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Theory of Block Copolymers. I. Domain Formation in A–B Block Copolymers

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Synopsis

Microphase separation occurs in many block copolymers to give domain structures. In this first paper in a series dealing with domain formation and the consequences thereof, a theory is presented for the formation of spherical domains in A–B block copolymers. The theory establishes criteria for the formation of domains and their size in terms of molecular and thermodynamic variables. It is shown that the considerable loss in configurational entropy due to the constraints on the spacial placement of chains in a domain structure requires that the critical block molecular weights required for domain formation are many-fold greater than required for phase separation of a simple mixture of the component blocks. The relation between domain radius R and molecular dimensions is obtained from the requirement that space in the domain must be filled with a constant density of segments. Segment densities are evaluated from solutions of the diffusion equation, treating the constraints on chain placement as boundary value problems. This gives the relationship $R = 4/3 \langle L^2 \rangle^{1/2}$, where $\langle L^2 \rangle^{1/2}$ is the root-mean-square end-to-end chain length. Because of chain perturbations in a domain system, $\langle L^2 \rangle^{1/2}$ is larger than the unperturbed value $\langle L^2 \rangle_0^{1/2}$ normally expected for bulk polymers. A means to evaluate the perturbations is shown. The agreement between the predictions of the present theory and the limited published experimental information appears quite satisfactory.

INTRODUCTION

A remarkable increase in interest in block copolymers has occurred in the past few years, probably inspired by the realization that new types of technologically important materials are possible by use of block copolymers, e.g., thermoplastic elastomers (1). The thermally reversible, physical "crosslinking" that occurs in the thermoplastic elastomers is generally recognized to result from a unique type of microscopic phase separation in which complete aggregation of the separate phases does not occur, in contrast to ordinary phase separation. The formation, size, shape, etc., of the microscopic phase regions, which will be called

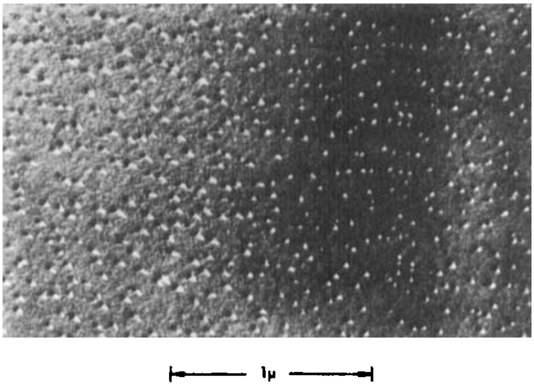

Fig. 1. Electron micrograph of S-I film.

domains, are functions of such molecular properties of a block copolymer as the nature of the block components, molecular weights, distribution of the blocks, etc. This paper is the first in a series concerning block copolymers in which theories of domain formation and the consequences thereof will be developed.

In this paper, we confine our attention to the simplest type of block copolymer, namely an A–B type in which the molecular weight of one component, A, is much less than that of the other. This stipulation ensures that the A-component will be the dispersed, domain-forming component and also fixes the domain shape. Our theoretical work on domain shapes (to be presented in a subsequent paper) and experimental evidence both show that the equilibrium domain shape is spherical when the component block molecular weights are greatly different and the components are amorphous. Other shapes, e.g., planar, cylindrical, etc., can, however, be the stable forms under other conditions (2,3). Figure 1 shows an example of the spherical domains formed from an amorphous block copolymer in which the block molecular weights are greatly different. This figure is an electron micrograph of a very thin film of a styrene-isoprene (S-I) block copolymer of 15,000–75,000 block molecular weights. The film was prepared by evaporation of a very dilute benzene solution of the block copolymer, followed by shadowing, and shows spherical domains of polystyrene projecting above the surface of the film. The domain diameters are approximately 260 Å.

MODEL AND APPROACH

The model domain structure to be treated in this paper is shown in Figure 2 (in which only a few of the chains that make up a domain are shown). The domain is assumed to be spherical, consisting predominately of the A component and is imbedded in a matrix of the B compo-

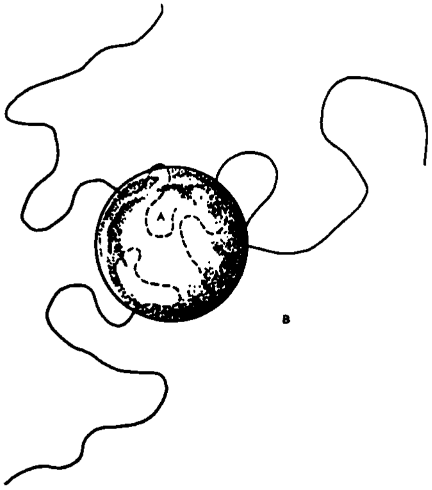

Fig. 2. Model domain structure.

nent. It can be shown that the "phases" that form in a domain system will be essentially pure, just as with phase separation of two mixed homopolymers in which the phases that form are almost pure homopolymers. Only at the domain surface will there be a thin region in which A and B segments remain mixed. This region will contain the junction between the A and B blocks. The surface of a domain is relatively well defined, as confirmed by electron microscopy.

