Block Copolymers, Polymer–Polymer Interfaces, and the Theory of Inhomogeneous Polymers

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Most of the polymeric materials one encounters so widely are heterogeneous. For instance, commercial plastics may be blends of immiscible polymers, they may contain antioxidants or other modifiers which are not totally soluble, and frequently they have added inorganic fillers. Other examples of inhomogeneity in polymer systems are composites, partially crystalline materials, surface layers, ionomers, and block and graft copolymers. In some cases the heterogeneity is the essence of the material's virtue (e.g., its mechanical properties). In other cases heterogeneity is an affliction. But, whether one's goal is to maximize or minimize the effect of nonuniformity, it is well to understand the factors which determine the features of inhomogeneous polymers. This we will attempt to do in a qualitative way by describing from a simple molecular point of view the entropy and energy terms which control the systems' physical features. Rather than dealing in generalities, however, let us focus on two particular cases: interfaces between immiscible polymers,[1–5] and block copolymers.[5–8] This should provide the reader with some insight into the myriad of recent developments in the field of polymer blends, composites, and microheterogeneities.

In an interfacial region (interphase) between immiscible polymers, A and B, some degree of interpenetration does occur. This produces an energy of mixing contribution to the interfacial tension. Also, the energy of AB adjacency leads to preferences for certain arrangements of the molecules in the interphase over others. Polymer states (spatial shapes called conformations) of low degrees of mixing are statistically favored. The rejection of those conformations with large interpenetration produces a loss of "conformational entropy". We will show how the statistical problem can be analyzed by a mean field theory, but our major concern will be to demonstrate that the results follow from simple dimensional arguments.

Similar concepts will serve in understanding block copolymer systems. Block copolymers[8] are molecules which contain within the same chain long sequences of one type of unit, A, followed by long sequences of another, B. The diblock copolymers, AB, have one such A chain covalently attached to a B chain. By using a triblock copolymer, ABA, a rubber which is fusible for processing can be made. Multiblock materials also find applications. In a typical case A may be polystyrene, of molecular weight in the tens of thousands, while B is polybutadiene with similar or higher sequence length. The tendency is for A and B to phase separate, but due to the covalent connection the two phases must stay in close proximity. The result is spherical, cylindrical, or lamellar microdomains (Figure 1) with typical sizes tens of nanometers.

With annealing, or techniques such as extrusion, the domains may form regular arrays over extensive regions.[9] Under more common conditions the structures do not form a lattice. In fact, the shapes described above are only an idealization of the distorted geometries observed.

The microdomains are directly observable by electron microscopy,[8,9] and are clearly inferred from small-angle X-ray scattering (SAXS) as well as from multiple glass relaxation peaks nearly corresponding to those of the pure materials.[8] A current problem is the cause and nature of the influence of one material on the other's relaxations. The boundary between phases is not sharp, as indicated by relaxation experiments, and the recent SAXS measurements.[10] Our prediction of interfacial widths for polystyrene–polyisoprene is 1.6 nm, while the SAXS value is 2.6 nm (using a slightly different measure and including surface roughness effects).

The behavior of block copolymers as thermoplastic elastomers is attributable to the microdomain morphology.[8] Let A be glassy or crystalline at the temperature of use (e.g., polystyrene) and let B be rubbery (polybutadiene, polyisoprene, polyolefin). If A agglomerates into spheres, then these microdomains serve as cross-links for the rubbery B chains. The "cross-links" can be temporarily melted or dissolved

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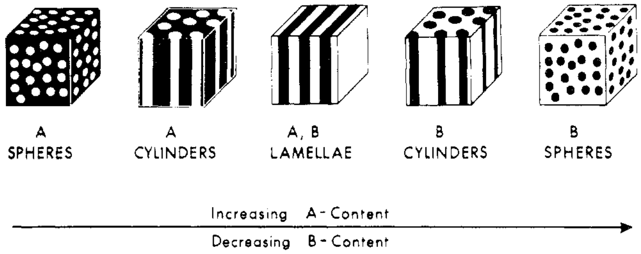

Figure 1. Microdomain structures of block copolymers schematically illustrated (from G. E. Molau, ref 8b; reproduced through the courtesy of Plenum Publishing Corp.).

for processing. Another consequence of the anchoring of the rubber chain ends is that one gets topologically permanent entanglements which greatly enhance, in fact dominate, the effective cross-link density. The tensile strength is very high because: (1) the hard domains serve as a reinforcing filler; (2) strain on the rubber chains can be redistributed more easily with entanglements than permanent cross-links; and (3) under sufficiently high stress the hard domains can yield.[11]

Besides their use as easily processed rubbers, other applications of block copolymers include adhesives, emulsifying agents, conventional rubbers, impact modifiers, protective coatings, and mosaic membranes.

