Simple Model for Enthalpic Effects in Homopolymer/Block Copolymer Blends

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ABSTRACT: A simple model is developed for estimating the extent to which a homopolymer, H, can form a mixed phase with the A segments of a block copolymer when there is a favorable enthalpy of mixing A and H. The model assumes a lamellar domain morphology and ignores any interfacial effects. Enthalpic and entropic terms in the free energy expression favor mixing of H and A, whereas conformational changes for both A and H chains oppose mixing. An equilibrium saturation composition of homopolymer in the mixed phase results from the balancing of these opposing effects. An exothermic interaction dramatically alters the phase behavior from that of an athermal system, e.g., polystyrene homopolymer blends with styrene-based block copolymers. The model predictions are compared with experimental results given in a companion paper for blends of poly(phenylene oxide) with styrene-based block copolymers with good semiquantitative agreement. The exothermic interaction of this system greatly increases the extent of homopolymer incorporation into the copolymer domains and makes the molecular weight of the homopolymer a relatively unimportant parameter compared to the athermal case. Limitations of the model are discussed.

Introduction

The recent literature contains several reports on blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with various styrene-based block copolymers.[1-6] Even though PPO and polystyrene (PS) homopolymers are well-known to be completely miscible[7-9] for all molecular weights, the constraints acting in block copolymers may prevent their PS segments and PPO homopolymer from forming a single mixed phase in some cases as demonstrated previously.[6,10] The companion paper[11] gives an extensive experimental investigation of the extent of phase mixing as a function of the molecular weights of the PPO homopolymer and the PS segments of block copolymers. It was shown that the latter is much more important than the former in determining phase behavior in these systems.

A complete thermodynamic theory for the phase behavior of blends of a homopolymer, H, with block copolymers of the type AB or ABA must describe a number of complex possibilities.[12-14] Various formulations of this problem have appeared the recent literature[12-17] that focus mainly on the special case where H is chemically identical with one of the blocks of the copolymer, e.g., A. The latter restriction amounts to the assumption that H and A mix athermally and, thus, ignores the consequences on blend phase behavior of any favorable energetic interaction between them. For the blends of interest here (i.e., H = PPO and A = PS), there is an exothermic interaction between the two types of segments that is an important factor driving miscibility of blends of the corresponding homopolymers. Because of the mathematical complexities of the theoretical formulations mentioned above, it is difficult to gain from them much insight about how a favorable interaction would alter the extent that H would be incorporated into domains of A for phase-separated block copolymers. For this purpose, we suggest here a simple physical picture and a model that identifies some of the main factors and gives a semiquantitative assessment of their relative importance. For this, we envision preexisting domains of A segments and examine some of the thermodynamic consequences of continued addition of H molecules to this phase including combinatorial entropy of mixing, heat of mixing, conformational extension of A blocks, and conformational compression of H chains. Any contributions from the B phase or the interface (interphase) are ignored; hence, the size of these blocks or their architecture, AB, ABA, etc., have no direct role in the model. The approach used has some similarities with the swelling of polymer networks by solvents.[18]

While the model is very simplistic in many regards, it will be seen that it does predict the trends seen in the companion paper in a semiquantitative manner. It is hoped that these results will stimulate more rigorous analysis of this interesting and important problem.

Physical Model

For simplicity, we assume the block copolymer domains are lamellar; however, some unique aspects of other morphological arrangements will become clear. The left side of Figure 1 shows a lamellar domain where A blocks with free ends emanate from both bounding surfaces as they would for AB or ABA architectures. The thickness of this domain, L_0, is related to the size of the A block by[19]

