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Conclusions

Several pertinent aspects emerge from the present photon correlation spectroscopic study of the diffusional dynamics in the poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO) mixture. The mutual diffusion coefficient D changes significantly with temperature for blend compositions near the critical concentration due to strong thermodynamic interactions. At extreme compositions, D exhibits a temperature dependence very similar to that of the shear viscosity.

At constant temperature and composition, the transport coefficient D^0 is rather insensitive to molecular weight variations, in agreement with the "fast mode" theory of mutual diffusion. The purely dynamic quantity D^0, which is a weighted average of the tracer diffusivities of the two components, can be extracted from the mutual diffusion D and the static structure factor $S(0)$ accessible from the same experiment.

At constant temperature, the mutual diffusion D in the PEO(1000)/PPO(1025) blend is strongly reduced near the middle of the composition range mainly due to the unfavorable segment–segment interactions. The positive interaction parameter χ_F leads to $D^0 < D$, in agreement with the theoretical prediction. Using the values of the self-diffusion coefficients of the blend components determined by NMR measurements, the computed values of D are in agreement with the experimental D in extreme blend compositions. However, near the middle of the composition range the φ dependence of D^0 cannot be described by either the "fast" or "slow" mode theories. Possible reasons for this discrepancy are discussed.

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Registry No. PEO, 25322-68-3; PPO, 25322-69-4.

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Lattice Model for Crystal–Amorphous Interphases in Lamellar Semicrystalline Polymers: Effects of Tight-Fold Energy and Chain Incidence Density[1]

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ABSTRACT: The partition function for polymer chains in the interphase of lamellar crystallites has been evaluated by the enumeration of the different ways of placing chain segments on a lattice. In essence, we have reformulated the earlier work of Flory, Yoon, and Dill. In the case of fully flexible chains involving no conformational energy for tight-folds, our expression for the partition function reduces to the form reported by Marqusee and Dill, who derived their partition function through probabilistic, space-filling arguments. However, the inclusion of an energy term E_η disfavoring tight-fold conformations is found to decrease significantly the fraction of regular adjacent folds and increase the thickness of the interphase. Quantitative results from our calculations are in good agreement with the Monte Carlo results of Mansfield. The effect of the chain incidence density at the crystal surface on the fraction of regular adjacent folds is also examined, and we show that both these factors are important in determining the structure of the crystal–amorphous interphase.

Introduction

Order–disorder transitions for small-molecule systems across interphases occur over distances comparable to the molecular size. However, since the extent of the phases themselves are frequently macroscopic, the interphase may essentially be ignored in the framework of classical thermodynamics of small molecules. Frequently, therefore, these interphases are idealized, following Gibbs,[3] to be

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infinitesimally thin. These arguments are essentially inapplicable to polymeric systems due to two factors. First, in most cases (for example, the domains in a microphase-separated block copolymer or a crystal–amorphous interphase) the size of the phase is comparable to the dimensions of the interphase itself. Second, the connectivity of the segments of a chain induces a "memory" in the molecule that persists over a length scale that is comparable to its unperturbed radius of gyration (R_g). Due to these two reasons the understanding of the effects of interfacial properties is very important in the case of macromolecular systems.

The general problem of polymers at interphases has received considerable interest and has been the source of much discussion in the past few years.[4-20] Problems that have been investigated include phase-separated block copolymers, the behavior of polymer melts and solutions in thin films, and the crystal–amorphous interphase in semicrystalline polymers. In this paper we concern ourselves with the crystal–amorphous interphase, i.e., the dissipation of order occurring when polymer chains traverse from lamellar crystals to an amorphous region, a situation encountered in the case of many semicrystalline polymers. Flory[4] first argued that compared to the crystal one must have a reduced chain "flux" in the amorphous phase, to allow for the chains to be disordered in this region. He concluded that more than half of the chain sequences emanating from the crystal surface must reenter the same crystallite but not necessarily at sites adjacent to those that they emerged from. Frank[5] presented more rigorous arguments on this problem. His theory, based purely on geometrical considerations, cannot quantitatively predict the fraction of chain sequences that fold back immediately. He estimated for a typical case, however, that at least 70% of all chain sequences emanating from a lamellar crystal must return by forming tight-folds near the surface. A consequence of these statements is that although models based on the geometry of crystal–amorphous phases can yield bounds on the fraction of chain sequences associated with reentry folds, they cannot be used in the quantitative determination of the structure of the interfacial region.

A technique to overcome the deficiencies of the geometric models is to develop theories based on statistical mechanics. The first quantitative treatment of this problem, on this basis, was attempted by DiMarzio and Guttman,[6,7] who modeled chains in the crystal–amorphous interphase through the use of random chain statistics. However, in this approach, the authors assumed that the configurations of chains followed unperturbed or Gaussian statistics. Since it is well-known that the presence of interphases modifies the chain conformations near these boundaries, it is clear that this assumption makes the model questionable for comparison to experimental or Monte Carlo results.

The assumption of unperturbed random chains has been relaxed subsequently in the work of Flory et al.[18] and, more subtly, in the work of Helfand.[8] Through an enumeration of the number of possible configurations of chains on a lattice, Flory et al.[18] have shown that ca. 42% of all the sequences of completely flexible infinite molecular weight chains emerging from the lamellar surface form tight hairpin bends, or regular folds, in the immediate vicinity of the crystal, i.e., in the first lattice layer (see the section on model description). Moreover, the fraction of adjacent reentry folds was shown to decrease further as chain flexibility wsa decreased.