The following additional assumptions are made for simplicity; none are thought to be unduly restrictive nor unrealistic: (a) random-flight statistics are applicable, with perturbations allowed for by the use of the familiar isotropic chain expansion parameter α (4), (b) A and B segments are equal in size, (c) the polymers are amorphous, and (d) the block molecular weights of each component are uniform.

The basic difference in a treatment of block copolymers are opposed to simple homopolymers or random copolymers is the additional complication that arises from the constraints that restrict the components to separate regions of space, i.e., in the domain structure the A component is constrained to stay within the domain and the B component to stay out. These constraints, of course, restrict the number of configurations available to the chain with a concomitant reduction in the entropy of the system. Rather than evaluate the number of configurations (and hence the entropy) with these constraints by the usual lattice-type model, we avoid this almost hopelessly complex approach by treating the constraints as a boundary value problem, using the diffusion equation to generate the applicable chain statistics (5,6).

DOMAIN SIZE

It has been mentioned that the size of a domain is fixed by molecular chain dimensions. The reason is obvious as Figure 2 will show. If the A–B junction is fixed near the domain surface, the domain cannot grow without limit since then space near the center of the domain could not be filled with A segments. A vacuole or region of low density is a region of very high energy and will not occur. In fact, we take as the criterion to evaluate domain sizes in terms of molecular variables that the density of segments in the domain be constant. In the use of this criterion, we are assuming that of the terms relating the free energy of the system to domain size the term associated with density is of overriding importance.

We require an expression for the (number) density of segments within the domain as a function of the ratio of domain size to molecular chain dimensions. That ratio which gives the most constant density of segments will then be taken as the predicted relationship between domain sizes and molecular dimensions.

We obtain the segment number density in the domain by first solving the diffusion equation for the probability $W(n; \bar{r}, \bar{r}', R)$ of finding the free end of a subchain of n elements at $\bar{r}$ when the first end is fixed at $\bar{r}'$ and all segments are constrained to stay within the spherical region of radius R. The origin of the coordinate system will correspond to the center of a domain. The number density $\rho(\sigma_A; \bar{r}, \bar{r}', R)$ of an A chain having a total of σ_A segments is then obtained by summing $W(n; \bar{r}, \bar{r}', R)$ over n, i.e.,

$$\rho(\sigma_A; \bar{r}, \bar{r}', R) = \sum_{n=1}^{\sigma_A} W(n; \bar{r}, \bar{r}', R) \tag{1}$$

The diffusion equation in the form applicable to the present problem is

$$\frac{\partial W(n; \bar{r}, \bar{r}', R)}{\partial n} = \frac{l^2}{6} \nabla^2 W(n; \bar{r}, \bar{r}', R) \tag{2}$$

where l is the length of a statistical segment. The boundary condition for this problem is $W(n; R, \bar{r}', R) = 0$, which removes from the ensemble of configurations those in which any segment of the chain has reached R, i.e., the surface is an absorbing barrier. The remaining configurations are given proper statistical weight by renormalization (5).

Equation (1) gives the number density of a single chain in the domain space. The total segment density $\Omega(\sigma_A; \bar{r}, R)$ is obtained by summing at $\bar{r}$ the number densities $\rho(\sigma_A; \bar{r}, \bar{r}', R)$ of the many chains that make up a domain. This summation requires specification of the placement $\bar{r}'$ of each chain origin. We have carried out the summation for 24 chains whose origins were equidistant from one another on the surface of a sphere, with results showing that the angular variation in total segment density becomes very small for this packing density of chains because of overlap of adjacent molecules. Since the packing density in a domain will, in general, be even greater than that used here, we may ignore the angular variables and consider only the radial variation in total segment density. With this simplification, the total number segment density Ω at r becomes from eqs. (1) and (2)

$$\Omega(\sigma_A; r, R) = \frac{\eta_A}{4R^3} \sum_{n=1}^{\sigma_A} \frac{\sum_{m=1}^{\infty} \frac{R}{r} \sin\left(\frac{m\pi r}{R}\right) \sin\left(\frac{m\pi r'}{R}\right) \exp\{-\sigma_A l^2 m^2 \pi^2/6R^2\}}{\sum_{p=1}^{\infty} (-1)^p \frac{1}{p} \sin\left(\frac{p\pi r'}{R}\right) \exp\{-\sigma_A l^2 p^2 \pi^2/6R^2\}} \tag{3}$$

where η_A is the number of A chains in the domain.

Equation (3) has been evaluated with an IBM 7040 computer for various values of r/R, r′/R, and $\sigma_A l^2/R^2$ and for $\sigma_A = 20$ and $\sigma_A = 100$ statistical elements. Normalized chain densities $\Omega' = (4R^3/\sigma_A\eta_A)\Omega$ were found to be independent of these values of σ_A. Since our domain model places the origins r′ of the A chains near the domain surface, we have restricted r′/R to the range 0.8–1.0. For r′ R > 0.9, segment densities were found to be negligibly dependent on the value chosen for r′/R. Since we shall later take r′/R to be greater than 0.9, we shall show results for only one value of r′/R, namely 1.0, to avoid clutter in the figure.