$$L_0 = k\langle r_A^2\rangle^{1/2} \quad (1)$$

where $\langle r_A^2\rangle^{1/2} = C_A M_A^{1/2}$ is the rms end-to-end distance of A blocks of molecular weight M_A, C_A is a constant depending on the molecular structure of A, and k is a factor related to copolymer architecture ($\cong$1.4 for the case on the left and 1.2 for the case on the right). As molecules of H are added, this domain swells to a larger thickness, $L = \alpha L_0$, because of the volume occupied by H. Owing to the thermodynamic tendency for A and H to mix uniformly, the A segments will extend; however, at some point the molecular extension factor will have to become less than the macroscopic factor α. This will result in a compositional gradient such that the concentration of A segments decreases toward the center of the domain[17] and in the extreme could result in a central region of pure H segments as implied in the bottom panel on the left in Figure 1. Meier[15] introduced an arbitrary constraint to ensure that the segment density within a domain remains essentially constant. In this model, we will avoid this difficulty by the simple but artificial means of treating only the problem where the A block is connected to *both* walls bounding the A domain as shown on the right in Figure 1. This is analogous to the situation for a BAB architecture. While this gives a simple means of dealing with the real but difficult problem illustrated on the left in Figure 1, it must be emphasized that this is an approximation to the real case where concentration gradients may exist, and further, such a constraint on the A block can be removed by morphological rearrangements of the type illustrated in

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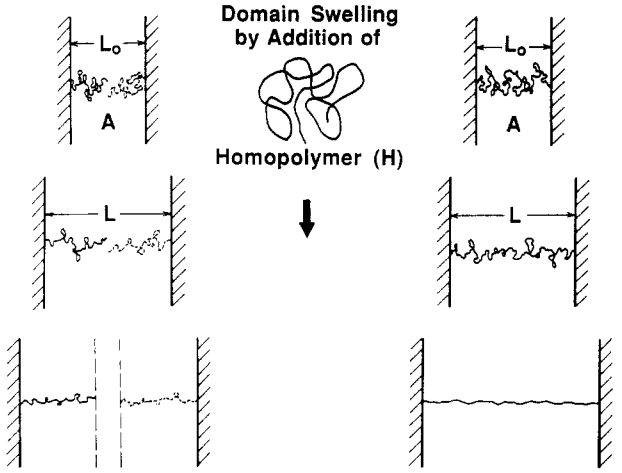

Figure 1. Lamellar domains of A segments of a block copolymer showing swelling as homopolymer chains H are added. On the left, separate chains emanate from both bounding surfaces, e.g., AB or ABA copolymers. On addition of homopolymer, the A segments tend to extend toward the center of the domain but composition gradients may exist as suggested at the bottom by a central zone nearly depleted of A units. On the right, these problems are avoided by having each chain connected to both surfaces as would by the case for a BAB copolymer.

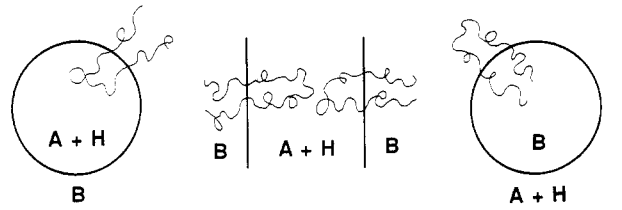

Figure 2. Illustrations of morphological arrangements for blends of BAB copolymer with homopolymer H that can occur in addition to that shown on the right in Figure 1.

Figure 2. Consequently, this approach cannot describe the detailed behavior of real systems at high contents of H.

Mathematical Formulation

In this section, the free energy change associated with adding homopolymer chains to A domains like the one shown on the right in Figure 1 is developed from estimates of the contributions from each of the four separate sources mentioned in the Introduction.

Combinatorial Entropy of Mixing. The combinatorial entropy of mixing for adding n_H moles of homopolymer to the A domains is given by

$$\Delta S_{mix}^{(c)} = -n_H R \ln \phi_H \quad (2)$$

where ϕ_H is the volume fraction of homopolymer that is assumed to be uniformly distributed throughout the domain. A corresponding term for the A segments is not included here following the argument by Meier[15] that they do not have spatial freedom.

Heat of Mixing. A van Laar type expression gives the following result for the total heat of mixing of A and H segments

$$\Delta H_{mix} = (n_H \tilde{V}_H + n_A \tilde{V}_A) B \phi_H \phi_A \quad (3)$$

where $\tilde{V}_i$ are molar volumes that may also be expressed in terms of molecular weights and densities, i.e., M_i/ρ_i, n_A is the moles of A blocks considered, and $\phi_A = 1 - \phi_H$. The interaction between segments of H and A is characterized by the parameter B which alternately can be expressed as the familiar "chi" parameter of the Flory–Huggins theory.[20]

