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Macromolecular
Systems**

Edited by

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THEORY OF STRESS DISTRIBUTION IN BLOCK COPOLYMER MICRODOMAINS

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INTRODUCTION

Much of this meeting is devoted to the fascinating domain structures formed by diblock copolymers whose blocks are strongly incompatible. These diblocks and more complicated block copolymers have become important in a wide range of applications. One important use of diblocks is in blends of incompatible homopolymers. Here diblocks made of the two polymeric species to be blended allow control of the domain morphology and inhibit macroscopic phase separation.

Our focus here is on the statistical mechanics of these diblocks, and how these differ from homopolymers in a melt. The free energy contributions which distinguish diblock domains have been appreciated for a long time [1]. On the one hand, the material has interfacial energy proportional to the total surface area. This energy tends to make the domains as large as possible. On the other hand, if the domains are large, the constituent polymer blocks must be elongated. This is true because all blocks must have one end at the domain interface, while the free ends must be distributed so as to fill the adjacent domain. Balancing the resulting elastic energy against the interfacial energy leads to a well-known scaling law for the domain size h as a function of the molecular weight M of the copolymer: $h \sim M^{2/3}$. This prediction has been verified by experiment [2] and numerical work [3]. Much theoretical effort has been devoted to fleshing out this simple scaling picture [4,3,5,6,7]. These theories use sophisticated numerical techniques of polymer statistics to give a detailed picture of the conformations and energetics of the polymer blocks. Complementing these are simple extensions of the Meier scaling ideas to give qualitative insights [8,9,10]. A recent approach [11,12] has made a satisfying connection between the scaling approach and the more systematic numerical approaches. This work has shown how the numerical solution for a chain at a copolymer interface reduces to an analytical form at asymptotically high molecular weight. The asymptotic theory confirms the 2/3 scaling power. Further, it gives the unknown proportionality constants in the scaling theories explicitly in terms of known polymer parameters, and it gives detailed predictions beyond the scope of the scaling theories.

SPONTANEOUS CURVATURE IN A DIBLOCK COMPATIBILIZER

In this contribution we illustrate the power of the recent theories by working out an example of practical interest. We wish to use diblocks to arrest phase separation of two blended homopolymers in an incompressible melt state. Like a surfactant, this diblock "compatibilizer" is forced to reside at a narrow bilayer near the homopolymer phase boundary. We wish to design the copolymer so that one of the homopolymers—denoted I for "interior"—is confined in spherical domains of a particular radius R . The other homopolymer—denoted E for "exterior"—lies outside these spheres. To achieve the desired radius, the stress within the E-I diblock bilayer itself must give rise to a spontaneous curvature of $1/R$. For concreteness, we shall require 1-micron domains of polybutadiene in polystyrene, a typical morphology in toughened-plastic applications.

The state of a polymer block in this bilayer closely resembles its state in the lamellar phase of the neat diblock material, as Leibler has discussed [10]. As in the neat material the number of diblock polymer chains σ per unit area is governed by a balance between interfacial energy and rubber-elastic energy. The interfacial energy per unit area γ resides in a narrow mixing zone which is small in relation to polymer dimensions. The local monomer interactions which determine γ are insensitive to the overall connectivity of the polymers. This γ is nearly the same with or without copolymers present.

The elastic energy of a chain is proportional to the mean squared extension of the blocks. Thus for e. g. the E blocks, the elastic energy $T_E \sim h_E^2/r_E^2$, where r_E^2 is the mean-squared unperturbed end-to-end distance. Since each block displaces some volume V_E in the melt, the height h_E must be at least large enough to accommodate the blocks which are present: $h_E \geq \sigma V_E$. Any penetration of homopolymer into the bilayer could only increase h_E ; we neglect such penetration here and justify this below. The mean-squared radius r_E^2 appearing in T_E is proportional to molecular weight, and thence to the volume V_E .

