Macromolecules **1991**, *24*, 5414–5420

A Lattice Model for Interphases in Binary Semicrystalline/Amorphous Polymer Blends. 2. Effects of Tight Fold Energy

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Received January 1, 1991; Revised Manuscript Received April 2, 1991

ABSTRACT: In a previous paper, we examined the crystal/amorphous interphase in a binary blend that is miscible in the melt but undergoes phase separation due to crystallization of one polymer in a lamellar morphology. It was assumed in these calculations that the chains were fully flexible, a situation that is not easily realizable in practice. In this paper, we extend these calculations to account for the limited flexibility of macromolecular chains, through the incorporation of an energetic parameter, $E_\eta(k_BT)$, that accounts for the reluctance of chains to assume tight fold conformations. It was found that the region of partial order for the semicrystalline component, which is essentially independent of $-\chi_{AB}$, increases slightly as one considers stiffer chains. The interphase of varying polymer composition, however, is affected strongly when bending energy effects are included, and its size increases monotonically with E_η and inversely with $-\chi_{AB}^{1/2}$. It is thus suggested that the interphase of partial order for the semicrystalline component is essentially pure when the interaction between the two polymers is not very strong, especially in cases where one deals with stiff crystalline polymers. However, the segments of the amorphous polymer penetrate the order–disorder interphase in cases where $-\chi_{AB}$ assumes a large value. These results are apparently in agreement with recent experimental findings on poly(ethylene oxide) blends where the interphase composition is found to be dependent on the nature of the amorphous polymer in the blend.

1. Introduction

Polymer blends are industrially important in several contexts. For example, the use of a rubbery polymer in a crystalline matrix allows one to produce materials that have significantly improved dynamic properties. Our interest in the recent past has focused on binary blends that are compatible in the melt but undergo phase separation on cooling due to the crystallization of one component in a lamellar morphology.[1]

We have modeled this interfacial situation through the device of a fully filled cubic lattice model in the Bragg–Williams mean-field approximation.[1] It was assumed that both chains were infinitely long and completely flexible under the constraints presented by the lattice. Under these assumptions, the only variable in this system was the energetic interactions between the segments of the two polymers, which was modeled through the use of the Flory–Huggins exchange energy parameter, χ_{AB}. In this case, χ_{AB} assumes a negative value since the polymers are compatible in the melt. It was found that the order–disorder interphase, defined as the region of the loss of crystalline order, spanned the first two layers from the crystal surface and is essentially unchanged when χ_{AB} was varied from −1.0 to −0.005. On the other hand, the region of varying polymer composition was strongly affected by χ_{AB}, with the interfacial thickness varying with the reciprocal of $|\chi_{AB}|^{1/2}$.

In this paper, we extend this theory to account for the reluctance of real polymers to assume tight fold conformations. This was modeled by incorporating an energetic parameter, $E_\eta(k_BT)$, that disfavors the formation of tight folds.[2] The approach to be adopted, therefore, closely follows our earlier work on the characteristics of the crystal/amorphous interphase in homopolymers that are not completely flexible.[2] The effects of including the parameter E_η on the interfacial characteristics of binary, melt-compatible blends will be examined.

2. Model Formulation

As in previous work,[1] we do not consider the crystalline regions and choose to model only the noncrystalline regions through the device of a lattice of coordination number z (=6 in the case of a cubic lattice). The lattice was set up so that its layers were parallel to the crystal surface, which is the origin of the lattice. Layers were numbered in ascending order, with the crystal surface being numbered 0. Each lattice site is isodiametric, so that each site is approximately 0.45 nm on a side in the case of polyethylene. It is assumed that the lattice is completely filled, an assumption that is appropriate in the modeling of a polymer system at meltlike densities.

The two polymer chains are assumed to be of infinite degree of polymerization, and it is postulated that all the stems of the crystalline polymer (termed A) are oriented normal to the lamellar surface. Segments of the two polymer chains interact energetically with each other, and the exchange energy between the unlike monomers is modeled through the use of the Flory–Huggins parameter, χ_{AB}. This quantity will always assume a negative value since the two polymers are of infinite length and miscible in the melt. In addition, an extra energy term, $E_{\eta K}(k_BT)$, is included in the formulation to account for the reluctance of chains of type K to assume "tight fold" conformations.[2] It should be emphasized that although we include bending energies that disfavor the formation of tight folds, no other bending energy effects (including the simple case of a right-angle bend involving two adjacent bonds) have been included in this formulation. The rationale for utilizing

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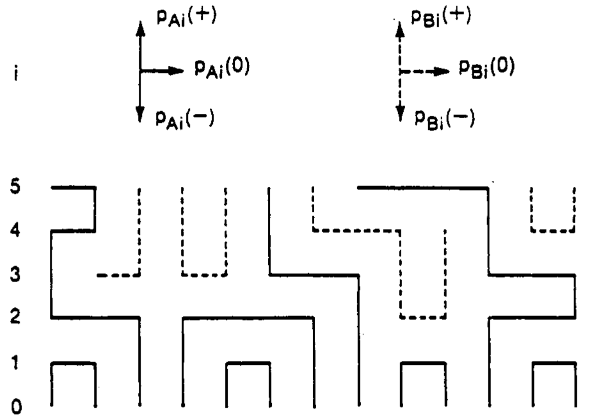

Figure 1. Schematic representation of the crystal/amorphous interphase and definitions for different probabilities used in the text. The semicrystalline polymer A is shown by solid lines and the amorphous polymer B by dashed lines.

