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Lattice Model for Interphases in Binary Semicrystalline/Amorphous Polymer Blends

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ABSTRACT: In this paper we examine the interphase in a system which consists of two polymers that are compatible in the melt but undergo phase separation due to the crystallization of one polymer in lamellar semicrystalline morphology. The problem is formulated on a cubic lattice in the Bragg–Williams mean-field approximation, under the assumption that the asymptotic amorphous phase of the system corresponds to the most favorable (for mixing) 50/50 composition. We find that the dissipation of the crystalline order through the interphase of partial order is little affected by the interaction energies between the two polymers. On the other hand, the interfacial region of varying polymer composition is strongly affected by the interaction parameter χ_{AB}, with the interfacial thickness varying with the reciprocal of $|\chi_{AB}|^{1/2}$. Hence, binary polymer mixtures with $\chi_{AB} \simeq 0$, which are miscible in the melts, are predicted to undergo nearly complete phase separation upon crystallization of one component, in agreement with experiments.

1. Introduction

The understanding of the behavior of polymer blends has taken on an increasing significance in the wake of the recent practical applications of these systems.[2] Of particular interest are systems that are completely miscible in the melt but phase separate on cooling due to the crystallization of one component. Examples of such blends include poly(vinylidene fluoride) (PVDF) as the crystallizable component, mixed with one of the following amorphous polymers: poly(methyl methacrylate) (PMMA),[3-10] poly(ethyl acrylate) (PEA),[11] poly(vinylpyrrolidone) (PVP),[12] poly(vinyl esters) like poly(vinyl acetate), poly(vinyl propionate), or poly(vinyl butyrate),[13] and a mixture of poly(ethylene oxide) as the crystallizable component mixed with PMMA.[14] Mixtures of crystallizable stereoregular polymers with atactic amorphous polymers from the same chemical monomers, isotactic/atactic polystyrene systems,[15] for example, have also been studied extensively in this regard.

In all cases, on cooling, the mixture separates into several distinguishable phases: the crystal phase, which has been assumed to be constituted purely of the crystallizable polymer, an interphase whose composition is not clearly known, and an amorphous phase that is either a homogeneous mixture of both polymers in the interlamellar region or is a pure phase of noncrystallizable material in the interfibrillar or interspherulitic space.

The presence of an interlamellar amorphous phase in which the two polymers are miscible due to the negative heat of mixing is expected to depress the melting point of the crystallizable component, a fact that has been observed in calorimetric experiments. For example, Nishi and Wang[4] used the depression of melting points of PVDF in PVDF/PMMA mixtures to derive interaction energies between the two polymers. (A Flory type analysis[16] was employed by the authors in this calculation.) From this calculation it has been suggested that the exchange energies between the polymers is relatively large, of the order $-{}^1/{}_2 k_B T$ per mole of chain segments.[4] Similar results were also obtained for the PVDF/PEA[11] and the PVDF/PVP[12] systems. It has also been pointed out that the structure and composition of the amorphous phase in these cases are sensitive to the technique of preparation, viz., melt crystallized versus solution crystallized.[4,6]

Recently, it has been suggested that the interphase between the crystal and amorphous phases constitutes an important facet of this problem that has not been considered properly in the past. Yoon and his co-workers,[7,8] Wendorff,[7,9] and Alfonso et al.[12] have illustrated the presence of the interphase and also delineated its importance in determining the behavior of the mixture when it is thermally treated.

In this paper we present a lattice theory that describes the structure and composition of the crystal–amorphous interphase in binary blends that are compatible in the melt. The size of the interphase and its dependence on the energy of interaction between the two polymers are investigated in detail.

2. Model Formulation

We consider chains placed on a lattice of coordination number Z. (For a cubic lattice $Z = 6$.) Each lattice layer has N_0 sites, and lattice layers are numbered as an ascending function of their distance from the crystal surface, which is numbered zero. Each lattice site is isodiametric, so that a lattice site is approximately 4.5 Å on a side in the case of polyethylene. For the sake of simplicity we limit the investigations to the chains of infinite molecular weights. It has been further assumed that the lattice is completely filled: i.e., no voids have been included in our calculations. The energy of interaction between two unlike monomers is characterized through the Flory–Huggins interchange energy parameter, χ_{AB}. It is assumed that only polymer A crystallizes and that the crystalline stems of polymer A are perfectly normal to the lamellar surface. It is also supposed that both A and B chains are completely flexible: i.e., the chains can take up any conformation afforded under the constraints of the lattice without any energy penalty. (We recognize that conformational energetic effects may play an important role in deter-

