Registry No. III, 69496-25-9; IV, 119071-30-6; IV (homopolymer), 119071-35-1; metacryloyl chloride, 920-46-7.

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Microphase Separation in Diblock-Copolymer Melts: Ordering of Micelles

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Introduction

Microphase-separated block–copolymer systems attract considerable attention from polymer scientists. One of the particular systems of that kind is a melt of diblock–copolymers A–B, incompatibility of A and B blocks being responsible for separation effects. It is well established that polymer melts are weakly fluctuating systems, so a mean-field approach (in a general sense) can be applied to the melts. The specific mean-field theories of block–copolymer melts were proposed by Helfand and Wasserman[1] for the case of narrow interphase width and by Leibler[2] for the opposite case. The final results of these papers[1] were obtained after some numerical work. More recent approaches[3,4] enable one to obtain essentially the same results in a purely analytical way. Moreover, a number of new analytical results were obtained in ref 3 and 4. In particular, it was shown that the interaction energy of two spherical domains (micelles) depends on the distance between them in a nonmonotonic manner. It was assumed that this prediction implied some special features of micelles formation and ordering. The aim of the present paper is to study quantitatively some equilibrium aspects of the process of formation and ordering of micelles.[5]

Let us consider a melt of block–copolymers A–B, A being the minor component: $f = N_A/N \ll 1$ ($N = N_A + N_B \gg 1$ is the number of links in a polymer chain). The radii of gyration of the blocks in a homogeneous melt are

$$R_A = N_A^{1/2} a_A; \qquad R_B = N_B^{1/2} a_B \tag{1}$$

where a_A and a_B are the characteristic sizes of A and B links. Let us consider the simplest symmetric case: $a_A = a_B = a$ and $v_A = v_B = v$, where v_A and v_B are the volumes per link in undiluted homopolymers A and B, respectively.

The excess free energy of mixing can be written as[7]

$$F_{int} = \chi T \int \varphi_A(r)\, \varphi_B(r)\, d^3r/v \tag{2}$$

where $\varphi_A(r)$ and $\varphi_B(r)$ are volume concentrations of A and B components relative to the pure polymers (an incompressibility condition, $\varphi_A(r) + \varphi_B(r) = 1$ is assumed), and χ is the (dimensionless) parameter of incompatibility.

Interaction of Micelles

If χ were sufficiently small, the melt would be homogeneous:

$$\varphi_A(r) = f; \qquad \varphi_B(r) = 1 - f$$

As χ increases, an effective repulsion of A and B blocks gives rise to aggregation of copolymer chains into spherical domains (micelles). The structure of a micelle was considered in ref 3 in detail: it includes a core filled by A blocks and a "coat" of B blocks "grafted" to the surface of the core (Figure 1). The size of the "coat" is of the order R_B; the radius of the core is[3]

$$R = 2.18(\chi N_A)^{1/6} R_A, \qquad R_A \ll R \ll R_B \tag{3}$$

It was also shown[3] that the free energy of an isolated micelle is

$$F_o = -TQN_A(\chi - \chi_c) \quad \text{if} \quad |\chi/\chi_c - 1| \ll 1 \tag{4}$$

where

$$Q = 4\pi R^3/3vN_A \gg 1 \tag{5}$$

is the number of polymer chains per micelle and

$$\chi_c \simeq N_A^{-1}\{\ln (1/f) + 2.06[\ln (1/f)]^{1/3}\} \tag{6}$$

Let $\mathcal{N}$ be the number of micelles in the system. If the concentration of micelles, $c = \mathcal{N}/V$, is small enough, an interaction between them can be neglected. Therefore, the free energy of the "gas" of micelles can be written as

$$\mathcal{F} = \mathcal{F}_{id} + \mathcal{N}F_o$$

where

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$$\mathcal{F}_{id} = \mathcal{N}T \ln (cR_B^3/e) \quad (7)$$

is an ideal-gas term.[8] The minimum of the free energy, $\mathcal{F}$, corresponds to the equilibrium concentration of the micelles:

$$c = R_B^{-3} \exp(Q\tau) \quad \text{for} \quad \tau < 0, \quad |\tau Q| \gg 1 \quad (8)$$

where

$$\tau \equiv N_A(\chi - \chi_c)$$

At larger concentrations, an interaction between micelles must be taken into account. The dependence of the interaction energy for two micelles,[9] U_{int}, on the distance between their centers, r, was obtained analytically in ref 3 (for the case $f \ll 1$):

$$U_{int}(r) = (T\upsilon N_B Q^2/8\pi R_B^3)\varphi(r/R_B) \quad (9)$$

where

$$\varphi(s) = 4\pi \int d^3q\ (2\pi)^{-3} \times \exp(iq_z s)[1 - \exp(-q^2)]^2/[q^2 + \exp(-q^2) - 1]$$

