dyad configurations of poly(propyl oxide) are termed as δ-meso and δ-racemo for dyad tactic structures. By the same way, those of polypropylene are termed as γ-meso and γ-racemo.
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Confined-Chain Statistics of Block Polymers and Estimation of Optical Anisotropy and Domain Size

Takeji Hashimoto,* Mitsuhiro Shibayama,[†] and Hiromichi Kawai[‡]

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Dale J. Meier*

Michigan Molecular Institute, Midland, Michigan 48640. *Received December 7, 1984*

ABSTRACT: Optical anisotropy of block polymer chains in lamellar microdomains has been calculated on the basis of a modified confined-chain statistics. The results show that the anisotropy associated with molecular orientation is an order of magnitude smaller than that associated with form anisotropy for polystyrene–polyisoprene and polystyrene–polybutadiene A–B type diblock and A–B–A type triblock polymers. Compared with the statistics originally proposed by one of us (D.J.M.), the modification involves elimination of the narrow-interphase approximation and use of a different functional form for the segmental density distribution across the interface. The modification is shown to give a better agreement with the experimental results.

I. Introduction

A–B and A–B–A type di- and triblock polymers form microdomain structure as a consequence of microphase separation of constituent block chains A and B under the strong segregation limit where they have a strong repulsive interaction. In this paper we will estimate the "intrinsic" optical anisotropy of block polymers forming lamellar microdomains, a special type of the microdomain morphology that is formed when the molecular volume of A (in the case of A–B diblock polymers) or of 2A (in the case of A–B–A triblock block polymers) is about equal to that of B.

We will restrict our treatment here to the case where both A and B are amorphous. The estimation of the intrinsic optical anisotropy involves the calculation of both molecular anisotropy and form anisotropy. The molecular anisotropy is the anisotropy due to molecular orientation of A and B chains in the domain space. The chemical junction points between A and B are localized somewhere in the interface, and the end-to-end vectors of A and B chains are statistically oriented normal to the interface. In this paper we will estimate this anisotropy based on an approximate method that involves two steps: (i) first we calculate the mean-square end-to-end distance of each block chain parallel ($\langle r^2\rangle$) and perpendicular ($\langle (z - z')^2\rangle$) to the interface on the basis of the "confined-chain statistics" proposed by one of us[1-3] and then (ii) knowing the results of (i), we calculate the orientational anisotropy of the chains based upon the Kuhn–Grün theory.[4,5] The Kuhn–Grün theory, which interrelates the anisotropy of a chain with its end-to-end displacement, is valid for the chains in free space but not for the block chains A and B in the confined space. Thus the second step involves an approximation, as will be discussed in section II-2.

The form anisotropy is the anisotropy arising from the distortion of the electric field strength of the incident light wave at the phase boundaries between the two coexisting phases[6] when there is a difference in their refractive indices. The greater the difference of the refractive indices and the greater the asymmetry in the shape of each phase, the larger is the form anisotropy. The form anisotropy (birefringence) was studied by Wiener[6] for two-phase systems in which each phase is optically isotropic and the boundary between the two phases is sharp, with the refractive index varying stepwise across the interface. Thus the estimation of the form anisotropy for the block polymer systems involves generalization of the theory to account for the finite thickness of the domain boundary region as well as for molecular anisotropy (see section III).

II. Molecular Anisotropy of Block Polymer Chains in the Domain Space

Let us take a reference axis z perpendicular to the interfaces between A and B lamellar domains. The A and B chains in the A–B diblock polymer are joined somewhere in the interface (chemical junction), and all their segments are restricted in the A and B domains (Figure 1a). Their end-to-end vectors orient uniaxially with respect to the reference axis.

The molecular anisotropy of the jth chain in A domain with its end-to-end vector $\mathbf{R}_j$ oriented at the polar angle θ_j with respect to the z axis is given by

$$P_{1j} - P_{2j} = (\pi_{1j} - \pi_{2j})(3\cos^2\theta_j - 1)/2 \qquad \text{(II-1)}$$

where P_{1j} and P_{2j} are the polarizabilities of a single chain parallel and perpendicular to z, respectively, and π_{1j} and π_{2j} are the polarizabilities parallel and perpendicular to the end-to-end vector $\mathbf{R}_j$ (Figure 1b).

1. Application of Kuhn–Grün Statistics for the Confined Chains.

The molecular anisotropy of the single chain A in the confined space, in turn, may be *approximately* given by Kuhn–Grün chain statistics.

$$\pi_{1j} - \pi_{2j} = \sigma_A(b_1 - b_2)_A f_s \qquad \text{(II-2)}$$

[†] Present address: Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan.

[‡] Present address: Hyogo University of Education, Hyogo-ken 673-14, Japan.

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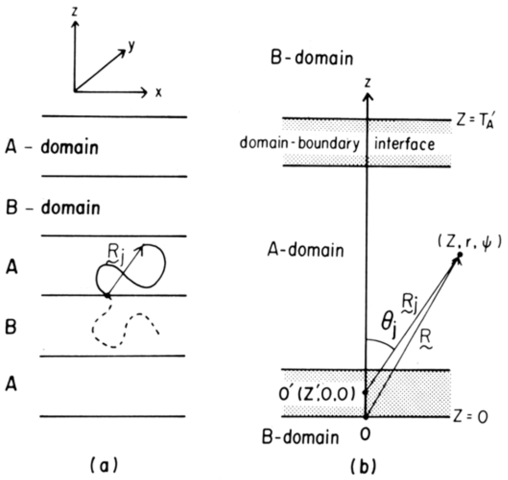

Figure 1. (a) Coordinate system 0_{xyz} fixed to an alternating lamellar microdomain and a single block chain in the domain. (b) Coordinates $(z',0,0)$ and (z,r,ψ) specifying the two ends of an A block chain whose segments are between two walls at $z = 0$ and $z = T_A'$.

σ_A is the number of segments per single A chain (monodispersity of molecular weight distribution is assumed here), $(b_1 - b_2)_A$ is the segmental anisotropy for A, and f_s is the second moment of the orientation distribution of the segments with respect to the end-to-end vector $\mathbf{R}_j$

$$f_s \equiv (3\langle\cos^2\theta_s\rangle - 1)/2 = 1 - 3[(R_j/\sigma_A l_A)/\mathcal{L}^{-1}(R_j/\sigma_A l_A)] \quad \text{(II-3)}$$

where θ_s is polar angle between the segment and $\mathbf{R}_j$, l_A is the length of the statistical segment for the A chain, and $\mathcal{L}^{-1}(x)$ is the inverse Langevin function as given by

$$\mathcal{L}(x) = \coth x - 1/x \quad \text{(II-4)}$$

$$\mathcal{L}^{-1}(x) = 3x + (9/5)x^3 + (297/175)x^5 + \ldots \quad \text{(II-5)}$$

For a Gaussian chain with $R_j \ll \sigma_A l_A$ (where $\sigma_A l_A$ is the contour length of a chain), eq II-3 is given by

$$f_s = \frac{3}{5}\frac{R_j^2}{\sigma_A^2 l_A^2} \quad \text{(II-6)}$$

If there are N block chains per unit volume, the molecular anisotropy of A lamella $(P_1 - P_2)_A$ is given by

$$(P_1 - P_2)_A = \sum_{j=1}^{N}(\pi_{1j} - \pi_{2j})(3\cos^2\theta_j - 1)/2 = N\langle(\pi_{1j} - \pi_{2j})(3\cos^2\theta_j - 1)/2\rangle \quad \text{(II-7)}$$

where the angular brackets indicate an average over all possible molecular conformations. Using the Lorentz–Lorenz equation, one can relate the anisotropy of the A domain to the orientational birefringence Δn_A of the A domain

$$\Delta n_A = \frac{2\pi}{9}\frac{(\bar{n}_A^2 + 2)^2}{\bar{n}_A}(P_1 - P_2)_A \quad \text{(II-8)}$$

where $\bar{n}_A$ is the average refractive index of the domain.