Conformational Change of A Segments. Swelling of the domains causes an extension of the A chains leading to a change in their conformational entropy that can be estimated by using the statistical theory of rubberlike elasticity (Flory): where α_i are the molecular extension

$$\Delta S_A^{(e)} = -\tfrac{1}{2} n_A R[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln \alpha_x \alpha_y \alpha_z] \quad (4)$$

factors in the three coordinate directions. Recent evidence from electron microscopy[10] suggests that macroscopically the swelling occurs equally in all three coordinate directions, hence

$$L/L_0 = \phi_A^{-1/3} \quad (5)$$

This may not be so at the molecular level. For the simple case of unentangled segments having their end-to-end vector parallel to the thickness direction, the molecular extension factor in the thickness direction, α_x, is given by eq 5 while the lateral extension factors, α_y and α_z, remain unity since swelling only serves to move the chains apart in these directions without deforming them. For this case, eq 4 reduces to

$$\Delta S_A^{(e)} = -\tfrac{1}{2} n_A R[\phi_A^{-2/3} - 1 + \tfrac{1}{3} \ln \phi_A] \quad (6)$$

However, appreciable entanglement of the A segments with each other or skewness of their end-to-end vectors from parallel to the thickness direction will result in a larger change in conformational entropy than estimated by eq 6.

Conformational Change of Homopolymer Chains. In the homopolymer phase, chains of H exist as random coils with a radius of gyration, R_G, that is related to their molecular weight, M_H, by[18]

$$R_G = b_H M_H^{1/2} \quad (7)$$

Since the dimensions of the block copolymer domains may be comparable or smaller than R_G, homopolymer coils may have to undergo a conformational rearrangement or compression to enter these regions. The conformational entropy or free energy change associated with this is analogous to that for partitioning of coils between pores and a dilute solution of H. The latter problem is of interest in gel permeation chromatography and expressions for the partition coefficient, K, for such cases have been developed[21-23] in terms of the ratio of the radius of gyration of the polymer coil, R_G, and the pore dimension, a, where $a = \frac{1}{2}L$ for slitlike pores and is the radius for cylindrical or spherical pores. The results are given below for various pore geometries.

slits: $K =$

$$(8/\pi^2) \sum_{m=0}^{\infty} (2m+1)^{-2} \exp\{-(2m+1)^2(\pi^2/4)(R_G/a)^2\} \quad (8)$$

cylinders:

$$K = 4 \sum_{m=1}^{\infty} \beta_m^{-2} \exp\{-\beta_m^2 (R_G/a)^2\} \quad (9)$$

spheres:

$$K = (6/\pi^2) \sum_{m=1}^{\infty} m^{-2} \exp\{-m^2 \pi^2 (R_G/a)^2\} \quad (10)$$

In eq 9, β_m are the roots of the zero-order Bessel function of the first kind. The free energy or entropy changes associated with the conformational rearrangement are given by

$$\Delta G_H^{(e)} = -T \Delta S_H^{(e)} = -n_H R T \ln K \quad (11)$$

Figure 3 shows the free energy increase associated with transferring a homopolymer coil from its bulk phase into block copolymer domains using this partition model. The

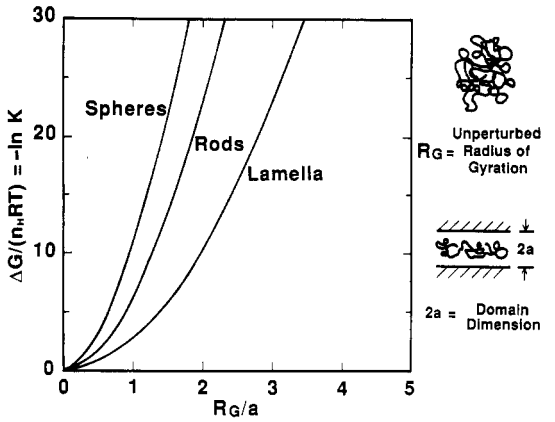

Figure 3. Conformational free energy change for transferring a randomly coiled polymer chain with an unperturbed radius of gyration R_G to a pore or a domain with spherical, cylindrical, or slitlike geometry having dimension $2a$.

free energy penalty is, of course, greater as the coil becomes larger relative to the domain dimension. The penalty is not as great for a rodlike domain as for a sphere because the chain can extend easily along the cylinder axis. Lamellar domains involve the least penalty since the chain can extend in both lateral directions. Thus, morphological rearrangements can have important effects on the thermodynamics of this process; however, the following discussion will continue to be restricted to lamellar-type structures.