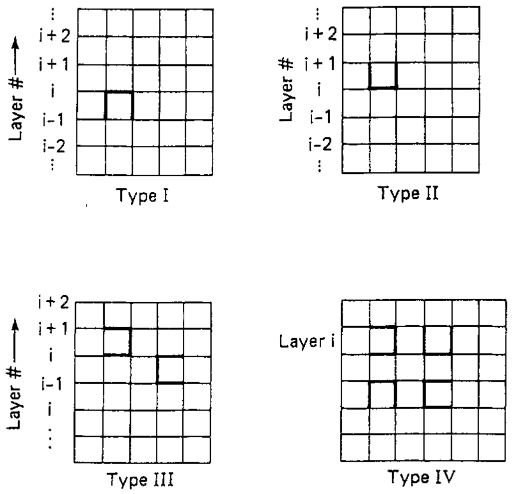

Figure 2. Schematic representation of the tight folds possible in the system for each component in the binary blend. Note the fact that loops of type IV occur completely in layer i, while all other loops span two different layers.

this simple model stems from previous work in this area, which suggests that the most important factor in the vicinity of a crystal surface is the reluctance of chains to form tight fold conformations.[2]

The notations to be adopted in this work closely follow the work presented in refs 1 and 2, which are motivated by the earlier work of Helfand[3] on the interface between two immiscible polymers. The volume fractions of the A segments in layer i is denoted by ϕ_{Ai}, while the corresponding quantity for the noncrystalline polymer B is ϕ_{Bi}. The volume fractions of the two components in any layer i must sum to unity. In addition, the probability of finding a bond belonging to chains of type K (either A or B) pointing in the three nonequivalent directions is denoted by $p_{Ki}(-)$, $p_{Ki}(+)$, and $p_{Ki}(0)$, respectively, as shown schematically in Figure 1. $p_{Ki}(-)$ represents the probability of the occurrence of a bond belonging to polymer species K spanning layers i and $i-1$, $p_{Ki}(+)$ spans i and $i+1$, and $p_{Ki}(0)$ is the probability of the occurrence of a bond that is completely in layer i. These probabilities follow the constraint equation

$$p_{Ki}(-) + p_{Ki}(+) + (z-2)p_{Ki}(0) = 1 \quad (1)$$

It has been found in our earlier calculations on homopolymer crystal/amorphous interphases that, at high values of E_η, a formulation based only on the probabilities described in eq 1 is insufficient.[2] It has also been found that one could correct for the flaws of this model if one also incorporated probabilities of the occurrence of a particular bond direction conditional on its immediately previous bond.[2] In the absence of an energy disfavoring any particular conformation, there are nine such different conditional probabilities for each species in any layer i: $p_{Ki}(0/-)$, $p_{Ki}(+/-)$, $p_{Ki}(-/-)$ [=0], $p_{Ki}(-/+)$, $p_{Ki}(0/+)$, $p_{Ki}(+/+)$ [=0], $p_{Ki}(0/0)$, $p_{Ki}(+/0)$, and $p_{Ki}(-/0)$. Note that the quantities $p_{Ki}(-/-)$ and $p_{Ki}(+/+)$ have been set to zero to avoid back-stepping of the bonds. If there is an energy disfavoring tight fold conformations, then all probabilities involving a right-angled bend will be disfavored relative to a straight conformation. Thus, the probability of a horizontal bond conditional on the previous being horizontal, $p_{Ki}(0/0)$, has been split into two components, $p_{Ki}{}^{s}(0/0)$ and $p_{Ki}{}^{b}(0/0)$, corresponding to a straight and a bent conformation, respectively. We include these extra terms in our expression for the free energy of the mixed interphase. The final expression for the entropy of the interphase, in this approximation, has been derived for the case of a homopolymer elsewhere[2,4,5] and is therefore not rederived for the case of a mixed interphase. The expression for this case can be written as

$$\frac{-S}{N_0K_B} = \sum\sum \phi_{Ki}p_{Ki}(-)\{(z-2)p_{Ki}(0/-)\ln p_{Ki}(0/-) + p_{Ki}(+/-)\ln p_{Ki}(+/-)\} + \phi_{Ki}p_{Ki}(+) \times \{(z-2)p_{Ki}(0/+)\ln p_{Ki}(0/+) + p_{Ki}(-/+)\ln p_{Ki}(-/+)\} + \phi_{Ki}(z-2)p_{Ki}(0)\,\{p_{Ki}(+/0)\ln p_{Ki}(+/0) + p_{Ki}(-/0)\ln p_{Ki}(-/0) + p_{Ki}{}^{s}(0/0)\ln p_{Ki}{}^{s}(0/0) + (z-4)p_{Ki}{}^{b}(0/0)\ln p_{Ki}{}^{b}(0/0)\} \quad (2)$$