Important features of a theory of domains in block copolymers were first discussed by Meier.[12] Other theories have been presented subsequently.[6,13–20]

Briefly, from the theory to be described below we can identify the following elements of the free energy of block copolymer systems. When microdomains are present there is interfacial free energy between the phases. The joints between A and B blocks are preferentially found in the interfacial regions. As a consequence there is a loss of entropy in two ways. One is due directly to this confinement of the joint degree of freedom. The other has its origin in the vast number of polymer conformations which are not allowed because they produce lower density near the domain centers than at the outer boundaries. As the microdomains grow, these two entropy losses increase until they finally outweigh the decrease of surface free energy, and a thermodynamically stable size is achieved.

Simple Conditions Governing Phase Separation

Let us review some elementary considerations with respect to phase separation of two-component systems. Consider n_A molecules of A and n_B of B. A and B are small molecules, and, let us say, equal in size. We use the language of nearest-neighbor interactions and a lattice model. In the process of going from pure phases to a mixture we form n_{AB} AB bonds with energy ϵ_{AB}, but first it is necessary to break $\frac{1}{2}n_{AB}$ AA bonds and the same number of BB's. An estimate of n_{AB}, neglecting correlations, is

$$n_{AB} \approx n_A z n_B/(n_A + n_B) \qquad (1)$$

i.e., (the number of A's) × (z, the number of neighbors of each molecule) × (the fraction of those neighbors which are B). Thus, an approximation to the energy of mixing is[21]

$$\Delta E = \frac{n_A n_B}{n_A + n_B} z[\epsilon_{AB} - \tfrac{1}{2}(\epsilon_{AA} + \epsilon_{BB})] \qquad (2)$$

A dimensionless parameter χ can be introduced as a measure of the degree of incompatibility of A and B by writing[22]

$$\Delta E = \chi k_B T n_A n_B/(n_A + n_B) \qquad (3)$$

Note: $2\chi k_B T$ is the energy required to take a unit of A out of pure A surroundings, take a B out of pure B, and interchange their original places. Generally χ is positive. It is this case we shall consider.

The reason that endothermic mixing occurs in many small-molecule systems is the greater randomness of a mixture. The entropy of mixing

$$\Delta S = -k_B\left[n_A \log \frac{V_A}{V} + n_B \log \frac{V_B}{V}\right] \qquad (4)$$

(where V is volume, and V_K is the volume of component K when pure) expresses the fact that a unit of K can be placed in a fraction V/V_K greater volume after mixing occurs. Complete mixing is found if the entropy of mixing outweighs the energy of mixing. Roughly speaking, this occurs if $\chi \lesssim 1$ (for $n_A \approx n_B$).

What happens if one links the A into molecules of Z units, similarly polymerizing B? This does not significantly affect the expression for the energy of mixing,[23] although one may have to readjust slightly the value of χ. Bear in mind that n_A and n_B must be interpreted as numbers of monomer units. By contrast, the entropy of mixing is profoundly altered. The extra freedom in placement of a molecule of A on mixing is available to only one out of Z degrees of freedom. Thus the entropy of mixing is down by a factor of $1/Z$, and the criterion for mixing to occur is

$$\chi \lesssim 1/Z \text{ or } \chi Z \lesssim 1 \qquad (5)$$

This explains the observation that most pairs of polymeric components are immiscible, even with $\chi \approx 0.01$ (since usually $Z > 100$, frequently much greater).

Another way of looking at this is that the Boltzmann factor for a molecule of A to come out of pure A into B and a molecule of B to go into A is $\exp(-2\chi Z)$. Thus the comparison of χZ with unity determines the likelihood of such interchanges.