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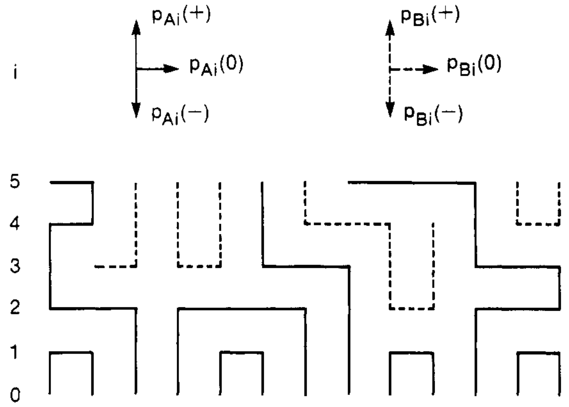

Figure 1. Schematic representation of the crystal–amorphous interphase and definitions for different probabilities used in the text. The semicrystalline polymer A is shown by solid lines and the amorphous polymer B by dashed lines.

mining the structure of the interphase:[17-19,23] however, these calculations are deferred to a future publication.)

The notations (Figure 1) and derivations adopted in this work closely parallel those presented initially by Helfand[20] for the immiscible amorphous polymer mixtures and reformulated later in ref 19 and 21 for the crystal–amorphous interphase of homopolymers. The volume fraction of A segments in layer i is denoted by ϕ_{Ai}, while the corresponding quantity for B is ϕ_{Bi}. Obviously, the two volume fractions in each layer sum to unity:

$$\phi_{Ai} + \phi_{Bi} = 1 \tag{1}$$

In addition, the probabilities of finding a bond belonging to polymer A in layer i pointing in the three directions are denoted by $p_{Ai}(-)$ (spanning layer $i-1$ and i), $p_{Ai}(+)$ (spanning layers i and $i+1$), and $p_{Ai}(0)$ (a bond in layer i), respectively. These probabilities obey the constraint equation

$$p_{Ai}(-) + p_{Ai}(+) + (Z-2)p_{Ai}(0) = 1 \tag{2a}$$

Analogously, $p_{Bi}(-)$, $p_{Bi}(+)$, and $p_{Bi}(0)$ are the corresponding probabilities for B segments in the same layer i. These probabilities also obey a constraint equation that is the B analogue of eq 2a.

$$p_{Bi}(-) + p_{Bi}(+) + (Z-2)p_{Bi}(0) = 1 \tag{2b}$$

The entropy of chain segments in the interphase can then be formulated in the spirit of the Bragg–Williams approximation. This derivation has been presented earlier[19-21] and hence is not repeated here. However, the final result is reported here:

$$-\frac{S}{k_B N_0} = \sum_{i=1}^{k} \phi_{Ai}[p_{Ai}(+)\ln p_{Ai}(+) + p_{Ai}(-)\ln p_{Ai}(-) + (Z-2)p_{Ai}(0)\ln p_{Ai}(0)] + \phi_{Bi}[p_{Bi}(+)\ln p_{Bi}(+) + p_{Bi}(-)\ln p_{Bi}(-) + (Z-2)p_{Bi}(0)\ln p_{Bi}(0)] \tag{3}$$

To obtain the Helmholtz energy associated with the interphase, we must obtain the energy associated with the mixing of the A and B segments in each layer. This can be simply obtained through the equation

$$\frac{U}{k_B T} = \sum_{i=1}^{k} \frac{\chi_{AB}}{Z} \phi_{Bi}[\phi_{A(i-1)} + (Z-2)\phi_{Ai} + \phi_{A(i+1)}] \tag{4}$$

The Helmholtz energy of the interphase, A, can then be obtained from eq 3 and 4.

$$A = U - TS \tag{5}$$

To obtain the equilibrium distribution of bond directional probabilities, eq 5 should be minimized with respect to all the p's with eq 1 and 2 as constraints. In addition, the geometry of the problem imposes the following boundary conditions

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

$$\phi_{B1} = 0 \tag{6b}$$

Also, the symmetry of the problem dictates that

$$p_{Ki}(-)\phi_{Ki} = p_{K(i-1)}(+)\phi_{K(i-1)} \tag{7}$$

where K is either A or B. Equation 7 is merely a restatement of the continuity condition[19,21] or flux constraint.[20]