It should be realized that eq 2 has eight unknown conditional probabilities for each species in a layer. However, there are six mathematical relationships, which are derived in Appendix I of ref 2, that relate some of these unknown probabilities. Thus, there are two unknown conditional probabilities per species in each layer that have to be determined to characterize the thermodynamic equilibrium state of the interphase.

To obtain the Helmholtz energy of the interfacial energy, one needs to obtain the energy of the chains in the interphase. This energy is split into two parts for convenience. The first term accounts for the energetic interaction between unlike segments through the use of the Flory χ_{AB} parameter.[1,3]

$$U^{AB}/(N_0k_BT) = \sum(\chi_{AB}/z)\phi_{Ai}[\phi_{B(i-1)} + (z-2)\phi_{Bi} + \phi_{B(i+1)}] \quad (3)$$

In addition, we also have to account for the energy associated with the formation of tight folds of the two polymeric species in each layer. Four different kinds of tight folds can be formed, and these are sketched schematically in Figure 2. If one terms the number of each of these loops as N_{1Ki}, N_{2Ki}, N_{3Ki}, and N_{4Ki} for species K in layer i, then the energy associated per lattice site due to the tight folds is

$$U^{\text{fold}}/(k_BT) = \sum\sum E_{\eta K}[N_{1Ki} + N_{2Ki} + N_{3Ki} + N_{4Ki}] \quad (4)$$

The expressions for the different kinds of loops are also derived in Appendix I of ref 2. The Helmholtz energy for the interfacial system can then be derived from eqs 2–4 as

$$A = U^{\mathrm{AB}} + U^{\mathrm{fold}} - TS \tag{5}$$

One can then derive the equilibrium structure of the interphase by the minimization of eq 5 under the appropriate constraints (i.e., eq 1). In addition, the geometry of the problem imposes the following constraints:

$$p_{\mathrm{A1}}(-) = 0.5, \qquad \phi_{\mathrm{A1}} = 1 \tag{6}$$

$$p_{\mathrm{A1}}{}^{\mathrm{s}}(0/0) = p_{\mathrm{A1}}{}^{\mathrm{b}}(0/0) = p_{\mathrm{A1}}(+/0) = p_{\mathrm{A1}}(0/+) = 0 \tag{7}$$

$$p_{\mathrm{A1}}(-/0) = p_{\mathrm{A1}}(-/+) = 1 \tag{8}$$

$$p_{\mathrm{B2}}(-) = p_{\mathrm{B2}}(-/0) = p_{\mathrm{B2}}(-/+) = p_{\mathrm{B2}}(+/-) = p_{\mathrm{B2}}(0/-) = 0 \tag{9}$$

Also, the number of bonds of polymer K pointing upward from layer $i - 1$ must equal the number of bonds pointing downward from layer i. This is an expression of the continuity condition inherent in the problem.

$$p_{K(i-1)}(+)\phi_{K(i-1)} = p_{Ki}(-)\phi_{Ki} \tag{10}$$

Along with these equations, the Helmholtz energy of the system is completely defined. The equilibrium state of the interphase can then be obtained from a minimization of this function with respect to the unknown probabilities in each layer. In our case, this was performed both numerically and analytically. In the numerical method, the minimization was achieved by using an IMSL subroutine (ZXMIN), which is a modified Fletcher–Powell algorithm.[6] In the analytical procedure, the Helmholtz energy was minimized with respect to the constraints inherent in the problem. A coupled set of nonlinear algebraic equations was obtained and solved by a modified Newton–Raphson solution procedure.

A note is made of the asymptotic value of the compositions of the two polymers in the "bulk", far from the crystal surface. As before,[1] ϕ_{Ki} asymptotically assumes a value of 0.5 for chains that are completely flexible or of the same degree of inflexibility (i.e., having same E_η). This is a direct manifestation of the assumption that chains are of infinite degree of polymerization (DP): under these conditions, the favorable interaction energy between the A and B segments is maximized at a volume fraction of 0.5. It is noted that this result would not, in general, be true for polymers of finite DP at equilibrium. However, the results obtained in this case would still be qualitatively true for chains that are not of infinite length.

3. Results

3.1. Interfacial Characteristics with No Bending Energy Effects. We begin by analyzing the results for the case where no bending energy effects are included. In our earlier work on this problem,[1] we have examined the same situation but with the expression for the entropy of chains derived in the Bragg–Williams approximation: i.e., we have computed the entropy without resort to the conditional probabilities that have been used in deriving eq 2. The aim of this section is to examine the validity of the earlier results[1] by comparison to a model that incorporates the chain structure of the molecules more accurately.