Combining these facts we find the scaling of elastic energy T_E per E-block with coverage σ . We find $T_E \sim \sigma^2 V_E$. The system chooses that coverage σ which minimizes the total energy per chain, $T_E + T_I + \gamma/\sigma$. Letting the two chain volumes vary in proportion, the optimal coverage evidently satisfies $\sigma^3 \sim V_E^{-1}$, so that $h_E \sim \sigma V_E \sim V_E^{2/3}$. The same scaling applies to the I side of the bilayer. Thus the bilayer thickness follows the 2/3 power law. Evidently h_E grows indefinitely larger than the ideal radius $r \sim V_E^{1/2}$. Thus the blocks become strongly stretched.

To understand the bilayer in greater detail, we must determine the conformational statistics of the blocks in each bilayer. This problem has been studied extensively for the lamellar phase of the neat material, as noted above. The problem may be reduced to that of a single chain with one end confined to the interface, moving in a height-dependent pressure $p(z)$, arising from interaction with the other chains [4,5,6]. (This pressure is equivalent to a height-dependent monomer chemical potential [12].) In an arbitrary pressure field $p(z)$ the ensemble of end-confined chains at coverage σ would produce a particular monomer concentration profile $\rho(z)$. The correct, self-consistent, $p(z)$ is that which achieves a constant $\rho(z)$ equal to the density of the melt in question.

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In the asymptotic limit of high molecular weight, the self-consistent $p(z)$ takes an exceeding simple form [12]. It becomes a parabolic function of height which falls from a maximum at the interface to zero at a particular height h . Since the pressure $p(z)$ is sufficient to extend the block chains far beyond their ideal dimensions, the work required to insert an additional block into the layer must be much greater than kT . This means that unattached chains are strongly excluded from the layer. This is equally true whether these outsiders are blocks attached to an opposing lamellar interface or are homopolymers. Any contribution to the density from such outsiders is confined [13] to a narrow zone of relative height $\lambda/h \sim V^{-1/3}$. Thus penetration by outside chains has a negligible impact asymptotically on the configurations of the attached blocks.

Recently we [14,15] used the asymptotic theory to find the energy of a slightly bent bilayer. We now use this theory to treat the concrete compatibilizer problem at hand. The first step is to find the elastic free energies per block T_E and T_I explicitly for the polymers in question. The energy to extend an E-block to height h_E may be written $(1/2)a_E h_E^2/V_E$, where the length a_E characterizes the intrinsic elasticity of the E-chains. The elastic energy per chain T_E is a universal multiple of this energy, viz. [11]

$$T_E = \frac{\pi^2 a_E h_E^2}{24 V_E} = \frac{\pi^2 a_E \sigma^2 V_E}{24} \quad (1)$$

and similarly for T_I .

Here, and throughout this discussion, we use V_E and V_I to measure molecular weight. Molecular weight enters our problem *only* through these volumes. Using this notation, the intrinsic elasticity of a polymer enters only through the single parameter a , which we call the "packing length". Such quantities as the length of a statistical segment are relevant only insofar as they affect the packing length. We list the packing lengths and other parameters of our system in Table I. Packing lengths for common polymers are a few Angstroms [16].

A bilayer made of two asymmetric polymers will not in general be flat; it will have a radius of curvature R (which proves to be spherical). This curvature changes the elastic energies. When the curvature is small and spherical, the asymptotic theory gives [14]

$$T_E = \frac{\pi^2}{24} \sigma^2 a_E V_E \left[1 - \frac{3 \sigma V_E}{2 R} + \frac{13}{5} \left(\frac{\sigma V_E}{R} \right)^2 + \dots \right] \quad (2)$$

For this exterior layer, the curvature allows the chains to splay out, thus reducing their energy in first order. For the interior layer the linear term has the opposite sign. The general form of this bending energy is the same for any thin layer, and is well known [18]. Even the numerical coefficients shown here are close to a recent estimate of Leibler [10].

