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Notes

Ordering Transition of Copolymer Micelles

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A considerable experimental interest has been devoted to polymer blends containing copolymer additives. Even the simplest blends of this type, the amorphous mixtures of a homopolymer A and of a block copolymer A–B, exhibit complex phase diagrams[1] and interesting mechanical and rheological properties.[2] In such blends, in contrast to ordinary mixtures of homopolymers, the incompatibility effects do not necessarily manifest themselves in a macroscopic phase separation.[3-5] Copolymer chains may aggregate into micelles or form ordered microdomain structures. Even for a relatively weak repulsion between monomers A and B, a critical micelle concentration behavior is to be expected.[3] When the volume fraction of copolymer monomers ϕ is smaller than the critical micelle concentration (cmc), ϕ_0, copolymer chains are homogeneously mixed with homopolymers and are not aggregated. For copolymer content higher than the cmc ($\phi > \phi_0$), a finite fraction of copolymer chains aggregates into nearly monodisperse micelles which may structurally be described by two regions: the core, containing B blocks, and the outer shell, the corona, containing both A blocks and homopolymer chains.[3] For copolymer concentrations close to the cmc, the micelles are randomly dispersed in a homogeneous matrix. The concentration of free (nonaggregated) copolymers remains approximately ϕ_0 and increases only very slowly when the overall copolymer content increases. The value of the cmc, ϕ_0, depends strongly on the degree of incompatibility of the copolymer blocks.

It should be stressed[3] that the corona of the micelle is swollen by homopolymer chains and consequently, the actual volume fraction of the system occupied by the micelles may be much higher than the volume fraction of copolymer monomers ϕ. Even for small copolymer volume fractions micelles may overlap. It is therefore important to study the interactions between micelles. The purpose of the present paper is to present a simple model describing micelle interactions in solutions of diblock copolymers A–B in homopolymers A. We predict that above a certain copolymer content the micelles should order and form a macrolattice rather than be disordered as in a dispersion.

In thermodynamic equilibrium, the size and the number of micelles in the system may be calculated by minimizing the total free energy of the system. A simple statistical model is discussed in detail in ref 3. In practice, for high molecular weight copolymers, the system may be not in thermodynamic equilibrium. Then the number of copolymer chains per micelle, for instance, may depend on the particular way the sample has been prepared (e.g., dissolution of chains A–B and A in a solvent and its subsequent evaporation, annealing at high temperature). However, the for study of interactions between micelles, the aggregation number, p, i.e., the average number of copolymer chains in a micelle, may be treated as a fixed parameter. It can be measured experimentally for a given system, or its equilibrium value may be calculated from a statistical model.[3] For spherical micelles, the radius of the core, R_B, is simply related to the aggregation number, p, through the packing condition

$$(4\pi/3)R_B{}^3\rho_B = pN_B \tag{1}$$

where ρ_B denotes the density of monomers B and N_B is the number of B monomers in the B block. In writing (1) it is assumed that homopolymers do not penetrate into the core. This is not the case for the corona, whose thickness, R_A, depends not only on the number of copolymer chains in a micelle but also on the number of A homopolymer chains penetrating into the corona. The volume fraction of homopolymer monomers in the corona, $1 - \eta$, and, consequently, the swelling degree of the micelle may be calculated by minimizing the free energy of the system with the aggregation number p being fixed.[3] The penetration of homopolymer chains into the corona has two opposite effects on the energy of the micelle: it increases the entropy of mixing which is energetically favorable, but at the same time it causes deformation of the A blocks which are "grafted" to the core. The volume fraction of monomers belonging to A blocks, η, and the volume fraction occupied by the micelles are essentially determined by the competition of these two effects. The concentration η is often small, and the average distance between micelles may be comparable with their dimensions even for a small copolymer content in the system.

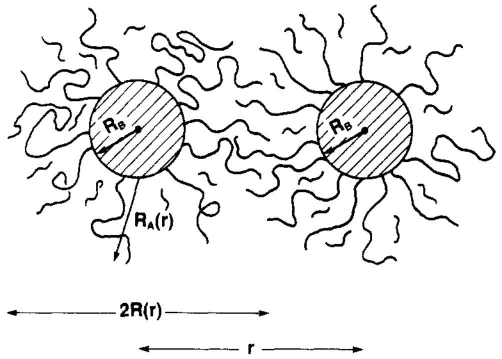

Figure 1. Schematic representation of two overlapping micelles. The cores contain B blocks of copolymer chains, and the outer shell contains both blocks A and homopolymers A.