Somewhat different results were obtained by Marqusee and Dill,[19] who have employed the expression for the entropy of the chains in the interphase as developed by Helfand[8] using probabilistic expressions for space filling. Through this formulation it has been shown that ca. 74% of the crystalline stems are involved in the formation of tight adjacent folds in the first layer of the lattice. This number is in good agreement with the Monte Carlo results of Mansfield,[17] who predicts that ca. 72% of the chain stems are involved in tight adjacent folds. The difference between the formulations of Flory et al.[18] and Margusee and Dill[19] are of particular significance since the application of unperturbed chain statistics[6,7] to this problem shows that 66% of chains issuing from the crystal will form adjacent folds in the first layer. The two models presented above therefore predict that lattice chains will not be unperturbed but predict departures that are in opposite directions.

In this paper we have reformulated the earlier work of Flory et al.[18] to account for some approximations inherent in their formulation of the appropriate partition function. For fully flexible chains our expression for the partition function reduces to the form reported by Helfand[8] and Marqusee and Dill.[19] Most importantly, we have incorporated an energy factor E_η that is associated with formation of tight-folds and show that the results of our calculations are in good agreement with Monte Carlo results.[17] This factor of tight-fold energy was considered in the analytical model of Flory et al.[18] Marqusee and Dill,[19] however, considered only the completely flexible chain, in deriving the analytical equations and comparing their results with the analytical results of Flory et al.[18] and the Monte Carlo results of Mansfield,[17] and hence did not include this factor, which is most critical for real polymer chains (see below).[25] The effect of changes in chain density at the crystal surface on the fraction of chains that form adjacent folds in the first layer is also examined for completely flexible chains.

Model

We consider infinite molecular weight chains emanating from a lamellar crystallite. It is assumed that the chains occupy only those configurations that may be accommodated on a lattice of coordination number z. (It must be stressed that a completely flexible chain, in this context, would involve only those conformations that are permitted under the constraints imposed by the lattice.) One axis of this lattice is normal to the crystal, while the other axes form a plane that is parallel to the surface. We have chosen to study completely filled lattices, i.e., the effects of changes in compressibility of the medium are ignored.

Our principal analysis has been restricted to chains on a cubic lattice ($z = 6$). Following earlier practice, a cell on this lattice is approximately 4.5 Å on a side, or a lattice site holds $\simeq$3.5 methylene groups.[18] Lattice layers are numbered sequentially, with the crystal being numbered as layer 0 and layers further from the crystal boundary being numbered in ascending order. It has been assumed that each site in the lattice has $(z - 2)$ nearest neighbors in the same layer and one each in its two immediately adjacent layers. Our initial investigation focuses on completely flexible chains placed on this lattice, with no energy effects associated with any conformation. Any effect of the interphase on the properties of the lattice chains will thus be an entropically driven phenomenon. Subsequently, we introduce an energy $E_\eta k_B T$ for each tight-fold conformation to model the difficulty of chains to form tight-folds. The effect of the variation of the dimensionless energy parameter, E_η, on the configurations of chains in the

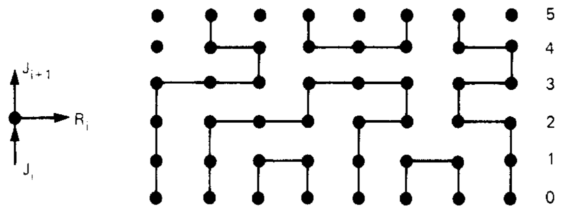

Figure 1. Schematic representation of the interphase in lamellar semicrystalline polymers. The layers are numbered sequentially with the last crystal layer being numbered zero. J_{i+1}, J_i, and R_i denote the number of different lattice connections in layer i.

crystal–amorphous interphase will then be studied.

Problem Formulation

Completely Flexible Chains. The notation used in this document closely follows that in ref 18, i.e.: the number of vertical bonds spanning layer $i-1$ to $i \equiv J_i$; the number of vertical bonds spanning layer i to $i+1 \equiv J_{i+1}$; the number of horizontal bonds in layer $i \equiv R_i$; the number of lattice sites per layer $\equiv N_0$. The geometrical basis for this model is sketched schematically in Figure 1. It has been assumed that we have a constant number of sites in each layer, an assumption that is valid for cubic lattices. Extension to spherical or cylindrical lattices will involve allowing for this number to be a function of the position of the layer.[16] In the case of a cubic lattice that is fully filled with infinite chains, the following constraint equation will have to be satisfied:[18]

$$J_i + J_{i+1} + 2R_i = 2N_0 \tag{1}$$

for each lattice layer i. Equation 1, which has also been termed as the conservation condition,[18] expresses the facts that each of the N_0 lattice sites in a layer will have two bonds connected to it and that these bonds will have to be apportioned between the J_i, J_{i+1} vertical and R_i horizontal bonds. We may rewrite eq 1 as

$$\frac{J_i}{2} + \frac{J_{i+1}}{2} + R_i = N_0 \tag{2}$$

An interesting aspect of eq 1 and 2 is that the number of vertical bonds related to layer i (namely, J_i and J_{i+1}) have been weighted by a factor of $^1/_2$ relative to the horizontal bonds (R_i). The rationale for this biased weighting is that although the horizontal bonds will be accounted for only in layer i, the contributions of the vertical bonds will be enumerated in two layers (for example, J_i vertical bonds will be accounted for in layer $i-1$ and also in layer i). Equations 1 and 2 are, therefore, consequences of the layer-by-layer approach that we will adopt toward the mathematical formulation of this problem.