The actual radius R is that which minimizes the total energy per chain, $T_E + T_I + \gamma/\sigma$. Thus the partial derivatives of this energy with σ and with $1/R$ must both vanish. For the $1/R$ derivative only the corrections to T_E and T_I contribute: one

Table I

Melt Properties for Polystyrene
and Hydrogenated Polybutadiene [16]

polymer	Temp- erature (Kelvin)	density (amu Å ⁻³)	m_0^a (amu)	b^b (Å)	C_∞^c	packing length (Å) ^d
polystyrene	400	0.61	52	1.54	9.4	11.5
hydrogenated 1,2 polybutadiene	373 ^e	0.49	27.7	1.54	5.5	12.9

- a. molecular weight per backbone bond [16]
 b. length of backbone bond [16]
 c. mean-square end-end distance relative to that of a freely jointed chain of backbone bonds [16]
 d. packing length defined in text, as calculated from preceding table data.
 e. We estimate less than 10% change from these values at 400 Kelvin.

Interfacial energy [17] at 423 Kelvin is taken to be 3 dyne/cm. for 4000-molecular-weight HPBD. From this data we estimate that this energy increases by about 6% at 400K. A further small increase is expected in the limit of high HPBD molecular weight. At 400K, 3 dyne/cm. = $5.5 \times 10^{-3} kT \text{ \AA}^{-2}$. This is the value of γ used for the estimates in the text.

finds

$$0 = V_E a_E \left[-\frac{3}{2} \sigma V_E + 2 \frac{13}{5} \frac{\sigma^2 V_E^2}{R} \right] + V_I a_I \left[\frac{3}{2} \sigma V_I + 2 \frac{13}{5} \frac{\sigma^2 V_I^2}{R} \right]. \quad (3)$$

The condition for a *flat* interface, $1/R = 0$, is independent of our numerical coefficients. Evidently

$$V_E^2 a_E = V_I^2 a_I. \quad (4)$$

For our polystyrene and hydrogenated polybutadiene, with $a_E/a_I = 0.9$, a balanced flat interface occurs when $V_I/V_E = 0.9^{1/2}$; i. e. the bilayer should be about 53% polystyrene by volume.

To achieve the desired curvature with the E polystyrene on the exterior, the E molecular weight must be slightly greater than this balancing value: $V_E^2 a_E = V_I^2 a_I (1 + \epsilon)$. Using Eq. (3) near the balance point, we find

$$\epsilon = \frac{52}{15} \sigma \frac{V_E + V_I}{R}. \quad (5)$$

The coverage σ is that which minimizes the total energy:

where we have again used the preceding.

We now work out the details. We suppose that the E, polystyrene, has a molecular weight of 61,000. At balance the packing length is $94,000 \text{ \AA}^3$. Using Eq. (4) we find $V_I/V_E = 0.9^{1/2}$ per 710 \AA^2 . The thickness of the bilayer, in comparison, an ideal, non-interacting chain, end distance perpendicular to the surface is smaller than the calculated value. The bending constant [14] K is a measure of the imbalance ϵ ($\equiv V_E^2 a_E / (V_I^2 a_I)$), e. g. by reducing the polymer molecular weight. An uncertainty of perhaps 10% in Temperature and finite molecular weight are surely somewhat inaccrued. More important than these are the details. We discuss the importance of these details in a later paper.

SIGNIFICANCE OF ?

We have seen that the simple model of the bilayer is the packing length. The recent notions of rubber elasticity, e. g. a may be altered by chemical crosslinking, influence the bilayer.

The name "packing length" is independent of chains packed together. The defining equation (above Eq. (3)) for the elastic energy in terms of the packing length a may also be expressed in terms of the chain segment of size r to the radius r the number of independent chains. The actual average number of chains is a numerical constant. Thus the number of independent chains is a numerical constant.

Recently Lin [16] has found an empirical connection between the modulus of polymer melts. The modulus is kT/V_e , where V_e is a characteristic volume of the polymer. A section of volume V_e is independent of polymer type [16]. Remarkably, the average number of independent chains a gives $G \simeq 0.13 kT a^{-3}$.

$$\sigma^3 = \frac{(12/\pi^2)\gamma}{(V_I + V_E)(a_I a_E)^{1/2}}, \quad (6)$$

where we have again used the condition (Eq. 4) that the bilayer is essentially balanced.