Total Free Energy. The total free energy change associated with adding n_H moles of homopolymer to n_A moles of A blocks from the above sources is

$$\Delta G_{total} = \Delta H_{mix} - T[\Delta S_{mix}^{(c)} + \Delta S_A^{(e)} + \Delta S_H^{(e)}] \quad (12)$$

It is convenient to divide this total free energy by the original volume of the A phase, $n_A\tilde{V}_A$, to get

$$\frac{\Delta G_{total}}{RTn_A\tilde{V}_A} = \frac{B\phi_H}{RT} + \frac{\rho_H\phi_H}{M_H(1-\phi_H)}\ln\phi_H + \frac{\rho_A}{2M_A}\left[(1-\phi_H)^{-2/3} - 1 + \frac{1}{3}\ln(1-\phi_H)\right] - \frac{\rho_H\phi_H}{M_H(1-\phi_H)}\ln K \quad (13)$$

The term K is a function of R_G/a, and since $a = {}^1/_2L$, it depends on the chemical structure of H and its molecular weight through R_G (see eq 7), the volume fraction of H in the domain through the relationship of L to L_0 (see eq 5), and the chemical structure of the A segment and its molecular weight through L_0 (equivalent of equation 1).

Application to Blends of PPO with Styrene-Based Block Copolymers. In this section the terms in eq 13 are made specific for blends of PPO and styrene-based copolymers and then examined individually to understand their relative importance to the overall process envisioned. Finally, the chemical potential of PPO chains in the domains of styrene segments is obtained from eq 13 and used to compute the amount of homopolymer that can be mixed with the PS block segments at equilibrium.

Estimated Free Energy Terms. In the following calculations we use 200 °C as the temperature. This is an arbitrary but reasonable choice for comparison with the experimental results in the companion paper. Polystyrene lamellar domain thicknesses were computed by using eq 1 with $k = 1.2$ and $C_s = 6.95 \times 10^{-9}$ cm as suggested by others.[19,24] The PPO radius of gyration was computed by using eq 7 with $b_{PPO} = 3.35 \times 10^{-9}$ cm.[24] The only other parameter needed is the van Laar interaction parameter, B, which can be estimated from the vast literature on PPO–PS blends; however, an unambiguous value is difficult to establish as revealed by the following discussion.

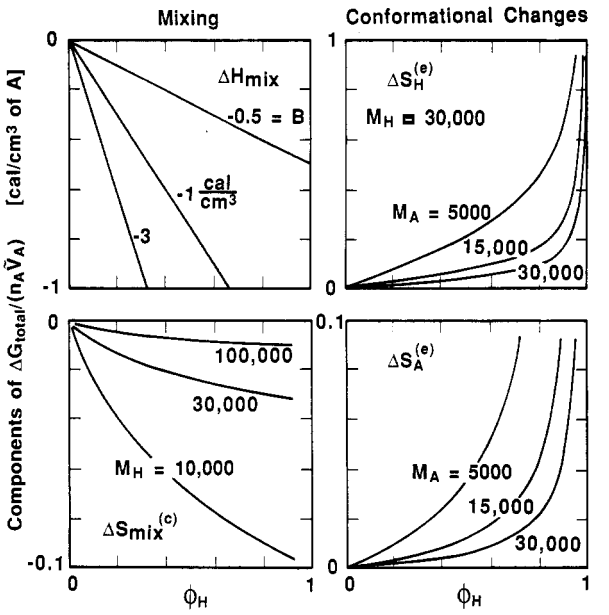

Figure 4. Individual contributions of the four terms considered by the model to the total free energy change when A domains are diluted with homopolymer to a volume fraction ϕ_H. Mixing terms are on the left while terms arising from conformational changes are on the right. Note differences in scale for top and bottom.

