scattered but it appears that the ratio decreases slightly with increasing CM_w. This result may imply that the ratio is somewhat different in different regions. However, if we consider that most of the ratio is almost constant in the range of 0.5 ± 0.2 (nearly equal to the value reported in the earlier work[14]) over wide ranges of concentration and molecular weight, we may conclude that there is no significant difference between dependences of τ_0 and τ_w on concentration, molecular weight, and solvent power over regions II and IV.

In highly entangled regions, τ_w or τ_0 is reported to be well represented by the longest relaxation times of the terminal relaxation process.[14] However, there are only a few studies on terminal relaxation processes in semidilute solutions.[18,19] Further work is needed to understand viscoelastic properties in semidilute solutions systematically.

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Incorporation of Molecular Orientation into Systems of Lamellar Morphology. 1. Effects of Packing Entropy on the Lamellar Thickness of Block Copolymers

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ABSTRACT: Equations for the dimensions of the A and B regions of monodisperse diblock copolymers with lamellar morphology are obtained. An important feature of the treatment is the incorporation of the orientation-dependent packing entropy into the formalism. The equations are believed to be accurate over the whole range of orientation of bonds, from random orientation to perfect alignment. Copolymer thicknesses vary as the $^2/_3$ power of molecular weight to the first power depending on the amount of orientation induced by the packing entropy and the energetics. The amount of bond orientation in stretched molecules in bulk material is twice what the molecules would have if they were stretched (by the same stretch ratio) in solvent. It is observed that this effect is important to those systems of micelles, vesicles, membranes, soaps, liquid crystals, and block copolymers that experimentally are known to display significant orientation, and it is suggested that extant theories can be modified to include the effect.

1. Introduction

This paper is concerned mainly with the effect of orientation of polymer bonds on the thermodynamics of monodisperse block copolymers. A simple calculation given previously[1] shows that the dimensions of the homopolymer portions in the direction perpendicular to the lamellar surfaces vary as the $^2/_3$ power of the molecular weight. This means that the bonds have a net preferential orientation in the perpendicular direction. It is meaningful to ask how this orientation affects the thermodynamics of such systems.

Previous theories of block copolymers do not predict significant orientation. However, these theories do not take into account the orientation-dependent packing entropy, which when properly treated leads to the liquid crystal phase[2-5] (and also substantial orientation of the polymer) if the molecules are stiffer than a critical value. That this effect is relevant to block copolymers is suggested by those few existing experiments that show that the shape of small molecules dissolved in the lamella is nonspherical even though these molecules are small compared to the thickness of the lamella in which they are imbedded.[6] Presumably these small molecules sense the background grain of larger molecules comprising the lamella. This is consistent with the observation that nematic liquid crystals orient dissolved η-alkanes.[7]

Another reason for believing that the orientation effects are important is the existence of liquidlike theories of rubber elasticity that allow for competition for space among chains touching each other in a bulk rubber.[8,9] These theories predict a significant contribution to the stress–strain relation arising from the packing entropy.

The third reason for treating orientation effects is that they are known to be important in membranes. Not only is the amount of bond orientation substantial, but also it is strongly dependent on the location of the bond in the lipid molecules.[10]

Although we will develop our equations in the context of a discussion of block copolymers, the treatment will have application also to membranes, soaps, and smectic liquid crystals. These four classes of materials are closely related to each other, there being examples of materials that simultaneously fall into two or more classes. This is true for each of the six pairs of classes. Let us consider, for example, the connection between block copolymers and soaps. Each have amphiphilic characteristics. The two parts of the molecule energetically dislike each other but like themselves; this allows for segregation so that in diblock copolymers there can be a spatial alternation of A and B lamellae, while in soaps there is also a spatial segregation of the hydrophobic and hydrophilic parts.[11] In soaps the separation is aided and abetted by solvent while in block copolymers one does not need solvent, but this difference should not mask the same root cause. One can understand the properties of these materials in terms of forces tending to phase separate portions of the molecules that are covalently linked. The lamellar, cylindrical, and spherical phases in block copolymers correspond to the neat, middle, and isotropic phases in soaps. In fact the existence of the classification of phases of soaps and micelles by Ekwall et al.,[12] which includes other phases in addition to the neat, middle, and isotropic phases, suggests to us that there are corresponding phases in block copolymers that have not yet been found. It seems to us that soaps and micelles are nothing more than block copolymers that happen to have short hydrophobic parts and even shorter hydrophilic parts. The characteristic that separates block copolymers from the other three classes of materials seems to be only molecular weight; the MW of the subblocks is large, while in soaps, membranes, and smectic liquid crystals the corresponding MWs are small.

Such a unity and identity of subject matter requires and deserves a unity of approach and understanding. Since the lattice model has a history of success and wide applicability and since the main differences between the various classes seems to be one of molecular weight, we will work within the context of the lattice model. We shall see that our improved version of the lattice model can handle the main features of these materials. Ideally we should be able to use the lattice model to treat those factors that are important for our four classes of materials. They are (1) Orientation. As we have pointed out it is important to block copolymers and it is even more important to membranes, micelles, soaps, and liquid crystals since they are known to be highly oriented. (2) Concentration effects. (3) Intramolecular energy (chain stiffness effects) as well as intermolecular energy effects. (4) Spatial variation of density (concentration) as well as of orientation. This is important for molecules at an interface. All of our systems have interfaces associated with them. (5) Molecular weight of each of the homopolymer parts of the molecules. We are aware of no treatment that correctly combines spatial variation of both orientation and density (item 4 above) except for a lattice model treatment of rigid rods.[13] For this reason we shall not treat item 4 at all. This is a serious omission. Eventually of course we would hope to include gradient effects along with orientation effects. A possible approach might come through a generalization of the work of Scheutjens and Fleer.[14,15] Their work does indeed allow for a description in terms of spatial variation of both concentration and bond orientation. However, their procedure must first be improved by incorporation of an orientation-dependent entropy of packing term. The packing entropy for a system of flexible polymers that have spatial dependence of both density and orientation has been obtained;[16] however, we have not yet incorporated it into the Scheutjen–Fleer formalism. Finally, we shall in this paper concern ourselves mainly with item 1. It is our hope that other existing treatments would be able to incorporate the orientation packing entropy into their formalisms.