We now proceed to the formulation of the partition function of the chain segments that are associated with lattice layer i. First of all, the different ways of arranging R_i indistinguishable horizontal bonds on the available N_0 sites will be enumerated. This quantity may be expressed in the spirit of the Bragg–Williams approximation as

$$\Omega_1 = \frac{N_0!}{R_i!(N_0 - R_i)!}(z-2)^{R_i} \tag{3}$$

The last factor in eq 3 [involving the $(z-2)$ term] is the result of the assumption that each horizontal bond in this layer has an internal degeneracy of $(z-2)$, i.e., it accounts for the fact that each site in layer i has $(z-2)$ nearest neighbors in the same layer.

We now have to calculate the number of different ways of placing J_i indistinguishable vertical bonds that span layers $i-1$ and i, and J_{i+1} vertical bonds spanning layers i and $i+1$ on the remaining $(N_0 - R_i)$ sites. This may be expressed, again in the spirit of the Bragg–Williams approximation, as

$$\Omega_2 = \frac{(N_0 - R_i)!}{(J_i/2)!(J_{i+1}/2)!} \tag{4}$$

As stated before, a weighting factor of $^1/_2$ is assigned to the vertical bonds to account for the fact that these sequences will also be included in the formulation for the respective adjacent layers. (That is, J_i will be accounted for in layers $i-1$ and i, and similarly J_{i+1} in i and $i+1$.) The partition function for polymer chains in this layer may be obtained by taking a product of eq 3 and 4. We may write the partition function of layer i, to within multiplicative constants, as

$$\Omega_i = \left[\frac{1}{z}\right]^{J_{i-1}/2}\left[\frac{1}{z}\right]^{J_{i+1}/2}\left[\frac{z-2}{z}\right]^{R_i}\frac{N_0!}{(J_i/2)!(J_{i+1}/2)!R_i!} \tag{5}$$

It is to be noted that in the derivation of eq 5, the connectivities of the molecules have not been explicitly accounted for. The only statement of the nature of molecules is eq 2, the conservation condition, which ensures that each lattice site has two bonds emanating from it. However, no other conditions such as the self-avoiding nature of the molecules or the symmetry of the conformations of bond-pair junctions have been built in. The symmetry criteria of bond-pair junctions, also termed as the continuity condition in ref 18 (see Appendix) have been considered an important factor in accurately determining the conformations of macromolecules in interphases. The effects of the exclusion of these criteria in this formulation will be examined in the Results and Discussion section.

We now introduce the following definitions:

$$p_i(-) = \frac{J_i}{2N_0} \tag{6a}$$

$$p_i(+) = \frac{J_{i+1}}{2N_0} \tag{6b}$$

$$p_i(0) = \frac{R_i}{N_0(z-2)} \tag{6c}$$

and the definition of entropy associated with the chains in the interphase spanning k lattice layers adjacent to the crystal surface:

$$S = k_B \sum_{i=1}^{k} \ln \Omega_i \tag{7}$$

where k_B is the Boltmann's constant, and Ω_i is defined as in eq 5. One may then show that entropy of chains in the interphase is, apart from additive constants

$$\frac{-S}{N_0 k_B} = \sum_{i=1}^{k} p_i(-) \ln p_i(-) + p_i(+) \ln p_i(+) + (z-2)p_i(0) \ln p_i(0) \tag{8}$$

This result is exactly the same as the one presented by Helfand[8] and later utilized by Marqusee and Dill.[19] The difference between the earlier formulation of Flory et al.[18] and this approach is that we have chosen to distinguish between J_i and J_{i+1} bonds and also correct for the overcounting of available configurations.

The analysis presented above has been extended to a case where we consider the effect of a previous neighbor (i.e., the two-segment conditional probabilities in the notation of Marqusee and Dill) on the probability of the occurrence of the current bond. This corresponds to the case where the continuity condition,[18] accounting for the symmetry of the conformations of bond-pair junctions, is included in the formulation. The mathematical treatment of this case is not presented here since the result obtained for the entropy of the system in this approximation is identical with the corresponding expression reported by Marqusee and Dill.[19] The current formulation, therefore, is identical with the alternate treatment of Helfand,[8] who used probabilistic space-filling arguments to derive the entropy of a set of chains on a fully filled lattice. Partition functions for this problem developed by enumerating the number of arrangements of molecules on a lattice are therefore completely equivalent to techniques based on probabilistic space-filling arguments, as long as both are developed consistently, in the spirit of the appropriate (either Bragg–Williams or any higher) approximation.

Effects of Tight-Fold Energy. To this point in our analysis we have considered only chains that are completely flexible and may adopt any conformation with no change in the conformational energy. However, it is known that the trans conformation for a chain is, in general, the most favored energetically, with the gauche$^+$, gauche$^-$ being associated with an energy penalty that disfavors these arrangements of torsion angles. In our lattice calculations we assume that each edge of a unit cell holds $\simeq 3.5$ methylene units. A tight-fold in the lattice formulation, therefore, for the case of polyethylene chains, must admit a number of gauche conformations. Furthermore, at the crystal surface, the tight adjacent folds involve additional energies for bond-angle bending to comply with the constraints of the crystal lattice. For example, Corradini et al.[21] estimated that the adjacent folds for polyethylene chains near the crystal correspond to an energy of ca. 4 kcal/mol. Clearly, therefore, a tight-fold must be disfavored due to energetic considerations. To mimic the behavior of real chains we have chosen to associate an energy $E_\eta k_B T$ that disfavors each of these tight-folds.