First of all, we examine the variation of the fraction of sites in the first lattice layer that were involved in the formation of tight folds as a function of χ_{AB}. These results, as well as the corresponding quantities from our earlier calculations,[1] are shown in Table I. It can be seen that the fraction of tight adjacent reentry loops follows the same trends in both of the approximations and also seems to be affected little by the presence of the second noncrystallizable component even for very favorable interaction energies, χ_{AB}. As found in the case of the homopolymer interphase,[2,4] however, it is seen that the two-segment approximation predicts somewhat lower values of adjacent reentry than the one-segment approximation. It is thus concluded that the formation of tight loops is slightly more favored in binary blends with favorable interactions, as compared to a pure component, regardless of the approximation employed in deriving the free energy of the chains in the interphase.

Table I
Variation of the Fraction of Stems Involved in Tight Adjacent Reentry with the Interaction Energy, χ_{AB}, with No Bending Energy Effects

	fraction of adjacent reentry	
χ_{AB}	one-segment approx	two-segment approx
0.00[a]	0.744	0.732
–0.01	0.747	0.736
–0.05	0.756	0.745
–0.10	0.764	0.756
–0.50	0.798	0.792
–1.00	0.812	0.809

[a] Results for the one-segment and two-segment approximations for $\chi_{\mathrm{AB}} = 0$ are results for a homopolymer crystal/amorphous interphase from Marqusee and Dill[4] and Kumar and Yoon.[2]

To probe the effect of the second polymer, we then examined the volume fraction of each species in a layer as a function of its position relative to the crystal surface. It is to be recognized that the composition at the crystal surface corresponds to pure A ($\phi_{\mathrm{A1}} = 1$) and that one has a 50 vol % mixture in the amorphous phase. The spatial region required to make this transition then corresponds to the size of the compositional interphase. The results obtained in these calculations utilizing the two-segment approximation closely parallel the trends that have been reported earlier in ref 1 and are hence not reported here in more detail. As before,[1] it is noted that the interphase was the smallest (ca. 4 layers or 2 nm) for large, negative values of χ_{AB} (≤ -0.5). As the interaction parameter is reduced toward zero, the compositional interphase broadens, and the drop off to the asymptotic value of 0.5 becomes much more gradual.

To characterize the variation of the size of this interphase with χ_{AB}, we define its thickness as corresponding to that lattice layer where the composition is different from the asymptote by 1 part in 1000. This thickness, termed t_{lat}, is plotted in Figure 3 as a function of $|\chi_{\mathrm{AB}}|$ on a log–log basis. Data obtained from the one-segment approximation[1] are also shown for comparison. Figure 3 illustrates that, regardless of the approximation, the thickness of the compositional interphase varies with the interaction energy as

$$t_{\mathrm{lat}} = C|\chi_{\mathrm{AB}}|^{-1/2} \tag{11}$$

where C depends on the exact details of the model itself. For example, the one-segment approximation yields $C = 3$, while the two-segment approximation yields $C = 4$. It is thus seen that, as expected, the two-segment approximation yields a compositional interphase that is somewhat broader than predicted by the one-segment approximation. This is due to the fact that the new formulation accounts for the connectivity of the molecules more accurately than the previous formulation, which treats the chain propa-

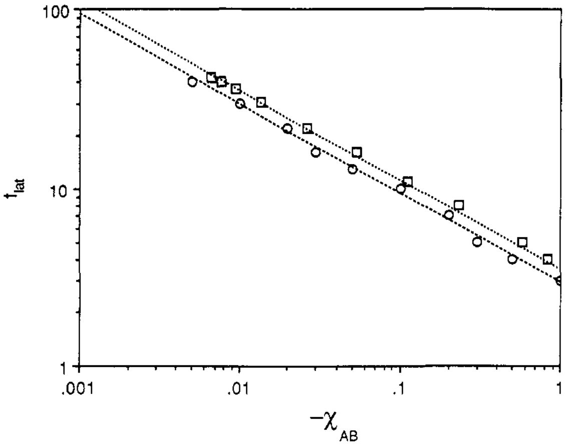

Figure 3. Variation of the thickness of the compositional interphase with the interaction energy parameter, $-\chi_{AB}$, in the absence of bending energy effects. ○ are results from the one-segment approximation,[1] while □ are from the two-segment approximation. Dotted lines represent the form illustrated in eq 11 for the dependence of t_{lat} on $-\chi_{AB}$.

Table II
Parameters Employed in Fitting the Concentration Profiles, in the Absence of Bending Energy Effects, Using Equation 12

χ_{AB}	ξ	x	χ_{AB}	ξ	x
−0.500	1.05	1.00	−0.025	5.50	1.27
−0.105	2.70	1.03	−0.020	6.20	1.29
−0.054	3.70	1.14	−0.007	11.0	1.35

gation as a truly Markovian process.