Figure 3 shows the relative segment densities $\Omega'(\sigma_A; r, R) = (4R^3/\sigma_A\eta_A)\,\Omega(\sigma_A; r, R)$ as a function of the radius r/R and for several values of $(\sigma_A l^2)^{1/2}/R$, i.e., the ratio of the rms end-to-end chain distance of a free chain to the domain radius R. Also shown in the figure is a curve giving the desired relative density of segments that would be obtained if the density of segments in a sphere were constant to r/R = 0.9 and then linearly decreased to zero at r/R = 1.0. The region 0.9 < r/R < 1.0 is taken to represent the interfacial region in which A and B segments are intermixed, with the A segment density decreasing from its uniform value characteristic of the "pure" A interior of the domain to zero at the surface. The B segment density, of course, increases in this model from zero at r/R = 0.9 to its "pure" value at r/R = 1.0. The particular value r′/R = 0.95, which gives the thickness $\Delta R/R = 0.1$ to the interfacial region, is used here to be consistent with a later choice, but the value has little influence on the present evaluation of the relationship between domain size and molecular dimensions.

In Figure 3, we see that the present model does not give the desired constant density of segments throughout the domain for any value of $(\sigma_A l^2)^{1/2}/R$. Obviously in a real domain there must be chain perturba-

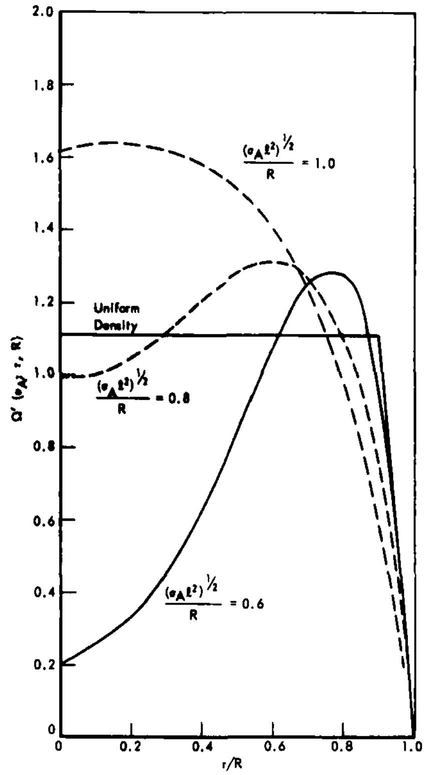

Fig. 3. Relative density of segments.

tions which smooth out these variations in segment densities that occur for purely random-flight statistics. The problem is now to choose that value of $(\sigma_A l^2)^{1/2}/R$ which minimizes the chain perturbations or movement of segments required to obtain constant segment density. A rigorous solution of this problem would be quite difficult, although possible by using the diffusion equation modified by a biasing potential. Rather than introduce this complexity, we take a simplified approach and minimize the absolute deviations from the desired density Ω'_0 over the domain, i.e., the expression

$$\int_{r/R=0}^{1} |\Omega'(\sigma_A;\, r,\, R) - \Omega'_0| \left(\frac{r^2}{R^2}\right) d(r/R)$$

is minimized as a function of $(\sigma_A l^2)^{1/2}/R$. The absolute value of the density difference is minimized rather than, say, the mean-square difference, since the number of segments that must be moved achieve constant density is directly proportional to the density difference. The above function has a minimum for $(\sigma_A l^2)^{1/2}/R \simeq 0.75$, which is now adopted as giving the desired relationship between domain radii and chain dimensions, i.e., $R = 4/3\ (\sigma_A l^2)^{1/2}$. However, this expression is still not adequate to enable prediction of domain radii in terms of molecular weights, even though the constant K in the relationship $<\sigma l^2>_0^{1/2} = KM^{1/2}$ between unperturbed rms end-to-end chain dimensions for a bulk polymer and molecular weight is known. The domain system has additional chain perturbations which do not exist in a bulk polymer and which must be evaluated before predictions of domain size can be made. If the ratio of perturbed to unperturbed chain dimensions is represented by α (4), then we may write

$$R = \frac{4}{3}\ (\sigma_A l^2)^{1/2} = \frac{4}{3}\ \alpha\ (\sigma_A l^2)_0^{1/2} = \frac{4}{3}\ \alpha\ KM_A{}^{1/2} \tag{4}$$

A method to evaluate α is presented in the following section which then allows prediction of R as a function of M_A (if K is known).