The difficulty of directly measuring the heat of mixing for two polymers is well-known;[25] however, an indirect route using heats of dilution[26,27] suggests for the PPO–PS system that B is about −4 to −5 cal/cm³ at 35 °C. For many systems melting point depression has proved useful,[28-31] and a recent study[32] employing *i*-PS/PPO blends suggests that B is about −3 cal/cm³ at 230 °C. Gas sorption experiments[33] at 35 °C are consistent with values of B in the range given above. Numerous estimates of the interaction parameter for this system have been deduced from neutron scattering studies, and Kramer et al.[34] recently attempted to unify the rather divergent values that have been reported. One problem is that interaction parameters obtained from phase behavior are expected to contain an entropic effect in addition to the purely enthalpic one. Using the temperature-dependent forms of the Flory–Huggins interaction parameter summarized by Kramer et al.,[34] we estimate a B in the range of −0.7 to −0.9 cal/cm³ at 25 °C and −0.2 to −0.4 cal/cm³ at 200 °C, which is very much less than the values indicated above. If the purely enthalpic contribution to the Flory–Huggins interaction parameter is evaluated from the temperature-dependent forms given by Kramer et al.[34] using standard thermodynamic relations,[18,35] then a temperature-independent value of −1.57 cal/cm³ results. Because of the uncertainty in the value of B, we will show the effects of varying this quantity within the ranges given above.

Figure 4 shows the contribution of each of the four terms in eq 12 and 13 to the total free energy change when homopolymer PPO of molecular weight M_H is incorporated into PS domains composed of segments of molecular weight M_A (see right side of Figure 1). Note that the mixing terms (ΔH_{mix} and $\Delta S_{mix}^{(c)}$ on the left in Figure 4) are always negative and favor addition of homopolymer while the terms stemming from conformational changes ($\Delta S_A^{(e)}$ and $\Delta S_H^{(e)}$ on the right) are always positive and inhibit addition of homopolymer. Each term increases in magnitude as the fraction of homopolymer in the domain increases. Note that the scale for the upper two panels is an order of magnitude greater than that for the two lower panels. Hence, the dominate terms will usually be

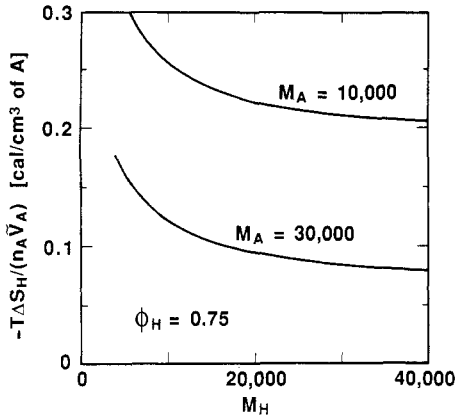

Figure 5. Variation in the contribution to free energy for the conformational change of homopolymer chains as their molecular weight increases at fixed values of M_A and ϕ_H.

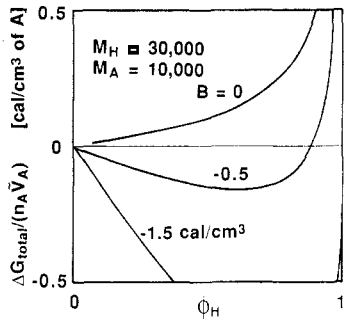

Figure 6. Total free energy change versus ϕ_H for M_H = 30 000 and M_A = 10 000 for different magnitudes of interaction parameter B.

ΔH_{mix} and $\Delta S_H^{(e)}$; however, all terms are considered in subsequent calculations. Both conformational contributions become smaller the larger M_A is. The term $\Delta S_H^{(e)}$ also depends on M_H, and its contribution to the free energy decreases as M_H becomes larger as illustrated in Figure 5. At first sight this seems contrary to intuition and to Figure 3; however, in eq 13 an increase in M_H amounts to a decrease in moles of H while Figure 3 is expressed per mole of H.

As seen in Figure 4, the heat of mixing term can be quite significant in comparison to the other terms. Its effect is best seen in Figure 6 where the total free energy change per volume of A is shown for typical molecular weight values.[11] When B = 0, the total free energy change is unfavorable for adding significant amounts of homopolymer to the A domains. However, when B = −0.5 cal/cm³, the total free energy favors adding substantial amounts of homopolymer and continues to be even more favorable for B = −1.5. Thus, we can see that the exothermic mixing of H and A units is a substantial driving force relative to the opposing terms when the interaction parameter is in the range expected for PPO–PS and other miscible blend systems.[36] The minimum in the total free energy versus ϕ_H stems from balancing the favorable mixing terms against the unfavorable conformational terms.