In this formulation we have chosen to use the same expression for entropy that was developed earlier in this work (eq 8) as a starting point. Alternately, this assumption is equivalent to dictating that the energy associated with tight-folds will not alter the assumptions made in deriving the entropy of chains in the interphase. To complete this formulation, we need to account for the associated energy terms (U), in the expression for the Helmholtz energy (A) for this system. Mathematically, we need to formulate

$$A = U - TS \tag{9}$$

The only contributions to the internal energy of this system is the total energy associated with the tight-folds in the system. To obtain this quantity, we need to enumerate the number of tight-folds in each layer of the system. Subsequently, to obtain the equilibrium distribution of bond propagation probabilities in each layer, therefore, we must minimize A with respect to all $p_i(+)$. One can show from an analysis of the geometry of the system that there are only four kinds of tight-folds possible in the system; these are sketched in Figure 2. From probabilistic arguments one can show that the number of different folds of each kind in layer i are

$$N_{1i} = 4N_0 p_i(-)[(z-2)p_i(0)]p_i(-) \tag{10}$$

$$N_{2i} = 4N_0 p_i(+)[(z-2)p_i(0)]p_i(+) \tag{11}$$

$$N_{3i} = 4N_0[(z-2)p_i(0)]p_{i-1}(-)p_{i-1}(0) \tag{12}$$

$$N_{4i} = 4N_0[(z-2)p_i(0)][(z-4)p_i(0)]p_i(0) \tag{13}$$

The factor 4 that has been introduced in each equation accounts for the fact that the probabilities in each layer have been obtained in terms of the $2N_0$ bonds associated with each layer (see eq 6) rather than with the N_0 sites.

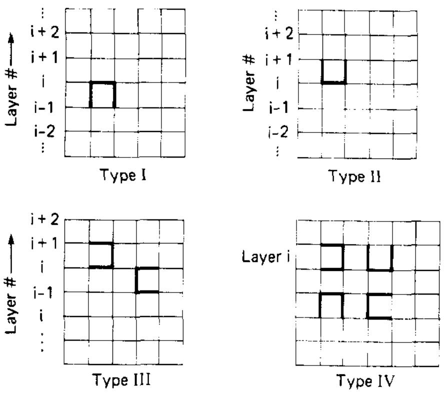

Figure 2. Schematic representation of the types of tight-folds possible in the system. Note is to be made of the fact that loops of type IV occur completely in layer i, while all other loops span two different layers.

The Helmholtz energy of this system, eq 9, may now be derived from the use of eq 8 and 10–13 and may be minimized with respect to all $p_i(+)$, the only undetermined variables in this system (see eq 17):

$$A = \sum_{i=1}^{k}[E_\eta k_B T[N_{1i} + N_{2i} + N_{3i} + N_{4i}] - k_B T \ln \Omega_i] \tag{14}$$

It must be recalled that the conservation condition (eq 1 or 2) will continue to be binding in this case. The minimization of A with respect to these variables results in coupled sets of algebraic equations that have been solved with the aid of a standard Newton–Raphson equation solver.

A note is made of the fact here that in the disordered amorphous region, regardless of the value of the energy parameter, the propagation probabilities must all take on the same value, i.e.

$$p_i(-) \equiv p_i(+) \equiv p_i(0) \equiv 1/z \tag{15}$$

Another interesting limit occurs when $E_\eta \rightarrow \infty$, i.e., when the energy disfavoring tight-folds becomes infinitely large. In the framework of the model, then, the crystal–amorphous transition will never occur, and the crystal will then represent the only stable phase.

Results and Discussion

Completely Flexible Chains from a Perfect Crystal. To obtain the equilibrium distribution of bond direction probabilities in each layer, one has to maximize the partition function expressed in eq 8 with respect to the variable $p_i(+)$ for all layers, subject to the constraint expressed in eq 2. Also, at a perfect crystal, the constraint

$$p_0(+) = 1/2 \tag{16}$$

must be fulfilled. In addition, the symmetry of the problem imposes the constraint

$$p_i(+) = p_{i+1}(-) \tag{17}$$

The solution obtained for this problem is exactly the same as in ref 19 and hence is not elaborated upon here. In brief it was found that 74.4% of chain sequences emerging from the lamellar crystal returned to the same crystal by forming tight adjacent folds in the first layer of the interphase. This result is in good agreement with the Monte Carlo results of Mansfield,[17] who reports 72% as the appropriate quantity from simulations of the crystal–amorphous interphase. It is clear that, at least in this case, the results

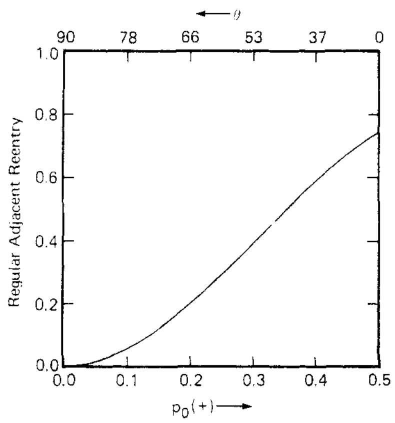

Figure 3. Variation of the fraction of sites in the first lattice layer that are involved in regular folds as a function of the chain incidence probability.