THERMODYNAMICS OF A–B BLOCK COPOLYMERS

The free energy difference ΔG between a random mixture of block copolymer molecules and the domain system can be separated into several entropic and enthalpic contributions. First, the restriction on the placement of the A–B junctions to the interfacial regions of domains decreases the entropy relative to random placement. This entropy decrease will be termed the "placement entropy" difference ΔS_p and will be evaluated by a lattice model. Second, the constraints on the placement of the A and B segments in the domain system (to the inside and outside regions of the domains, respectively) also reduces the entropy of the domain system relative to a random mixture. This entropy difference will be termed the "restricted volume" entropy difference ΔS_v and will be evaluated by generation of the applicable chain statistics with the diffusion equation. Third, the perturbation of chain dimensions in the domain system from their random-flight values also decreases the entropy. This will be called the "elasticity entropy" difference ΔS_{el} and will be taken from standard elasticity theory.

The enthalpy difference ΔH between the domain and random mixture systems will be taken as the heat of mixing of a simple mixture of A and B molecules, i.e., the fact that the component blocks are joined together in the block copolymer is ignored. In a random mixture of A–B molecules, the effect of the A–B junction on the relative number of like- and unlike-segment interactions can hardly extend more than a few segments away from the junction. The errors introduced by ignoring this effect are trivial compared to those inherent in the pair-interaction model (4) used to evaluate ΔH.

The "residual" interaction of the A and B segments at the domain surface will be treated as a surface free energy G_s and characterized by an interfacial tension γ. This interaction energy could, in principle, also be obtained from the pair-interaction model, but would require knowledge of the distribution of A and B segments in the interfacial region. It appears simpler to treat the interaction as a surface energy.

Placement Entropy Difference ΔS_p

We evaluate here the entropy difference between the random placement of one segment per molecule (the junction segment) on a lattice and the placement of the segment on a lattice of domains in which the segment is restricted to a domain surface. It is emphasized that at this point we are concerned with only one segment per molecule and are not concerned with the configurational entropy of the remaining segments.

A random mixture of N_{AB} copolymer molecules having σ_A and σ_B A and B segments, respectively, has $N_{AB}(\sigma_A + \sigma_B)$ total lattice sites available. The number of possible sites available for the first segment of the i^{th} molecule after $i - 1$ molecules have been placed on the lattice is $(N_{AB} - i + 1)(\sigma_A + \sigma_B)$. Thus the total number of distinctive ways Ω_1 of placing one segment each of N_{AB} identical molecules on the lattice is

$$\Omega_1 = \frac{1}{N_{AB}!} \prod_{i=1}^{N_{AB}} (N_{AB} - i + 1)(\sigma_A + \sigma_B) = (\sigma_A + \sigma_B)^{N_{AB}}$$

and the entropy S_1 associated with Ω_1 is $S_1 = N_{AB}k \ln(\sigma_A + \sigma_B)$.

In the domain system, we assume that the interfacial region of a domain is divided into η cells, where η is the number of molecules in a domain, and only one AB junction will occupy the lattice sites within a cell, i.e., multiple occupancy by the origins of the A and B chains (their junction) is prohibited. This assumption appears reasonable since the density of segments from a given molecule is greatest near the chain origin and thus to maintain constant density the origins will tend to be as far away from one another as possible. If the junction segment is restricted to an interfacial region of thickness ΔR, then each molecule added to the system will fill $3\sigma_A\,\Delta R/R$ sites. This follows from the number of lattice sites on a domain surface $4\pi R^2\,\Delta R/v$, where v is the volume required for a segment, and the domain volume $4/3\ \pi R^3 = \eta\sigma_A v$. In this last equation, we have neglected the small contribution of B segments to the domain volume. After $i - 1$ molecules have been placed in domains, the number of sites available on the domain surfaces to place the i^{th} molecule is merely $(N_{AB} - i + 1)(3\sigma_A\,\Delta R/R)$. If the probability of placing a junction segment on a lattice site within a cell is equivalent for all sites, then the number of ways Ω_2 of placing the junction segments of N_{AB} identical molecules on the domain surfaces becomes

$$\Omega_2 = \frac{1}{N_{AB}!} \prod_{i=1}^{N_{AB}} (N_{AB} - i + 1)(3\sigma_A \, \Delta R/R) = (3\sigma_A \, \Delta R/R)^{N_{AB}}$$

and the entropy becomes

$$S_2 = kN_{AB} \ln (3\sigma_A \, \Delta R/R) \tag{5}$$

This probably represents an upper limit to the placement entropy on the domain surface since it appears likely that our assumption of equal probability of all sites within a cell overestimates Ω_2 because of the tendency of the chain origins to avoid one another. The lower limit of Ω_2 is of the order of one representing the extreme case where the junction segments are fixed at specific sites on the surface. It will also be noted that we have neglected the minor contribution to the entropy in the domain system arising from the possible arrangements of domains in space. It is easy to show that the entropy gained from this source is of the order of k/η per molecule, and is negligible since η is a relatively large number for systems of interest.