Table I
Variation of the Fraction of Stems Involved in Tight Adjacent Reentry with the Interaction Energy χ_{AB}

χ_{AB}	fraction of adjacent reentry	χ_{AB}	fraction of adjacent reentry
0	0.744	−0.1	0.764
−0.003	0.745	−0.5	0.798
−0.01	0.747	−1.0	0.812
−0.05	0.756		

The minimization of the Helmholtz energy of the interphase was performed using two different methods. In the first method, eq 5 was analytically minimized with respect to the constraints. A coupled set of nonlinear algebraic equations were obtained for the probabilities and the mole fractions in each layer i. These equations were solved with the aid of a Newton–Raphson solver. In the second case, the Helmholtz energy was minimized numerically with respect to the unknown probabilities and mole fractions through the use of a modified Fletcher–Powell algorithm. The results of the two techniques are in excellent agreement for all cases examined.

A note is made here of the asymptotic value of ϕ_{Ai} that we obtain far from the crystal surface. In all cases where χ_{AB} is negative, this value is equal to 0.5. This is not a surprising result, since the number of A–B contacts will be maximized in this situation. In practice, the asymptotic amorphous composition is determined by the external constraints, such as overall polymer concentration, the degree of crystallinity, etc. The general features of the interphase, however, are expected to be little affected by the asymptotic composition (see below).

3. Results and Discussion

The first result we examine here is the change in the fraction of sites in the first lattice layer that are associated with adjacent reentry folds as a function of χ_{AB}. It has been understood for sometime that the quantity of tight adjacent reentry folds is an important variable in determining the structure of the crystal–amorphous interphase in semicrystalline polymers. It is seen in Table I that the fraction of sites in regular folds seems relatively insensitive to the value of the interaction parameter, χ_{AB}. For example, this number rises from a value of 74.4% for a χ_{AB} value of 0 to 81.2% for a χ_{AB} value of −1. Clearly, the presence of a second, noncrystallizable component does not significantly affect the behavior of the interphase in the immediate vicinity of the lamellar surface.

To further delineate the effect of the existence of the second polymer better, we then proceeded to examine the variation of the volume fraction of each species in a layer as a function of its position relative to the crystal surface. Several different values of the interaction parameter were examined, and these results are sketched in Figure 2. For the largest negative χ_{AB} examined, (−1.0), it is seen that the composition is perceptibly different from the asymptotic value in only the first three lattice layers. On this basis, the interface in this case is three layers, or ca. 15 Å thick. As the χ_{AB} value is increased toward zero, it is seen that the interphase becomes broader, and the composition drop-off to the asymptote is much more gradual. This clearly reflects the importance of entropy constraints in the interphase relative to the contribution of the enthalpy of mixing.

To study the dependence of the thickness of the interphase on the value of χ_{AB}, we have plotted the thickness against the absolute value of χ_{AB} on a log–log basis in Figure 3. (The thickness of the interphase in this figure corresponds to the lattice layer where the concentration is different from the asymptotic value by less than one part in a thousand. Different definitions for the thickness have

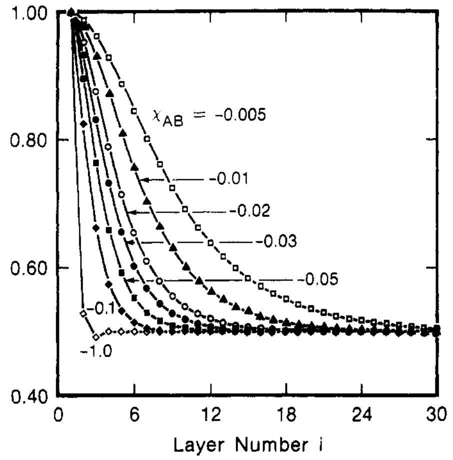

Figure 2. Variation of the volume fraction of polymer A in each layer for different values of χ_{AB} indicated in the figure.