2. Theory

As an entre to the problem we begin with a simple treatment that results in the $^2/_3$ law. The free energy per chain can be written as a sum of four terms:

$$\frac{F}{kT} = \frac{3}{2}\left(\frac{l_1^2}{b_1^2 r_1}\right) + \frac{3}{2}\left(\frac{l_2^2}{b_2^2 r_2}\right) + \frac{\lambda^2\sigma}{kT} - 2\ln\lambda \qquad (2.1)$$

The first term arises from stretching the A portion a distance l_1. The number of statistical lengths is r_1, and the statistical length is b_1. The third term is a surface energy term, λ being the mean separation between adjacent chains and σ the surface free energy. The fourth term allows for the chain to be at any of the λ^2 positions within the area allowed to each chain (entropy of delocalization term). It gives only small corrections, and we shall henceforth ignore it (see also the Discussion). There are two equations of constraint, each of which state that the density, ρ_1 in monomer units per unit volume times the volume spanned by one polymer chain equals the number of monomer units:

$$\rho_1\lambda^2 l_1 = r_1, \qquad \rho_2\lambda^2 l_2 = r_2 \qquad (2.2)$$

These equations are obtained by counting the total number of monomer units within each lamella.

Of the subchains in a given lamella, a certain fraction are covalently connected to the lamella above, and the remainder are connected to the lamella below. We shall assume that a given subchain does not move from one lamella to another (there is a large energy barrier preventing this) and that therefore there is no attendant entropy contribution. Also the densities of the A type lamellae are taken to be the same (from lamella to lamella) and similarly for the B type lamellae.

Substituting from eq 2.2 into eq 2.1 and then minimizing F with respect to λ give

$$\frac{3r_1}{b_1\rho_1^2\lambda^5} + \frac{3r_2}{b_2^2\rho_2^2\lambda^5} - \frac{\lambda\sigma}{kT} = 0 \qquad (2.3)$$

Elimination of λ from eq 2.2 yields[1]

$$\frac{l_1}{r_1} = \left[\left(\frac{3\rho_1^3 kT}{\sigma}\right)\left(\frac{r_1}{b_1^2\rho_1^2} + \frac{r_2}{b_2^2\rho_2^2}\right)\right]^{-1/3} \qquad (2.4)$$

$$\frac{l_2}{r_2} = \left[\left(\frac{3\rho_2^3 kT}{\sigma}\right)\left(\frac{r_1}{b_1^2\rho_1^2} + \frac{r_2}{b_2^2\rho_2^2}\right)\right]^{-1/3} \qquad (2.5)$$

This approximation is expected to be valid for large molecular weights where Gaussian statistics hold. The physics behind these equations is simple. The interfacial tension term seeks to minimize area and therefore to diminish λ. By virtue of the equations of constraint this tends to make l_j large. But the configurational entropy of the chain resists stretching. The result is a balance between the interfacial tension and the elastic restoring force.

The equations predict that the chains are stretched in the direction perpendicular to the lamellar surface. This in turn means that the polymer bonds are oriented preferentially in the perpendicular direction, the amount of orientation varying with the parameters of our system. The question of whether these effects are large enough to be important is answered by calculation of the packing entropy, to which we now address ourselves.

We shall try to be as explicit as possible in listing the assumptions as we develop the theory. Hidden assumptions are damaging to the direction of future work. (1) We shall use the cubic lattice model oriented so that the z axis runs perpendicular to the lamellar surface. (2) Each configuration of the polymer chain is imagined to fit onto the lattice. (3) The two ends of each subchain are forced to lie within the planes separating the blocks, one end of the subchain lying in a different plane than the other end. This simplifying assumption was shown to lead to the same equations for lamellar thickness as when the free end is allowed to terminate anywhere within the lamella.[17] See the Appendix for further discussion of this point. (4) In ref 17 we observed that an A type polymer should be confined to walk between the planes that define the A block lamella (called model B[17]). We shall use the less accurate model C,[17] which allows the chain segments to spill over to the other side of each plane. The formulas for model B, which assumes constant density, are unwieldy and would, we feel, obscure the clarity of presentation of this initial effort. (5) We assume constant spatial density of polymer when calculating the packing entropy term as well as the elasticity term. This assumption is expected to be correct for the bulk phase but will be unrealistic when there is much solvent.