The placement entropy difference ΔS_p equals $S_2 - S_1$ or

$$\Delta S_p = kN_{AB} \ln \frac{3\sigma_A \, \Delta R}{(\sigma_A + \sigma_B)R} \tag{6a}$$

when the lattice sites in a cell are equally accessible and

$$\Delta S_p = - kN_{AB} \ln (\sigma_A + \sigma_B) \tag{6b}$$

as the lower bound when only one site per cell can be occupied by the junction.

Restricted Volume Entropy Difference ΔS_v

In the preceeding section, the entropy change associated with the nonrandom placement (i.e., on the domain surface) of the junction segment was evaluated without regard to the configurational statistics of the remaining segments of the chain. In this section we consider the remaining segments and determine the change in entropy resulting when constraints are applied to keep the A segments within the domain and the B segments outside. As has been mentioned previously, the diffusion equation offers a means to evaluate this entropy change; the constraints become boundary values in the solution. In the present case, since we wish to remove those configurations which have chain elements across the domain boundary, the boundary is taken as a completely absorbing barrier. For the A chains, the diffusion equation gives (7) the probability $Q(\sigma_A; \bar{r}, \bar{r}', r < R)$ (per unit volume) that the second (free) end of the chain will be found at $\bar{r}$ when the fixed end is at $\bar{r}'$ and all segments are at $r < R$ as

$$Q(\sigma_A; \bar{r}, \bar{r}', r < R) =$$

$$\sum_{m=0}^{\infty} \sum_{\beta} \frac{\exp\{-\sigma_A l^2 \beta^2/6\}\, j_m(\beta r)\, j_m(\beta r')\,(2m+1)\, P_m(\mu)}{[j_m'(\beta R)]^2}$$

where $j_m(z)$ is the spherical Bessel function of order m, $P_m(\mu)$ is the Legendre polynomial of order m, $\mu = \cos\theta$, $j_m'(z) = dj_m(z)/dz$, and the β's are the positive roots of $j_m(\beta R) = 0$.

Correspondingly, for the B chains the probability that the free end of the chain is at $\bar{r}$ when the fixed end is at $\bar{r}'$ and all segments are at $r > R$ is

$$Q(\sigma_B; \bar{r}, \bar{r}', r > R) = \frac{1}{4\pi r^{1/2} r'^{1/2}} \sum_{m=0}^{\infty} (2m+1) Pm(\mu) \cdot$$

$$\int_0^{\infty} \frac{C_{m+1/2}(ur)\, C_{m+1/2}(ur')\, \exp\{-\sigma_B\, l^2\, u^2/6\}}{J^2_{m+1/2}(uR) + Y^2_{m+1/2}(uR)}\, du$$

where $J_m(z)$ and $Y_m(z)$ are Bessel functions of the first and second kinds, respectively, of order m, and

$$C_{m+1/2}(z) = J_{m+1/2}(z)\, Y_{m+1/2}(uR) - Y_{m+1/2}(z)\, J_{m+1/2}(uR)$$

In the above equations the free ends of the chains are at the particular locations $\bar{r}$. Since in the domain system the free A chain end may be anywhere within the domain and the free B end may be anywhere outside of the domain, the above equations are integrated over the accessible volume to remove the constraints on the free ends. Thus, the desired probability $P(\sigma_A; r', r < R)$ that all σ_A chain elements are inside the domain when the chain origin is at r' becomes

$$P(\sigma_A; r', r < R) = \int Q(\sigma_A; \bar{r}, \bar{r}', r < R)\, d^3\bar{r}$$

$$= 2 \sum_{i=1}^{\infty} (-1)^{i+1}\, j_0(i\pi r'/R)\, \exp\{-i^2 \pi^2 \sigma_A l^2/6R^2\} \qquad (7a)$$

The probability $P(\sigma_B; r', r > R)$ that all σ_B chain elements are outside the domain becomes

$$P(\sigma_B;\, r',\, r > R) = \int Q(\sigma_B;\, \bar{r},\, \bar{r}',\, r > R)\, d^3\bar{r}$$

$$= 1 - \frac{R}{r'} \operatorname{Erfc}\left[\left(\frac{3}{2\sigma_B l^2}\right)^{1/2} (r' - R)\right] \quad (7b)$$

where Erfc (z) = 1 − Erf (z) and Erf (z) is the error function.

The loss in entropy due to restricted volume ΔS_v is from eqs. (7a) and (7b)

$$\Delta S_v = N_{AB} k\, [\ln P(\sigma_A;\, r',\, r < R) + \ln P(\sigma_B;\, r',\, r > R)] \quad (8)$$

and is easily evaluated given molecular sizes, domain sizes, and the placement r′ of the origins (junction segment) of the A and B chains.* Results are shown in Table I for various values of r′/R and for various ratios of the molecular sizes of the A and B blocks. For the domain radius R we have used $R = (4/3)\, (\sigma_A l^2)^{1/2}$ as established in a previous section.