The interaction energy between two micelles U is a function of the distance between the centers of the micelles and is equal to the difference of the free energy $F(r)$ of the complex built up of two cores (Figure 1) and the free energy of two nonoverlapping spherical micelles, F_0

$$U(r) = F(r) - 2F_0 \tag{2}$$

For short-range interactions, $2F_0$ is equal to the energy $F(r)$ of the complex with just touching coronas, i.e., with $r = 2(R_A + R_B)$.

The interaction arises solely from the change of concentration of penetrating homopolymers chains in the outer shell of the complex and related entropic effects. If we neglect the bulk compressibility of the polymeric liquid, the incompressibility condition implies that the volume fraction of monomers A belonging to copolymer chains in the outer shell, $\eta(r)$, equals

$$\eta(r) = 2pN_A/[\rho_A V(r)] \tag{3a}$$

where N_A denotes the number of monomers in an A block

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and ρ_A the density of monomers A. The volume $V(r)$ of the outer shell of the complex depends on the distance r and is equal to the volume of two intersecting spheres each of radius $R(r) = R_B + R_A(r)$ with two spherical cavities (holes) of radius R_B:

$$V(r) = \frac{4\pi}{3}\left\{R^3(r) + \frac{3}{4}rR^2(r) - \frac{1}{16}r^3 - 2R_B^3\right\} \quad (3b)$$

$R_A(r)$ denotes the thickness of the outer shell. In general, the thickness $R_A(r)$ will depend on the degree of interpenetration of two micelles, i.e., on the distance r between the micelles.

In a simple Flory–de Gennes type model[3,6,7] we may approximate the energy of formation of the complex of two overlapping micelles by a sum of three contributions arising from the constraints imposed by the very structure of the complex (cf. ref 3):

$$F(r) = G(p) + 2kTp\left\{\frac{3}{2}\left[\frac{R_A^2(r)}{N_A a^2} + \frac{N_A a^2}{R_A^2(r)}\right] + \delta\frac{[1-\eta(r)]}{\eta(r)}\ln\,[1-\eta(r)]\right\} \quad (4)$$

with $\delta = N_A/N_h$, N_h being the polymerization index of the homopolymer chains; $G(p)$ denotes the contributions dependent only on the aggregation number p and independent of $\eta(r)$. This includes for example the interfacial energy and the deformation energy of the B blocks in the micelle cores. The last term in (4) is the translational entropy of homopolymer chains penetrating into the outer shell of the complex. The second term represents the deformation energy of the A blocks. We have assumed that copolymer blocks A have an average end-to-end distance of order $R_A(r)$. The thickness of the outer shell $R_A(r)$ adjusts itself so that the energy $F(r)$ is minimized. In particular, the minimization of $F(r)$ in the limiting case of tangent micelles, i.e., $r = 2(R_B + R_A)$, provides both the radius $R = R_B + R_A$ and the concentration η of copolymer monomers in the corona of an isolated spherical micelle.[12] The minimization of $F(r)$ for any r yields $R_A(r)$, $\eta(r)$, and also the interaction energy $U(r)$.

The essential result of this calculation is that the energy of two overlapping micelles is repulsive. In fact, when micelles start to overlap, the concentration of homopolymer chains in the outer shell decreases, which is energetically unfavorable. It is to be noted that as the distance r decreases the thickness of the outer shell $R_A(r)$ first decreases and then increases again. This can be understood in terms of a changing balance between the deformation energy of A blocks and the entropy of mixing of A blocks and homopolymers. The detailed variation of U with the distance r depends on the copolymer architecture, the ratio δ, and the aggregation number p.

Figure 2 shows some examples of the dependence of the interaction $U(r)/kT$ on the distance r for a relatively long copolymer and different polymerization indices of homopolymer chains. We have assumed that the system is in thermodynamic equilibrium so that the aggregation number p and the radius R of an isolated micelle is calculated by minimizing the free energy per copolymer chain in a micelle. The most interesting result is a strong repulsion even when micelles are only slightly overlapping. Hence, the range of interactions is essentially determined by the swelling of the micelle corona and is bigger in the case of shorter homopolymer chains.