We must replace the terms appearing in eq 2.1 by more accurate ones and add the packing term. The expression for the elastic free energy is valid only for small elongation, and we replace it by a version of the venerable Kuhn–Grun formula[18] appropriate to our geometry. There are

$$W = \frac{r_1!}{(\alpha_{11}r_1)!(\alpha_{21}r_1)!}4^{\alpha_{21}r_1}\frac{(\alpha_{11}r_1)!}{\left(\dfrac{\alpha_{11}r + l_1}{2}\right)!\left(\dfrac{\alpha_{11}r_1 - l_1}{2}\right)!} \tag{2.6}$$

configurations accessible to a chain of r_1 links of unit length whose end points are l_1 links apart. The first factor gives the number of ways to arrange $\alpha_{21}r_1$ bonds parallel to the lamellae and $\alpha_{11}r_1$ bonds perpendicular to the lamellae ($\alpha_{11} + \alpha_{21} = 1$). The first subscript of α indicates direction, while the second subscript indicates species A or B. The second factor allows each of the parallel bonds to lie in any of the four allowed directions radiating out (parallel to the lamellae) from a lattice point. The third factor allows for the two kinds of perpendicular bonds, $(\alpha_{11}r_1 + l_1)/2$ stepping in the positive direction and $(\alpha_{11}r_1 - l_1)/2$ stepping in the negative direction. This term selects out from W only those configurations that have a z component of end-to-end length of value l_1. The contribution to the stretching entropy, S_e, arises from both of the subchains:

$$S_e/k = -\sum_{j=1,2}[r_j \ln 2 - \alpha_{2j}r_j \ln (2/\alpha_{2j}) - ((\alpha_{1j} + L_j)r_j \ln (\alpha_{ij} + L_j))/2 - ((\alpha_{1j} - L_j)r_j \ln (\alpha_{ij} - L_j))/2] \tag{2.7}$$

where our calculations are on a per chain basis, and $L_j = l_j/r_j$.

The packing entropy, S_p, is given by[8]

$$\frac{S_p}{k} = \sum_{j=1,2}\lambda^2 l_j\left[-\upsilon_{0j}\ln \upsilon_{0j} + \left(1 - \frac{(r_j - 1)\upsilon_{xj}\alpha_{1j}}{r_j}\right)\times \ln\left(1 - \frac{(r_j - 1)\upsilon_{xj}\alpha_{1j}}{r_j}\right) + 2\left(1 - \frac{(r_j - 1)\upsilon_{xj}\alpha_{2j}}{2r_j}\right)\times \ln\left(1 - \frac{(r_j - 1)\upsilon_{xj}\alpha_{2j}}{2r_j}\right) - \frac{\upsilon_{xj}}{r_j}\ln\left(\frac{\upsilon_{xj}}{r_j}\right)\right] \tag{2.8}$$

where υ_{0j} and υ_{xj} are the volume fractions of solvent and polymer. This expression requires some explanation. In 1956 Flory observed that the Flory–Huggins lattice model could be generalized to treat rigid rod liquid crystals.[3] A crucial modification occurred in the calculation of the competition of the chains for space. The expectation that a site was empty given that the previous site (in direction $-\Omega$) was empty was shown to depend on the orientation of the previously placed molecules. *Rods that lie in orientation Ω contribute according to their mole fraction, while rods perpendicular to Ω contribute according to volume fraction.* The physics behind this is that every one of the r segments of the rod perpendicular to Ω is a possible interference site, while the rod parallel to Ω can show only the one end site as a possible interference site. Each of the $r - 1$ other segments is shielded by its adjacent segment lying in the $-\Omega$ direction. These simple ideas were generalized to the case of flexible molecules that were oriented.[8] The number of possible interference sites on each molecule is r minus the number shielded by their adjacent sites. This later number is $\alpha_\Omega(r - 1)$, where α_Ω is the fraction of bonds in the Ω direction. These ideas were successfully used to generalize the lattice model to systems of flexible but oriented polymers and to develop the foundation of a liquidlike theory of rubber elasticity.[8,9]

The total free energy per chain can now be written as

$$\frac{F}{kT} = -S_e - S_p + \frac{\lambda^2\sigma}{kT} + \lambda^2\sum_{j=1,2} l_j\upsilon_{0j}\upsilon_{xj}\chi_j \tag{2.9}$$

We have used simple nearest-neighbor statistics in our expressions for the energy, believing that an improved energy expression is not warranted at this time. χ as usual is the dimensionless energy of mixing term.

The four equations of constraint are

$$\alpha_{1j} + \alpha_{2j} = 1, \qquad j = 1, 2 \tag{2.10}$$

$$\lambda^2 l_j = r_j/\upsilon_{xj}\rho_{0j}, \qquad j = 1, 2 \tag{2.11}$$

The volume constraint equations show that the bulk energy terms can be made not to depend on λ, L_j, or the α_{ij}. Therefore, they need not be considered in a minimization of free energy with respect to those variables. Of course, if we allowed the solvent to form a separate phase, as actually does happen for membranes, soaps, and micelles, and can happen for copolymers, then the bulk energies would be important determinants of how the solvent apportions itself between the polymer lamellae (solvent poor) phase and the solvent (solvent rich) phase. We do not consider this question here, nor do we concern ourselves with how the solvent apportions itself between the two species of polymer. These complications can be easily dealt with whenever we wish. If we now minimize the free energy with respect to the variables α_{1j} and L_j, we obtain using $\rho_{0j} = 1$ for simplicity and $(r_j - 1)/r_j = 1$

$$\frac{\alpha_{2j}(1 - \upsilon_{xj}\alpha_{2j}/2)}{2({\alpha^2}_{1j} - {L_j}^2)^{1/2}(1 - \upsilon_{xj}\alpha_{1j})} = 1 \tag{2.12}$$

$$\frac{2\sigma\lambda^4}{kT} = \sum_{j=1,2}\frac{r_j}{\upsilon_{xj}}\ln\left(\frac{\alpha_{1j} + L_j}{\alpha_{1j} - L_j}\right) \tag{2.13}$$

These equations turn out to be the expected generalizations of equations derived earlier for block copolymers with one block crystalline such as, for example, a diblock copolymer composed of polystyrene and poly(ethylene oxide).[17] They can be solved numerically for the lamellar thicknesses, for the orientations, and for λ. It is instructive

