22 The Viscoelastic Effect on the Formation of Mesoglobular Phase of Dilute Heteropolymer Solutions

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INTRODUCTION

The formation of polymeric nanoparticles actually contains two main parts: 1) the micronization of a material into nanoparticles and 2) the stabilization of the resultant nanoparticles. As for the micronization, one can start with either small monomers or long chain polymers. Emulsion including mini- and micro-emulsion polymerization as a conventional method can make polymeric particles in the size range 10-10^4 nm. Miller and El-Aasser (1997) have summarized recent advances in this area. It is well known that in microemulsion polymerization, a large amount of surfactant/co-surfactant has to be added to make small nanoparticles. The addition of surfactant limits not only the solid content in the dispersion but also their applications. The removal of surfactant from a resultant dispersion without affecting its stability is extremely difficult, if not impossible. Much effort has been spent on how to increase the solid content and reduce the amount of surfactant added. Up to now, it still remains a challenge to prepare concentrated uniform surfactant-free polymeric nanoparticles (10-50 nm in size) stable in water. Besides using surfactant, protein and other natural polyelectrolytes are often used in food and pharmaceutical industries to stabilize nanoparticles. Polymeric nanoparticles in water can also be stabilized by ionic groups introduced by copolymerization, initiation, and surface modification, and by hydrophilic polymer chains adsorbed or grafted on the particle surface.

In this chapter, we will concentrate on the formation of novel polymeric nanoparticles via the self-assembly of heteropolymer chains in dilute solutions, i.e., the formation of mesoglobular phase. Thermodynamically, for a given dispersion in water, the average area (s) occupied per stabilizer (ionic or hydrophilic group) on the particle surface approaches a constant, which enables us to control the size of the mesoglobular phase by varying the polymer-to-stabilizer weight ratio. We intend to emphasize that the formation of mesoglobular phase is not only governed by thermodynamics, but also greatly affected by the viscoelasticity of long chains even in dilute solutions.

THE FORMATION OF MESOGLOBULAR PHASE

Linear homopolymer chains in poor solvent exist either as individual crumpled single-chain globules or as macroscopic precipitate, depending on whether the solution is in one- or two-phase region (Wu and Zhou, 1995 and 1997; Wang *et al.* 1998; Wu and Wang, 1998). But for linear heteropolymers in dilute solutions, there exists an additional mesoglobular phase in which a limited number of chains are self-assembled together to form stable polymeric nanoparticles under a proper experimental condition. The typical and simplest example would be the self-assembly of diblock copolymers to form a core-shell nanostructure in a selective solvent in which only one block is soluble, or in other words, block copolymers are amphiphilitic in such a solvent. In general, Timoshenko and Kuznetsov (2000) stated that for N copolymer chains and each is made of M monomers A and B in a dilute solution, the effective Hamiltonian is given by

$$H=\frac{k_BT}{2L^2}\sum_a(\mathbf{Y}^a-\mathbf{Y})^2+\frac{k_BT}{2l^2}\sum_{a,n}(\mathbf{X}_n^a-\mathbf{X}_{n-1}^a)^2+\sum_{j\geq 2}\sum_{\{A\}}u_{\{A\}}^{(J)}\prod_{i=1}^{J-1}\delta\,(\mathbf{X}_{A_{i+1}}-\mathbf{X}_{A_i}) \qquad (1)$$

where $\mathbf{X}_n^a$ is the coordinate of the nth monomer in the ath chain, $\mathbf{Y}^a \equiv (1/M)\sum_n \mathbf{X}_n^a$ and $\mathbf{Y} \equiv (1/M)\sum_n \mathbf{Y}^a$ are the coordinates of the center-of-mass of a chain and the total system, respectively, L is the box size, l is the statistical segment length, and $u_{\{A\}}^{(J)}$ is the set of site-dependent virial coefficient. Using the Gaussian variational method, they showed that in a region of the phase diagram within the conventional two-phase coexistence region, the *mesoglobules* of equal size possess the lowest free energy and the matrix of the second virial coefficients $u_{\{A\}}^{(J)}$ could be related to the degree of amphiphilicity of the copolymer chain (Δ) and its primary chain sequence (chemical composition).