To understand the shapes of the concentration profiles in the interphase as a function of χ_{AB}, we have attempted to fit these to a number of standard, mean-field results for concentration profiles in a typical interface.[3] It was found, empirically, that the best fit to the data was obtained if one employed an equation of the type

$$\phi_{A_i} = 1 - 0.5 \tanh^x ((z-1)/\xi) \qquad (12)$$

Mean-field calculations on amorphous interfaces show a similar profile for the concentration of the appropriate species near the boundary, except that the power x is always equal to unity. In this case, however, the exponent x can assume a value different from unity. The prediction of eq 12 was also found to be clearly superior to the standard hyperbolic tangent function, thus verifying that it is an appropriate form to be utilized in this context.

There are two variables in eq 12. These are the power of the hyperbolic tangent function, x, and the correlation length in the system, ξ. Values of x and ξ used in fitting eq 12 to the composition data at different values of χ_{AB} are shown in Table II. It is seen that the correlation length does vary with the interaction parameter in the form

$$\xi \propto |\chi_{AB}|^{-1/2} \qquad (13)$$

This result is similar to the corresponding result obtained by Helfand[3] through a mean-field analysis of the interface between two immiscible polymers and may thus be a manifestation of the mean-field lattice treatments that have been employed in both calculations. Further, it is noted that x, the power for the tanh function in eq 12, is equal to unity for $|\chi_{AB}|$ greater than ca. 0.1, while it is larger than 1 for other values. These results suggest that the compositional decay to the bulk value proceeds slowly when one considers polymers that are only slightly attracted to each other and emphasize that the mixing process occurs slower than that predicted by the mean-field lattice theory of Helfand.[3] As we will show below, this is because, in contrast to the case considered by Helfand,[3] the mixing of the two polymers does not constitute the most urgent process in this interphase, thus allowing for it to occur in a slower fashion than that predicted by the mean-field theory.

In addition to the variation of the composition of the two polymers in the interphase, we have also examined the orientations of the segments of the two chains in the vicinity of the crystal surface.[1] The order parameter, which is defined as $3/2\langle\cos^2\theta\rangle - 0.5$, where θ is the angle of the bond relative to the surface normal,[1,2] is employed in studying the disordering process. It should be recognized in this context that the stems of the A polymer are oriented perfectly normal to the lamellar surface, while their orientations in the amorphous phase should be isotropic. The region where this disordering process occurs is termed the order–disorder interphase for the crystalline polymer and was found to span ca. 3–4 lattice layers depending on the value of χ_{AB}. Similar results were found for the amorphous component. The orientations of the two polymers as determined through this approximation are similar to those found by utilizing the one-segment approximation and suggest that the most urgent process in the vicinity of the crystal surface is the disordering of the crystalline stems. The essential conclusion of these calculations is that the characteristics of interphase as calculated from the two-segment approximation are similar to those determined from the earlier, more approximate one-segment approximation.

3.2. Interfacial Characteristics with Inclusion of Bending Energy Effects.

We now proceed to include the bending energy parameter, E_η, to study its influence on the characteristics of the crystal/amorphous interphase. For the sake of simplicity, it has been assumed in these calculations that both chains disfavor the formation of tight folds to the same extent; i.e., E_η has the same value for both polymers. This may not be the best assumption in this case since Corradini et al.[7] have shown that the crystal stems in the immediate vicinity of the crystal have higher energies associated with tight-fold conformations, since they involve significant bond angle bending in addition to the gauche conformations that have to be formed at any tight-fold location. Thus, the amorphous B chains which presumably do not have to undergo bond angle bending will be expected to have lower values of E_η than the A chains. We, however, choose to ignore these complications in these computations and choose to deal with the case where both chains have the same E_η in this aspect of the work.

We first examined the variation of the fraction of sites in the first lattice layer that were involved in the formation of tight adjacent reentry with changes in E_η. These results are shown in Figure 4 where the fraction of sites in tight adjacent reentry is plotted as a function of E_η for four different values of χ_{AB}. It is noted that the results corresponding to $\chi_{AB} = 0$ are those obtained from the homopolymer crystal/amorphous work that we have presented earlier.[2] It is seen that, for all values of χ_{AB}, the fraction of tight adjacent reentry in the first lattice layer decreases significantly as the energy disfavoring these folds, E_η, is increased. For example, at $\chi_{AB} = -1$, this fraction decreases from 81% (at $E_\eta = 0$) to 43% (at $E_\eta = 5$). In addition, it can also be seen that the number of tight adjacent reentry conformations is essentially independent of χ_{AB} for values of interaction parameter that are larger than ca. −0.1 and increases slightly for χ_{AB} that are smaller. In the limit of small energetic interactions between the