We can evaluate the average in eq II-7 on the basis of confined-chain statistics in the domain space. Let $P_A(\mathbf{R};z';\sigma_A)$ be the probability that an A chain with σ_A statistical segments of length l_A has one of its ends (chemical junction) at 0′ (whose position is specified by $(z',0,0)$ in cylindrical coordinates) and the other end at $\mathbf{R} = (z,r,\psi)$ (see Figure 1b). The probability P_A should simultaneously satisfy the conditions that all chain segments be confined in the space between the two planes at $z = 0$ and $z = T_A'$ and that the segment density be uniform everywhere in the domain space, the latter condition resulting from incompressibility of polymeric liquids. Using Gaussian statistics (eq II-6) and noting that

$$\cos^2\theta_j = (z - z')^2/[(z - z')^2 + r^2] \quad \text{(II-9)}$$

one obtains the molecular anisotropy of domain A, $(P_1 - P_2)_A$

$$(P_1 - P_2)_A = \frac{3}{5}\frac{(b_1 - b_2)_A}{\sigma_A l_A^2}N[\langle(z - z')^2\rangle - \langle r^2\rangle/2] \quad \text{(II-10)}$$

wherein

$$\begin{pmatrix}\langle(z - z')^2\rangle \\ \langle r^2\rangle\end{pmatrix} = \int\int\int P_A(z,r,\psi;z';\sigma_A)\begin{pmatrix}(z - z')^2 \\ r^2\end{pmatrix} d\psi\, r\, dr\, dz \quad \text{(II-11)}$$

for the chain with its junction at a fixed point z'. In the case when the junction can be anywhere in the interface, the integration has to be performed with respect to dz' over the narrow interfacial region. A similar equation is obtained for the molecular anisotropy of the B domain. Therefore the problem reduces to that of evaluating $\langle(z - z')^2\rangle$ and $\langle r^2\rangle$. The probability P_A in eq II-11 was given by Meier[1]

$$P_A(z,r,\psi;z';\sigma_A) = \frac{3}{\pi\sigma_A l_A^2}\frac{1}{T_A'}\exp[-3r^2/2\sigma_A l_A^2] \times \sum_{m=-\infty}^{\infty}\sin\frac{m\pi z'}{T_A'}\sin\frac{m\pi z}{T_A'}\exp\left[-\frac{m^2\pi^2\sigma_A l_A^2}{6T_A'^2}\right] \quad \text{(II-12)}$$

A similar equation holds for the B chain. The requirement of uniform volume filling invokes a constraint that T_A' depend upon chain dimension $(\sigma_A l_A^2)^{1/2}$

$$s \equiv (\sigma_A l_A^2)^{1/2}/T_A' \quad \text{(II-13)}$$

Among a number of possible values for s, the equilibrium value of s is the one that minimizes free energy of the microdomain ΔG

$$\partial\Delta G/\partial s = 0 \quad \text{(II-14)}$$

For such equilibrium conformation it was shown by Meier[2] that

$$\langle(z - z')^2\rangle \simeq T_A^2/4 \quad \text{(II-15)}$$

The lateral dimension is simply given by

$$\langle r^2\rangle = (2/3)\sigma_A l_A^2 \quad \text{(II-16)}$$

since there are no chain perturbations in the lateral direction. Consequently for the A–B diblock polymer the anisotropy, $(P_1 - P_2)_K$ (K = A or B), is given, from eq II-10, II-15, and II-16, by

$$(P_1 - P_2)_K = \frac{3}{5}\frac{(b_1 - b_2)_K}{\sigma_K l_K^2}N\left[\frac{T_K^2}{4} - \frac{\sigma_K l_K^2}{3}\right] \quad (\text{K} = \text{A or B}) \quad \text{(II-17)}$$

N is given for an A–B diblock polymer by

$$N = (v_A + v_B)^{-1} \quad \text{(II-18)}$$

where v_K (K = A or B) is molecular volume of the K chain. T_K should be calculated in terms of the confined-chain

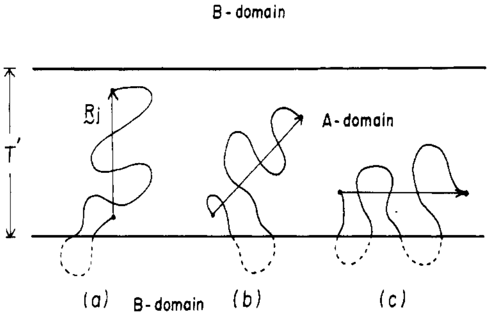

Figure 2. Forbidden chain conformations in the confined space.

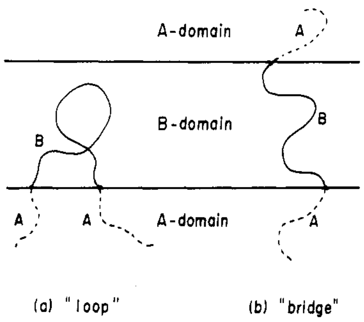

Figure 3. Loop (a) and bridge (b) conformations of central B block chains in A–B–A triblock polymers.

statistics (section IV). Thus total intrinsic birefringence Δn_t is given by

$$\Delta n_t = \Delta n_A + \Delta n_B \tag{II-19a}$$

$$\Delta n_K = \frac{2\pi}{9} \frac{(\bar{n}_K{}^2 + 2)}{\bar{n}_K} (P_1 - P_2)_K \qquad (K = A \text{ or } B) \tag{II-19b}$$

2. Validity of the Kuhn–Grün Statistics for the Confined Chains. Before we advance our arguments for the A–B–A triblock polymer, it may be useful to discuss here the validity of the Kuhn–Grün chain statistics for the chain in confined domain space. Kuhn–Grün chain statistics, leading to eq II-3, were originally derived for chains in free space and assumed cylindrical symmetry for the orientation of the segments with respect to the end-to-end vector $\mathbf{R}_j$. Thus all the chain conformations as depicted in Figure 2 are allowed in the Kuhn–Grün theory. On the other hand, in the confined chains all the segments must lie in the space between the walls, and hence all the conformations as shown in Figure 2 should be rejected.

In the calculation we present here, we could properly estimate the optical anisotropy for a chain with its end-to-end vector $\mathbf{R}_j$ oriented normal to the interface (as in Figure 2a), since (a) the cylindrical symmetry of the segmental orientation is valid for this type of the confined chains and (b) the confinement of the segments in the wall is taken into account in the calculation (eq II-12). However, for the chains with $\mathbf{R}_j$ inclined to the walls (as in Figure 2 parts b and c), the segmental orientation is no longer cylindrically symmetric, and hence the Kuhn–Grün statistics cannot be used for these chains. This is especially true for chains with the $\mathbf{R}_j$ vectors oriented parallel to the walls, as in Figure 2c, where the segments can be on only one side of space. Thus the validity of the approximation of cylindrical symmetry depends on the orientation of $\mathbf{R}_j$. However, since chains with their $\mathbf{R}_j$ vectors oriented normal to the interface are much more prevalent than those with $\mathbf{R}_j$'s parallel to the interface, the approximation of Kuhn–Grün statistics for this problem will be rather good. It seems intuitively obvious that the approximation underestimates the molecular anisotropy of the chains.

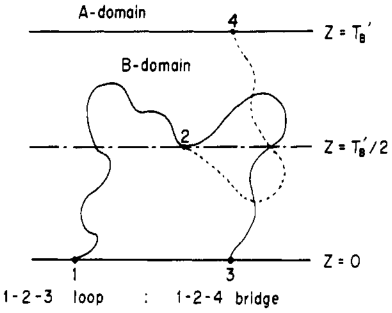

Figure 4. Loop and bridge conformations having identical molecular anisotropy. Note that the 2–3 portion (solid line) and the 2–4 portion (broken line) are mirror images with respect to the plane at $z = T_B'/2$.

3. Estimation for the A–B–A Triblock Polymers. The molecular anisotropy of the A domain in A–B–A triblock polymers can be calculated similarly to that in A–B diblock polymers.

The center block chain B can take either loop (a) or bridge (b) conformations as shown in Figure 3. The most probably position of the center of the B block chains has been shown to be in the middle of walls[2] (see Figure 4). For those chains whose centers lie in the middle of walls, a given loop conformation (1–2–3 in Figure 4) has a corresponding bridge conformation (1–2–4 in Figure 4). These bridge and loop conformations should have identical molecular anisotropy since the portion 2–3 of the chain is a mirror image of the portion 2–4. Thus from a physical point of view, the bridges and loops may have identical molecular anisotropy. Keeping this fact in mind, one obtains for the B chain

$$(P_1 - P_2)_B = \frac{3}{5} \frac{(b_1 - b_2)_B}{\sigma_B l_B{}^2} N \left[T_B{}^2 - \frac{\sigma_B l_B{}^2}{3} \right] \tag{II-20}$$

where N is given by

$$N = (2v_A + v_B)^{-1} \tag{II-21}$$

On the basis of eq II-8, II-17, II-20, and II-21, one can estimate the orientational birefringence of A–B–A triblock polymers

$$\Delta n_{\text{orient}} = \sum_K \Delta n_K \qquad (K = A, B) \tag{II-22a}$$

$$\Delta n_K = \frac{2\pi}{9} \frac{(\bar{n}_K{}^2 + 2)^2}{\bar{n}_K} (P_1 - P_2)_K \qquad (K = A, B) \tag{II-22b}$$

where $(P_1 - P_2)_B$ is given by eq II-20 and $(P_1 - P_2)_A$ by

$$(P_1 - P_2)_A = \frac{3}{5} \frac{(b_1 - b_2)_A}{\sigma_A l_A{}^2} 2N \left[\frac{T_A{}^2}{4} - \frac{\sigma_A l_A{}^2}{3} \right] \tag{II-22c}$$

It should be noted that one polymer chain has two A block chains; thus $2N$ rather than N appears in eq II-22c.