Monte Carlo simulation confirmed that as long as Δ is sufficiently large, the mesoglobules could be stabilized due to microphase separation, which introduces a preferred length scale. The existence of such mesoscopic structures is related to a delicate balance of energetic and entropic terms under the connectivity constraints. Experimentally, we found that in a microphase inversion process, i.e., the addition of an organic solution of ionomers (hydrophobic chains contain a few per cent of ionic monomers) dropwise into water, the insoluble chains could form stable surfactant-free mesoglobules with a core-shell nanostructure. The core was made of a limited number of collapsed and self-assembled chain backbones, while the shell contains ionic groups. For the first approximation, we could assume that all ionic groups (N_{ionic}) were on the periphery because they are hydrophilic. In the formation of each mesoglobule, its volume (V) is proportional to the cubic of its size ($V \sim R^3$), while its surface area (S) is proportional to the square of its size ($S \sim R^2$). Note that both V and N_{ionic} are proportional to the number of chains inside each mesoglobule (N). Therefore, the average surface area occupied per ionic group (s) is inversely proportional to N, i.e., $s \propto N^{-1}$. During the microphase inversion, s decreases as more chains are self-assembled into the mesoglobule. However, for each given system, s has a minimum value at which the surface of the mesoglobule is fully "covered" by the ionic groups and further

aggregation becomes impossible because of electrostatic repulsion. Figure 1 shows typical hydrodynamic radius distributions of such formed mesoglobules in water. Using a combination of static and dynamic light scattering (LLS) results, Li *et al.* (1997) showed that when carboxylated polystyrene ionomers were used, s remained a constant (~3 nm^2) even the average size of the resultant mesoglobules varied in the range 8-20 nm, depending on experimental condition.

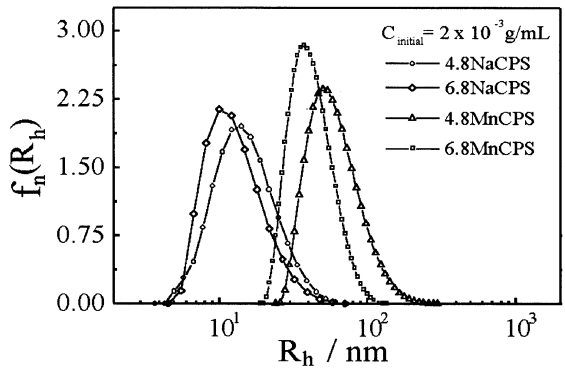

Figure 1. Hydrodynamic radius distribution of stable surfactant-free polystyrene nanoparticles prepared by microphase inversion.

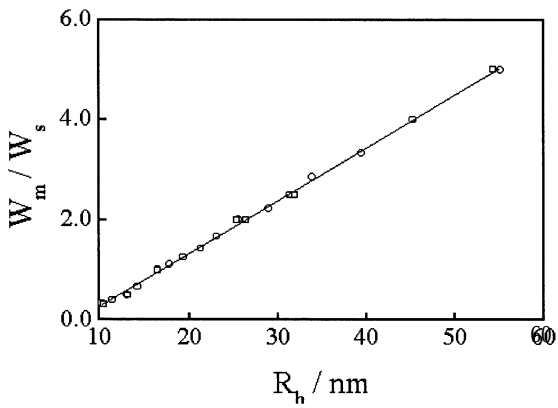

Figure 2. Polymer/stabilizer weight ratio (W_m/W_s) dependence of hydrodynamic radius R_h of polystyren nanoparticles.