It is well-known that classical systems of particles with purely repulsive two-body interactions freeze into an ordered crystalline phase if they are sufficiently dense.[8] Therefore, in our micellar system we should expect an analogous phenomenon of ordering of micelles into a macrolattice above a critical concentration of micelles. In order to estimate the copolymer content for which the transition occurs, we replace the actual interaction energy $U(r)$ by that of two hard spheres with effective radius R_{eff}. The value of R_{eff} is defined so that the second virial coefficient of the micellar liquid and hard-sphere systems is the same; i.e.

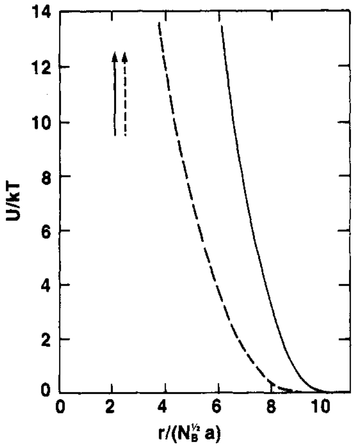

Figure 2. Interaction energy U between two micelles as a function of the distance r between them for two polymerization indices of homopolymer chains: $N_h = 50$ (solid line); $N_h = 360$ (dashed line). Diblock copolymers contain $N_A = 1800$ monomers A and $N_B = 200$ monomers B. The interaction parameter is assumed to be $\chi = 0.1$. For longer homopolymers ($N_h = 360$) the cmc is 2.4×10^{-7}, the aggregation number $p \simeq 123$, and the volume fraction of homopolymers penetrating the corona $1 - \eta \simeq 0.834$. For $N_h = 50$ the cmc is estimated to be 5.1×10^{-5}, $p \simeq 77.6$, and $1 - \eta \simeq 0.914$. $N_B^{1/2}a$ represents the end-to-end distance of an unperturbed B block and we assume that the density of monomers A and B is $\rho_A = \rho_B = a^{-3}$. The values of ρ, η, and the cmc are calculated by minimizing the total free energy along the lines of ref 3.

$$R_{\text{eff}} = R_B\left\{z_0^3 - 3\int_1^{z_0} dz\, z^2 \exp[-U(z)/kT]\right\}^{1/3} \quad (5)$$

where $z = r/(2R_B)$ measures distance in units of the core diameter and

$$z_0 = \frac{R}{R_B} = \left\{1 + \frac{N_A}{N_B\eta}\right\}^{1/3}$$

describes the swelling of the micelle. In writing (5) we assumed that $U(r) = \infty$ for $r < 2R_B$. The integral term in (5) is related to the fact that the interaction is not infinite for $r < R$ so that the micelles may still overlap. This calculation estimates the importance of this effect.

The hard-sphere system orders for particle volume fractions of the order of $v \simeq 0.45$. Therefore, we would expect the formation of macrolattice for the copolymer content higher than

$$\phi^* = v\left(1 + \frac{N_A}{N_B\eta}\right)\left\{z_0^3 - 3\int_1^{z_0} dz\, z^2 \exp[-U/kT]\right\}^{-1} \quad (6)$$

In writing (6) we have assumed that all copolymer chains form micelles. If the system is in thermodynamic equilibrium, ϕ^* denotes the difference between the actual transition concentration and the critical micelle concentration since the cmc provides roughly the number of nonaggregating copolymer chains.

In summary, we have approximately calculated the value of the copolymer content ϕ^* above which a macrolattice

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is formed. ϕ^* depends crucially on δ, the ratio of the length of block A and homopolymer chains. For high δ, for which micelles are expected to be fairly swollen, ϕ^* may be very small. For example, for systems considered in Figure 2 we find ϕ^* equal to 0.046 and 0.11 for shorter and longer homopolymer chains, respectively. It should be stressed that the transition concentration will depend weakly on temperature unless the system is close to the cmc.