III. Form Optical Anisotropy of Domain Systems

The form anisotropy or birefringence was first studied by Wiener[6] for the ideal two-phase system with zero interfacial thickness. It was also assumed that each phase is optically isotropic. Recently, Franklin et al.[7] generalized the theory for multiphase systems in which each phase has its own optical anisotropy due to the molecular orientation. In this section we apply the Franklin theory to the lamellar microdomain with finite thickness of the domain boundary region.

Cvikl, Moroi, and Franklin[7] developed a theory for a system having an unlimited number of alternating lamellae

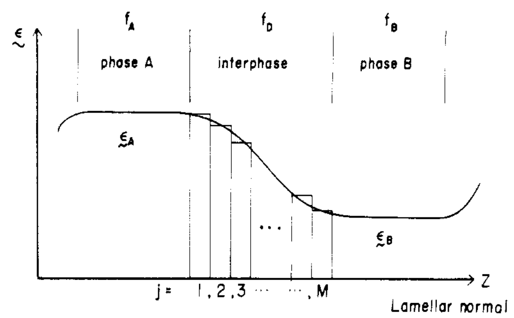

Figure 5. Spatial distribution of dielectric tensor ϵ along the lamellar normal z. The interface is divided into M sublayers with constant dielectric tensor ϵ_{jD} (j = 1–M).

of arbitrarily anisotropic homogeneous materials. For a special case where the principal axes of the dielectric tensors ϵ_i in each lamella have the same orientation and one of the principal axes is parallel to z, i.e., the lamellar normal, the effective dielectric tensor ϵ of the system is given by

$$\epsilon = \begin{pmatrix} \epsilon_x & 0 & 0 \\ 0 & \epsilon_y & 0 \\ 0 & 0 & \epsilon_z \end{pmatrix} \qquad \text{(III-1)}$$

$$\epsilon_x = \sum_{i=1}^{M} f_i \epsilon_{ix} \qquad \epsilon_y = \sum_{i=1}^{M} f_i \epsilon_{iy} \qquad \epsilon_z^{-1} = \sum_{i=1}^{M} f_i \epsilon_{iz}^{-1} \qquad \text{(III-2)}$$

where ϵ_{ix} is the dielectric constant of the ith lamella along the x axis, for example, and f_i is volume fraction of the ith lamella.

The theory may be applied to the lamellar microdomain system having the domain-boundary interphase as shown in Figure 5. The domain structure has a repeating unit that contains (i) the lamella of pure component A with dielectric tensor ϵ_A and volume fraction f_A, (ii) the interface of volume fraction f_D where the dielectric tensor varies from ϵ_A to ϵ_B, and (iii) the lamella of pure component B with dielectric tensor ϵ_B and volume fraction f_B. The interface can be further divided into a finite number of sublayers M, each layer having dielectric constant ϵ_{jD} and volume fraction f_{jD}.

Application of the theory to such a system immediately gives

$$f_A + f_B + f_D = 1 \qquad f_D = \sum_{i=1}^{M} f_{jD} \qquad \text{(III-3)}$$

$$\epsilon_i = \begin{pmatrix} \epsilon_{ix} & 0 & 0 \\ 0 & \epsilon_{ix} & 0 \\ 0 & 0 & \epsilon_{iz} \end{pmatrix} \quad (i = \text{A or B}) \qquad \text{(III-4)}$$

$$\epsilon_{jD} = \begin{pmatrix} \epsilon_{jDx} & 0 & 0 \\ 0 & \epsilon_{jDx} & 0 \\ 0 & 0 & \epsilon_{jDz} \end{pmatrix} \quad (j = 1\text{–}M) \qquad \text{(III-5)}$$

and for the effective ϵ

$$\epsilon = \begin{pmatrix} \epsilon_x & 0 & 0 \\ 0 & \epsilon_x & 0 \\ 0 & 0 & \epsilon_z \end{pmatrix} \qquad \text{(III-6)}$$

$$\epsilon_x = f_A \epsilon_{Ax} + f_B \epsilon_{Bx} + f_D \epsilon_{Dx} \qquad \text{(III-7)}$$

$$\epsilon_z^{-1} = f_A \epsilon_{Az}^{-1} + f_B \epsilon_{Bz}^{-1} + f_D \epsilon_{Dz}^{-1} \qquad \text{(III-8)}$$

ϵ_{Dx} and ϵ_{Dz} are given by

$$\epsilon_{Dx} = (1/f_D) \sum_{j=1}^{M} f_{jD} \epsilon_{jDx} \qquad \text{(III-9)}$$

$$\epsilon_{Dz}^{-1} = (1/f_D) \sum_{j=1}^{M} f_{jD} \epsilon_{jDz}^{-1} \qquad \text{(III-10)}$$

A sigmoidal density variation across the interface would cause a variation of the dielectric constants as given by

$$\epsilon_{Dx}(z) = (\epsilon_{Ax} - \epsilon_{Bx}) \phi_A(z) + \epsilon_{Bx} \qquad \text{(III-11)}$$

and

$$\epsilon_{Dz}(z) = (\epsilon_{Az} - \epsilon_{Bz}) \phi_A(z) + \epsilon_{Bz} \qquad \text{(III-12)}$$

where $\phi_A(z)$ may be given by

$$\phi_A(z) = \cos^2 (\pi z / 2\lambda) \qquad \text{(III-13)}$$

or by

$$\phi_A(z) = [1 + \exp(z/a)]^{-1} \qquad \text{(III-14)}$$

where λ and a are the parameters associated with the interfacial thickness and are related to the characteristic interfacial thickness as defined by

$$t \equiv |\mathrm{d}\phi(z)/\mathrm{d}z|^{-1}{}_{\phi(z)=1/2} \qquad \text{(III-15)}$$

$$t = 0.6366\lambda \quad \text{or } 4a \qquad \text{(III-16)}$$

The calculation of the form birefringence for the case where the density profile is given by eq III-13 was previously treated by Hashimoto et al.[8] In this case the analytical expression for ϵ_{Dx} and ϵ_{Dz} can be obtained by replacing the summations in eq III-9 and III-10 by integrals

$$\epsilon_{Dx} = (1/\lambda) \int_0^{\lambda} \epsilon_{Dx}(z)\, \mathrm{d}z \qquad \text{(III-17a)}$$

$$\epsilon_{Dz}^{-1} = (1/\lambda) \int_0^{\lambda} \epsilon_{Dz}^{-1}(z)\, \mathrm{d}z \qquad \text{(III-17b)}$$

One obtains

$$\epsilon_{Dx} = (\epsilon_{Ax} + \epsilon_{Bx})/2 \qquad \text{(III-18a)}$$

$$\epsilon_{Dz} = (\epsilon_{Az} \epsilon_{Bz})^{1/2} \qquad \text{(III-18b)}$$

Using Maxwell's equation, one can estimate the x and z components of the refractive indices

$$n_x = (\epsilon_x)^{1/2} \qquad n_z = (\epsilon_z)^{1/2} \qquad \text{(III-19)}$$

Then the net birefringence Δn_t of the lamellar microdomain is given from eq III-7, III-8, and III-19

$$\Delta n_t \equiv n_z - n_x \qquad \text{(III-20a)}$$

$$\Delta n_t = (f_A n_{Az}^{-2} + f_B n_{Bz}^{-2} + f_D n_{Dz}^{-2})^{-1/2} - (f_A n_{Ax}^{2} + f_B n_{Bx}^{2} + f_D n_{Dx}^{2})^{1/2} \qquad \text{(III-20b)}$$

where n_{Az} and n_{Ax} can be estimated from the average refractive index $\bar{n}_A$ of an A domain and from the orientational birefringence of an A domain, the latter being calculated by the procedure described in the previous section

$$\bar{n}_A = (n_{Az} + 2n_{Ax})/3 \qquad \text{(III-21)}$$

$$\Delta n_A = n_{Az} - n_{Ax} \qquad \text{(III-22)}$$

Similarly n_{Bz} and n_{Bx} can be estimated from $\bar{n}_B$ and Δn_B, and hence one can estimate Δn_t from eq III-20b. f_A, f_B, and f_D can be converted into the measurable quantities

$$f_D = 2\lambda / D$$

$$\psi_A \equiv T_A/D = f_A + \tfrac{1}{2} f_D$$

$$\psi_B \equiv T_B/D = f_B + \tfrac{1}{2} f_D$$

$$D = T_A + T_B \qquad \text{(III-23)}$$

where D is the domain identity period, T_K (K = A or B) is the thickness of the Kth domain, and f_D is the volume fraction of the interface.