This introductory discussion illustrates the simple molecular level on which we shall attempt to achieve

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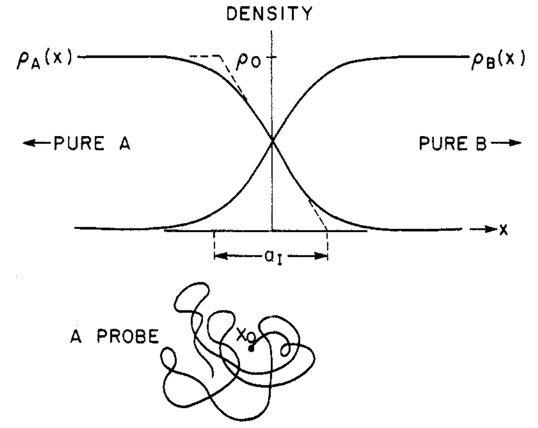

Figure 2. Concentration profiles of A and B through an interphase. The light dotted line is a wedged-shaped approximation to this profile, and is used to define an interfacial thickness, a_I. The conformation of a typical A probe with one end anchored at x_0 is indicated.

an understanding of several problems involving inhomogeneous polymers.

Polymer–Polymer Interfaces

Let us consider two polymers, A and B, which are incompatible, but with χ small, while χZ is large, compared with unity. To avoid extraneous complexity we will assume that the components are symmetric in the sense that, when pure, A and B have the same: (1) density of monomer units, ρ_0; (2) degree of polymerization, Z, which will later be taken as approaching infinity; (3) effective length of a repeat unit, b, selected so that the unperturbed mean-square end-to-end distance is Zb^2; and (4) compressibility, κ.

The asymptotic phases A and B in contact remain essentially pure. In the interphase, however, mixing occurs as the concentration of one polymer falls, being replaced by the other. This is shown in Figure 2.

To learn more, imagine that we take a probe molecule of type A and insert it. For the moment specify that one end of that probe chain is fixed at a point $\mathbf{r}_0$, and look at what the rest of the molecule does. Energetically the probe prefers A surroundings. If energetics were all that mattered the chain would stretch out away from the B phase. However, this is but one of the probe's many possible states. The various conformations will be taken on with probabilities weighted by Boltzmann factors disfavoring high degrees of contact with B. Typically the probe will have a coiled shape with some bias toward the A side of $\mathbf{r}_0$ (Figure 2). From an entropy–energy point of view, because some conformations appear less frequently, due to their higher degree of penetration into B, there is a loss of conformational entropy. Furthermore, the probe does have contacts with polymer B, indicating that there is an extra energy of mixing in the interphase.

In the sense that the probe has one end fixed at $\mathbf{r}_0$, it is not truly an indicator of a typical macromolecule's behavior. When its end is released, a solution to its dilemma of avoiding B phase while using all conformations equally might be to move further into the A phase. But it is well to recall the categorical imperative of Kantian ethics: "Act only on that maxim which you can at the same time will that it should become a universal law".[24] From this point of view it would be immoral for the probe to leave the interface, for when the other molecules follow suite the joint would fall apart.

In physical terms, the result of a movement apart of the phases would be to create a dip in the overall density, $\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$, away from the value ρ_0. In condensed media of low compressibility there is a high free-energy price for density deviations. Rather than pay that price, the system will tend to keep molecules in the interface, paying the lesser toll of mixing energy and conformational entropy loss discussed above. However, this introduces another conformational entropy loss, namely that associated with maintaining uniform density: $\rho_A + \rho_B = \rho_0$. [When the densities of pure A and B are different, ρ_{0A} and ρ_{0B}, and there is zero volume change on homogeneous mixing, a sum of reduced densities stays constant[2] (eq 6)]

$$(\rho_A/\rho_{0A}) + (\rho_B/\rho_{0B}) = 1 \tag{6}$$

These arguments provide a qualitative understanding of the sources of surface free energy. Let us indicate briefly what the ingredients of a quantitative theory are. A monomer unit of an A probe is acted on by a chemical potential, which is the work required to take the unit from pure A surroundings to a point x where the densities are $\rho_A(x)$, $\rho_B(x)$. It has two parts. The first, due to interaction with B, is proportional to χ and the square of the fraction of B present,[25] $(\rho_B/(\rho_A + \rho_B))^2$. The second part keeps the density essentially uniform. It is proportional to any density deviation which may occur, $[\rho_A(x) + \rho_B(x) - \rho_0]$, and to the inverse of the compressibility, $1/\kappa$. (The density deviation is very small, but so is κ. The limit $\kappa \to 0$ is appropriate, and produces a $0 \times \infty$ which turns out to be a finite contribution.)