Applying this idea to other polymer dispersions stabilized by surfactant (Wu, 1994), grafted chains (Wu *et al.*, 1997), adsorbed chains (Gao and Wu, 1999), and soluble polymer blocks (Wu and Gao, 2000), we have confirmed that s is indeed an important parameter. In general, $s = A_t/N_s$ with A_t and N_s being the total available surface area of the resultant particles and the total number of stabilizers on the surface. $A_t = 4\pi R_c^2(W_p+\gamma W_s)/(^4/_3\pi R^3\rho)$ with W_p and W_s, respectively, the

macroscopic weights of polymer and stabilizer, R_c and R, respectively, the radii of the core and the mesoglobule, γ the weight fraction of stabilizer on the surface, and ρ the average density of particles. $N_s = N_A(\gamma W_s)/M_s$ with N_A and M_s, respectively, the Avogadro's constant and the molar mass of stabilizer. Therefore,

$$\sigma = \frac{A_t}{N_s} = \left[\frac{4\pi R_c^{\,2}(W_p + \gamma W_s)}{\frac{4}{3}\pi R^3 \rho} \right] / \left(\frac{N_A \gamma W_s}{M_s} \right) \tag{2}$$

Assuming that the thickness of the stabilizer layer ($\Delta R = R - R_c$) is much smaller than R, we can rewrite Equation (2) as

$$\frac{W_p}{W_s} = \gamma \left(\sigma \frac{N_A \rho}{3M_s} \frac{R^3}{R_c^{\,2}} - 1 \right) \cong \gamma \sigma \frac{N_A \rho}{3M_s} R + \gamma \left(\sigma \frac{N_A \rho}{3M_s} \Delta R - 1 \right) \tag{3}$$

It clearly shows that Wp/Ws is a linear function of R. The slope and intercept can, respectively, lead to σ and ΔR if we know γ since both ρ and Ms are constants for a given system. Figure 2 shows a typical plot on the basis of Equation (3).

THE VISCOELASTIC EFFECT ON MICROPHASE INVERSION

Noted that the above discussion has not considered possible incomplete relaxation of the heteropolymer chains to their thermodynamically stable states during the formation of mesoglobular phase. Li *et al.* (1999) showed that in the microphase inversion, the insolubility of the chain backbone in selective solvents (often water) leads to a competition between intrachain contraction and interchain association. The fast intrachain contraction can result in smaller mesoglobules. The stability of such formed mesoglobular phase mainly depends on the coarsening dynamics. Picarra and Martinho (2001) showed that in the phase demixing of a dilute *homopolymer* solution, the collision would not be effective as long as the collision (or contact) time (τ_c) is relatively less than the time (τ_e) needed to establish a permanent chain entanglement between two approaching globules. Quantitatively, Tanaka (1993) stated that τ_c and τ_e can be roughly characterized as

$$\frac{r_o}{\langle v \rangle} < \tau_c < \frac{r_o^2}{D_R} \qquad \text{and} \qquad \tau_e \sim \frac{a^2 M^3 \phi_p^{3/2}}{D_m} \tag{4}$$

where r_o is the range of interaction, $\langle v \rangle$ is the thermal velocity of globules, D_R is the transition diffusion coefficient of globules with radius R, ϕ_p is the polymer concentration inside the globule, and a, M and D_m are the length, number and diffusion coefficient of monomer, respectively. When $\tau_c \ll \tau_e$, two collided globules have no time to stick together and they behave as elastic bodies. Such an effect is exactly attributed to the viscoelasticity of long polymer chains. Therefore, in order to obtain a stable globular phase, it is necessary to decrease τ_c and increase τ_e. Equation (4) shows that for a given type of polymer solution, r_o, α and D_m are constants. One has to promote the intrachain contraction and reduce the interchain association to decrease the size of initial globules. In this way, D_R increases so that τ_c decreases.

Experimentally, this can be achieved by diluting the solution and quenching the solution to a desired phase transition temperature as fast as possible. The addition of an ionomer solution dropwise into water to induce the microphase inversion and the formation of stable surfactant-free polystyrene nanoparticles, as shown in Figure 1, is a good example to illustrate this point.