A prediction of the macrolattice structure is a delicate problem. Strictly speaking, for hard-sphere systems a closely packed cubic structure is to be expected. However, for actual "softer" interaction potentials the body center cubic lattice may occur on the ordering curve as has been argued in general by symmetry considerations[9] and shown for pure copolymers.[10] In practice, due to very long diffusion times a true long-range order may not actually be observed and a glassy phase of micelles may obtain. In any case the rheological properties of the system will be strongly affected at the transition because the micelle motions will be strongly correlated. This will result at ϕ^* to a more or less sharp increase in relaxation times. Rheological effects of this type have been observed in block copolymer solutions in selective solvents and have been interpreted in terms of the ordering transition of micelles.[11]

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(12) Strictly speaking, η is given by the minimization of the total free energy as discussed in detail in ref 3. However, for long copolymers for which the cmc is very small the difference between η obtained by the minimization of $F(r)$ with $r = R_A + R_B$ and the actual value is negligibly small.

Effect of Swelling on the Short-Chain Reinforcement Observed in Bimodal Elastomeric Networks

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Elastomers which contain a large mole fraction of very short chains as part of a bimodal distribution of network chain lengths have been shown to be unusually tough, even in the unfilled state.[1-5] The primary reason for the increased toughness is a marked upturn in the stress at high elongations, and this has been attributed to the limited extensibility of the very short chains.[1-3] This explanation, which is entirely intramolecular in nature, is supported by insensitivity of the strengthening upturns to temperature and the absence of any deviations from linearity in the force–temperature and birefringence–temperature relationships.[6] The most stringent test, however, for the possible importance of intermolecular effects (for example, strain-induced crystallization),[7] is the dependence of the stress–strain isotherms on degree of swelling. Should any strain-induced crystallization be present it would be greatly diminished by incorporation of diluent into the network, through the depression of the melting point.[8,9] Effects of limited chain extensibility, in contrast, would not be diminished by swelling and could in fact be enhanced because the swelling dilation causes some stretching of the chains prior to their additional deformation in the elongation experiments.

The present investigation thus focuses on determination of the effects of swelling on the stress–strain isotherms of bimodal elastomeric networks.

Experimental Details

The two bimodal elastomers investigated were portions of two poly(dimethylsiloxane) networks which had previously been studied in the undiluted state.[1] They had been prepared by end-linking very short chains having a number-average molecular weight of 220 with relatively long chains of 18.5×10^3. The first consisted of 90 mol % short chains and the second 85 mol %. Both had been extracted to remove the 5 wt % soluble matlerial they contained.[1]

The nonvolatile solvent chosen as swelling diluent was a mixture of linear dimethylsiloxane oligomers having 8–11 repeat units; it was generously provided by Dow Corning Corp. Two portions of the network containing 90 mol % short chains were swollen to give values of the volume fraction v_2 of polymer present of 0.61 and 0.41, respectively. Three portions of the other network were swollen to $v_2 = 0.76$, 0.60, and 0.39, respectively.

Stress–strain measurements in elongation were carried out on both the unswollen and swollen networks at 25 °C in the usual manner.[1,2,10,11] The elastomeric quantity of primary interest was the reduced stress or modulus defined by[8,11,12]

$$[f^*] \equiv f v_2^{1/3} / A^*(\alpha - \alpha^{-2}) \qquad (1)$$

where f is the elastic force, A^* is the cross-sectional area of the unstretched and unswollen sample, and $\alpha = L/L_i$ (where L and L_i are the stretched and unstretched lengths, respectively, in the swollen state). The measurements were carried out to the rupture points.

Results and Discussion

The representation of the stress–strain data was based on the Mooney–Rivlin equation[13,14]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (2)$$

where $2C_1$ and $2C_2$ are constants. These plots, of the reduced stress against reciprocal elongation, are shown in Figures 1 and 2. Only the curves for the unswollen networks ($v_2 = 1.00$) have any portions which show the usual decrease in $[f^*]$ with increasing α,[13,14] which is due to the increasingly nonaffine nature of the deformation.[15,16] The rest of the results all show very strong increases in $[f^*]$ at high elongations, with the upturns in some cases being very nearly vertical. Of greatest importance is the observation that swelling does not diminish this toughening effect; in fact, it generally seems to enhance it! These results thus give very strong support to the interpretation[1-3] of this interesting behavior in terms of the limited extensibility[17] of the short chains in the network structure. Contributions

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