In the statistical mechanical treatment of the problem[5-7] attention focuses on a function $Q_A(x,t;x_0)$ proportional to the probability that one end of a probe molecule will be at x_0 while the other end is at x, if the probe has degree of polymerization t. In pure A phase, Q_A is the familiar Gaussian end-to-end distribution; i.e., Q_A satisfies the diffusion equation. In an inhomogeneous region this diffusion equation is to be augmented with the chemical-potential terms just considered (eq 7), with a similar equation for Q_B.

$$\frac{\partial Q_A}{\partial t} = \frac{b^2}{6}\frac{\partial^2 Q_A}{\partial x^2} - \left[\chi\left(\frac{\rho_B(x)}{\rho_0}\right)^2 + \frac{1}{\kappa \rho_0 k_B T}\frac{\rho_A(x) + \rho_B(x) - \rho_0}{\rho_0}\right] Q_A \tag{7}$$

This is not a straightforward equation because it contains the unknown density patterns $\rho_A(x)$ and $\rho_B(x)$. However, if one knows Q_A and Q_B, the densities are calculable,[1-7] and one is called upon to find a self-consistent solution.

For the interface problem (even unsymmetric) solutions can be obtained analytically,[1,2] and the concentration profile is

$$\rho_A(x)/\rho_0 = \{1 + \exp[2(6\chi)^{1/2}x/b]\}^{-1} \tag{8}$$

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[24] I. Kant, "Groundwork of the Metaphysics of Morals", H. J. Paton, Translator, Harper and Row, New York, N.Y., 1964.

[25] Usually[22] the term proportional to χ in the chemical potential of A goes as $\chi(\rho_B/\rho_0)^2$. Working to zero order in compressibility it turns out that the first or second power of ρ_B/ρ_0 yields the same answer, because of the constancy of $\rho_A + \rho_B$. The matter has been discussed in ref 5 and a general proof follows from material in ref 2.

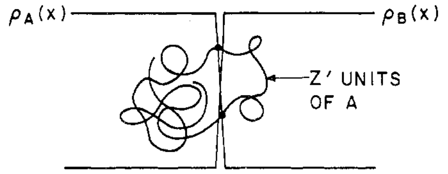

Figure 3. An imagined sharp interface between A and B, and the conformation of a typical A probe which penetrates B.

We are less interested in the detailed formula than in qualitative features. Define a characteristic width of the interphase by approximating the sigmoidal concentration profile with a wedge-shaped function of matching slope at $x = 0$ (dotted curve in Figure 2). The interfacial thickness, a_I, will be defined as the width of the wedge:

$$a_I = 2b/(6\chi)^{1/2} \tag{9}$$

To qualitatively appreciate the dependence on b and χ, consider a sharp AB boundary as in Figure 3. From earlier considerations we expect that A chains of Z' units such that $\chi Z' \lesssim 1$ can enter the B phase. Such chains will extend

$$b(Z')^{1/2} \approx b/\chi^{1/2} \tag{10}$$

into B, which establishes the functional dependence of a_I. For $b = 0.65$ nm and a χ of 0.05, $a_I = 2.4$ nm. For χ's much larger, the interface becomes of the size of the monomer. The Gaussian model then would not be a priori appropriate (although, in practice, we find it to be unexpectedly good[2]). A lattice model has been developed.[3,4]

The theory also produces a formula for the surface tension[1,2]

$$\gamma = (\chi/6)^{1/2} b \rho_0 k_B T \tag{11}$$

(In practice, χ is found to be temperature dependent and eq 3 represents both energy and entropy contributions. This affects the temperature dependence of γ.) One can understand qualitatively the magnitude of this result also. We have pointed out that there is significant mixing in an interphase of width $0(b/\chi^{1/2})$. This width times $0(\rho_0)$ is an estimate of the number of A units with important amounts of B contacts. Each has a mixing energy $0(\chi k_B T)$. Multiplying factors produces a surface energy of the form of eq 11. But the surface entropy and surface energy have similar dependencies on the parameters, since the whole interphase structure was determined by balancing forces arising from energy and entropy. Hence the functional form of the surface tension is established.