The function $\varphi(s)$ can be represented by the following asymptotic values:

$$\varphi(s) = 1/s \qquad s \ll 1$$

$$\varphi(s) = 0.5\pi^{-1/2} \exp(-s^2/4) - (15.56/s) \exp(-2.218s) \sin(1.682s + 0.273) \qquad s \gg 1$$

In the region $0 < s \lesssim 8$, the function $\varphi(s)$ shows a fast monotonic decrease; $\varphi(s)$ can be approximated by

$$\varphi(s) = 0.5\pi^{-1/2} \exp(-s^2/4) \quad (10)$$

to within an error less than 10% in the range $3 \lesssim s \lesssim 7$. For $s \gtrsim 8$, the function $\varphi(s)$ exhibits damped oscillations. The absolute minimum of the function $\varphi = -\varphi^* = -0.989 \times 10^{-8}$ corresponds to $s = 8.23$.

Thus, the interaction of two micelles is alternatively attractive and repulsive, the absolute minimum of the energy of interaction being negative:

$$\min U_{int} = -U^* \qquad U^* = (T\upsilon N_B Q^2/8\pi R_B^3)\varphi^* \quad (11)$$

Formation of Ordered Structure

As τ increases, the concentration of micelles, c, increases, and ordering of the micelles into a macrolattice can occur. The features of the ordering process crucially depend on the parameter U^*/T. In the case $U^*/T \gg 1$,[10] the stability of a micelle increases appreciably if there is another micelle at the distance $r = s^*R_B$. Hence, an ordered arrangement of the micelles would already be thermodynamically advantageous at $\tau < 0$. The most stable structure obviously should satisfy the following conditions: (1) the separation between the nearest micelles, d, must correspond to min U_{int}, i.e., must be equal to $d = s^*R_B = 8.23R_B$; and (2) the number of the nearest neighbors must be maximal, i.e., equal to 12. Thus, the free energy per micelle can be written as[11]

$$F = -6U^* + F_0 \quad (12)$$

where 6 is half of the number of nearest neighbors (the contribution of next-nearest neighbors to F is negligible); $F_0 = -TQ\tau$ is the free energy of an isolated micelle (see eq 4). The ordering transition corresponds to $F = 0$; i.e.,

$$\tau_c = -6U^*/QT \quad (13)$$

Substituting eq 13 into eq 8, we get the concentration of the gas of micelles at the transition point, $\tau = \tau_c$:

$$c_1 = R_B^{-3} \exp(-6U^*/T)$$

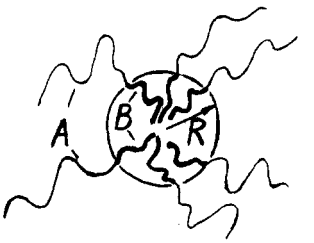

Figure 1. Isolated micelle: a core of radius R is filled by A blocks, B blocks being "grafted" to the surface of the core.

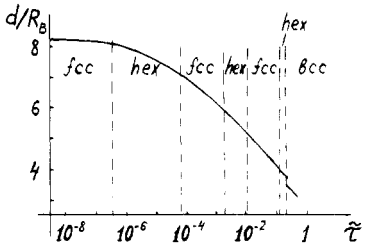

Figure 2. Dependence of the reduced interdomain separation, d/R_B, on the reduced interaction parameter, $\tilde{\tau} = \tau(8\pi R_B^3)/(\upsilon N_B Q)$. The vertical dashed lines separate the regions of stability of different micellar structures: fcc, face-centered cubic; hex, hexagonal; bcc, body-centered cubic.

The concentration, c_1, is extremely small since $U^* \gg T$. Thus, at $\tau = \tau_c$ an extremely dilute gas of micelles would be replaced by an ordered structure, the concentration of micelles in the structure being $c_2 \sim 1/(d^*)^3 \gg c_1$ (i.e., a substantial jump of the concentration at the transition point is predicted).