Elasticity Entropy Difference ΔS_{el}

The positive interfacial free energy in the domain system will tend to cause an increase in domain dimensions. However, the increase in dimensions can occur only if the average dimensions of chains in the domain are increased. This increase in dimensions over the unperturbed random flight values can be characterized by α (4), the ratio of perturbed to unperturbed end-to-end chain distances, and gives an entropy decrease (4) (for chains that have one free end) of

$$\Delta S_{el} = -3/2\; N_{AB} k\, (\alpha^2 - 1 - 2 \ln \alpha) \quad (9)$$

In an earlier section dealing with domain sizes, it was noted that other chain perturbations must occur if a constant density of segments in the domain is to be attained. We neglect the entropy decrease due to these perturbations for two reasons: (a) the fraction of the total number of

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*It will be noted that the same R is used in the steps leading to eqs. (6) and (7) for both the A and B chains. Actually, in our model, the values of R used for the two types of chains should differ by ΔR, where ΔR is the thickness of the interfacial region ($\Delta R \simeq 2\,|R - r'|$). However, electron micrographs of domains in block polymers show that the interface is relatively sharp, indicating that ΔR/R is small. The same R may then be used for both chains and also identified as the domain radius. In obtaining eq. (7b), we have neglected the volume excluded to a B chain by domains surrounding the one being considered. This can be shown to introduce a negligible error for the present model.

TABLE I

Restricted Volume Entropy Decrease

r'/R	$P(\sigma_A;\, r',\, r < R)$	$\dfrac{\sigma_B l^2}{\sigma_A l^2} \sim \dfrac{M_B}{M_A}$	$P(\sigma_B;\, r',\, r > R)$	$\Delta S_v/N_{AB}k$
0.90	0.0914	1	0.284	−3.7
		6	0.175	−4.2
		10	0.158	−4.3
		∞	0.100	−4.7
0.95	0.0440	1	0.142	−4.4
		6	0.0875	−4.8
		10	0.079	−4.9
		∞	0.050	−5.4

segments that must move to achieve constant density and the movement required (perturbation) are both small and (b) a satisfactory treatment of this (small) entropy decrease is not apparent.

Enthalpy Change ΔH

It has been mentioned that the enthalpy change for domain formation from a random mixture of block copolymer molecules will be taken as the negative of the heat of mixing of a simple mixture of the component blocks of the block copolymer. The pair-interaction model then gives ΔH as

$$\Delta H = N_{AB}kT\chi\phi_A \tag{10}$$

where χ is the Flory interaction parameter (4) and ϕ_A is the volume fraction of A segments, $\phi_A = \sigma_A/(\sigma_A + \sigma_B)$.

Surface Free Energy

If the residual interaction of the A and B segments at the domain interface is characterized by an interfacial energy γ, the total surface free energy of the domain system becomes $G_s = \eta_d 4\pi R^2\gamma$, where η_d is the total number of domains. Using our previously established relationship between R and $(\sigma_A l^2)^{1/2}$, i.e., $R = (4/3)\,(\sigma_A l^2)^{1/2} = (4/3)\,\alpha K M_A^{1/2}$, we obtain

$$G_s = \frac{9}{4}\,\frac{N_{AB}M_A{}^{1/2}\gamma}{\bar{A}\,\rho\alpha\,K} \tag{11}$$

where $\bar{A}$ is Avogadro's Number and ρ is the density.

Free Energy of Domain Formation ΔG_d

The free energy change associated with the formation of domains from a random mixture of A–B molecules is from eqs. (6a), (8), (9), (10), and (11).

$$\begin{aligned}\Delta G_d/N_{AB}kT &= \ln\left(\frac{\sigma_A + \sigma_B}{3\sigma_A}\right)\left(\frac{R}{\Delta R}\right) - \ln P(\sigma_A;\, r',\, r < R)\\ &\quad - \ln P(\sigma_B;\, r',\, r > R) + \frac{3}{2}\,(\alpha^2 - 1 - 2\ln\alpha) + \frac{9M_A{}^{1/2}\gamma}{4\alpha K\bar{A}\rho kT}\\ &\quad - \chi\sigma_A/(\sigma_A + \sigma_B)\end{aligned} \tag{12}$$

where we have used the expression for the minimum placement entropy difference, i.e., eq. (6a).

The chain expansion parameter α appears only in the terms relating to the interfacial energy (tending to increase α) and the elastic free energy (tending to decrease α). The equilibrium value α_m is obtained by differentiation and is

$$\alpha^3{}_m - \alpha_m = \frac{3}{4}\,M_A{}^{1/2}\gamma/Kk\rho\bar{A}T \tag{13}$$

which then leads to the minimum value of ΔG_d as

$$\begin{aligned}(\Delta G_d/N_{AB}kT)_{min} &= \ln\left(\frac{\sigma_A + \sigma_B}{3\sigma_A}\right)\left(\frac{R}{\Delta R}\right) - \ln P(\sigma_A;\, r',\, r < R) -\\ \ln P(\sigma_B;\, r',\, r > R) &+ \frac{9}{2}\,(\alpha^2{}_m - 1) - 3\ln\alpha_m - \chi\sigma_A/(\sigma_A + \sigma_B)\end{aligned} \tag{14}$$