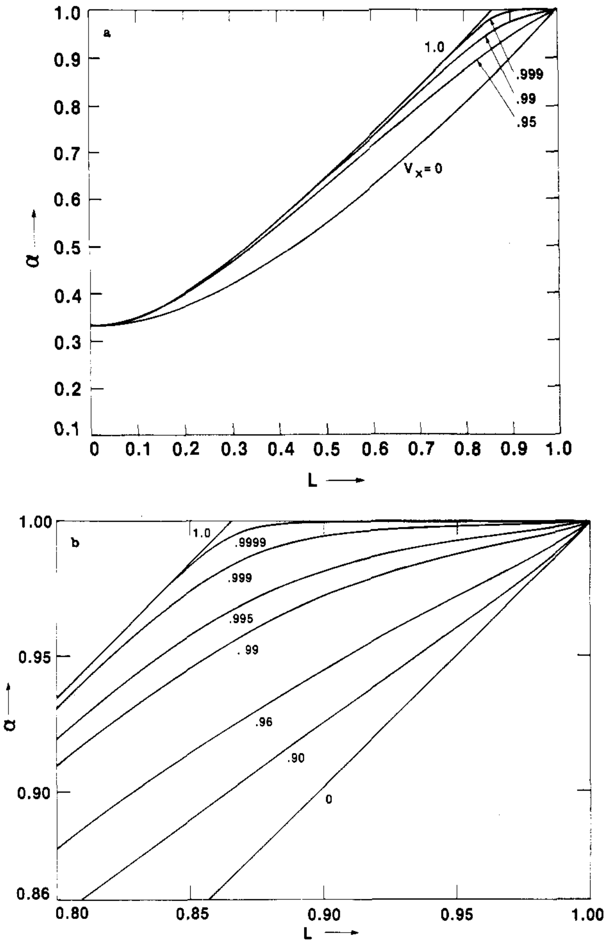

Figure 1. (a) Fraction of bonds, α, oriented in the direction perpendicular to the lamellae as a function of the normalized stretch ratio, L, for various volume fractions of polymer, V_x. This figure shows that bond orientation is enhanced by the presence of other nearby oriented polymer bonds. The connection between α and $P_2(\theta)$ is $P_2(\theta) = (3\alpha^2 - 1)/2$. (b) Bond orientation is a sensitive function of the volume fraction is polymer at high stretch ratio. See also eq 2.14. At high extensions, for bulk polymer, there can be a sudden snapping of the chains into the fully extended form.

to observe that for a given v_{xj}, L_j is a unique function of α_{1j}. The equation determining the dimensionless lamella thickness L ($L = l/br$) and orientation α within one lamella is decoupled from that for the other lamella (see eq 2.12). Figure 1 is a plot of α, the fraction of bonds perpendicular to the lamella versus L for various v_0. α varies from $^1/_3$ to 1, while L varies from 0 to 1. For small L the deviation of α from $^1/_3$ is quadratic in L. A simple calculation gives

$$\delta\alpha \simeq \frac{3 - v_x}{3 - 2v_x} L^2 \qquad (2.14)$$

Notice that the effect is twice as large for bulk polymers ($v_x = 1$) as for polymers in dilute solution ($v_x = 0$). This fact was first observed by Tanaka and Allen in a paper dealing with a liquidlike theory of rubber elasticity.[9] Finally, if we put $\alpha_{1j} = {}^1/_3$ in eq 2.13 and assume L_j to be small, then eq 2.4 and 2.5 are easily recovered ($\rho_j = V_{xj}\rho_{0j}$, $\rho_{0j} = 1$, and $b_j = 1$).

3. Discussion

The fact that lamellar thickness in block copolymers varies approximately as the $^2/_3$ power of molecular weight was confirmed experimentally by Hashimoto et al.[19] Earlier Helfand[20] and Meier[21] had developed theories that contained variation of lamellar thickness with MW of approximately $^2/_3$ power. The theory we developed here gives the $^2/_3$ power exactly in the limiting case of no entropy of packing term ($S_p = 0$). Because of the coupling of α to L we can expect MW variation from as low as $^2/_3$ to the first power of MW. In this theory it is the orientation-dependent packing entropy that gives rise to the higher power. Note should be made of experimental systems that seem to show linear dependence[22] and of theories of Alexander[23] and de Gennes[24] that predict linear dependence of thickness with MW for some adsorbed systems. Indeed the simple packing condition of eq 2.4 imply linear dependence provided λ is maintained close to 1 by strong attractive energies of the end groups. This is easily seen as follows. If the first segment of an A chain (the one connected to the B chain) occupies a lattice site in the plane separating A and B layers, and if the adjacent lattice sites in this plane are occupied by first segments of the neighboring A chains ($\lambda = 1$), then the second segment of the central chain must occupy the lattice site vertically above the plane. Therefore, each A chain prolongates itself in order not to overfill space. This effect is probably important for membranes made from low molecular weight chains.

Comments on the Entropy. A main result is that we have a unique relation between the lamellar thickness and the bond orientation within each lamella. This is embodied in eq 2.12. Thus any of the points along the curve of Figure 1 are permissible, the actual values of L and α being determined by eq 2.13. This curve is more accurate for large elongations than for small, the reason being that the packing term is exact for rigid rods oriented in a unique direction,[25] and the Kuhn–Grun formula is accurate over all extension values. Also, the idea that the end-to-end length determines lamellar thickness is exact in the limit of full extension of the molecules. On the other hand, for very small L it is not correct to identify the z component of the chain end-to-end length with L. These considerations have been discussed previously, and an improved but more difficult to implement version of the packing calculation has been developed,[17] but since our chains are expected to be somewhat extended, varying as the $^2/_3$ power of the MW (or higher) we shall not need those results here.