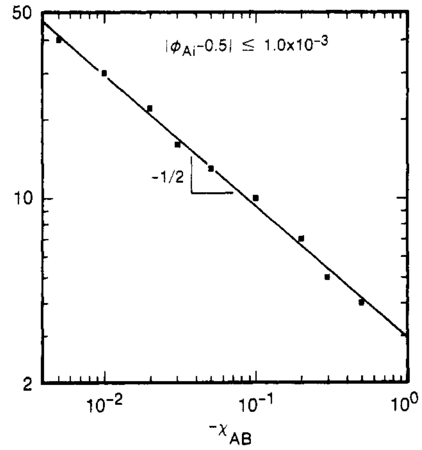

Figure 3. Thickness of interfacial layers as a function of χ_{AB}. The interface is defined as the region in which the polymer composition deviates by more than 0.001 from the asymptotic value of 0.5.

been employed, but the qualitative results obtained were not different from those demonstrated in Figure 3.) It is immediately seen that the points fall on a straight line of slope −0.5. Hence, we may write a simple equation

$$t_{\text{lat}} = \frac{3}{(-\chi_{\text{AB}})^{1/2}} \tag{7a}$$

Here t_{lat} is the thickness of the interphase in units of lattice layers. The dependence of the thickness of the interphase on the interaction parameter follows qualitatively the earlier calculation of Helfand[20] on immiscible polymers. It is surprising to note this similarity between the case of immiscible and miscible polymers, since the very nature of the interphase in the two cases is quite different.

An interesting prediction of eq 7 is that the binary polymer mixtures with $\chi_{\text{AB}} \simeq 0$, which are miscible in the melts, will no longer be miscible in the semicrystalline blends. That is, the noncrystalline polymer will be expelled completely from the interlamellar zone. This is consistent with the experimental results. For example, Warner et al.[15] found that the atactic polystyrene is completely absent in the interlamellar region of isotactic polystyrene crystallites, although the isotactic/atactic polystyrene systems are completely miscible in the melts. Similar situations are also expected in other stereoregular/atactic polymer mixtures as well as linear/branched (polyethylene) polymer mixtures wherein the χ_{AB} should be nearly 0.

An alternate way to characterize the interphase is to study the orientational order of the A and B segments in each lattice layer. This is represented by the order parameter, which has been defined earlier[17]

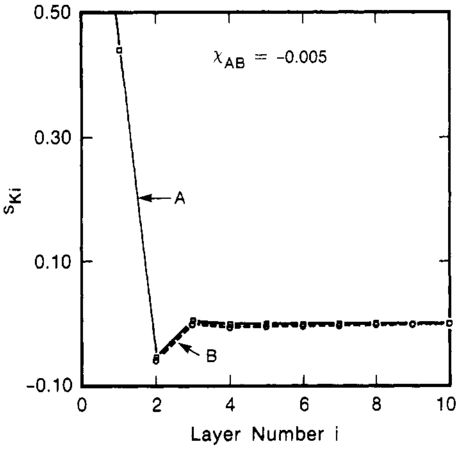

Figure 4. Variation of the segmental order parameters of polymer A (solid line) and B (dashed line) in each lattice layer, calculated for χ_{AB} = −0.005.

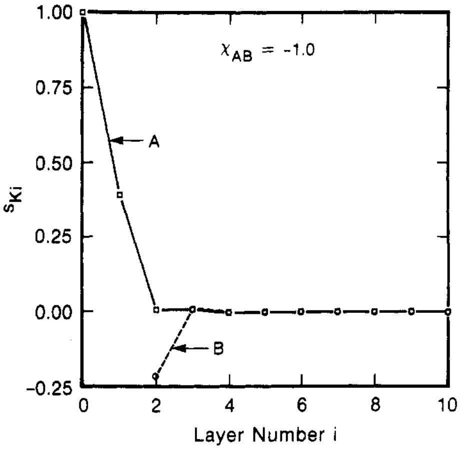

Figure 5. Variation of the segmental order parameters of polymer A (solid line) and B (dashed line) in each lattice layer, calculated for χ_{AB} = −1.0.

$$s_{Ki} = (3\langle\cos^2\vartheta\rangle_{Ki} - 1)/2 \tag{8}$$

where we calculate the order parameter separately for A and B segments in each layer (denoted here by the K subscript). Here, ϑ represents the angle made by a segment in a layer to the normal to the crystal surface. In Figures 4 and 5 we plot s_i for both A and B segments as a function of the distance of the layer from the crystal surface for two χ_{AB} values, −0.005 and −1.0, respectively. These results show that the effect of χ_{AB} is limited only to the first two layers, and complete isotropy of segment orientation is obtained from the third layer on, regardless of the value of χ_{AB}. On this basis, we conclude that the interphase of partial order is approximately three layers (or 15 Å) thick in all practical cases for completely flexible chains. However, it should be recognized that, in the case of χ_{AB} = −0.005 beyond the third layer, the order parameter while smaller than 10^{-3} is different from zero to the 35th layer, which is the location where the polymer composition reaches its asymptotic value.