Let us consider the equilibrium structure of the macrolattice. Conditions (1) and (2) point to a closely packed arrangement, i.e., in particular, to hexagonal (hex) or face-centered cubic (fcc) structure. An analysis of the interactions between micelles (not only between the nearest neighbors) shows that at $\tau = \tau_c$ the absolute minimum of the free energy of the system corresponds to an fcc structure. As τ increases, the interdomain separation, d, decreases and a number of structural phase transitions from fcc to hex arrangement and vice versa occur (see Figure 2). The final transition from a hex to a body-centered cubic (bcc) structure occurs at $\tau_f = 0.27\upsilon N_B Q/8\pi R_B^3$; at $\tau = \tau_f$ the separation, d, changes from $d = 3.5R_B$ to $d = 3.4R_B$. (A jump of d accompanies every structural transition considered above since all these phase transitions are of the first order. Nevertheless, a jump of separation, d, is noticeable only for the hex–bcc transition: for other structural transitions, it is extremely small.)

Let us consider now another (more realistic) case: $U^*/T \ll 1$. This inequality implies that the attractive part of the interaction energy is negligible. The ordering transition is thus caused principally by the repulsion, an ordered micellar structure being formed from a rather concentrated gas of micelles.[12] At the transition point, the interaction energy per micelle (which is approximately equal to $6U_{int}(d)$) must be of the order T:

$$6U_{int}(d) \sim T \quad (14)$$

Using eq 9 and 10, we get, from eq 14,

$$d_c = 2R_B[\ln (3\upsilon N_B Q^2/8\pi^{3/2}R_B^3)]^{1/2} \quad (15)$$

The value τ_c can be easily obtained by using eq 15 and the plot in Figure 2. Depending on τ_c, the structure of the macrolattice at the transition point may be fcc, hex, or bcc. As τ increases, the separation, d, decreases (in the way shown in Figure 2) and a number of structural transitions (which are shown in Figure 2 for $\tau > \tau_c$) occur.

Let us estimate the values of d_c/R_B which can be expected for real polymers. Using eq 15, 5, 3, and 6, we get for PI–PS block-copolymers for $f \sim 0.1$:

$$d_c/R_B = 2^{1/2}(\ln M)^{1/2} \quad (16)$$

where M is the total molecular weight of a copolymer. The range $M = 10^4$–10^6 corresponds to $d_c/R_B = 4.3$–5.2. Taking into account Figure 2, we thus predict the following most probable picture of the ordering and structural transitions as a function of τ in the PI–PS melt: the gas of micelles–fcc structure–hex structure–bcc structure.

Registry No. (I)(S) (block copolymer), 105729-79-1.

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(8) The form (eq 7) of the ideal-gas term is used instead of the canonical form, $F_{id} = \mathcal{N}T \ln (c/e)$, since the argument of the logarithm should be dimensionless. The length, R_B, in eq 7 can be substituted by any other length: this substitution can be apparently compensated by the corresponding change of χ_c. Note that substitution of R_B by, say, R_A would produce an extremely small change of χ_c: $\chi_c \rightarrow \chi_c + \Delta\chi$, $\Delta\chi = 3Q^{-1}N_A^{-1} \ln (R_B/R_A) \ll \chi_c$.
(9) Note that, as was shown in ref 3, the interaction between micelles is a pair (two-body) interaction (provided that the distance between the nearest neighbors is larger than the radius of the core).
(10) The quantity U^*/T is equal to the product of the large parameter $vN_BQ^2/8\pi R_B^3 \sim N_B^{1/2}a^3/v$ and the small numerical factor φ^* so that both situations $U^*/T \gg 1$ and $U^*/T \ll 1$ are possible in principle. For real block-copolymer systems, the parameter U^*/T is always small. Nevertheless, the case $U^*/T \gg 1$ is considered here in order to obtain a complete picture of structural transitions.
(11) The ideal-gas term can be neglected since $U^* \gg T$.
(12) The concentration change at the transition point is expected to be rather small. Therefore, this ordering transition is in some sense analogous to a liquid-crystal phase transition.