We now work out the explicit prediction for ϵ for a particular molecular weight. We suppose that the E, polystyrene, block has a volume V_E of 10^5 \AA^3 , i. e. a molecular weight of 61,000. At balance, the I, polybutadiene, block must have a volume V_I of $94,000 \text{ \AA}^3$. Using Eq. (4) and the data in Table I, the coverage σ is then one chain per 710 \AA^2 . The thickness of the bilayer $h_E + h_I = \sigma(V_E + V_I)$ is 270 \AA . For comparison, an ideal, noninteracting diblock would have a root-mean-square end-to-end distance perpendicular to the interface of $(V_E/a_E + V_I/a_I)^{1/2} = 130 \text{ \AA}$ —somewhat smaller than the calculated bilayer height. The elastic energy is 1.9 kT/diblock . The bending constant [14] K is $80kT$. To achieve the desired 1-micron radius, requires an imbalance ϵ ($\equiv V_E^2 a_E / (V_I^2 a_I) - 1$) of 9%. The required imbalance can be achieved e. g. by reducing the polybutadiene molecular weight by 4.5%. These results have an uncertainty of perhaps 10%, owing to the uncertainty in the data in Table I. Temperature and finite molecular weight effects could influence these data by this amount. More importantly these explicit results rely on our asymptotic theory; they are surely somewhat inaccurate for the small molecular weights of our example. We discuss the importance of these inaccuracies in the Discussion section.

SIGNIFICANCE OF THE PACKING LENGTH

We have seen that the single polymer chain parameter controlling the properties of the bilayer is the packing length a . In this section we show that a is related to recent notions of rubber elasticity in entangled polymer melts. We also discuss how a may be altered by chemical changes in the polymer, and how such changes should influence the bilayer.

The name "packing length" is natural, because a describes the number of independent chains packed into a given small volume of the melt. Comparing the defining equation (above Eq. 1) for a with the conventional expression $1/2 h^2 (r^2/3)^{-1}$ for the elastic energy in terms of the unperturbed end-to-end distance r , we see that a may also be expressed by $r^2 = 3V/a$. This same law relates the size of a small chain segment of size r to the volume V it displaces. In an arbitrary small sphere of radius r the number of independent chains represented is of order $r^3/V(r) \simeq r/a$. The actual average number of chains represented differs from this value by an unimportant numerical constant. Thus the packing length a is the parameter determining the number of independent chains present in a given small volume of the melt.

Recently Lin [16] and Kavassalis and Noolandi [19] have shown a striking empirical connection between this packing property and the characteristic (plateau) moduli of polymer melts. In the ordinary language of rubber elasticity, this modulus is kT/V_e , where V_e is a characteristic chain volume which depends on the type of polymer. A section of volume V_e has a corresponding size r_e as discussed above. Remarkably, the average number of chains sharing the volume r_e^3 appears to be *independent* of polymer type [16,19]. Expressing this fact in terms of the packing length a gives $G \simeq 0.13kTa^{-3}$.

C_∞	packing length (\AA) ^d
9.4	11.5
5.5	12.9

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Evidently a is related to two separate properties of the melt. It governs the rubber modulus and thus influences the chain entanglements. But also, it controls the elastic stretch energy relevant for the equilibrium properties of a copolymer bilayer. This latter property bears no essential relation to entanglement, since the equilibrium properties in question are independent of any (finite-lived) entanglement constraints.

Polymers with large a values appear to offer interesting potential for their bilayer properties. A diblock made with such polymers would contain a large elastic energy per chain, as compared with a diblock of the same volume and interfacial energy. The large a results in a large elastic energy per chain, and hence enhances the distinctive features of the bilayer.

We also expect large a values to reduce processing problems which often occur in diblock compatibilizers. It is observed [20,21] that when the diblocks have too-high molecular weight or the blocks are too incompatible, the resulting material has an intractably high viscosity. This behavior is natural in view of the expected entanglement [13] properties of the end-confined blocks. Such blocks are not able to release their entanglements by the normal mechanism of reptation, since their ends are confined to the phase boundary. We estimate that the viscosity of the layer grows exponentially with molecular weight [13].