Thus if T_A, T_B, and λ are estimated from the statistics of confined chains, one can estimate the net birefringence Δn_t. The total orientational birefringence Δ_{orient} and form birefringence Δ_{form} may be defined as

$$\Delta_{orient} \equiv \Delta n_A + \Delta n_B \qquad \text{(III-24a)}$$

$$\Delta_{form} \equiv \Delta n_t - \Delta_{orient} \qquad \text{(III-24b)}$$

These quantities can also be estimated from confined-chain statistics.

In the case where the density profile is given by eq III-14, one cannot really separate the domain and domain-boundary interface as in eq III-3, III-7, and III-8, since with eq III-14, $\phi_A(z)$ goes to zero only at $z = \infty$. In this case one can directly calculate ϵ in eq III-6 by noting that

$$f_A = f_B = 0 \quad \text{and} \quad f_D = 1 \qquad \text{(III-25)}$$

Thus from eq III-9, III-10, and III-25, one obtains

$$\epsilon_z^{-1} = \epsilon_{Dz}^{-1} = \frac{2}{T_A + T_B}\int_{-T_A/2}^{T_B/2} \epsilon_{Dz}^{-1}(z)\ dz \qquad \text{(III-26)}$$

$$\epsilon_x = \epsilon_{Dx} = \frac{2}{T_A + T_B}\int_{-T_A/2}^{T_B/2} \epsilon_{Dx}(z)\ dz \qquad \text{(III-27)}$$

By substituting eq III-11, III-12, and III-14 into eq III-26 and III-27, one obtains

$$\epsilon_z^{-1} = \frac{2a}{D}\left\{\epsilon_{Az}^{-1} \times \log\left(\frac{[\epsilon_{Az} + \epsilon_{Bz}\exp(-T_A/2a)]\exp(T_B/2a)}{[\epsilon_{Az} + \epsilon_{Bz}\exp(T_B/2a)]\exp(-T_A/2a)}\right) + \epsilon_{Bz}^{-1}\log\left(\frac{\epsilon_{Az} + \epsilon_{Bz}\exp(T_B/2a)}{\epsilon_{Az} + \epsilon_{Bz}\exp(-T_A/2a)}\right)\right\} \qquad \text{(III-28)}$$

and

$$\epsilon_x = \frac{2a}{D}(\epsilon_{Ax} - \epsilon_{Bx}) \times \log\left\{\frac{[1 + \exp(-T_A/2a)]\exp(T_B/2a)}{[1 + \exp(T_B/2a)]\exp(-T_A/2a)}\right\} + \epsilon_{Bx} \qquad \text{(III-29)}$$

In the limit of narrow interphase with $T_A \gg 2a$, and $T_B \gg 2a$, eq III-28 and III-29 become much simpler

$$\epsilon_z^{-1} = \phi_A\epsilon_{Az}^{-1} + \phi_B\epsilon_{Bz}^{-1} + (2a/D)(\epsilon_{Az}^{-1} - \epsilon_{Bz}^{-1})\log(\epsilon_{Az}/\epsilon_{Bz}) \qquad \text{(III-30)}$$

and

$$\epsilon_x = \phi_A\epsilon_{Ax} + \phi_B\epsilon_{Bx} \qquad \text{(III-31)}$$

From eq III-28 and III-29, one can estimate Δn_t and Δ_{form}.

IV. Domain Size and Domain-Boundary Thickness

From the results of the sections II and III, the birefringence of a domain system can be estimated from the parameters characterizing a microdomain (i.e., T_A, T_B, and a or λ). In this section we estimate these parameters based upon a confined-chain statistics that is slightly modified from the original version proposed by Meier.[2,3] In general, the free energy of microdomain formation ΔG from molecular mixture is given by

$$\Delta G = \Delta E_{int} - T(\Delta S_p + \Delta S_c) - N\chi_A k_B T\phi_B \qquad \text{(IV-1)}$$

where the last term of right-hand side of eq IV-1 is the enthalpy of demixing (N being the number of block polymer chains, ϕ_B the volume fraction of the B chain, and k_B Boltzmann's constant). The first term represents the interfacial energy, and the second and third terms are respectively the free energy associated with placement entropy and with the entropy of confining the A and B segments in their respective domains.

1. A–B Diblock Polymers. (a) Interfacial Energy ΔE_{int}. The unlike segments intermix at the interface, contributing to the interfacial energy

$$\Delta E_{int} = \frac{\chi_A k_B T}{v_A} S \int_{-\infty}^{\infty} \phi_A(z)\phi_B(z)\ dz \qquad \text{(IV-2)}$$

where $\phi_A(z)$ and $\phi_B(z)$ are the segmental density profile across the interface; $\phi_A(z) + \phi_B(z) = 1$. χ_A is the interaction parameter, defined by

$$\chi_A = \frac{(\delta_A - \delta_B)^2}{\rho_{A0} k_B T} = v_A \frac{(\delta_A - \delta_B)^2}{k_B T} \qquad \text{(IV-3)}$$

where δ_K is the solubility parameter of the K polymer and ρ_{A0} is the number density of the K polymer. S is the interfacial area given by

$$S = 2Nv_A/T_A \qquad \text{(IV-4)}$$

In previous work, $\phi_A(z)$ was assumed to be given by eq III-13, but in this work $\phi_A(z)$ as given by eq III-14 will be used, based upon the statistical mechanical studies of interfacial properties.[12–16] Substituting eq III-14 and IV-4 into eq IV-2, one obtains

$$\frac{\Delta E_{int}}{Nk_B T} = \frac{2\chi_A a}{T_A} = \frac{\chi_A t}{2T_A} = y\frac{\chi_A}{2} \qquad \text{(IV-5)}$$

where t is given by eq III-16 and y is defined as

$$y \equiv t/T_A \qquad \text{(IV-6)}$$

(b) Placement Entropy ΔS_p. Loss of entropy in placing the chemical junctions somewhere in the interface is given by

$$\frac{\Delta S_p}{Nk_B} = \ln\left[\frac{2\xi t}{T_A + T_B}\right] - 1 = \ln\left[\frac{2\xi y}{1 + q}\right] - 1 \qquad \text{(IV-7)}$$

where the chemical junctions are assumed to locate within ξt in the interface, ξ being an adjustable parameter characterizing the greater space available for the junctions in the interface than is given by the characteristic interfacial thickness t. In the case when $\phi_A(z)$ is given by eq III-14, one cannot really separate the interface from a domain, and hence specification of the parameter ξ is necessary. The quantity q is defined as a ratio of molecular volume of A and B and is equal to T_B/T_A for diblock polymer.

$$q \equiv v_B/v_A = T_B/T_A \qquad \text{(IV-8)}$$

(c) Constraint-Volume Entropy ΔS_c. Let $P_A(z_A;z_A')$ be the probably that the chemical junction of the A chain locates at z_A' within the interface of thickness ξt and the other free end of the A chain locates between z_A and $z_A + dz_A$, with all the A segments lying between walls of

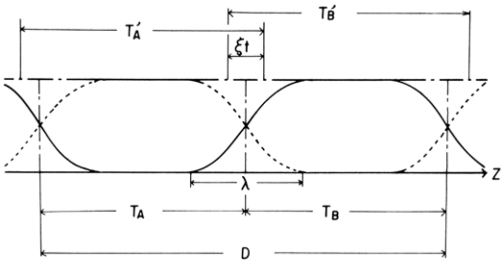

Figure 6. Spatial distribution of segmental densities (broken line for A segments and solid lines for B segments) and definitions of D, T_A, T_B, T_A', T_B', and ξt.