Therefore, it is clear that the need to dissipate order is more urgent for the system than allowing for the mixing of the A and B segments. Alternately, this might assert the importance of "entropic" effects over "energetic" factors in determining the structure of such interphases. These conclusions follow directly from the results shown in Figures 2–5, where it is seen that the region for the dissipation of order seems relatively insensitive to the chosen

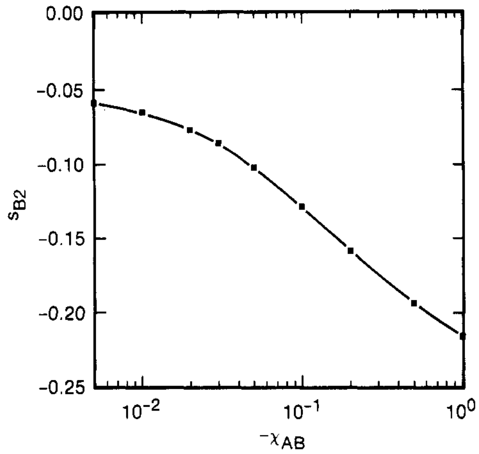

Figure 6. Segmental order parameters of amorphous polymer B in the second lattice layer plotted against χ_{AB}.

value of the interaction energy between the segments of the two different polymers. On the other hand, the region required to obtain isotropy in terms of composition can be much broader and depends strongly on the value of χ_{AB}.

Finally, we have examined the effect of the interaction parameter, χ_{AB}, on the order parameters in the first two layers that show significant segmental orientation. Specifically, in Figure 6, we plot the order parameter of the B segments in the second layer as a function of χ_{AB}. It is seen that for small values of the interaction energy the s_{B2} value reaches an asymptotic value of roughly -0.05. This corresponds to the value obtained in a homopolymer crystal-amorphous interphase in the second lattice layer.[19,21] However, as one increases the absolute value of χ_{AB}, it is seen that the order parameter in this layer decreases significantly toward an asymptotic value of -0.22, which corresponds to the polymer melts at the hard wall, considered first by Helfand.[22] This reflects the fact that the B segments are present in significant numbers but cannot penetrate the first layer (eq 6b). (The slight dip below 0.5 in Figure 2 may be a reflection of this fact.) These results again are a manifestation of the competition between the energetic and entropic factors in determining the structure of the crystal-amorphous interphase in such situations. Clearly, at extremely large negative χ_{AB} the energetic gain obtained by mixing A and B segments becomes comparable to the entropic gain in disorienting segments in the immediate vicinity of the crystal surface. In this regard, it is anticipated that the inclusion of conformation energy terms disfavoring the formation of tight folds will have very interesting consequences in determining the structure of this interphase.

4. Conclusions

We have developed here a lattice model, in the spirit of the Bragg-Williams approximation, to analyze the interphase in a binary mixture where phase separation occurs due to the crystallization of one component. It must be stressed that this formulation attempts to minimize the Helmholtz energy of the noncrystalline phase only, a fact that assumes that it is this phase controlling the equilibrium of the entire system. Under these conditions we show that the most urgent process in the interphase involves the disordering of the crystalline A segments to an isotropic phase. The mixing of the A and B segments, driven by the favorable interaction energy, does play a role in determining the concentration profile in the interphase. However, this seems to be of secondary importance in determining the interphase of partial order. Consequently, the equilibration of order and composition tends to occur more or less independent of each other. This general conclusion is expected to be valid in more practical situations wherein the composition of the amorphous phase is controlled by the external constraints such as the overall polymer concentration and conditions of crystallization.

Finally, the theory predicts that the entropic constraints at the crystal surface lead to nearly complete phase separation of binary polymer mixtures with $\chi_{AB} \simeq 0$ upon crystallization of one component, though they are completely miscible in the melts. This is in agreement with the experimental results of isotactic/atactic polystyrene mixtures,[15] for example.

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