Contemporary Topics in
POLYMER SCIENCE
Volume 6
Multiphase Macromolecular Systems

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PLERUM PRESS · NEW YORK AND LONDON
DE DICATION

As this book was in preparation, the Editor was greatly saddened to learn that R. Stille, a distinguished polymer chemist and an author. Stille was among the most productive polymer chemists, with over 270 publications. A member of the faculty, Department of Chemistry, a University Distinguished Professor, he received his B.A. and M.S. from the University of Illinois and his Ph.D. degree. He held a research career at the University of Illinois for 20 years prior to joining Texas Tech University, where he served as a faculty member for many years. Stille was known for his contributions to the field of organic chemistry, and his participation in the "International Symposium on Multifunctional Macromolecular Systems" is highly regarded. He is remembered for his dedication to science and his contributions to the field of polymer chemistry.

May 8, 1988
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 [4,5,6,7]. 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 $\sigma$ per unit area is governed by a balance between interfacial energy and rubber-elastic energy. The interfacial energy per unit area $\gamma$ resides in a narrow mixing zone which is small in relation to polymer dimensions. The local monomer interactions which determine $\gamma$ are insensitive to the overall connectivity of the polymers. This $\gamma$ 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 hence to the volume $V_E$.

Combining these facts we find the scaling of elastic energy $T_E$ per E-block with coverage $\sigma$. We find $T_E \sim \sigma^2 V_E$. The system chooses that coverage $\sigma$ 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 $\sigma$ 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.

In the asymptotic limit of an exceeding simple form for $p(z)$ from a maximum at the interface $p(z)$ is sufficient to extract the work required to insert a chain of length $L$ into the melt, $kT$. This means that unconfined chains are equally free whether they are at the interface or are homopolymer chains confined to a narrow mixing zone by outside layers.

Recently we [14,15] have examined a bent bilayer. We now use the same ideas as above. The first step is to understand $p(z)$ for the polymers in question. It may be written $(1/2) \alpha_E h_E^2 V_E / V_E$, where $\alpha_E$ is the width of the E-chains. The elastic energy for the bilayer, viz. [11]

$$T_E = \pi^2 \frac{\sigma V_E}{24}$$

and similarly for $T_I$.

Here, and throughout, we report on the weight. Molecular weight $\sigma$ has been defined. In this notation, the intrinsic length parameter $\alpha$, which we choose to scale the statistical segment in the melt, is given by $\alpha = \sqrt{3} \sigma$. The packing lengths and $\sigma$ are characteristic for common polymers.

A bilayer made of polymers with a fixed $\sigma$ have a radius of curvature $R$ which is some function of the elastic energies. When $R < \sigma/\gamma$ it gives [14]

$$T_E = \frac{\pi^2 \sigma^2 V_E}{24}$$

For this exterior layer, the bilayer energy is in first order the result of the external pressure, which is well known [18]. Even the estimate of Leibler [10].

The actual radius $R$ is equal to $\sigma/\gamma$. Thus the particle is capable of vanishing. For the $1/R$ derivative
COMPATIBILIZER

Composites are made by working out an epitome of the last phase separation of the homopolymer matrix. Like a surfactant, this block is located near the homopolymer interface. By reducing the length of the homopolymers—a particular radius $R$. Inside these spheres, To form a bilayer itself must give to the bilayer shall require 1-micron on the energy in toughened-plastic

Spheres with depth as in the the subsection discussed [10]. As in the previous the contact area is governed by a constant $\gamma$. The interfacial energy $\gamma$ is typically related to polymer $\gamma$ is insensitive to the polymer is the same with or without

For the confined extension of radius $r^2 \sim \h_E^2 / \sigma^2$, where $r^2$ is the chain, each block displaces some polymer, enough to accomodate the confinement of homopolymer into the bilayer. We therefore take this to be $\h_E \sim \sigma$, proportional to molecular weight.

The energy $T_E$ per E-block is $\h_E \sim \sigma$, so that coverage $\sigma$ which gives the two chain volumes $V_E \sim \sigma^2$, $V_{E \pm} \sim \sigma^2$, so that $h_E \sim \sigma$ in the bilayer. Thus the bilayer is infinitely larger than the elastomer, $\h_E \sim \sigma$.

We can now determine the conformations of the problem. This problem has been studied extensively as described above. The problem is reduced to an epitome of the interface, which interacts with the other component. Provided monomer chemical interaction is an ensemble of end-confined chains, $\rho(x)$ is the concentration profile $\rho(x)$. The constant $\rho(0)$ equal to the

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 outsides 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

$$T_E = \pi^2 a_E h_E^2 / 2 V_E = \pi^2 a_E \sigma^2 V_E,$$

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]

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

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, $T_E + T_I + \eta / \sigma$. Thus the partial derivatives of this energy with $\sigma$ and with $1/R$ must both vanish. For the $1/R$ derivative only the corrections to $T_E$ and $T_I$ contribute: one
where we have again used the notation $16$.

We now work out the interfacial energy in detail. We suppose that the E, polystyrene, has a molecular weight of 61,000. At balance point, $W_E = 94,000 \, \text{Å}^2$. Using Eq. (4) we calculate the area per $710 \, \text{Å}^2$. The thickness of the bilayer, determined by comparison, an ideal, non-bonded end distance perpendicular to the surface, is $20 \, \text{Å}$, smaller than the calculated value. The bending constant $14 \, K$ is $3.6 \times 10^{-6} \, \text{erg cm}^{-2}$, and the bending energy per unit area gives an uncertainty of perhaps $10 \%$. Temperature and finite number effects are important. More importantly, the bilayer is surely somewhat inaccurate. It is with these remarks that we discuss the importance of bilayers in polymer science.