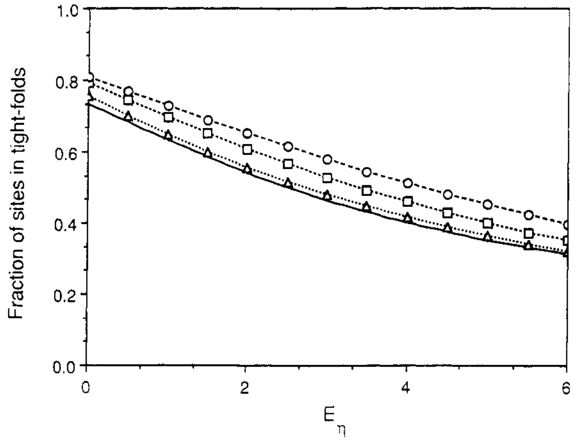

Figure 4. Variation of the fraction of crystalline stems in the first lattice layer involved in the formation of tight folds with changes in E_η ($=E_{\eta A} = E_{\eta B}$). Four different values of χ_{AB} are shown: (—) 0.0, (△) −0.1, (□) −0.5, (○) −1.0.

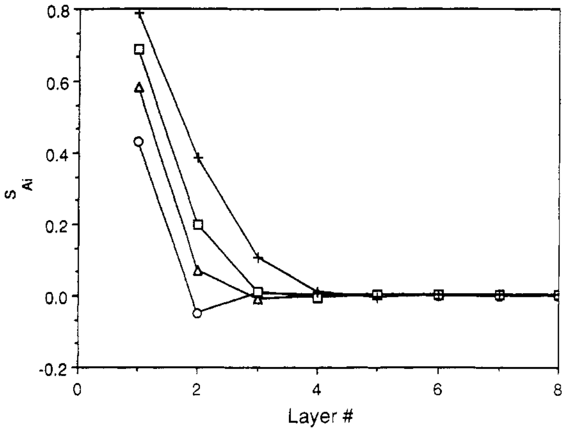

Figure 5. Order parameter of the segments of the crystalline polymer as one traverses from the crystal into the amorphous phase for $\chi_{AB} = -0.1$. Both A and B chains have the same bending energy (E_η) of (○) 0, (△) 2, (□) 4, and (+) 7.

two polymers, therefore, the crystal/amorphous interphase, on this basis, begins to closely resemble the behavior that has been observed earlier for a homopolymer.[2] The essential result from this calculation is that the structure of the A chains in the immediate vicinity of the crystal in systems without large favorable interaction energies will be similar to that of the pure crystalline homopolymer; the presence of B chains in the inter-lamellar regime has only a minor effect in determining the folding behavior of the A chains in the vicinity of the crystal surface.

Having examined the fraction of tight fold conformations in the first layer, we proceeded to analyze the orientations of the segments of the two chains as a function of distance from the crystal surface. The disordering of the crystalline stems is examined first. It can be seen in Figure 5, for a favorable value of χ_{AB} (=−0.10), that the segments in the vicinity of the crystal surface are oriented in a direction that is preferentially normal to the surface. As one proceeds into the amorphous phase, however, this order is dissipated quickly, and the segments assume random orientations. The distance required for this disordering process is seen to be dependent on the value of E_η and closely parallels the interfacial behavior observed in the case of a homopolymer.[2]

An alternate way of examining these data is to examine the orientation of segments as a function of the interchange parameter, χ_{AB}, at a constant value of the bending energy, E_η. It was found that the ordering of the segments of the

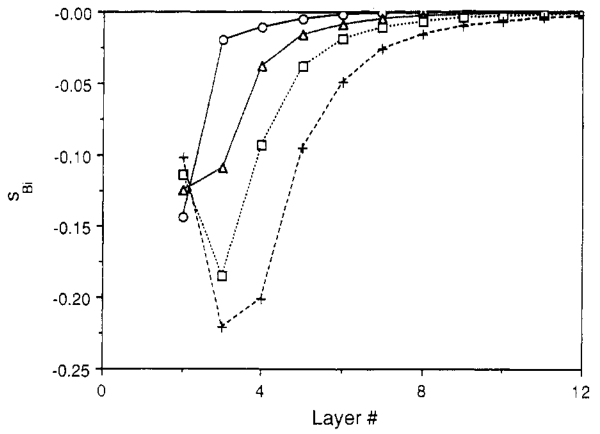

Figure 6. Order parameter of the segments of the amorphous polymer, B, as one traverses from the crystal into the amorphous phase for $\chi_{AB} = -0.1$. Both A and B chains have the same bending energy (E_η) of (○) 0, (△) 2, (□) 4, and (+) 7.

crystalline species was essentially unaffected by changes in χ_{AB} for all values of E_η examined ($0 \leq E_\eta \leq 10$). These results are consistent with earlier results[1] for freely jointed chains that have suggested that the most urgent process in the vicinity of the crystal surface is the disordering of the crystal segments, suggesting that this process must be essentially independent of χ_{AB}, although it is affected by chain flexibility characterized by E_η.