Another question about the entropic contribution is whether the use of three orientations rather than a continuum of orientations is sensible. For the configurational contribution, consideration of the central limit theory shows us that the distribution functions (for end-to-end length) are identical provided that the variances are chosen to be equal. This is achieved by making the bond length in the continuous case equal to the bond length for the discrete case. For the packing entropy contribution it was shown previously[4] that a continuum of orientations gave the same results as the case of a discrete set of orientations provided we chose the value of the coordination number properly. A related question has to do with the orientation of the end-to-end vectors of the chains. We placed them all vertical (perpendicular to the lamellae) in the simple treatment (eq 2.1), but in the more accurate treatment (eq 2.6) we allowed for the chain ends to be displaced horizontally. Yet the results are identical when $S_p = 0$. Perhaps the best test of an entropic theory is rubber elasticity since the elastic force is (almost) entirely entropic. But it is well-known that the three-chain model gives good results for rubber.[26] Therefore, we expect that more careful accounting of the distribution of end-to-end length vectors will not alter our results.

A subject that is both entropic and energetic dependent is the notion of statistical length. We should like our formulas to be valid when the beads have their own internal structure. There are two aspects to this problem.

The first concerns the isolated chain. Given that there is a correspondence between a real chain and its equivalent chain at zero applied field, does this correspondence persist for stretched chains? Specifically, we are concerned with whether the isomeric state model of a polymer exhibits the same stress–strain relationship as its equivalent chain. The answer, given by Volkenstein[27] and by Scott and Tobolsky[28] is that the stress–strain curves are different but only by a few percent over the whole extension range.

The second aspect concerns the spatial interference among equivalent chains. Our observation is that the equivalent bead should not be viewed as spherical. The equivalent bead model of a polymer chain defines the distance between adjacent beads and the number of beads. It does not concern itself with the shape or size of the (equivalent) bead, since only (equivalent) bead number and (equivalent) statistical length are needed to determine an end-to-end length distribution which is identical with that of the original chain. Now because we are dealing with dimensions of the molecules, we need to retain the equivalent chain model. However, because we are packing the chains together on the lattice, we also need to assign a proper volume and shape to each bead. A model that allows these possibilities simultaneously is a variant of the n-broken-rod model. The n-broken-rod model consists of n freely jointed rods each of length b and of thickness d (asymmetry ratio $\mu = b/d$). We can transform the rod model into a bead model by representing each rod as μ rigidly connected beads and allowing only every μth bead to be flexible. This bead model, which we shall call the n-broken-necklace model, seems to be a sensible model for an all-trans chain such as polyethylene when the fraction of flexes happens to be small. It allows us to assign a volume $V = nbd^2$ to each chain. Further, it allows us to picture the chain as fitting onto a lattice, each site of which has a volume of b^3. Such a picture is easily adapted to the Flory–Huggins lattice model.[29] It is immediately obvious that the orientation effects in this model are enhanced over what they would be if we had supposed the statistical length were spherical.

Another entropic effect is the confinement of a chain by its tube. A block copolymer molecule in a lamella would not be able to escape its tube because of the energetic improbability of the A portion of a molecule moving through the B type lamella (and conversely). Tube renewal times then are much larger for molecules in the lamellar phase. One wonders to what extent the initial conditions influence the final state. Certainly for the isotropic or spherical phase the number of molecules per sphere is determined by initial conditions rather than by end-state thermodynamics.[30] This tube effect can be used as a justification for ignoring the ln λ^2 term in the entropy.

An important aspect of tube confinement is that the dimensions of the chains in the horizontal directions are drastically affected by the confinement. In rubber elasticity theory the tube was assumed to deform affinely,[31] resulting in corrections to the stress–strain relations[32] and also resulting in lateral contraction of the confined (stretched) chain. In the block copolymer problem, tube confinement will certainly act to reduce chain dimensions in the horizontal directions in accord with experimental results.[33] One is tempted toward a simple-minded application of the tube concept and assume the horizontal dimensions to be proportional to λ. We will resist this temptation but observe that tube confinement considerations are an essential part of the block copolymer problem as well as the problem of rubber elasticity.

Comments on the Energy. Our choice of the energy is the simplest possible. We should be open to the possibility that there is an orientation-dependent energy between chains and that this energy can serve to increase the extent of alignment. It is known, for example, that van der Waals forces between two cylinders strongly favor parallel alignment. This means that we should be open to the possibility of a cooperative locking-in of the stretched state arising from an energy so that stretched chains are favored. It is also possible for strictly intramolecular energies to favor extension. All that is needed is that the internal energy cooperatively depend on the amount of orientation. Thus, for example, the coupling of the helix–random coil transition within a single polymer chain to the nematic liquid crystal to isotropic plane transition treated by Matheson and Flory results in enhanced alignment.[34] If these chains were part of a block copolymer, there would then be an additional alignment pressure over and above what we have predicted. Figure 1 suggests that the system can jump from partial to total alignment.

Six Simple Generalizations. The reason for discussing, however briefly, these generalizations is first to display the richness of the subject and second to observe that the packing entropy is relevant to each of them. The packing entropy should materially affect results whenever there is an appreciable amount of bond orientation and, for flexible polymers, when the volume fraction of polymer is large.