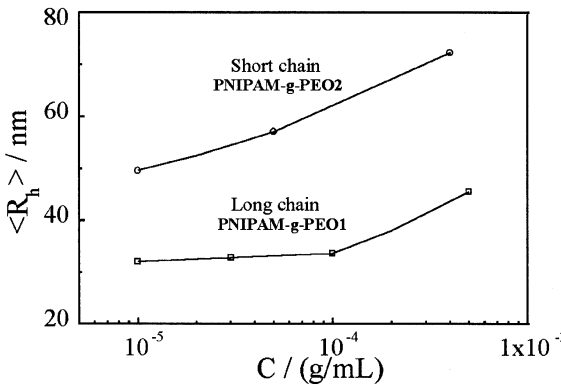

Figure 3. Chain-length and concentration dependence of average hydrodynamic radius $\langle R_h \rangle$ of mesoglobules made of the copolymer chains in water.

On the other hand, using long chains (larger M) is a more effective way to increase τ_e. To demonstrate it, Qiu and Wu (1997) studied the temperature-induced self-assembly of copolymers, poly(*N*-isopropylacrylamide) (PNIPAM) grafted with a few per cent of short poly(oxide ethylene) (PEO) chains. At the room temperature, both PNIPAM and PEO are water-soluble, while at temperatures higher than ~32 °C, PNIPAM segments become hydrophobic and undergo the intrachain contraction and the interchain association to form mesoglobules with the hydrophilic PEO chains on the surface as stabilizer. As expected, the size of the mesoglobules decreases with increasing the number of the PEO chains grafted on the PNIPAM chain backbone. A lower copolymer concentration or a fast heating rate can also lead to smaller mesoglobules. The more interesting result is that when a pair of PNIPAM-*g*-PEO copolymers with an identical comonomer composition, but different chain lengths, were used, long copolymer chains resulted in smaller mesoglobules, as shown in Figure 3. This is against our conventional wisdom; namely, we normally thought that under the same condition, the self-assembly of long chains would lead to larger particles than that of shorter chains. However, we forgot that long chains can reach the condition of $\tau_e > \tau_c$ much easier than short chains so that the association of long chains stops at a much earlier stage of the microphase transition. Qiu and Wu (1999) further showed that in a dilute solution long PNIPAM-*g*-PEO chains could even fold to form a stable single-chain core-shell nanostructure in which interchain association was completely suppressed.

In the collapsed state, Wu and Zhou (1995) showed that ϕ_p could be as high as 30 wt% even though the overall concentration was very low. Therefore, the relaxation of long chains inside globules is extremely slow, suggesting that long homopolymer chains would also be able to form mesoglobules in solution. However, it is well known that such formed mesoglobules are thermodynamically unstable. This is because unlike heteropolymer chains, homopolymers have no stabilizing groups on the chain backbone. Therefore, the interaction range between two approaching aggregates in the two-phase region is very long, resulting in a long contact time τ_c, so that they have sufficient time to fuse together to form macroscopic precipitation. This is why the addition of polystyrene homopolymer solution dropwise into water only resulted in macroscopic precipitation, not stable nanoparticles. Moreover, on the basis of Equation (4), we know that for a given polymer solution, smaller globules are more stable because τ_c is smaller, which is also apparently in contradiction to thermodynamics; namely, smaller particles with larger surface area and higher free energy should be less stable. In reality, in the microphase separation, as soon as long polymer chains are collapsed inside small mesoglobules, their relaxation become so slow that further entanglements between the chains in different mesoglobules become impossible in the experimental time scale. In other words, the viscoelastic effect "overwrites" thermodynamics in this case. The results in Figure 3 showed the importance of the viscoelastic effect on the formation of mesoglobular phase of dilute heteropolymer solutions.

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