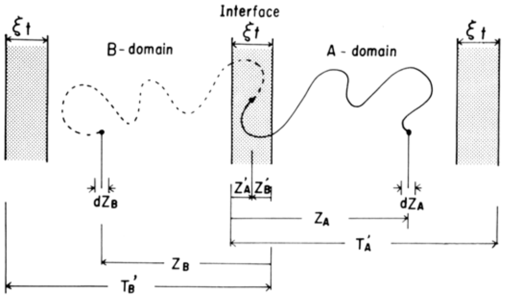

Figure 7. Locations of two chain ends and a chemical junction for an A–B diblock polymer chain in a domain.

thickness T_A' (see Figure 6). $P_A(z_A;z_A')$ is given from eq II-12 by

$$P_A(z_A;z_A') = \frac{2}{T_A'}\sum_m \sin\frac{m\pi z_A'}{T_A'} \sin\frac{m\pi z_A}{T_A'} \exp\left[-\frac{m^2\pi^2\sigma_A l_A^2}{6T_A'^2}\right] dz_A \qquad \text{(IV-9)}$$

A similar equation is obtained for the B block chain

$$P_B(z_B;z_B') = \frac{2}{T_B'}\sum_n \sin\frac{n\pi z_B'}{T_B'} \sin\frac{n\pi z_B}{T_B'} \exp\left[-\frac{n^2\pi^2\sigma_B l_B^2}{6T_B'^2}\right] dz_B \qquad \text{(IV-10)}$$

In the previous treatment the interface was assumed to be narrow so that $z_A' \ll T_A'$ and $z_B' \ll T_B'$. In this case $P_A(z_A;z_A')$ is given by

$$P(z_A;z_A') \simeq \frac{2\pi z_A'}{T_A'^2}\sum_m m \sin\frac{m\pi z_A}{T_A'} \exp\left[-\frac{m^2\pi^2\sigma_A l_A^2}{6T_A'^2}\right] dz_A \qquad \text{(IV-11)}$$

However, in the modified statistics presented here, this assumption will not be used. From eq IV-9 and IV-10 one can calculate the probability $P(z_A,z_B;z_A')$ that the chemical junction of the A–B block polymer locates at z_A', free ends of A and B locate respectively at z_A and z_B, and all A and B segments lie respectively between walls of thickness T_A' and T_B' (see Figure 7)

$$P(z_A,z_B;z_A') = P_A(z_A;z_A')P_B(z_B;\xi t - z_A') \qquad \text{(IV-12)}$$

The probability $P(z_A,z_B;\xi t)$ that the chemical junction is somewhere in the interface, keeping other conditions unchanged, is given by

$$P(z_A,z_B;\xi t) = \frac{1}{\xi t}\int_0^{\xi t} P(z_A,z_B;z_A')\, dz_A' \qquad \text{(IV-13)}$$

One can further calculate the probability of the confined chain, i.e., the probability $P(T_A',T_B';\xi t)$ that the free ends z_A and z_B are somewhere in the domains T_A' and T_B', respectively, keeping other conditions unchanged.

$$P(T_A',T_B';\xi t) = \int_0^{T_A'}\int_0^{T_B'} P(z_A,z_B;\xi t)\, dz_A\, dz_B \simeq P(\langle z_A^2\rangle^{1/2},\langle z_B^2\rangle^{1/2};\xi t)\, dz_A\, dz_B \qquad \text{(IV-14)}$$

with

$$\langle z_A^2\rangle^{1/2}/T_A' = \langle z_B^2\rangle^{1/2}/T_B' = \tfrac{1}{2} \qquad \text{(IV-15)}$$

Equations IV-14 and IV-15 were obtained previously by Meier[2,3] and suggest that the most probably positions of the free ends are in the middle of the respective domains when segmental densities are uniform. Noting that

$$dz_K = rT_K \qquad (K = A \text{ or } B) \qquad \text{(IV-16)}$$

where r should be a constant, and defining a parameter c associated with the asymmetry of the block polymer

$$c \equiv \sigma_B l_B^2/\sigma_A l_A^2 \qquad \text{(IV-17)}$$

one obtains

$$P(T_A',T_B';\xi t) = \frac{4\alpha\beta r^2}{\pi(\alpha-1)}\sum_{\substack{m,n\\ \text{odd}}}(-1)^{(m+n+2)/2} \times \frac{m\beta \sin\dfrac{n\pi(\alpha-1)}{\beta} - n\alpha \sin\dfrac{m\pi(\alpha-1)}{\alpha}}{m^2\beta^2 - n^2\alpha^2} \times \exp\left[-\frac{\pi^2}{6}\left(\frac{\sigma_A l_A^2}{T_A^2}\right)\left(\frac{m^2}{\alpha^2} + \frac{cn^2}{\beta^2}\right)\right] \qquad \text{(IV-18)}$$

where α and β are defined as

$$\alpha \equiv 1 + \xi y \qquad \beta \equiv q + \xi y = q + \alpha - 1 \qquad \text{(IV-19)}$$

$$\Delta S_c/k_B N = \ln P(T_A',T_B';\xi t) \qquad \text{(IV-20)}$$

From eq IV-1, -5, -7, -18, and -20, one finally obtains the expression for ΔG, the free energy of the microdomain of the A–B diblock polymer

$$\frac{\Delta G_{AB}}{Nk_BT} = \frac{\chi_A y}{2} - \left[\ln\frac{2(\alpha-1)}{1+q} - 1\right] - \ln\left\{\alpha\beta\sum_{\substack{m,n\\ \text{odd}}}(-1)^{(m+n+2)/2} \times \frac{m\beta \sin\dfrac{n\pi(\alpha-1)}{\beta} - n\alpha \sin\dfrac{m\pi(\alpha-1)}{\alpha}}{m^2\beta^2 - n^2\alpha^2} \times \exp\left[-\frac{\pi^2}{6}\left(\frac{\sigma_A l_A^2}{T_A^2}\right)\left(\frac{m^2}{\alpha^2} + \frac{cn^2}{\beta^2}\right)\right]\right\} - \ln\frac{4r^2}{\pi(\alpha-1)} - \frac{\chi_A q}{1+q} \qquad \text{(IV-21)}$$

From eq IV-21, ΔG is a function of a set of independent variables $(y,\sigma_A l_A^2/T_A^2,\xi)$ or $(a,\sigma_A l_A^2/T_A^2,\xi)$. We treat here ξ as an adjusting parameter. Then for a given set of molecular parameters such as $\sigma_A l_A^2$, χ_A, q, and c, one can estimate equilibrium values of a and $\sigma_A l_A^2/T_A$ by minimizing the free energy of the microdomain, that is, by solving simultaneously the following equations.

$$\partial\Delta G_{AB}/\partial a = 0$$

$$\partial\Delta G_{AB}/\partial(\sigma_A l_A^2/T_A^2) = 0 \qquad \text{(IV-22)}$$

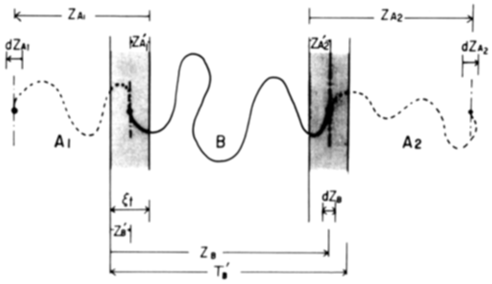

Figure 8. Locations of two chain ends and two chemical junctions for an A–B–A triblock polymer chain in a domain.

From the equilibrium values one can estimate $D = T_A + T_B$, t, and T_K (K = A or B).

2. A–B–A Triblock Polymers. (a) Interfacial Energy ΔE_{int}. From eq III-14 and IV-2, one obtains

$$\Delta E_{int} = Sa\chi_A k_B T/v_A \qquad \text{(IV-23)}$$

which is identical with ΔE_{int} for A–B diblock polymer. The total interfacial area S for A–B–A triblock polymer is given by

$$S = 2Nv_B/T_B = 4Nv_A/T_A \qquad \text{(IV-24)}$$

Noting that

$$T_B/T_A = v_B/2v_A = q/2 \qquad \text{(IV-25)}$$

and from eq IV-23 to IV-25

$$\frac{\Delta E_{int}}{Nk_BT} = \frac{\chi_A t}{T_A} = \chi_A y = \frac{\chi_A(\alpha - 1)}{\xi} \qquad \text{(IV-26)}$$

(b) Placement Entropy ΔS_p. In a manner similar to that used for an A–B diblock polymer, one can calculate ΔS_p for an A–B–A triblock polymer. Noting that for an A–B–A polymer T_B and T_A are mutually related by eq IV-25 rather than eq IV-8 for an A–B polymer

$$\Delta S_p = \ln \frac{2\xi y}{1 + q/2} - 1 = \ln\,[4(\alpha - 1)/(2 + q)] - 1 \qquad \text{(IV-27)}$$