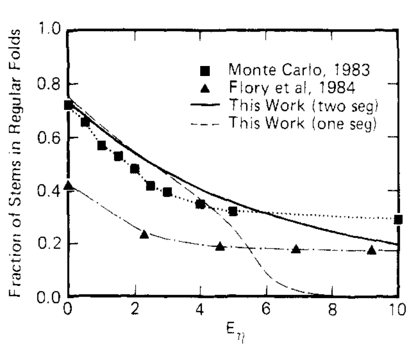

Figure 4. Variation of the fraction of sites in the first layer that are involved in regular folds as a function of the energy parameter, E_η. Squares represent data from Mansfield,[17] while triangles are the results of Flory et al.[19] The dotted line is the result of the one-segment calculation, while the dark line is the result of the two-segment approximation.

obtained from the analytical calculations are not very sensitive to the approximations inherent in its formulation. We are therefore led to believe that the conservation constraint (eq 2) is the dominant factor in determining the number of chains that return to the crystal in the first lattice layer. The continuity condition[18] seems to play a relatively minor part in this case.

This is a somewhat surprising result, since we may show using eq 11 and 12 that in this case the model predicts the existence of approximately 2% loops of type II and 1.5% of loops of type III in the first lattice layer. This result is in disagreement with the physical situation at hand since the geometry of the perfect crystal (as has been stated earlier)[18] prevents the existence of any kind of loops in the first layer except of type I. The presence of these loops in the model may be the origin of the difference between the analytical calculations and Monte Carlo results. Also, we will show in the section on the effect of tight-fold energies that the presence of the continuity constraints will play a significant role for chains that disfavor the presence of tight-folds strongly.

Effects of Changes in Surface Chain Density. The effects of changes in the chain density at the crystal surface, i.e., changes in $p_0(+)$, were examined next, in the context of this model. One motivation for this study is the prior experimental knowledge that the axes of chain sequences in the crystal may be inclined an angle φ_t, from the normal to the lamellar surface. In polyethylene, for example, φ_t lies in the range 18–45°.[20,22,23] The reduction in surface chain density may be expressed as a decrease in $p_0(+)$ following ref 18 as

$$p_0(+) = \frac{1}{2}\cos\varphi_t \tag{18a}$$

Another case may be found in polymers that have larger cross-sectional area per crystal segment (A_c) than for a corresponding segment in the amorphous phase (A_a). This could happen in a situation where the crystalline conformation corresponds to a helix with a large diameter. In this case

$$p_0(+) = \frac{1}{2}\frac{A_a}{A_c} \tag{18b}$$

To obtain the equilibrium distribution of $p_i(+)$ for all layers, we need to maximize the entropy of chains in the interphase (eq 8) with respect to all the $p_i(+)$ under the constraints expressed in eq 2 and 18. The required distributions of bond probabilities have been calculated for $p_0(+)$ values in the range 0–0.5. From these results we may calculate the number of loops that are of type I in the first lattice layer (N_{11}) using eq 10. The fraction of crystal stems in this layer that are associated with type-I folds (i.e., $2N_{11}/N_0$) is plotted against the chain tilt angle φ_t and also $p_0(+)$ in Figure 3.

It can be seen in this figure that the fraction of crystal stems involved in regular adjacent reentry decreases monotonically with decreasing surface chain density. For example, in the case of a perfect crystal 74.4% of all sites in first layer have loops of type I passing through them, while for a crystal with φ_t of 40°, or $A_a/A_c = 0.7$, this number is seen to drop to approximately 50%. The rationale for these results is that as one increases φ_t, the chain incidence probability is reduced. Hence the need to form tight loops to dissipate order is diminished, leading to the observed result.

In summary, therefore, it is clear that decreasing the chain density at the crystal surface owing to chain tilt or the larger cross-sectional area of the crystal sequences plays an extremely important role in determining the number of regular adjacent reentry folds in the immediate vicinity of the crystal. Accounting for this fact is therefore crucial in understanding the characteristics of the interphases in these situations.

Effects of Tight-Fold Energy. Another facet of real chains that also needs to be accounted for is the fact that chains seldom are completely flexible as explained in the previous section. We examined the behavior of the crystal–amorphous interphase for values of E_η ranging between 0 and 20 in the case of a crystal with zero tilt angle.

Material constraints dictate that of all the possible types of loops (see Figure 2), only loops of type I can be formed in the first layer for chains issuing from a perfect crystal. The variation of the number of horizontal bonds, or alternately the number of tight-folds, in the first layer with changes in E_η may thus be calculated under this constraint. We performed these calculations in the case of an interphase adjoining a perfect crystal. The results from our formulation (the one-segment results in Figure 4) are in good agreement with simulation results, up to an E_η value of 3. However, beyond this value, the Monte Carlo results suggest that the fraction of regular folds in the first layer becomes practically constant at approximately 30%, while our model predicts that it decreases sharply and asymptotically approaches 0 with increasing E_η. The mathematical approach presented above, therefore, predicts that we have a rapid change from disorder to order around an E_η value of 3.