The disordering of the noncrystallizable segments is examined next (Figure 6) as a function of E_η at $\chi_{AB} = -0.1$. As one increases the value of E_η, it can be seen that s_{B2}, the order parameter for the B segments in the second layer, decreases initially and then increases. At the same time, s_{B3} decreases continuously and is lower than s_{B2} in the region where s_{B2} is increasing. The essential conclusion of these results is that the segments of the amorphous polymer in the second and third lattice layers are oriented parallel to the surface and, at high values of E_η, assume values similar to that obtained for a polymer melt near a hard wall (where $s_1 = -0.22$).[3] The fact that s_{B3} is more negative than s_{B2}, especially at high values of E_η, can be rationalized in light of the fact that in this limit the quantity of B segments in the second layer is almost, but not exactly, equal to zero. In effect, therefore, at high bending energies, the second layer is practically impenetrable to the B segments, thus leading to the observed trends for s_{B2}.[3]

Having examined the effects of chain flexibility on the ordering of chain segments, we proceed to explore its effects on the compositional interphase. Again, we examine the variation of composition of the two polymers near the crystal surface as a function of χ_{AB}, at two different values of E_η (0 and 4, respectively) in Figure 7.

At each value of E_η, it can be seen clearly that the compositional interphase becomes smaller as the magnitude of the interchange energy parameter, $|\chi_{AB}|$, becomes larger, a result that is consistent with our earlier findings on fully flexible chains. It should be stressed, however, that the interphase for systems with equal values of χ_{AB} is always larger for higher values of E_η. These results can be rationalized by realizing that chains become "stiffer" as the value of E_η is increased. Hence, the dissipation of crystalline order becomes harder, making it more difficult for amorphous stems to penetrate the A-rich region in the immediate vicinity of the crystal, especially in the case where the enthalpy gain in mixing the two segments is minimal.

Let us now focus on two extreme values of χ_{AB} corresponding to −0.75 and −0.05. For the case where χ_{AB} assumes a value of −0.05, it can be seen that the

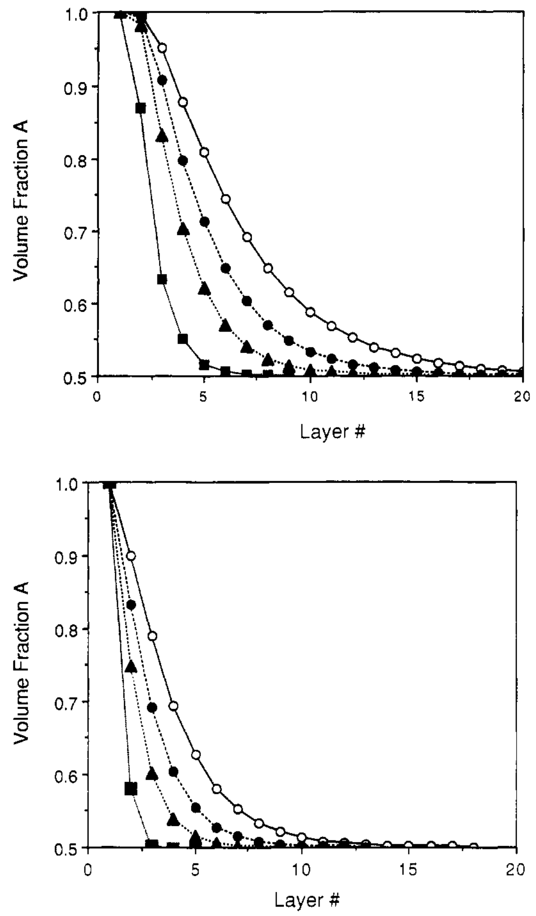

Figure 7. (a, top) Volume fraction of crystalline polymer A as one traverses from the crystal into the amorphous phase for the case where both A and B chains have the same bending energy (E_η) of 4. (■) $\chi_{AB} = -0.75$, (▲) $\chi_{AB} = -0.2$, (●) $\chi_{AB} = -0.1$, (○) $\chi_{AB} = -0.05$. (b, bottom) Same as in a, except for $E_\eta = 0$.

compositional interphase is large for both values of E_η examined and that one has essentially pure A in the zone where the disordering process occurs for the stems of the A polymer. However, when one proceeds to the case where χ_{AB} assumes a value of −0.75, it is clear that the composition changes from pure A to a mixed, amorphous phase (50% of each component) over the same spatial region where the disordering process occurs. The favorable energy of interaction between the two polymers in the second case thus results in the penetration of the amorphous polymer into the interphase of partial order for the semicrystalline polymer. It should be recognized, however, that the penetration will occur for larger values of $-\chi_{AB}$ as one proceeds to more inflexible chains due to the fact that the penetration is associated with increased folding for the A polymers in the vicinity of the crystal surface, a process that becomes increasingly difficult as one increases E_η.