(c) Constraint-Volume Entropy ΔS_c. A–B–A triblock polymers have two possible conformations (bridges and loops) as shown in Figure 3. Let us first estimate ΔS_c for bridges. Let us define the probability $P_{ABA}(z_{A1},z_{A2};\xi t)$ that the A and B chains are confined in the A and B domains, respectively, with the free ends of A at z_{A1} and z_{A2} and the chemical junctions somewhere in the interface of thickness ξt for A–B–A block polymers. P_{bridge} is given in terms of $P_A(z_{A1};z_{A1}')$, $P_A(z_{A2};z_{A2}')$, and $P_B(z_B;z_B')$ defined in eq IV-9 and IV-10, where $P_A(z_{Ai};z_{Ai}')$ ($i = 1, 2$) are the probabilities for the two A chains and $P_B(z_B;z_A')$ is the probability for the bridge chain B (see Figure 8).

$$P_{bridge}(z_{A1},z_{A2};\xi t) = \frac{1}{\xi t} \times \int_{z_B'=0}^{\xi t}\int_{z_B=T_B'-\xi t}^{T_B'} P_A(z_{A1};z_{A1}')P_B(z_B;z_B')P_A(z_{A2};z_{A2}')\ dz_B'\ dz_B \qquad \text{(IV-28)}$$

It should be noted that, upon integration of eq IV-28, junctions 1 and 2 (z_{A1}' and z_{A2}' in Figure 8) are related to z_B' and z_B

$$z_{A1}' = \xi t - z_B'$$
$$z_{A2}' = z_B - T_B = z_B - T_B' + \xi t \qquad \text{(IV-29)}$$

Table I
Effect of Choice of ξ on Domain Parameters for Sample L-6 at 293 K[a,b]

ξ	T_{PS}, nm	D, nm	t, nm
1	33.6	58.0	2.08
2	32.1	55.4	1.84
3	30.6	52.9	1.68
4	29.6	51.2	1.56

[a] SI Diblock polymer with total number average molecular weight 102 × 10³ and 61 wt % polystyrene. [b] T_{PS} is the thickness of a polystyrene lamella and t is the characteristic interfacial thickness.

The probability $P_{ABA}(T_A',T_B';\xi t)$ that the free ends of the A chains are somewhere in the interface, keeping other conditions unchanged, is given by

$$P_{bridge}(T_A',T_B';\xi t) = \int\int P_{bridge}(z_{A1},z_{A2};\xi t)\ dz_{A1}\ dz_{A2} \simeq P_{bridge}(\langle z_{A1}{}^2\rangle^{1/2},\langle z_{A2}{}^2\rangle^{1/2};\xi t)\ dz_{A1}\ dz_{A2} \qquad \text{(IV-30)}$$

From eq IV-9, -10, -16, -17, -25, and -30, one obtains

$$P_{bridge}(T_A',T_B';\xi t) = \frac{8r^2\alpha^2\beta}{\pi^2(\alpha - 1)} \sum_{\substack{p\\ \text{integer}}} \sum_{\substack{m,n\\ \text{odd}}} (-1)^{p+1} \times \frac{m\beta \sin\dfrac{p\pi(\alpha - 1)}{\beta} - p\alpha \sin\dfrac{m\pi(\alpha - 1)}{\alpha}}{m^2\beta^2 - p^2\alpha^2} \times \frac{n\beta \sin\dfrac{p\pi(\alpha - 1)}{\beta} - p\alpha \sin\dfrac{n\pi(\alpha - 1)}{\alpha}}{n^2\beta^2 - p^2\alpha^2} \times (-1)^{(m+n+2)/2} \exp\left[-\frac{\pi^2}{6}\left(\frac{\sigma_A l_A{}^2}{T_A{}^2}\right)\left(\frac{m^2 + n^2}{\alpha^2} + \frac{cp^2}{\beta^2}\right)\right] \qquad \text{(IV-31)}$$

Thus the constraint-volume entropy $\Delta S_{c,bridge}$ for bridges is given by

$$\Delta S_{c,bridge} = N_{bridge}k_B \ln P_{bridge}(T_A',T_B';\xi t) \qquad \text{(IV-32)}$$

where N_{bridge} is the number of A–B–A block chains having bridge conformations.

Let us now consider the constraint-volume entropy for loops, $\Delta S_{c,loop}$. In order to satisfy the requirement of uniform filling of the space with the segments, a loop is treated as two separate chains (A–B/2) with ends of the chains corresponding to the center segment of the loop. In this manner, one can estimate the probability $P_{loop}(T_A',T_B';\xi t)$ based on the statistics of A–B diblock polymers. Noting that B in A–B diblock polymer should be replaced by $^1/_2$B for an A–B–A triblock polymer

$$P_{loop}(T_A',T_B';\xi t) = \left\{\frac{4r^2\alpha\beta}{\pi(\alpha - 1)} \sum_{\substack{m,n\\ \text{odd}}} (-1)^{(m+n+2)/2} \times \frac{m\beta \sin\dfrac{n\pi(\alpha - 1)}{\beta} - n\alpha \sin\dfrac{m\pi(\alpha - 1)}{\alpha}}{m^2\beta^2 - n^2\alpha^2} \times \exp\left[-\frac{\pi^2}{6}\left(\frac{\sigma_A l_A{}^2}{T_A{}^2}\right)\left(\frac{m^2}{\alpha^2} + \frac{cn^2}{2\beta^2}\right)\right]\right\}^2 \qquad \text{(IV-33)}$$

Thus constraint-volume entropy $\Delta S_{c,loop}$ for loops is given by

$$\Delta S_c = 2N_{loop}k_B \ln P_{loop}(T_A',T_B';\xi t) \qquad \text{(IV-34)}$$

where N_{loop} is the number of A–B–A block polymer molecules with loop conformations.

From eq IV-26, -27, -32, and -34, one obtains the free energy of microdomains for A–B–A triblock polymers

$$\begin{aligned}\frac{\Delta G_{\text{ABA}}}{Nk_{\text{B}}T} = {} & \chi_{\text{A}}y - \ln\left[\frac{2(\alpha-1)}{1+q/2}\right] + 1 - \\ & 2f_{\text{l}} \ln\left\{\frac{4r^2\alpha\beta}{\pi(\alpha-1)}\sum_{\substack{m,n\\ \text{odd}}}(-1)^{(m+n+2)/2} \times \right. \\ & \frac{m\beta\sin\dfrac{n\pi(\alpha-1)}{\beta} - n\alpha\sin\dfrac{m\pi(\alpha-1)}{\alpha}}{m^2\beta^2-n^2\alpha^2} \times \\ & \left.\exp\left[-\frac{\pi^2}{6}\left(\frac{\sigma_{\text{A}}l_{\text{A}}{}^2}{T_{\text{A}}{}^2}\right)\left(\frac{m^2}{\alpha^2}+\frac{cn^2}{2\beta^2}\right)\right]\right\} - \\ & f_{\text{b}} \ln\left\{\frac{8r^2\alpha^2\beta}{\pi^2(\alpha-1)}\sum_{\substack{p:\text{ integer}\\ m,n:\text{ odd}}}(-1)^{p+1} \times \right. \\ & \frac{m\beta\sin\dfrac{p\pi(\alpha-1)}{\beta} - p\alpha\sin\dfrac{m\pi(\alpha-1)}{\alpha}}{m^2\beta^2-p^2\alpha^2} \times \\ & \frac{n\beta\sin\dfrac{p\pi(\alpha-1)}{\beta} - p\alpha\sin\dfrac{n\pi(\alpha-1)}{\alpha}}{n^2\beta^2-p^2\alpha^2} \times \\ & \left.(-1)^{(m+n+2)/2}\exp\left[-\frac{\pi^2}{6}\left(\frac{\sigma_{\text{A}}l_{\text{A}}{}^2}{T_{\text{A}}{}^2}\right)\left(\frac{m^2+n^2}{\alpha^2}+\frac{cp^2}{\beta^2}\right)\right]\right\} \\ & - \frac{\chi_{\text{A}}q}{1+q/2} \end{aligned} \qquad \text{(IV-35)}$$

where f_{l} and f_{b} are the fractions of A–B–A forming loops and bridges, respectively. Minimizing the free energy with respect to a and to $\sigma_{\text{A}}l_{\text{A}}{}^2/T_{\text{A}}{}^2$ and solving the resulting two equations simultaneously

$$\frac{\partial\Delta G_{\text{ABA}}}{\partial a} = \frac{\partial\Delta G_{\text{ABA}}}{\partial(\sigma_{\text{A}}l_{\text{A}}{}^2/T_{\text{A}}{}^2)} = 0 \qquad \text{(IV-36)}$$

one obtains equilibrium values of a and $\sigma_{\text{A}}l_{\text{A}}{}^2/T_{\text{A}}{}^2$ for a given ξ, from which $D = T_{\text{A}} + T_{\text{B}}$, t, T_{K} (K = A or B) also are estimated.

