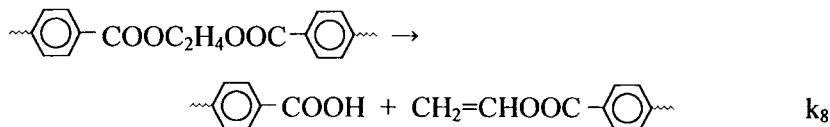
Water formation reactions



Diethyleneglycol (DEG) formation reaction



Diester group degradation reaction



Kinetic parameters

Reaction	Activation energy [kcal/mol]	Frequency factor [ml/mol·min]	Equilibrium constant
$k_1$	18.5	$1.36 \times 10^9$	0.5
$k_2$	29.8	$8.32 \times 10^{3(1)}$	–
$k_3$	18.5	$3.56 \times 10^{10}$	–
$k_4, k_7$	29.8	$8.32 \times 10^{10}$	–
$k_5$	17.6	$2.08 \times 10^9$	2.5
$k_6$	17.6	$2.08 \times 10^9$	1.25
$k_8$	37.8	$7.2 \times 10^{9(1)}$	–

<sup>(1)</sup> Unit: is [1/min]

$$D_c = 5.67 \times 10^{-8} \text{ [cm}^2\text{/sec] at } 230^\circ\text{C}$$

$$\text{Activation energy for } D_c = 28 \text{ [kal/g}\cdot\text{mol]}$$

$D_c$ : diffusion coefficient of ethylene glycol in solid states poly(ethylene terephthalate), [cm<sup>2</sup>/sec]

$k_1, k_3$ – $k_7$ : second order rate constants, [ml/mol·min]

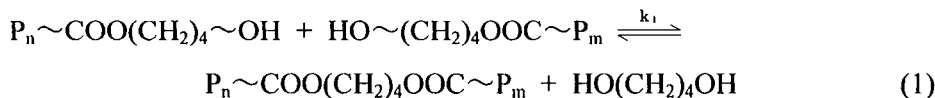
$k_2, k_8$ : first order rate constants, [ml/mol·min]

Yoon, K. H., Kwon, M. H., Jeon, M. H., and Park, O. O., *Polym. J.*, **25**, 219 (1993)

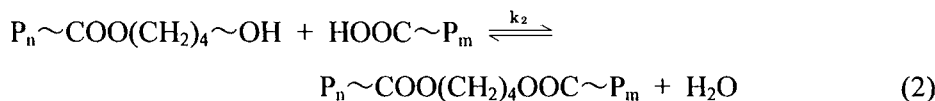
## 4.6 Polycondensation of solid-state polybutylene terephthalate

Temperature: 214°C

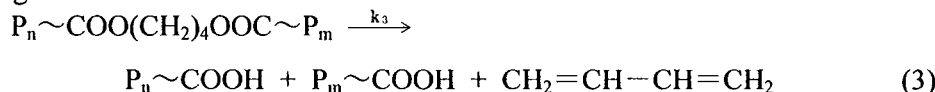
Transesterification reaction



Esterification reaction



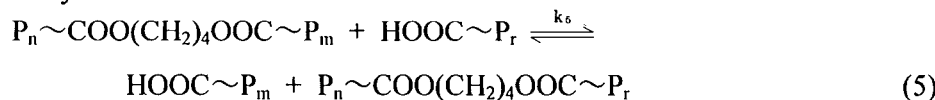
Degradation reaction



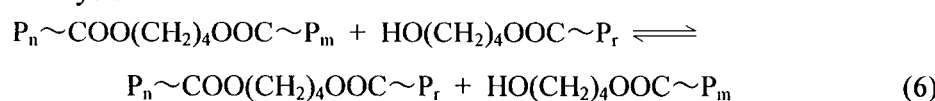
Side reaction



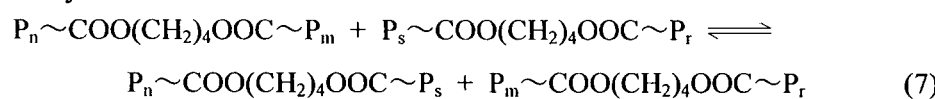
Acidolysis



Alcoholysis



Esterolysis



## Kinetic and equilibrium data for relevant chemical reactions

Reaction	Equilibrium constant	Kinetic constant	Reference
Eq(1)	0.4	$6.1 \times 10^{-4}$ [l/mol·sec]	(1)(2)
Eq(2)	1.0	$7.6 \times 10^{-4}$ [l/mol·sec]	(1)(2)
Eq(3)	-	$3.5 \times 10^{-8}$ [1/sec]	(3)(4)
Eq(4)	-	$0.9 \times 10^{-5}$ [1/sec]	(4)
Eq(6)	1.0	$1.25 \times 10^{-5}$ [l/mol·sec]	(5)

<sup>(1)</sup>Pilati, F. et al., *Polymer*, **24**, 1479 (1983).

<sup>(2)</sup>Pilati, F. et al., Short communication and posters, AIM, 6° Convegno Italiano di Scienza e Tecnologia delle Macromolecole, Pisa, 10-14 October 1983, p393.

<sup>(3)</sup>Passalacqua, V. et al., *Polymer*, **17**, 1044 (1976).

<sup>(4)</sup>Pilati, F. et al., *Polymer*, **22**, 1566 (1981).

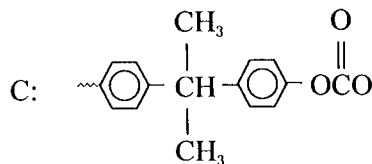
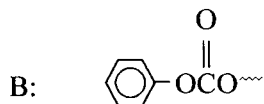
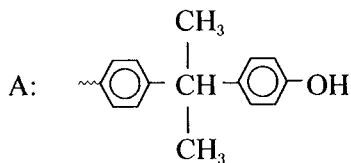
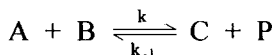
<sup>(5)</sup>Devaux, J., *Polym, Eng. Sci.*, **22**, 229 (1982).

Gostoli, C., Pilati, F., Sarti, G. C., and Giacomo, B. DI., *J. Appl. Polym. Sci.*, **29**, 2873 (1984). Copyright © 1984 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

#### 4.7 Transesterification of diphenyl carbonate with bisphenol

Catalyst:  $\text{LiOH} \cdot \text{H}_2\text{O}$

Temperature:  $150\text{--}180^\circ\text{C}$



$$k = 4.890 \times 10^{17} \exp(-21048/RT) \quad [\text{ml}^2/\text{mol}^2 \cdot \text{min}]$$

$$k_{-1} = 8.180 \times 10^{15} \exp(-16884/RT) \quad [\text{ml}^2/\text{mol}^2 \cdot \text{min}]$$

$k$ : forward reaction rate constant,  $[\text{ml}^2/\text{mol}^2 \cdot \text{min}]$

$k_{-1}$ : backward reaction rate constant,  $[\text{ml}^2/\text{mol}^2 \cdot \text{min}]$

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