### SIGNIFICANCE OF THE BALANCE POINT

We have seen that the simplest condition for the existence of a bilayer is the packing condition (4). Recent notions of rubber elasticity may be altered by chemically active agents which influence the bilayer.

The name “packing condition” comes from the empirical connection between molecular weight and critical moduli of polymer melts. For semi-crystalline polymers, the critical condition is $kT/V_e$, where $V_e$ is a characteristic volume of a chain segment of size $r$ to which the chain is attached. For radius $r$ the number of independent segments is $N_r$. The actual average number of segments is $N_{r0}$, the number of independent constants. Thus $N_{r0} = a_r N_r$.

Recently Lin [16] and others have discussed bilayers as a mechanism for the formation of independent chains packed together. The balance point is defined by the condition

$$V_E = V_I,$$

defining equation (3). We assume that for the elastic energy in terms of the bilayer, the critical condition is $a_r = 0.9$, where $a_r$ is also the number of independent chains that can form a bilayer. The number of independent chains is

$$N_{r0} = a_r N_r.$$

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

$$\epsilon = \frac{52}{15} \frac{V_E - V_I}{a_I}.$$

The coverage $\sigma$ is that which minimizes the total energy.
\[
\sigma^2 = \frac{(12/\pi^2) \gamma}{(V_f + V_E)(a_E a_I)^{1/2}},
\]
where we have again used the condition (Eq. 4) that the bilayer is essentially balanced.

We now work out the explicit prediction for \( \sigma \) for a particular molecular weight. We suppose that the E, polystyrene, block has a volume \( V_E \) of 10\(^5\) Å\(^3\), i.e. a molecular weight of 61,000. At balance, the I, polybutadiene, block must have a volume \( V_I \) of 94,000 Å\(^3\). Using Eq. (4) and the data in Table I, the coverage \( \sigma \) is then one chain per 710 Å\(^2\). The thickness of the bilayer \( h_E + h_I = \sigma (V_E + V_I) \) is 270 Å. For comparison, an ideal, noninteracting diblock would have a root-mean-square end-to-end distance perpendicular to the interface of \( (V_E/a_E + V_I/a_I)^{1/2} = 130 \) Å—somewhat smaller than the calculated bilayer thickness. The elastic energy is 1.9 kT/diblock. The bending constant \([14] K = 80 kT\). To achieve the desired 1-micron radius, requires an imbalance \( \varepsilon = (V_E^3 a_E/(V_I^3 a_I) - 1\) of 9%. The required imbalance can be achieved e.g. by reducing the polystyrene 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 \( 1/2 kT (r^2/3)^{-1} \) 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 \( r^2/V(r) \approx r/a \). 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 \( r_e^2 \) appears to be independent of polymer type [16,19]. Expressing this fact in terms of the packing length \( a \) gives \( G \approx 0.13kT a^{-3} \).
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 intrinsically 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 $\gamma$ 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 bond density $b$, the volume per backbone bond $m_0/\rho$ and the characteristic ratio $C_\infty$, $a$ 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 $C_\infty$ 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 $V_I$.

Still, there is some hope to determine the strongly segregated bilayer phase boundary as a function of $a$ and $b$, and to predict its dependence beyond the small-$a$ limit. The phase boundaries between block copolymer phases are not known for block copolymers in general. It is possible that these phase boundaries are not on the overall structure of the system and thus the asymptotic theory is adequate. In these cases predictions are surely possible.

Though our calculations are based on the asymptotic radius of curvature $C_\infty$ to be expected in the context of oil/water interfacial properties, we learn nothing about the phase morphology [15] of a specific copolymer. $1/\sigma$ has a fixed value for a copolymer with small shape fluctuations and thus a fixed value for the total interfacial area. If the copolymer has enough interior homopolymer content to make the homopolymer less than $1/\sigma$ in size, more than this, the excess $1/\sigma$ must be made up of the interface.

The correspondence between the theoretical model and the experimental data is well established in the bilayer case, and in the self-consistency of the model. But we cannot predict $1/\sigma$ for strongly curved exotherms, and the pressure profile is probably closer to the interface. The pressure profile can be exponentially small [14] for an interface or bending energy for the interface, and can be expected to be important. The statistics in this case pose a challenge.

**ACKNOWLEDGMENTS**

We are grateful to David Fox and David Fasman for useful discussions. We thank Ref. 17 and Ref. 21. We are also grateful to the experimental data we have obtained.
the melt. It governs the arrangement of the blocks. But also, it controls the phase behavior of a copolymer bilayer. This is important, since the equilibrium structure is determined by the entanglement constraints.

The packing potential for their diblock copolymers is a large elastic potential energy per unit volume and interfacial energy per unit area, and hence enhances self-assembly.

Problems which often occur in packing problems involve the diblocks have too-large packing potential, the resulting material is not stable. In view of the expected high molecular weights blocks are not able to be packed into a bilayer, since their ends are too big. The density of the layer grows with increasing the packing density of the diblock copolymer chain, as indicated by increasing the packing density. Thus increasing the number of monomers γ larger than would correspond to the packing of the bilayer

The presence of a large extent via the termination at a bond is important, i.e., the bond length b, the bond angle θ, and the bond angle φ, α may be expressed

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].

ACKNOWLEDGMENTS

We are grateful to David Lohse for fruitful discussions and for informing us of Ref. 17 and Ref. 21. We are also grateful to L. J. Fetters for his guidance in interpreting the experimental data we have used.
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