V. Results of Numerical Calculations

The molecular volume of the K polymer v_{K} (K = A or B) can be calculated from molecular weight M_{K} and mass density d_{K} of the K polymer

$$v_{\text{K}} = M_{\text{K}}/(d_{\text{K}}N_{\text{A}}) \qquad \text{(V-1)}$$

where N_{A} is Avogadro's number. The mass densities[10] of polystyrene (PS) d_{PS} and polyisoprene (PI) d_{PI} are

$$d_{\text{PS}} = 1.052 \text{ g cm}^{-3} \qquad d_{\text{PI}} = 0.925 \text{ g cm}^{-3}$$

The unperturbed chain dimensions of PS and PI are estimated from

$$(\sigma l^2)_{\text{PS}} = K_{\text{PS}}{}^2 M_{\text{PS}} \qquad (\sigma l^2)_{\text{PI}} = K_{\text{PI}}{}^2 M_{\text{PI}} \qquad \text{(V-2)}$$

where the following values for K's are used:[10]

$$K_{\text{PS}} = 6.7 \times 10^{-2} \text{ nm} \qquad K_{\text{PI}} = 7.2 \times 10^{-2} \text{ nm}$$

In order to calculate χ_{A} one needs a value for $(\delta_{\text{A}} - \delta_{\text{B}})^2/k_{\text{B}}T$. Here the formula obtained by Rounds and McIntyre is used

$$(\delta_{\text{A}} - \delta_{\text{B}})^2/k_{\text{B}}T = -900 + 7.5 \times 10^5/T \text{ (mol/m}^3) \qquad \text{(V-3)}$$

These parameters are sufficient to estimate the domain size T_{K} (K = A or B), the domain identity period D, and the characteristic interfacial thickness t.

In the calculations of domain properties of A–B–A triblock polymers, f_{l} and f_{b} were assumed to be equal to $^1/_2$.

In order to estimate the optical properties of the domain system, one further needs parameters such as the average refractive indices of polystyrene ($\bar{n}_{\text{PS}}$) and polyisoprene ($\bar{n}_{\text{PI}}$) and the segmental anisotropy of polystyrene ($(b_1 - b_2)_{\text{PS}}$) and polyisoprene ($(b_1 - b_2)_{\text{PI}}$). The following values are used:[9]

$$\begin{gathered}\bar{n}_{\text{PS}} = 1.59 \qquad \bar{n}_{\text{PI}} = 1.52 \\ (b_1 - b_2)_{\text{PS}} = -145 \times 10^{-4} \text{ nm}^3 \\ (b_1 - b_2)_{\text{PI}} = 50.6 \times 10^{-4} \text{ nm}^3\end{gathered} \qquad \text{(V-4)}$$

Table I shows the effect of the adjustable parameter ξ on the polystyrene (PS) lamellar thickness T_{PS}, the domain identity period D, and the characteristic interfacial thickness t at 293 K for sample L-6,[10] which is a polystyrene–polyisoprene diblock polymer (SI) with total number-average molecular weight $M_{\text{n}} = 102 \times 10^3$ and 61 wt % PS block. As ξ increases, t decreases. This is reasonable since ΔG_{AB} is a function of $\chi_{\text{A}}y$, y, and $\sigma_{\text{A}}l_{\text{A}}{}^2/T_{\text{A}}$, and hence increasing ξ is qualitatively equivalent to decreasing t (or y). It should be noted that ξt is not constant because free energy depends not only on ξt (or ξy) but also on $\chi_{\text{A}}t$ (or $\chi_{\text{A}}y$).

Table II shows comparisons of the domain parameters obtained from the present modified statistics and from the original version for SI and SIS block polymers. In the modified statistics ξ is assumed to be 2. The SI diblock polymer has $M_{\text{n}} = 10^5$ and the SIS triblock polymer has $M_{\text{n}} = 2 \times 10^5$. Both polymers have weight percent of PS (W_{PS}) equal to 50. Besides the fact that modified treatment gives a much thinner interface, the two treatments give almost identical results for T_{PS} and D. This is because the narrow-interphase approximation is good enough for these polymers.

Table III shows comparisons of calculated and experimental domain dimensions for a series[10] of SI diblock polymers having lamellar microdomains. The calculated values are obtained for $\xi = 2$ and at $T = 293$ K. The values obtained from the original version of the statistics are also included in parentheses in the table. The specimens L-4 and L-5 may have tapered block structures.[10] It is clearly seen that the modified statistics gives better agreement with the experimental results,[10] especially for the characteristic interfacial thickness.

Table II
Comparisons of Domain Parameters (nm) Estimated from Modified and Original Statistics for SI and SIS Block Polymers

	SI[b]			SIS[c]		
statistics	T_{PS}	D	t	T_{PS}	D	t
modified[a]	25.5	54.5	2.07	25.8	55.1	1.93
original	25.5	55.1	2.75	23.8	54.8	3.42

[a] ξ is assumed to be 2. [b] Polystyrene–polyisoprene (SI) diblock polymer with $M_{\text{n}} = 10^5$ and $W_{\text{PS}} = 0.5$ at 293 K. [c] SIS triblock polymer with $M_{\text{n}} = 2 \times 10^5$ and $W_{\text{PS}} = 0.5$ at 293 K.

Table III
Comparisons of Calculated and Experimental Domain Parameters for a Series of SI Diblock Polymers

polymers	$M_n \times 10^{-3}$ PS/PI	D, nm calcd[a]	D, nm exptl[b]	t, nm calcd[a]	t, nm exptl[b]
L-1	11.1/9.9	20.3 (19.8)	17.2	2.54 (3.4)	1.7 ± 0.2
L-2	12.4/18.6	26.3 (26.2)	24.3	2.53 (3.4)	1.7 ± 0.2
L-3	22/27	35.9 (36.0)	31.9	2.17 (3.3)	1.9 ± 0.2
L-4[c]	25.3/29.7	38.3 (38.7)	34.0	2.18 (3.2)	2.3 ± 0.2
L-5[c]	49.5/47.5	54.2 (55.5)	46.3	1.82 (2.8)	2.6 ± 0.2
L-6	62.2/39.8	55.4 (56.9)	50.3	1.84 (2.8)	1.7 ± 0.2

[a] Calculated values are obtained for $\xi = 2$ at $T = 293$ K and the values in parentheses are obtained from the original version of the statistics.[10] [b] See ref 10. [c] "Tapered" block polymer.[10]

Table IV shows calculated domain parameters T_{PS}, D, t, and optical properties such as Δn_{PS}, Δn_{PI}, Δ_{orient}, Δ_{form}, and Δn_t for a series of SI diblock polymers and SIS triblock polymers on the basis of the modified chain statistics with $\xi = 2$ and at $T = 293$ K. N is the number of block polymer chains per cm^3 as calculated with eq V-1 and with eq II-18 for diblock polymers and eq II-21 for triblock polymers. Δn_K (K = PS or PI) is the orientational birefringence of K lamellae as calculated from eq II-19 for diblock polymers and from eq II-20 to II-22 for triblock polymers. Δ_{orient} is the total orientational birefringence as calculated from eq II-19a and II-22a. Δn_t is the total birefringence of the lamellar microdomains as calculated from eq III-19, -20a, -28, and -29, and Δ_{form} is the form birefringence as defined by eq III-24b.

It will be noted in Table IV that $\Delta_{form} \simeq \Delta n_t$ or that $|\Delta_{orient}| \ll |\Delta n_t|$. That is, the intrinsic birefringence of the lamellar microdomains can be attributed primarily to form birefringence, with the orientational birefringence making an almost negligible contribution to Δn_t (equal to or less than about 10% of Δn_t). This conclusion supports the experimental observation of Folkes and Keller on extruded SBS triblock polymers.[11] Note that Δ_{form} is negative; i.e., $n_z < n_x = n_y$.

The orientational birefringence of polystyrene lamellae is negative because of the negative segmental anisotropy (eq V-4) used in the calculation. The absolute value of birefringence $|\Delta n_{PS}|$ and $|\Delta n_{PI}|$ decreases with increasing molecular weight of the block polymers. As the molecular weight increases, (i) the absolute value of the birefringence of a single chain increases because of the increased chain stretching involved in domain thickening (see $[T_K^2/4 - \sigma_K l_K^2]$ in eq II-17 and $[T_B^2 - \sigma_B l_B^2/3]$ in eq II-20), but (ii) the number of chains per unit volume N decreases according to eq II-18 for A–B and eq II-21 for A–B–A block polymers. The orientational birefringence is proportional to a product of these two factors, which have an opposite molecular weight dependence. Therefore, the birefringence decreases because the latter factor (ii) outweighs the former (i).