This excessive increase in viscosity can be mitigated by increasing the packing length a . Larger packing length means fewer entanglements per chain, as indicated above. This should allow faster disentanglement and lower viscosity. Thus increasing a may allow use of molecular weights and interfacial energies γ larger than would otherwise be possible. At the same time the distinctive elastic energy of the bilayer is increased.

It seems feasible to control the packing length a to a large extent via the polymer's architecture. In terms of the conventional backbone bondlength b , the volume per backbone bond m_0/ρ and the characteristic ratio C_∞ , a may be expressed as

$$a = \frac{m_0}{\rho} \frac{3}{C_\infty b^2}.$$

To decrease a below that seen in the simplest polymers appears difficult. But to increase a requires only that the chain be made more bulky, e. g. by increasing m_0 without increasing C_∞ too much. This could be accomplished in principle by attaching short side chains at frequent intervals along the backbone. If the side chains are composed of the same parent material, their presence should not affect compatibility properties markedly.

DISCUSSION

We first discuss the applicability of our asymptotic formulas to real copolymers. The asymptotic theory assumes that the elastic energy per chain is large compared to kT , or that the layer thickness h is much larger than the ideal chain radius r . We have seen above that neither of these conditions is well satisfied for the example we took: the elastic energy was only slightly larger than kT . The situation is not much improved by taking high molecular weight, since the elastic energies T_E and T_I increase only as the $1/3$ power of the chainlengths V_E and V_I .

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Still, there is some evidence that the asymptotic theory works even for moderate elastic energies, provided that the blocks are strongly segregated. Throughout the strongly segregated regime, one observes the asymptotic $2/3$ -power scaling between molecular weight and domain size [2]. If our estimates were strongly corrected by finite-molecular-weight effects, there should be some additional molecular-weight dependence beyond the asymptotic $2/3$ power. Another indication comes from the phase boundaries between spherical, cylindrical, lamellar, and double-diamond domain morphologies in neat copolymers [22,23,24]. The asymptotic theory implies that these phase boundaries should depend only on the volume fractions of the two blocks and not on the overall molecular weight. This is what is observed. Any departure from the asymptotic T_E and T_I should affect interior and exterior domains unequally and thus shift the phase boundaries at small molecular weight. Since the boundaries are not in practice sensitive to molecular weight, it appears that the asymptotic theory is adequate. Better estimates [25] of the pre-asymptotic corrections are surely possible. In any case, the experimental results must approach the asymptotic predictions above as the molecular weights are scaled up.

Though our calculation describes how to produce a bilayer with a given spontaneous radius of curvature R , we have so far said little about the actual domain morphology [15] to be expected. Happily, this question has been studied extensively in the context of oil/water/surfactant microemulsions [26,27]. This work depends on nothing about the phase boundary except that it has a fixed total area per surfactant $1/\sigma$ and has a fixed spontaneous radius of curvature R and bending modulus K . When $K \gtrsim kT$, as in our polymeric bilayers, the domains are spherical, with only minor shape fluctuations. The (small) amount of copolymer present forces a fixed total interfacial area. If the interface is to form spheres of radius R , there must be enough interior homopolymer to fill the corresponding volume. If the actual amount of homopolymer is less than this, the spheres are smaller than R ; if the amount is more than this, the excess homopolymer is expelled.

The correspondence between copolymers and surfactant interfaces is good only if these interfaces are weakly curved. When the curvature is stronger, the diblock interface exhibits new phenomena which are only beginning to be explored. Briefly, the self-consistency of the parabolic pressure profile $p(z)$ described above breaks down [11] for strongly curved exterior layers, though it remains valid for interior layers. The exterior pressure profile is believed to be divided into two zones of height. The zone closer to the interface contains no free chain ends. This "exclusion zone" is believed to be exponentially small [14] in $1/R$, and it has no effect on the spontaneous curvature or bending energy for the nearly flat bilayers discussed above. But this zone is expected to be important for strongly curved domains, and calculating the chain statistics in this case poses a challenging theoretical problem [28].

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