The effects of external fields are easily incorporated into the formalisms by adding a work term to the free energy. To illustrate, imagine that a constant force of magnitude f acts on the ends of the chains in a direction perpendicular to the lamellae. We simply add $f(l_1 + l_2)$ to the expression for free energy, either eq 2.1 or 2.9, depending on our level of approximation. It is instructive to use the simpler approximation, which when we minimize the free energy leads to a cubic equation (in λ^2):

$$-((3r_1/b^2{}_1\rho^2{}_1) + (3r_2/b^2{}_2\rho_2{}^2)) + \sigma\lambda^6/kT - (f/kT)((r_1/\rho_1) + (r_2/\rho_2))\lambda^2 = 0 \quad (3.1)$$

A cubic equation of the above reduced form will have three real roots whenever[35]

$$-[(f/3\sigma)((r_1/\rho_1) + (r_2/\rho_2))]^3 + [(3kT/2\sigma)((r_1/b_1{}^2\rho_1{}^2) + (r_2/b^2{}_2\rho_2{}^2))]^2 < 0 \quad (3.2)$$

Thus, for large enough f the free energy will display two minima. This supports the idea of a sudden snapping-in of an extended chain form as suggested above. A strong enough orienting energy, either from an external force f or from a very large surface free energy σ, which in combination with the volume constraint forces orientation, or from intra- and intermolecular energies that are directly orientation dependent, can cause a jump to the extended chain form.

Another simple generalization concerns the equilibrium between a lamellar system and solvent. As usual this problem is solved by equating the chemical potential of the solvent in the lamellar phase to the chemical potential of the solvent-rich phase, which we approximate as pure solvent. The value of this generalization lies in the fact that one can prepare isolated membranes by adding solvent to certain block copolymers or smectic liquid crystals.

The other phases that we need to compare the lamellar phase to are the cylindrical and spherical phases and the random amorphous phase. One suspects that we can add a patch consisting of our orientation-dependent packing term suitably generalized to cylindrical and spherical geometry to the manifold of existing treatments.[36] See also below.

A fourth generalization is to molecules that are not linear. Let us take as an example a star molecule of $n + m$ branches, n of type A each of length r_1 and m of type B each of length r_2. The expression for the free energy, eq 2.1, is altered by multiplying the first term on the right-hand side by n and the second by m. Equation 2.2 is altered by multiplying the right-hand side of the first equation by n and the right-hand side of the second equation by m. λ is interpreted to be the distance between the star centers lying in the plane separating the two phases. These new equations can be made identical in form with the old equations by the substitutions $r_1' = nr_1$, $r_2' = mr_2$, $b_1' = b_1/n$, and $b_2' = b_2/m$. Thus the equations for the lamellar thicknesses are obtained directly from eq 2.4 and 2.5. They are

$$\frac{l_1}{nr_1} = \left[\left(\frac{3\rho_1^3 kT}{\sigma}\right)\left(\frac{n^3 r_1}{b_1^2\rho_1^2} + \frac{m^3 r_2}{b_2^2\rho_2^2}\right)\right]^{-1/3} \quad (3.3)$$

$$\frac{l_2}{mr_2} = \left[\left(\frac{3\rho_2^3 kT}{\sigma}\right)\left(\frac{n^3 r_1}{b_1^2\rho_1^2} + \frac{m^3 r_2}{b_2^2\rho_2^2}\right)\right]^{-1/3} \quad (3.4)$$

Note that for $n = m$ the thicknesses are unchanged but λ increases by $m^{1/2}$!

Perhaps the most interesting thing about these equations is that they force us to face the problem of the buckling and bending of lamella. It is evident that there is a choice of b_i and r_i, for which there is no tendency to buckle. Increasing the length of say the B block molecules would favor the formation of a sphere whose center is surrounded on the inside by the A shell and on the outside by the B shell. Similarly, increasing the A block length would bend the lamella the other way.

We can easily determine the radius of the sphere in the region of gentle curvature where $R \gg (l_1 + l_2)$. Imagine a spherical micelle (vesicle) of one layer whose radius R is large compared to the lamellar thicknesses l_1 and l_2. The volume allowed to an A type strand can be represented by a truncated pyramid of height l_1 and width $Rd\theta$, where R is the distance from the center and $d\theta$ is the angle between centers of nearest-neighbor chains. The volume of the truncated pyramid is to first order in $1/R_0$:

$$V_1 = l_1[(R_0 + l_1/2)d\theta]^2 = l_1\lambda^2 + l_1^2\lambda^2/R_0 = r_1/\rho_1 \quad (3.5)$$

Where we have used the relation $\lambda = R_0 d\theta$. Similarly, for the B layer we obtain

$$V_2 = l_2[(R_0 + l_2/2)d\theta]^2 = l_2\lambda^2 - l_2^2\lambda^2/R_0 = r_2/\rho_2 \quad (3.6)$$

The minus sign appears in the constraint equation for the phase on the interior of the sphere. The free energy is now implicitly a function of R_0, and minimization of the free energy, which retains the form of eq 2.1, with respect to R_0, λ, l_1, and l_2 subject to the above equations of constraint yields after a considerable amount of algebra

$$R_0 = \frac{2r_1r_2}{\rho_1\rho_2}\left(\frac{r_1}{b_1^2\rho_1^2} + \frac{r_2}{b_2^2\rho_2^2}\right)^{2/3}\left(\frac{3kT}{\sigma}\right)^{-1/3} \times \left(\frac{r_1^2}{b_1^2\rho_1^3} - \frac{r_2^2}{b_2^2\rho_2^3}\right)^{-1} \quad (3.7)$$

This equation is valid only for large R_0, which occurs when $r_1^2/b_1^2\rho_1^3$ and $r_2^2/b_2^2\rho_2^3$ are approximately equal. For the star molecules we easily obtain by the same argument leading to eq 3.3 and 3.4

$$R_0 = \frac{2r_1r_2mn}{\rho_1\rho_2}\left(\frac{n^3r_1}{b_1^2\rho_1^2} + \frac{m^3r_2}{b_2^2\rho_2^2}\right)^{2/3} \times \left(\frac{3kT}{\sigma}\right)^{-1/3}\left(\frac{n^4r_1^2}{b_1^2\rho_1^3} - \frac{m^4r_2^2}{b_2^2\rho_2^3}\right)^{-1} \quad (3.8)$$

The formulas for l_1 and l_2 are again given by eq 3.3 and 3.4 to zeroth order in $1/R_0$.