The variation of interphase thickness (based on composition) with χ_{AB} and E_η was examined next. The interphase thickness was defined as the number of layers required before one approached the bulk composition of 0.5 to within 1 part in 1000. On this basis, it was found that the interphase thickness still varied with χ_{AB} as

$$t_{\text{lat}} \propto |\chi_{AB}|^{-1/2} \qquad (14)$$

In addition, it was found that the interfacial thickness also depended on E_η. The final expression that incorporates both of these effects were found empirically to be

$$t_{\text{lat}} \propto |\chi_{AB}|^{-1/2}(1 + CE_\eta^{\,0.7}) \qquad (15)$$

where C is a constant, ca. 0.35, apparently independent of χ_{AB}. Equation 15 implies that the compositional interphase broadens when one considers polymers with a relatively weak interaction (as characterized by the χ parameter) or when one deals with inflexible polymers.

It was found, however, that the form of the compositional variation in the interphase as proposed in eq 12 does not fit the data accurately especially in the range where the E_η values of the two chains are large. The reason for this failure is not clearly understood at this time.

4. Discussion

The results presented above have several consequences on the behavior of real semicrystalline/amorphous polymer blends. In the case of flexible chains, these results suggest that the interphase based both on composition and disordering will be somewhat broader than thought before.[1] The interfacial thickness based on composition depends on the interaction energy parameter, χ_{AB}, as $|\chi_{AB}|^{-1/2}$ and slightly less than linearly on the chain stiffness parameter, E_η. This suggests that systems such as isotactic polystyrene/atactic polystyrene[8] and high density polyethylene/low-density polyethylene[9] (at temperatures below the melting point of the former but above the melting point of the latter), which have χ_{AB} values nearly equal to zero, will not have a mixed phase in the interlamellar region. However, the second polymer will be expelled completely from the interlamellar region and finds itself in the interspherullitic space. These results are in complete agreement with experimental findings on such systems.[8,9]

The primary conclusion of this analysis is that the order–disorder interphase, especially for the crystalline polymer, is apparently affected little when one includes bending considerations and increases from ca. 3–4 layers (depending on the value of χ_{AB}) for freely jointed chains to ca. 6–9 for chains with a stiffness $E_\eta \approx 10$. This result suggests that the most urgent process in the immediate vicinity of the crystal surface is the disordering of crystal stems regardless of their stiffness. The mixing of the two chains in the interphase, however, seems to be a process that is only of secondary importance and is seen to be essentially independent of the disordering process except for cases where one has extremely favorable energetic interactions between the two polymers. The theory presented here therefore suggests that essentially two primary classes of behavior should be observed if one examined such blends experimentally:

(i) If one considered blends with small absolute values of χ_{AB}, but with increasing values of E_η, then the analysis suggests that the width of the order–disorder interphase should increase slightly. Coupled with the broadening of the composition interphase, therefore, it is suggested that there should be a broader region corresponding to essentially pure, "disordered" crystalline polymer that could be detected by an experimental technique such as dynamical mechanical measurements or dielectric spectroscopy. Such results are consistent with reported experimental findings for the poly(vinylidene fluoride)/poly(methyl methacrylate) (PMMA) blends.[10–12]

(ii) If one considered different blends characterized by the same value of E_η but with different values of χ_{AB}, then the analysis suggests that one should obtain an order–disorder interphase for the crystalline polymer that should be essentially pure A for small values of $|\chi_{AB}|$. However, the interphase will no longer be pure A as the interchange parameter becomes more favorable, and this can be attributed to the penetration of the amorphous polymer into the order–disorder interphase. In such a situation, one can no longer detect the presence of an interphase corresponding to a pure, disordered A phase.

An important check of the predictions of this theory is to examine the behavior of several miscible polymer blends with components having the same value of E_η but with varying χ_{AB}. To our knowledge the only experimental work in this area was conducted by Runt et al.,[13] who have examined three different blends involving poly(ethylene oxide) (PEO) as the crystalline component. The amorphous polymers chosen for these experiments were PMMA, poly(vinyl acetate) (PVAc), and poly(hydroxystyrene) (PHS) and were selected since the first two display small interactions with PEO, while PHS, which can hydrogen bond with PEO, has a relatively large energetic interaction. An essentially pure PEO interphase was found in the blends involving PMMA and PVAc, which experience weak interactions with PEO. In contrast, these workers find a relaxation that is suggestive of the existence of an interphase of partial order for the PEO/PHS blend, which is a mixture of the two polymers, implying that the segments of the amorphous polymer penetrate into the interphase of partial order for the semicrystalline polymer. These results are in qualitative agreement with the predictions of the theory presented here. It should be emphasized that more quantitative comparisons need to be performed before the validity of this theory can be examined in more detail.

Acknowledgment. We gratefully acknowledge the many useful discussions with J. P. Runt, which have shed much light on our understanding of this problem. S. K. gratefully acknowledges partial financial support from the Philip L. Walker professorship at The Pennsylvania State University.

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