In the theory of interfaces which are rather narrow it is important to take into account the nonlocality of interactions,[1-5] i.e., the fact that a unit at a point $\mathbf{r}$ interacts with another at a point $\mathbf{r}' \neq \mathbf{r}$. When χ is small, such effects change the interfacial tension of polymers by only a few percent, because the interphase widths are several times the range of forces. Nevertheless, nonlocality has been included in the full theories.[1-5]

The reader is directed to ref 2a for a comparison between theory and experiment. Generally, the results are good, especially in view of the large uncertainties associated with the values of the parameters.

We conclude this section with a comment on the widely used Fowkes theory,[26] which presupposes a sharp interface with no mixing, but only interactions across the boundary plane. This is contrary to what we have just established to be the case for polymer pairs of low, or even moderately sizable, χ. Hence the Fowkes ideas, which work so well when appropriate, must be applied with caution.

Block Copolymers

The above discussion of interfaces contains many ideas relevant to general inhomogeneous polymer systems, particularly microdomain formation in block copolymers. For simplicity, restrict attention to diblock copolymers composed of symmetric materials A and B. Assume the parameters are such that these separate into well-defined lamellar domains having a periodicity distance d, as illustrated in Figure 4.

With A and B separated, there must be interfaces between domains, and associated interfacial free energy. For the moment assume that these interfaces are much like those between semi-infinite phases, discussed above. This will be especially appropriate if the interphase is much narrower than the domain size ($\chi Z \gg 1$). The total free energy per unit volume, $f = F/V$, can be reduced by decreasing the surface to volume ratio. As the domains grow, this part of f falls like $1/d$.

Limitations on domain growth arise from the preference for the AB joint to be located in the interphase. Application of random-walk statistics, even modified to produce the kind of interphase we have learned to expect, results in an excess of polymer near the boundaries of the domains, and density deficiencies in the domain centers. This is because each chain has the bias of having one point, the joint, near the boundary. Again we have the situation where the system rejects a major number of the possible conformations, preferentially accepting those rarer conformations which reach into, and uniformly fill, the domain centers. The loss of conformational entropy becomes more severe as the domains grow. Detailed numerical calculations, using eq 7, produce a free energy fitted extremely well by a $d^{2.5}$ power law.

Another entropy loss is associated with the joint's confinement. It grows as the logarithm of the ratio of the volume available to the joint in a homogeneous system to the volume available in the microdomain structure, roughly log $(d/2a_I)$.

The result is a total free energy per unit volume, relative to a homogeneous system, of

$$\frac{f}{kT} = 2\left(\frac{\chi}{6}\right)^{1/2}\frac{\rho_0}{d} + \frac{\rho_0}{Z_A + Z_B}\log\frac{d(6\chi)^{1/2}}{\pi b} + 0.13_9\rho_0\frac{Z_A{}^{5/4} + Z_B{}^{5/4}}{(Z_A + Z_B)^{7/2}}\left(\frac{d}{b}\right)^{2.5} - \chi\rho_0\frac{Z_A Z_B}{(Z_A + Z_B)^2} \tag{12}$$

(easily modified for unsymmetric polymers). A similar equation holds for triblock copolymers. Without entering into details, the domain sizes of triblock copolymers are predicted to be only slightly different from those of the diblock copolymers obtained by cutting the triblocks in the middle of the central block. This is as is indicated experimentally.[27]

A typical f vs. d curve, Figure 5, possesses a mini-

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[26] F. M. Fowkes, *Ind. Eng. Chem.*, **56** (12), 40 (1964).

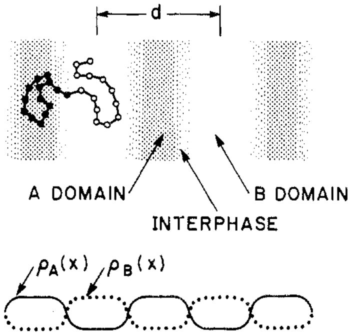

Figure 4. Schematic diagram of a lamellar microdomain structure in a block copolymer system.