Clearly, the approximations inherent in the formulation with only the conservation constraint make it increasingly inapplicable to the physical situation as the energy parameter, E_η, is increased. In the spirit of this approximation we have assumed that the continuity constraints do not play a significant role in the determination of the conformations of macromolecules at the interphase. Indeed Marqusee and Dill[18] have found previously that this is exactly the case for completely flexible chains.

To explore the effects of the inaccurate representation of entropy in the development presented above, we reformulated the statistics of polymer chains in the interphase in terms of the two-segment approximation of Marqusee and Dill.[19] In this approximation, it is assumed that the probability of the orientation of a bond is dependent on the configuration of the immediately previous bond, while in the earlier approximation a polymer molecule is essentially viewed as a Markovian chain with a renewal probability that is a function of the layer number of the segment. This "two-segment" approximation also allows one to build the continuity conditions explicitly in the formulation, since we can now account for the symmetry of bond-pair junctions to be built in. The development of this approximation, very similar to the "one-segment" approximation presented earlier, has been deferred to the Appendix. The Helmholtz energy of the chains in the interphase, as obtained from this approach, was then minimized numerically with a modified Fletcher–Powell algorithm (a Harwell routine) to yield the distribution of bond orientations in the different layers. The results in this calculation are presented in Figure 4. For comparison, Monte Carlo results and the results from the one-segment approximation are also presented in this figure. In addition, the numerical calculations of Flory et al.[18] are also shown. To allow for the representation of the results of Flory et al.[18] in this figure, we have converted their parameter η to the energy parameter E_η through the equation

$$\eta = \exp(-E_\eta) \tag{19}$$

It is clear that the two-segment approximation yields a better agreement with the Monte Carlo results over the range of E_η that was examined, especially at high values of the energy parameter. Also, the agreement of this model with Monte Carlo results are much better than the calculations of Flory et al.,[18] which consistently predict a lower value of the number of regular adjacent reentry folds. It can also be seen that the rapid changes from disorder to order that was observed for the one-segment formulation at an E_η value of 3 disappears in the new formulation. Clearly, this rapid change in the number of loops in the first layer was an artifact of the model employed earlier. Imposing the continuity constraints, therefore, allows one to model the behavior of the interphase with greater accuracy over the whole range of E_η.

However, it must be noted that the quantitative results of the model are not in very good agreement with Monte Carlo results at high values of E_η. Both the Flory et al.[18] and the Monte Carlo results suggest that the number of adjacent reentry folds reach an asymptotic value of E_η greater than ca. 5. Our calculations show that the number of loops in the first layer decreases monotonically with increasing E_η and approaches zero for values of E_η of approximately 20. The reason for this discrepancy is not clear at this time. However, note should be made of the fact that Monte Carlo results should predict that the number of regular folds in the first layer must necessarily approach zero at high values of E_η, as has been discussed earlier.

An interesting value of the energy parameter is $E_\eta \simeq 0.5$. In the framework of the one segment model, at this point, one-third of the bonds entering the first layer proceed to the second lattice layer, independent of $p_0(+)$. Bond propagation probabilities in all other layers take on values close to that found in the bulk, as defined by eq 15.

$$p_i(+) = p_i(-) = p_i(0) = 1/z \tag{15}$$

At this energy value, therefore, the interphase is exactly one layer thick and all chains obey unperturbed-chain statistics in the entire interphase. It may, therefore, be concluded that the net effect of the crystal surface on the conformation of chains is not very significant in the case of flexible chains.

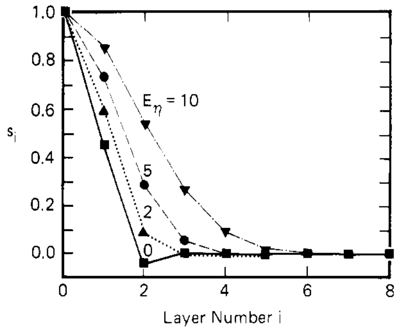

Figure 5. Variation of the segmental order parameter as a function of the distance of the layer from the crystal surface. Results for four different values of E_η are shown.

Having studied the effects of tight-fold energy on the number of adjacent reentry folds, we examined the effect of the energy parameter (E_η) on the thickness of the crystal–amorphous interphase. We characterized the interphase as the region where the orientation of segments is different from that in a truly random amorphous phase. A measure of the anisotropic distributions of bond orientations in lattice layer i is the order parameter, s_i, which is defined as

$$s_i = (3\langle\cos^2\varphi\rangle - 1)/2 \tag{20}$$

Here φ is the angle made by a segment to an axis normal to the crystal surface. Since bonds on a cubic lattice can take on only those orientations that are parallel or perpendicular to this axis, we may rewrite eq 20 in terms of our formulation as

$$s_i = \frac{3}{2}[p_i(-) + p_i(+)] - \frac{1}{2} \tag{20a}$$

The order parameter will take on a value of 1 at the crystal surface and 0 in the amorphous phase. We have computed the order parameters in the interfacial layers at different values of E_η. In Figure 5 we plot the variation of the order parameter as a function of layer number for four different values of E_η. A rough measure of the interphase size is the number of layers in which the order parameter deviates significantly from zero. It can be observed in Figure 5 that the interphase is approximately 2 lattice layers (or approximately 10 Å) thick for E_η value of 0. At larger values of E_η the interphase becomes broader and is 5 layers (25 Å) thick for an E_η of 10. Since it is expected that this range of values E_η will span most real systems, these calculations suggest that interfacial thickness will normally range between 10 and 30 Å in most cases. The effect of the energy associated with tight-folds is thus seen to have a strong effect on the size of the crystal–amorphous interphase in lamellar semicrystalline polymers.