In order to evaluate α_m, we require values of the interfacial tension γ. As far as the author is aware, only one report of the interfacial tensions between pairs of polymers has appeared in the literature (8). The polymer pairs and the results reported were nylon–polystyrene (5–6 dynes/cm), nylon–polyethylene (6.4 dynes/cm), and polyethylenephthalate–polyethylene (15 dynes/cm). In view of the lack of data on other systems of interest, we shall merely show α_m for several representative val-

TABLE II

Equilibrium Expansion Factors α_m

M_A	α_m		
	$\gamma = 1$ dyne/cm	$\gamma = 5$ dynes/cm	$\gamma = 15$ dynes/cm
10^3	1.04	1.18	1.40
10^4	1.12	1.43	1.86
3×10^4	1.20	1.62	2.16
10^5	1.31	1.87	2.56

ues of γ. Table II shows such α_m data for $\gamma = 1$, 5, and 15 dynes/cm for various values of M_A. In the use of eq. (13), we have taken T = 400°K, $\rho = 1$ g/cm^3 and $K = 7.5 \times 10^{-9}$ (an average value from a number of investigators (9–13) for polystyrene).

PREDICTED RADII OF POLYSTYRENE DOMAINS

With the data in Table II and with eq. (4), we may predict the size of domains as a function of molecular weight. Figure 4 shows such results for polystyrene domains (the results shown are calculated for 400°K but they are not very sensitive to temperature). The curves are nearly linear on a log–log plot, and give the following values of the exponent β in an equation of the type $R = kM^{\beta}$ as a function of γ.

γ, dynes/cm	β
1	0.55
5	0.60
15	0.65

There are few data concerning domain sizes in the literature and no data concerning γ for those polymers for which domain sizes have been reported. Hence, the direct comparison of theory and experiment is impossible at the present time. However, it is still of interest to see if the theoretical results agree with experiment for reasonable values of γ. The radii of the domains shown in Figure 1 are approximately 130 Å. This size would be predicted if γ were slightly less than 1 dyne/cm, a not unreasonable value for this system since the domains shown were formed in the presence of a third component which was a good solvent for both component blocks and hence might be expected to lead a low value for the interfacial free energy. However, this "agreement" may

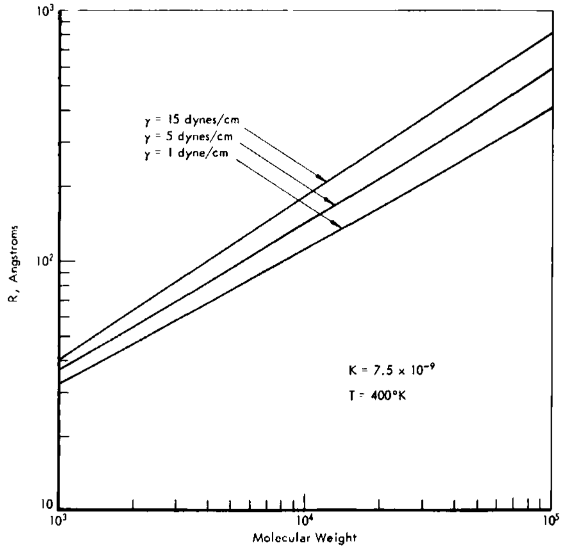

Fig. 4. Predicted polystyrene domain radii as a function of molecular weight.

be somewhat fortuitous since this theory does not treat the possible effects on domain size of the third (solvent) component that is later removed.

CRITERION FOR DOMAIN FORMATION

It is, of course, necessary that ΔG_d be negative if domains are to form. Thus, from equation (14) the criterion for domain formation is

$$\chi\sigma_A/(\sigma_A + \sigma_B) > \ln\left(\frac{\sigma_A + \sigma_B}{3\sigma_A}\right)\left(\frac{R}{\Delta R}\right) - \ln P(\sigma_A;\, r',\, r < R)$$

$$- \ln P(\sigma_B;\, r',\, r > R) + \frac{9}{2}(\alpha^2{}_m - 1) - 3 \ln \alpha_m \qquad (15)$$

The left-hand side of this inequality is almost directly proportional to the molecular weight of the A block (when $\sigma_B >> \sigma_A$, as assumed), while the right-hand side is only a slowly varying function of molecular weight. Thus, there will be a critical molecular weight of the A block above which the inequality is satisfied and domains will form. However, if predictions are to be made of critical molecular weights, values of χ (as well as γ, K, etc., must be known). Unfortunately, there are few literature data of χ for pairs of polymers and the few results that have been given differ greatly among themselves. For example, two results have been reported for the polybutadiene–polystyrene system (14,15). The reported values of $\chi/\bar{V}$, where $\bar{V}$ is the molar volume, differ by a factor of more than 200, and are obviously of little value in making predictions. In order to circumvent this problem, we shall compare the ratios of predicted critical molecular weights for domain formation with predicted critical molecular weights for phase separation of a simple mixture of A and B homopolymers. In this way, we eliminate the necessity that χ be known.