It is a simple matter to show that for cylindrical geometry the radius is exactly half that given by eq 3.8 or 3.7.

Our treatment, which is a treatment of a vesicle (micelle with a central solvent region), should be contrasted to that of Leibler et al.,[3] who treat a spherical micelle without a central solvent region. Rault also has calculated dimensions in the lamellar, cylindrical, and spherical diblock copolymer mesophases.[38] His formulas for lamellar thickness of the lamellar phase, though different from ours, does give variation with the $^2/_3$ rds power of molecular weight.

These formulas show that the radius is very sensitive to the parameters of the system such as relative chain lengths, relative lamellar densities, and in star molecules the relative number of branches of the A and B kind. Another important aspect of the problem is hysteresis. A spherical micelle or vesicle has a problem adding or taking away a molecule. To reach the interior A region of the micelle, the A part of the molecule has to traverse the B region. The energy barrier is of the order of $\sigma_{ab}r_a$, which can be very large. One predicts that the number of AB molecules in a micelle or vesicle is resistant to change.

A sixth generalization is to a mixed system consisting of an AB block copolymer whose A block has A type homopolymer molecules dissolved in it. If the unperturbed dimensions in the homopolymer molecules are larger than the lamellar thickness, then the deviations from sphericity are towards oblateness, since for energetic reasons the homopolymer will want to remain within the lamella. However, if the molecule is small compared to the lamellar thickness, then the molecule will be a prolate spheroid with the long axis perpendicular to the lamellae. The reason is simply that it is easier to step in the direction of elongation in a stretched system than perpendicular to it. This was the reasoning behind the derivation of eq 2.8. The problem of determining the probability distribution for the chain is the same as determining the probability distribution for a particle moving in a medium of asymmetric diffusion coefficient. This has already been done in the context of a particle diffusing in a liquid crystal medium.[39] A more comprehensive treatment by Ben-Shaul et al. calculates the stretching for an isomeric state model of chains dissolved in a nematic substrate.[40]

Experiments exist that have measured the prolate character of the dissolved homopolymer.[6]

At this point it would be beneficial to examine the existing theories to see to what extent they include orientation effects and to determine if packing entropy considerations can easily be incorporated into the various formalisms. Some theories use a simple volume fraction to account for competition for space; they therefore do not correctly account for the orientation-dependent packing entropy. The Scheutjens–Fleer treatment[14,15] would seem logically to be the one to attempt to incorporate the packing entropy because the theory is set up to yield the number of bonds of each orientation at each level (depth within the lamella) for each kind of molecule. Of course,

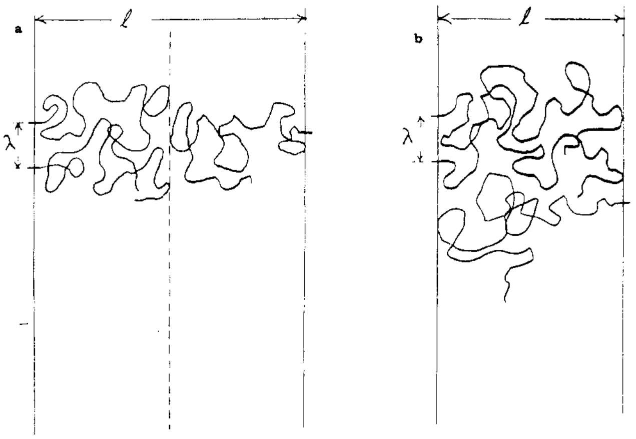

Figure 2. Noninterpenetration model of a is favored over the interpenetration model of b. The free energy is less because the chains are stretched less in the noninterpretation model.

some theories are concerned only, or mainly, with copolymers of large molecular weight that may not have significant orientation. Here the question is unimportant. However, for those systems of micelles, vesicles, membranes, soaps, liquid crystals, and block copolymers that experimentally do display bond orientation the question is important.

The theories of Dill and Cantor do account for some aspects of orientation-dependent interferences,[41] but it is not evident that the orientation-dependent packing entropy is correctly computed in their treatments. The relation between this treatment and theirs requires further elucidation.

Appendix

The chains that comprise an A lamella in a diblock copolymer of lamellar morphology cannot very easily thread through an adjacent B lamella and thereby become part of the next A lamella since the energy barrier is so high. A traverse requires many A monomers of one chain to be in the B region simultaneously. Therefore, we can expect that the number of A chains entering from each side of an A lamella is fixed by initial conditions. In the body of the paper we assumed that a chain samples the full width of the lamella. This assumption is appropriate to the case where all the chains comprising a lamella enter from one side. For the more usual case where equal numbers of chains enter from both sides of the lamella, we now show that the chains should be viewed as being stretched only half of the lamellar width.