On the Limitation of Comparative Quenching as a Measure of Electronic Energy Transfer in Polymers

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In some of the earliest work on electronic energy transfer (EET) in polymers by Fox et al.[1] and David et al.[2] it was noted that one manifestation of this phenomenon is that the polymeric excited state may be more easily quenched than the corresponding monomeric model compound. This is especially striking in low-temperature glasses in which no diffusion can occur. The physical idea is straightforward: if EET occurs, the excitation travels over a large volume, hence increasing the probability that a quencher species is encountered.

In some of these papers and our own publications[3] this idea was applied by using the extension by Voltz et al.[4] of the Smoluchowski–Einstein equation:

$$k_q = 4\pi(D_Q + D_{seg} + \Lambda_E)R_QP_Q \quad (1)$$

where k_q = quenching rate constant, R_QP_Q = product of interaction radius and probability of quenching per encounter, D_Q = the diffusion constant of the quencher, D_{seg} = the segmental diffusion constant of the chromophore bound to a polymer chain, and Λ_E = down-chain EET rate, expressed as a diffusion constant.

In our work we have determined k_q for a model polymer (k_q^{model}) in which there is a very low loading of chromophore[5] and for which it is assumed that $\Lambda_E \cong 0$. The quenching constant is then determined for a polymer in which it is assumed that $\Lambda_E > 0$ is possible (k_q^{polym}). It is further assumed that $D_{seg} \cong 0$ for both cases and that $R_Q^{model}P_Q^{model} \cong R_Q^{polym}P_Q^{polym}$. With these assumptions

$$(k_q^{polym} - k_q^{model})/k_q^{model} = \Lambda_E/D_Q \quad (2)$$

While all the assumptions that lead to eq 2 may be questioned, the underlying concept is simple: The faster the excitation moves along the coil (and hence the larger the volume swept out per unit time), the more efficiently the excited state is quenched. We wish to point out here that this is not always correct and that the use of eq 2 may lead to an underestimate of Λ_E.

We were led to reconsider the use of eq 1 and 2 because the Λ_E values for several different polymers were strikingly different using CCl_4 and O_2 as quenchers.[6,7] These data are summarized in Table I along with the Forster R_0 values for self-transfer.[8] These data illustrate the following: (1) for the phenanthrene polymers $\Lambda_E > 0$ is obtained for CCl_4

Table I
Comparison of the Fluorescence Quenching Parameters

(A) CCl_4

polymer	$\langle\tau\rangle^g$, ns	k_q, M^{-1} s^{-1}	Λ_E/D_{CCl_4}	R_0,[a] Å
r-MPh(42)$_{est}$[b]	32.9	2.2×10^8	0.50	8.8 (Phen)
PVPh[b]	17.0	5.4×10^8	2.64	
a-MPh$_{est}$[b]	42.5	2.6×10^8	0.78	
P(2VN-*co*-MMA)[c]	14.3	2.3×10^9	0.51	12 (2-MeNp)
P2VN-M[d]	7.4	1.2×10^9	0	
P(2VN-*alt*-MMA)[c]	43.4	3.0×10^9	0.97	
PVCz-M[d]	2.45	2.0×10^{10}	1.4–1.7	21 (MeCz)
PDPA-*co*-PS[e]	6.5	1.1×10^9	0	27 (DPA)
PDPA[e]	7.2	0.96×10^9	0	

(B) O_2

polymer	$\langle\tau\rangle^g$, ns	k_q, atm^{-1} s^{-1}	Λ_E/D_{O_2}	R_0, Å
r-MPh(42)$_{est}$[b]	32.9	7.4×10^7	0	8.8 (Phen)
PVPh[b]	17.0	7.9×10^7	0.03	
a-MPh$_{est}$[b]	42.5	7.8×10^7	0.01	
PDPA-*co*-PS[f]	6.8	1.7×10^8	0.09	27 (DPA)
PDPA[f]	7.1	1.5×10^8	0	

[a] Reference 8. Phen, phenanthrene; 2-MeNp, 2-methylnaphthalene; MeCz, *N*-methylcarbazole; DPA, 9,10-diphenylanthracene. [b] Reference 6. [c] Reference 3b. [d] Reference 3c. [e] Reference 7a. [f] Unpublished data. [g] $\langle\tau\rangle = \sum a_i\tau_i^2/\sum a_i\tau_i$ for multiexponential fluorescence decay.

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