For a simple mixture of homopolymers, Flory-Huggins theory (4,16) gives the free energy of mixing as

$$\Delta G_m = kT(n_A \ln \phi_A + n_B \ln \phi_B + \chi n_B \phi_A) \tag{16}$$

where n_A and n_B are the numbers of A and B molecules, respectively. Since we wish to compare phase separation under conditions which are similar to those that occur in domain formation (equal numbers of A and B molecules) we take $n_A = n_B$ and find that $\Delta G_m = 0$ when

$$\chi\sigma_A/(\sigma_A + \sigma_B) = \ln \left\{\frac{(\sigma_A + \sigma_B)^2}{\sigma_A\, \sigma_B}\right\} \tag{17}$$

If we now divide eq. (15) by eq. (17), we find the critical ratio of $\sigma_A{}^d$ for domain formation to $\sigma_A{}^m$ for phase separation of the simple mixture to be

$$\frac{\sigma_A{}^d}{\sigma_A{}^m} = \frac{\ln\left(\frac{\sigma_B}{3\sigma_A{}^d}\right)\left(\frac{R}{\Delta R}\right) - \ln P(\sigma_A;\, r',\, r < R) - \ln P(\sigma_B;\, r',\, r > R)}{\ln(\sigma_B/\sigma_A{}^m)} + \frac{\frac{9}{2}(\alpha_m{}^2 - 1) - 3 \ln \alpha_m}{\ln(\sigma_B/\sigma_A{}^m)} \tag{18}$$

where we have taken $\sigma_B \gg \sigma_A$. In Table II, we see that for molecular weights M_A below about 10^4 and for γ less than 5 dynes/cm, α_m will be less than about 1.5. Thus, under these conditions, the term $(9/2)(\alpha_m{}^2 - 1) - 3 \ln \alpha_m$ will vary between 0 and 4.41. In Table I we see that $\ln P(\sigma_A;\, r',\, r < R) + \ln P(\sigma_B;\, r',\, r > R)$ ($\equiv \Delta S_v/N_{AB}k$) is not a sensitive function of the ratio σ_B/σ_A and for $\Delta R/R = 0.10$ ($r'/R = 0.95$) their sum may be taken as -5.0. With these values eq. (18) becomes after collecting numerical values

$$\frac{\sigma_A{}^d}{\sigma_A{}^m} = \frac{\ln(\sigma_B/\sigma_A{}^d) + (6.3 - 10.7)}{\ln(\sigma_B/\sigma_A{}^m)} \tag{19}$$

where the term (6.3 – 10.7) represents a range of values arising when γ is between 0 and 5 dynes/cm. For σ_B in the range $10^2 - 10^4$ ($M_B \approx 10^4 - 10^6$), eq. (19) indicates that the ratio of critical molecular weights will be between about 2.5 – 5 (and would be even larger for larger values of γ). The much larger molecular weight of the A block required for domain formation than for simple phase separation is, of course, the consequence of the additional configurational constraints and interfacial energies of a domain system.

In his studies on the miscibility of polystyrene and polybutadiene, Paxton (15) reported that equal weight mixtures of polystyrene of $M_n = 2720$ and polybutadiene of $M_n = 1100$ (both polymers unfractionated) were not miscible. Assuming the applicability of the Flory-Huggins equation [eq. (16)] here, the minimum value of χ/M_B required for Paxton's results is 2×10^{-3}. With this minimum value of χ, we then find the results shown in Table III for the critical molecular weights M_c of polystyrene for phase separation from polybutadiene when equal numbers of molecules are mixed and the molecular weight of the polybutadiene is as shown.

TABLE III

Critical Molecular Weights for Phase Separation of Polystyrene and Polybutadiene $\chi/M_B = 2 \times 10^{-3}$

M_B polybutadiene	M_c polystyrene
10^4	1100
10^5	1970
10^6	2900

Since we have predicted that the critical molecular weights for domain formation would be at least 2.5 – 5 times larger than for simple phase separation, we would then predict that the critical molecular weights for domain formation in a styrene–butadiene block copolymer would be between about 5000 and 10,000 when the polybutadiene block molecular weight is of the order of 50,000. Data presented by Holden, Bishop and Legge (1) give some confirmation to these predictions. Their data show that the tensile strengths of A–B–A block copolymers of styrene and butadiene change from 150 psi for a 6000 – 81,000 – 6000 molecular weight polymer to 3350 psi for a 10,000 – 53,000 – 10,000 molecular weight polymer, i.e., a 20-fold increase in tensile strength when the polystyrene molecular weight is changed only from 6000 to 10,000. We interpret these data as evidence for the onset of domain formation in that molecular weight range, as predicted by present theory.

Although their data were obtained with A–B–A block copolymers and present theory deals with A–B polymers, it will be shown in a following paper that the thermodynamics of the A–B–A system is not greatly different from the A–B system and hence the comparison of critical molecular weights from a theory of A–B polymers with data from A–B–A polymers is valid.

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