Let us evaluate the free energy of the two systems depicted in Figure 2. The case of no interpenetration, Figure 2a, is identical with that treated in the text except for the fact that we use $L_i/2$ rather than L_i in the formulas (eq 2.2). The free energy per molecule is

$$F_N = \frac{3}{8}\left(\frac{l_a^2}{b_a^2 r_a}\right) + \frac{3}{8}\left(\frac{l_b^2}{b_b^2 r_b}\right) + \frac{\lambda^2\sigma}{kT} \tag{A1}$$

$$\lambda^2 l_a = 2r_a, \quad \lambda^2 l_b = 2r_b \tag{A2}$$

where λ is the mean separation between neighboring chains. λ lies in the plane separating the A lamella from the B lamella and connects the covalent bridges between A blocks and B blocks. If the number of chains in one lamella is $2N$, then $\lambda^2 N$ is the area of the interface separating the A and B regions. For the case of interpenetration, Figure 2b, we have for the free energy per molecule

$$F_I = \frac{3}{2}\left(\frac{l_a^2}{b_a^2 r_a}\right) + \frac{3}{2}\left(\frac{l_b^2}{b_b^2 r_b}\right) + \frac{\lambda^2\sigma}{kT} \tag{A3}$$

$$\lambda^2 l_a = 2r_a, \quad \lambda^2 l_b = 2r_b \tag{A4}$$

where λ has the same meaning as above. The solution to the above sets of equations is again given by eq 2.4 and 2.5, with the only difference being that for the case of no interpenetration we use 2σ in place of σ and $2b_i$ in place of b_i. This means only that the values of the lamellar thicknesses are doubled, but the functional forms remain the same. For the case of interpenetration the only change is to use 2σ in place of σ in eq 2.4 and 2.5. Here the only effect is to increase the lamellar thicknesses by a factor of the cube root of 2.

When these values for the lamellar thicknesses are substituted into the expressions for the free energy, we find that

$$F_N/F_I = 2^{2/3} \tag{A5}$$

which means that the noninterpenetrating situation prevails. This is in accord with a recent experimental observation by Han that deuteriated ends of a diblock copolymer prefer to be located in the middle regions within a lamella rather than be uniformly distributed throughout. It is also in accord with studies on micelles and low molecular weight bilayers by Szleifer et al.[42]

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fraction rather than the volume fraction for the interference term. The second step is to break the line of $N = N_0 + xN_x$ sites into $N^{2/3}$ lines each of $N^{1/3}$ sites. The problem of placing the N_x molecules on these $N^{2/3}$ lines is the same as the problem of placing N_x molecules in a three-dimensional cubic lattice when the molecules all have the same orientation. It is easy to show that to first order in N the entropy is the same for the $N^{2/3}$ lines of length $N^{1/3}$ as for the one line of length N.

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Role of Excluded Volume in the Configurational Properties of Uniform Star Polymers: Iterative Convolution and Monte Carlo Simulation

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ABSTRACT: The dimensional properties of three-dimensional uniform athermal self-avoiding star polymers of small to intermediate molecular weight are determined in the iterative convolution (IC) approximation. The results are compared with continuum Monte Carlo (MC) simulations and with lattice-based and renormalization group (RG) estimates that relate to the large-N limit. In particular, the present analysis provides direct structural and dimensional assessment of the interior star regimes proposed by Daoud and Cotton, which are inaccessible to the lattice-based and RG treatments. We find no evidence to support the Daoud–Cotton proposals. On the basis of the iterative convolution approximation, the central core structure of the star terminates at a density discontinuity followed by secondary radial structural features. These features are confirmed by Monte Carlo simulation. The relative mean square radii of gyration $g(f) = \langle S_N^2(f)\rangle / \langle S_N^2(1)\rangle$ is determined as a function of branching number f, and contrary to the Daoud–Cotton proposals we find $g \sim f^{-1}$ for small-to-intermediate uniform star systems. The particle scattering function $P(Q)$ is also determined, and comparisons are made with its random walk counterparts for a variety of star configurations.

Introduction

Interest in the theoretical description of the configurational properties of star-branched polymers has developed considerably with the increasing body of experimental data, largely based on recent light-scattering[1] and rheological/hydrodynamic studies.[2] Since the classic paper of Zimm and Stockmayer[3] based on the random-walk model (RW) of a polymer star, subsequent attention has been focused largely on the incorporation of the excluded volume effects appropriate to a real molecule. Notwithstanding these attempts, considerable attention has been devoted to the configurational statistics of star polymers in Θ solvents, and these studies have been complemented by experimental studies in Θ solutions. However, as has been frequently observed, there may not exist a unique Θ point at which the Zimm–Stockmayer theory would be appropriate due to the strong radial variation in monomer concentration about the star's vertex. Indeed, Daoud and Cotton[4] identify three distinct concentration regimes outward along a radial vector from the star center: in the central close-packed core the monomer concentration is essentially constant, while at intermediate distances interbranch effects dominate, excluded-volume effects are effectively screened, and the behavior is assumed to be Gaussian. In the outermost regions the full intrachain excluded-volume effect obtains, and in conjunction with a variable blob size representation of the sequence along each star branch, Daoud and Cotton established a functional form for the radial distribution of monomer concentration on the basis of scaling arguments in terms of the number of branches f and distance from the central vertex. Implicit in their treatment is the assumption of a monotonically decreasing monomer concentration along a radius vector, together with a somewhat arbitrary choice of blob size. Despite these objections, some of their results are in good agreement with light-scattering data[1] and recent exact enumeration studies,[6] although the model remains open to the above criticisms. Two of the characteristics of scaling arguments are their restriction to a power law representation of the configurational properties upon density and molecular weight and their inability to predict prefactors and distribution functions; in this regard the analysis of Daoud and Cotton is no exception. Indeed, many of the power law exponents are independent of the number of branches, the structure of the star polymer emerging solely from the prefactors, clearly emphasising the importance of their explicit determination.

More recently a chain conformational renormalization group (RG) technique has been applied to star polymers by Miyake and Freed[5] whose specific objectives were to

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