The orientational birefringence of polyisoprene lamellae in SIS triblock polymers, $\Delta n_{PI,SIS}$, is greater than that for corresponding SI diblock polymers, $\Delta n_{PI,SI}$. This is a consequence of the polyisoprene chains in SIS being constrained at both ends, while those in SI are constrained only at one end. This difference is clearly seen by comparing eq II-17 and -20. It should be noted that the SIS triblock polymers under consideration have molecular weights twice as large as those of the SI diblock polymers and have chemical compositions identical with those of the diblock polymers (i.e., in this regard the triblock polymers may be written as S–2I–S). From eq II-17 and II-18, the anisotropy of the B lamellae in A–B diblock polymer is given by

$$(P_1 - P_2)_{B,AB} = \frac{3}{5}\frac{(b_1 - b_2)_B}{\sigma_B l_B^2}(\upsilon_A + \upsilon_B)^{-1}\left[\frac{T_B^2}{4} - \frac{1}{3}\sigma_B l_B^2\right] \tag{V-5}$$

From eq II-20 and -21, the anisotropy of the B lamellae in the corresponding A–B–A triblock polymer is given by

$$(P_1 - P_2)_{B,ABA} = \frac{3}{5}\frac{(b_1 - b_2)_B}{(2\sigma_B) l_B^2}(2\upsilon_A + 2\upsilon_B)^{-1}\left[T_B^2 - \frac{1}{3}(2\sigma_B) l_B^2\right] = \frac{3}{5}\frac{(b_1 - b_2)_B}{\sigma_B l_B^2}(\upsilon_A + \upsilon_B)^{-1}\left[\frac{T_B^2}{4} - \frac{1}{6}\sigma_B l_B^2\right] \tag{V-6}$$

Thus by comparing eq V-5 and -6, it is clear that

$$(P_1 - P_2)_{B,ABA} > (P_1 - P_2)_{B,AB}$$

and hence

$$\Delta n_{PI,SIS} > \Delta n_{PI,SI}$$

The orientational birefringence of polystyrene lamellae in the diblock polymer is about equal to that for the corresponding triblock polymer. The small difference is attributed to small differences in the domain parameters (T_{PS}, D, and t).

The total orientational birefringence Δ_{orient} is negative since the negative birefringence of the polystyrene lamellae outweighs the positive birefringence of the polyisoprene lamellae. Absolute values of the orientational birefringence of the A–B–A triblock polymers $|\Delta_{orient}|_{ABA}$ are smaller than those of the corresponding diblock polymers $|\Delta_{orient}|_{AB}$ because of the greater $\Delta n_{PI,SIS}$ compared with $\Delta n_{PI,SI}$. The opposite signs of birefringence for the two kines of lamellae cause the total orientational birefringence to be small. It is conceivable that the total orientational birefringence

Table IV
Calculated Domain Parameters and Birefringence for SI and SIS Block Polymers

		domain parameters, nm				optical properties				
polymer	$M_n \times 10^{-3}$, S/I or S/I/S	T_{PS}	D	t	N, nm^{-3}	$\Delta n_{PS} \times 10^4$	$\Delta n_{PI} \times 10^4$	$\Delta_{orient} \times 10^5$	$\Delta_{form} \times 10^3$	$\Delta n_t \times 10^3$
SI-1	25/25	16.6	35.5	2.49	1.19×10^{-2}	−2.62	1.09	−15.2	−1.44	−1.59
SI-2	50/50	25.5	54.5	2.07	5.93×10^{-3}	−1.82	0.734	−10.8	−1.49	−1.60
SI-3	100/100	38.1	81.4	1.67	2.97×10^{-3}	−1.10	0.439	−6.63	−1.52	−1.59
SI-4	250/250	63.1	134.8	1.18	1.19×10^{-3}	−0.513	0.202	−3.11	−1.55	−1.58
SIS-1	25/50/25	16.8	35.9	2.31	5.93×10^{-3}	−2.73	1.65	−10.8	−1.46	−1.57
SIS-2	50/100/50	25.8	55.1	1.93	2.97×10^{-3}	−1.89	1.02	−8.71	−1.50	−1.59
SIS-3	100/200/100	38.5	82.3	1.45	1.48×10^{-3}	−1.15	0.583	−5.62	−1.53	−1.59
SIS-4	250/500/250	62.3	133.2	1.17	5.93×10^{-4}	−0.494	0.247	−2.48	−1.55	−1.57

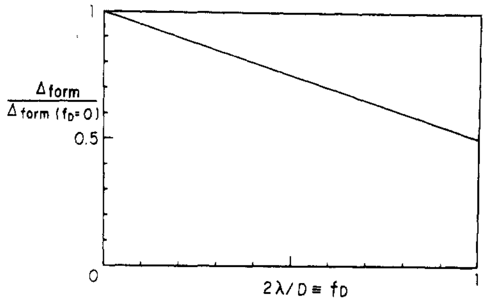

Figure 9. Form birefringence of a pseudo-two-phase system as a function of interfacial volume fraction $f_D = 2\lambda/D$. The form birefringence relative to the ideal two-phase system $\Delta_{\rm form}$ (f_D = 0) is plotted for the case where $\phi_A(z)$ is given by eq III-13. $\Delta_{\rm form}$ was calculated from eq III-20b.

may become quite large for systems in which the two block chains have large segmental anisotropies with same sign.

Figure 9 shows the effect of the interface on form birefringence for the case where the polystyrene and polyisoprene lamellae are optically isotropic and the density profile across the interface is given by eq III-13. In this case $\Delta_{\rm form}$ is equal to Δn_t in eq III-20 with $f_A = f_B = (1 - f_D)/2$, $n_{Ax} = n_{Az} = \bar{n}_A$, and $n_{Bx} = n_{Bz} = \bar{n}_B$, where f_D is the volume fraction of the interface ($f_D = 2\lambda/D$). It is clearly seen that the absolute value of the form birefringence decreases with increasing volume fraction of the interface. When $2\lambda/D = 1$, the form birefringence becomes as low as half of the value with zero interfacial thickness, i.e., when $2\lambda/D = 0$.

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Uniformity of Microdomain Size of Block Polymers As Compared with Uniformity of Their Molecular Weights

Takeji Hashimoto,* Hideaki Tanaka, and Hirokazu Hasegawa

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received December 11, 1984*

ABSTRACT: The uniformity of the microdomain sizes of polystyrene–polyisoprene block polymers is found to be much higher than the uniformity of molecular weights of the block polymers comprising the microdomains; the heterogeneity index for the distribution of microdomain size ($\bar{D}_w/\bar{D}_n$) is typically 1.001, while that for the molecular weight distribution of the block polymers studied ($\bar{M}_w/\bar{M}_n$) is typically 1.1 ($\bar{D}_w$ and $\bar{D}_n$ are the weight- and number-average domain identity periods and $\bar{M}_w$ and $\bar{M}_n$ are the corresponding average molecular weights). This implies that the molecules are packed in the domain space so as to compensate their molecular weight distributions.

Introduction

In this paper we are concerned with uniformity of the microdomain sizes of typical block polymers such as polystyrene–polyisoprene block polymers as compared with that of the molecular weights of the polymers comprising the microdomains. We wish to emphasize that the uniformity of the former is higher than that of the latter (e.g., $\bar{D}_w/\bar{D}_n \simeq 1.001$ and $\bar{M}_w/\bar{M}_n \simeq 1.1$; see eq 10 and 11) and that the molecules are packed in the domain space so as to compensate for the molecular weight and compositional distributions.

It is well-known that block polymers exhibit microdomain structures in the strong segregation limit. The size of these microdomains has to be closely related to the size of individual molecules,[1-9] the physics of which originates from the incompressibility of polymeric liquids and solids.[10,11] Incompressibility demands that the segments uniformly fill all space of the microdomains and their densities in the respective microphases should be equal to those in the corresponding homopolymers. Thus the molecules in the domain space have to adjust their dimensions and conformations according to the size of the microdomains as schematically shown in Figure 1. For example, if the domain space composed of A molecules expands from D_{A1} to D_{A2}, the A block molecules also have to expand their dimensions (with the root-mean-square end-to-end distance from $\langle Z_{A1}{}^2\rangle^{1/2}$ to $\langle Z_{A2}{}^2\rangle^{1/2}$) in the direction perpendicular to the interface in order to satisfy the demands of uniform space filling with the segments. The expansion of the molecules has to be accompanied by a decrease of the average intermolecular distance from a_1 to a_2 in order to satisfy the demands invoked by incompressibility. The equilibrium domain size is the one which minimizes the free energy of the system.

It has been found both theoretically and experimentally that the microdomain size (R_A) and the identity period (D)

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