Since we now understand the effect of the energy parameter, E_η, on the thickness of the interphase, we proceed to study the effect of this energy on the structure of the interphase. To this end we examine in Figure 6 the variation of the average length of horizontal chain sequences in layer i, $\langle l_i\rangle$, as a function of the layer number for dif-

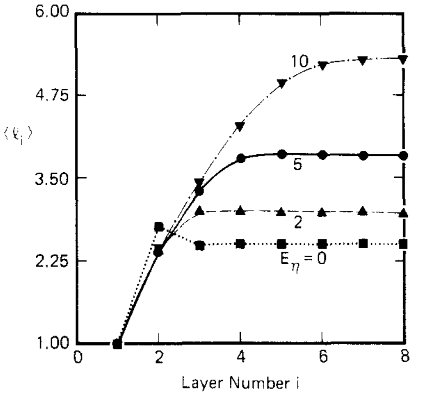

Figure 6. Dependence of the length of horizontal sequences in a layer as a function of the distance of the layer from the surface. Results for four different values of E_η are shown.

ferent values of E_η. This value of $\langle l_i \rangle$ is calculated through the equation

$$\langle l_i \rangle = \sum_{j=1}^{\infty} l_j p_j \Big/ \sum_{j=1}^{\infty} p_j \tag{21}$$

Here p_j is the probability of the occurrence of a horizontal sequence of length j in lattice layer i. We point out the fact that our formulation, being a two-segment probabilistic one, cannot differentiate between different kinds of horizontal sequences.

In all cases it may be seen that in the first lattice layer adjoining a perfect crystal, as has been pointed out earlier, the only kind of folds that exist are those that involve exactly one horizontal bond. The sequence length of horizontal sequences may, however, be different from unity is the second lattice layer. It can be seen that the value of $\langle l_i \rangle$ in this lattice layer is greater than the bulk value (2.5) for small values of E_η and then gradually drops to a value close to 2.25 for values of E_η close to 10. These results are in disagreement with those of Flory et al.,[18] who show that the sequence length of horizontal bonds in layer 2 asymptotically approach a value of 2, corresponding to a leapfrogging effect,[24] for high values of E_η. The reason for this difference, however, is not clear at this time. In all cases the asymptotic value of $\langle l_i \rangle$ is attained by the time one goes out to the sixth lattice layer. These results, as well as those shown in Figure 5, consistently demonstrate the broadening of the interphase as one proceeds to larger values of E_η. Also, these results must be contrasted to those of Flory et al.,[18] where the interfacial thickness increases from 2 to 3 lattice layers when one goes from fully flexible chains to the case of chains of limited flexibility (i.e., for $E_\eta \simeq 10$).

A note is made here of the fact that the asymptotic value of l_i increases with increasing values of the energy parameter, E_η. This is a direct manifestation of the assumptions in our formulation, wherein a tight-fold is obtained by the probabilistic existence of two consecutive right-angled bends. As E_η increases, the probability of the formation of tight-folds, and hence right angled bends, is reduced. This directly results in an increase in the average length of horizontal sequences, thus making the chains less flexible. It must be recognized that this result demonstrates an inherent deficiency in the model, since it results in the decreased probability of a right-angled bend, although we had desired to reduce the occurrence of tight-folds only. A potential remedy to this problem, not examined here, is to extend the formulation to a higher approximation, for example as a three-segment approximation. The problems encountered in the case of the two segment approximation will then be mitigated.

In summary, we demonstrate that the effects of tight-fold energy play an important role in determining the structure of chains sequences in the immediate vicinity of the crystal surface. These effects will therefore have to be considered if one desires to model the crystal–amorphous interphase accurately.

Conclusions

In this paper an expression for the entropy of completely flexible lattice chains of infinite molecular weight in an interphase has been derived, correcting for the overcounting problem in the approximation of Flory et al.[18] It has been shown that, under appropriate definitions, this expression for entropy is identical with the results obtained by Helfand for the same problem using probabilistic arguments for space filling. This formulation has been applied to the study of the crystal–amorphous interphase in lamellar semicrystalline polymers where the chain incidence probability is attenuated at the surface. (This may be due either to the tilting of the crystal stems relative to the axis normal to the crystal surface or owing to the larger cross-sectional area of crystal stems relative to that of the amorphous chains.)

We then considered the case of chains that mimic the behavior of real chains by associating an energy that disfavors the formation of tight-folds. While we have not considered the effect of chain flexibility explicitly by accounting for all the right-angle "gauche" connections, previous calculations[18] show that tight-fold energies are more important in this regard.

It is shown that the size and the structure of the crystal–amorphous interphase in semicrystalline polymers depend strongly on the tight-fold energy and also on the surface chain density. Insofar as polymer chain statistics are determined by the local segmental interactions and geometries unique to the constituent chemical structure of each polymer, it becomes impossible then to draw any simple conclusion on the structure of the crystal–amorphous interphase of semicrystalline polymers. It should also be borne in mind that our calculations are concerned with the state of equilibrium, thus ignoring important constraints due to the kinetic aspects of polymer crystallization. Therefore, problems of entanglement and limited chain mobility, especially prominent for very high molecular weight polymers, are not taken into account. These factors, however, are more likely to enhance the interphase by making it more difficult to dissipate the order through tight-folds.