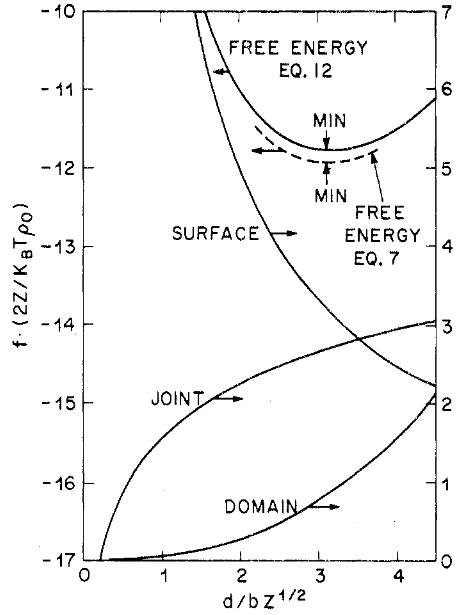

Figure 5. Free energy per unit volume of a lamellar block copolymer system as a function of the periodicity distance d (in dimensionless units). The plot is for $\chi Z = 37$. The full line is calculated according to eq 12; SURFACE, JOINT, and DOMAIN stand for the first three terms on the right-hand side of that equation, respectively. The dotted curve is a more exact result from solution of eq 7.

Table I
Comparison of Calculated and Experimental Domain Size

Polymer^a	Mol wt × 10^{-3}	T,^{b} °C	d_{exp}, nm	d_{calcd}, nm
SI^c	62–43	90	66	56
SI^d	23–21	20	31	30
SBS^e	14–28–14	20	27–30	27

^{a} S = polystyrene, I = polyisoprene, B = polybutadiene. ^{b} Estimates of the temperature at which the domain size was fixed due to glass transition on cooling or evaporation. ^{c} Reference 10. ^{d} Reference 28. ^{e} Reference 16.

mum, which is the predicted domain size. Comparisons between experiments and theory are contained in Table I. Agreement is reasonably good considering the parameter uncertainties. Also, one does not know well the temperature at which the domain size was "frozen in" by the polystyrene glass transition.

It is clearly not rigorous to view the block copolymer structure as pure domains joined to a narrow, unperturbed interface. One way to relieve the entropy losses associated with joint confinement and the difficulty of filling the domain centers is to broaden the interphase and the AB interpenetration. Actually one can abandon completely the artificial constructs of domains and interphases. Instead one solves equations like eq 7, merely seeking solutions with periodicity d. This we have done for a typical value of $\chi Z = 37$ with $Z_A = Z_B = Z$. The free energy is quite close to eq 12, as indicated in Figure 5.

For smaller values of χ (corresponding to higher temperatures) it is possible that the microdomain structure will be less stable than a homogeneous phase. Equation 12 possesses an instability at $\chi Z = 8.1$. However, for such a low χZ the division into interphase and pure domains is inappropriate. We find evidence of a great deal of mixing, but still heterogeneity, in the range of $\chi Z = 6$ to 8. Definitive answers await further numerical and analytical work.

The Challenge to Experimentalists

What experimental studies would be complementary to the present theoretical research in gaining greater understanding of inhomogeneous polymeric systems?

(1) Good measurements of χ between two polymers are essential. At present there are almost none available, in spite of the central role of this parameter. Of great import is the temperature dependence of χ. Furthermore, it would be desirable to go beyond the simple form of eq 3 for the energy of mixing. Obviously, it is difficult to measure thermodynamic properties of incompatible polymers. In the few studies which have been made, oligomers have been utilized to enhance the entropy of mixing contribution. The use of random copolymers may be an effective approach. An experiment of interest would be measurements of the solubility of oligomers of A in copolymers of A and B.

(2) More studies of interfacial tensions between pairs of polymers would be desirable. Polymers should be chosen with known parameters, so that the results can be checked against theory. If the present theory is confirmed, surface tensions will be useful in determining the compatibility characteristics of binary polymer pairs. In any event, it may be valuable to establish such a correlation on an empirical basis. Similarly the interfacial properties of solvent-saturated solutions and of concentrated solutions against hard surfaces have received inadequate attention. The theory is akin to that described in this Account.

(3) Much useful information is available on block copolymer domain size and geometry as a function of molecular weight. Less is known about the concentration profile in these domains, especially the interphase. There is a hiatus in our knowledge of conditions above the glass transition or melting point of the "hard" segments, and in the neighborhood of instability of the domain structure.

(4) Finally, great care must be taken to separate the equilibrium from the nonequilibrium aspects of polymers, especially inhomogeneous polymeric systems.

I am most grateful to Mrs. Zelda Wasserman, Dr. Yukiko Tagami, and Professor Anne Marie Sapse for their contributions to this research.

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