Appendix

Derivation of Equation 14 in the Two-Segment Approximation. In this formulation, apart from the "one-segment" probabilities, we must also define probabilities of the occurrence of a particular bond direction, conditional on its immediately previous neighbor. In the absence of an energy disfavoring any particular conformation there are nine such different conditional probabilities in each layer i: $p(0/-)$, $p(+/-)$, $p(-/-)$ [$\equiv 0$], $p(-/+)$, $p(0/+)$, $p(+/+)$ [$\equiv 0$], $p(0/0)$, $p(+/0)$, $p(-/0)$. We note here that the quantities $p(-/-)$ and $p(+/+)$ are identically equal to zero since two bonds may not overlap. However, if there is an energy disfavoring loops, then all probabilities involving a right-angled bend will be disfavored as relative to a "straight" conformation. In this situation we have to split the probability $p(0/0)$ into two parts: $p_s(0/0)$ corresponding to a straight conformation, and $p_b(0/0)$ corresponding to a bent conformation. In the framework of this approximation the number of loops corresponding to eq 9–13 are

$$N_{1i} = p_i(-)(z-2)p_i(0/-)p_i(-/0) \qquad (\mathrm{A1})$$

$$N_{2i} = p_i(+)(z-2)p_i(0/+)p_i(+/0) \qquad (\mathrm{A2})$$

$$N_{3i} = 2(z-2)p_i(0)p_i(-/0)p_{i-1}(0/+) \qquad (\mathrm{A3})$$

$$N_{4i} = (z-2)p_i(0)(z-4)p_{\mathrm{b}i}(0/0)p_{\mathrm{b}i}(0/0) \qquad (\mathrm{A4})$$

The constraint and continuity equations have been presented in the work of Marqusee and Dill.[19] The continuity equations, as stated earlier, express the symmetry of bond-pair junctions. For example, the number of (+/−) connections should exactly equal the number of (−/+) connections in each layer i. Mathematically this may be written as

$$p_i(+/-)p_i(-) = p_i(-/+)p_i(+) \qquad (\mathrm{A5})$$

Similarly, two more conditions may be written:

$$p_i(0/+)p_i(+) = p_i(+/0)p_i(0) \qquad (\mathrm{A6})$$

$$p_i(0/-)p_i(-) = p_i(-/0)p_i(0) \qquad (\mathrm{A7})$$

Equations A5–A7 represent the continuity equations. The constraint equations, however, are slightly modified to account for the bent and straight conformations of horizontal bonds:

$$p_i(+/-) + (z-2)p_i(0/-) = 1 \qquad (\mathrm{A5})$$

$$p_i(-/+) + (z-2)p_i(0/+) = 1 \qquad (\mathrm{A6})$$

$$p_i(-/0) + p_i(+/0) + p_{\mathrm{s}i}(0/0) + (z-4)p_{\mathrm{b}i}(0/0) = 1 \qquad (\mathrm{A7})$$

The entropy expression for the chain segments in the interface may then be written in analogy to ref 19:

$$\begin{aligned} -\ln \Omega_{2i}/k_{\mathrm{B}}N_0 = {} & p_i(-)p_i(+/-)\ln p_i(+/-) + p_i(-)p_i(0/-) \times \\ & (z-2)\ln p_i(0/-) + p_i(+)p_i(-/+)\ln p_i(-/+) + \\ & p_i(+)p_i(0/+)(z-2)\ln p_i(0/+) + \\ & (z-2)p_i(0)p_i(-/0)\ln p_i(-/0) + (z-2)p_i(0)p_i(+/0) \times \\ & \ln p_i(+/0) + (z-2)p_i(0)p_{\mathrm{s}i}(0/0)\ln p_{\mathrm{s}i}(0/0) + \\ & (z-2)p_i(0)p_{\mathrm{b}i}(0/0)(z-4)\ln p_{\mathrm{b}i}(0/0) \qquad (\mathrm{A8}) \end{aligned}$$

The total entropy of the chain segments in the interphase, Ω_2, may then be obtained by summing eq A8 over all k layers of the interphase. We may write the Helmholtz energy of the system in this approximation as

$$A = \sum_{i=1}^{k} E_\eta k_{\mathrm{B}}(N_{1i} + N_{2i} + N_{3i} + N_{4i}) - k_{\mathrm{B}}T\ln\Omega_2 \qquad (\mathrm{A9})$$

where Ω_2 is the total entropy of chains as represented in the two-segment approximation.

To derive the asymptotic probabilities of the bent and straight conformations, we set all the quantities in eq A9 to either of these quantities and maximize the partition function for either p_{s} or p_{b} under the constraint eq A5–A7, which collapse into a single equation:

$$p_{\mathrm{s}} + (z-2)p_{\mathrm{b}} = 1 \qquad (\mathrm{A10})$$

The resulting equation which defines p_{b} as a function of E_η is

$$p_{\mathrm{b}} = \frac{1}{(z-2) + \exp(2E_\eta p_{\mathrm{b}})} \qquad (\mathrm{A11})$$

This results in the appropriate limits for p_{b} as E_η tends to 0 (i.e., $1/(z-1)$) or ∞ (i.e., $p_{\mathrm{b}} = 0$).

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