Predicted Equilibrium Phase Behavior. The chemical potential of H in the mixed domains relative to a phase of pure H is obtained as follows:

$$\mu_H - \mu_H^\circ = \left(\frac{\partial \Delta G_{total}}{\partial n_H}\right)_{T,P,n_A} \tag{14}$$

Comparison of chemical potential values is more meaningful on a volumetric than a molar basis so we define a new term as follows:

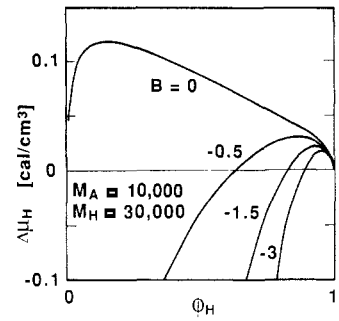

Figure 7. Chemical potential of homopolymer in A domains relative to pure state for same case shown in Figure 6. Point where $\Delta\mu_H$ crosses zero corresponds to saturation concentration $(\phi_H)_s$.

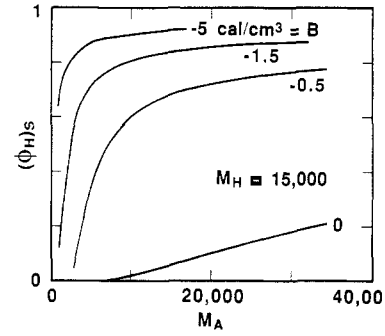

Figure 8. Effect of copolymer segment molecular weight and interaction parameter on saturation concentration when M_H = 15 000.

$$\Delta\mu_H = \frac{(\mu_H - \mu_H^\circ)}{\tilde{V}_H} \tag{15}$$

Performing these operations on eq 13 yields

$$\frac{\Delta\mu_H}{RT} = \frac{B}{RT}(1-\phi_H)^2 + \frac{\rho_H}{M_H}[\ln\phi_H + (1-\phi_H)] + \frac{\rho_A}{6M_A}[2(1-\phi_H)^{1/3} - 1 + \phi_H] - \frac{\rho_H}{M_H}\left[\ln K - \frac{1}{3}\phi_H\left(\frac{d\ln K}{d\ln x}\right)\right] \tag{16}$$

where

$$x = \frac{R_G}{a} = \frac{R_G}{(L/2)} = \frac{R_G(1-\phi_H)^{1/3}}{(L_0/2)} \tag{17}$$

Figure 7 shows the chemical potential, as defined in eq 15, of homopolymer dissolved in the A domains relative to a pure homopolymer phase for the same case as Figure 6. In all cases, $\Delta\mu_H$ goes to minus infinity as $\phi_H \to 0$, owing to the form for the entropy of mixing, and to zero as $\phi_H \to 1$ since this limit corresponds to a pure H phase. The mixed phase becomes saturated with homopolymer at an intermediate composition $(\phi_H)_s$ and is in thermodynamic equilibrium with the pure H phase when $\Delta\mu_H = 0$. This composition is quite small when B = 0 for the example in Figure 7; however, this saturation composition is considerable when mixing is exothermic to the extent expected for the PPO–PS system. The effect of enthalpic interaction on $(\phi_H)_s$ is shown for several cases in Figures 8–11.

It is instructive to examine first results for athermal mixing, B = 0, which is the situation when A = H = polystyrene. Experimental observations for this case[37-44]

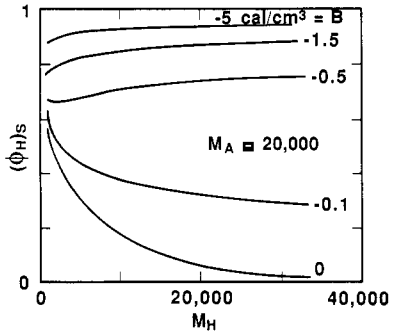

Figure 9. Effect of homopolymer molecular weight and interaction parameter on saturation concentration when $M_A = 20000$.

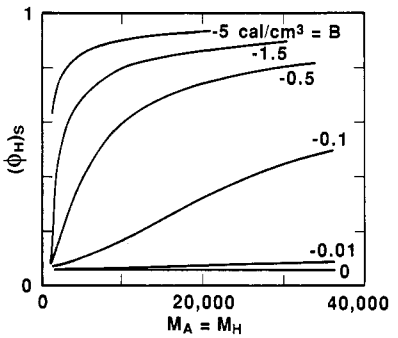

Figure 10. Effect of interaction parameter, M_H, and M_A on saturation concentration when $M_A = M_H$.

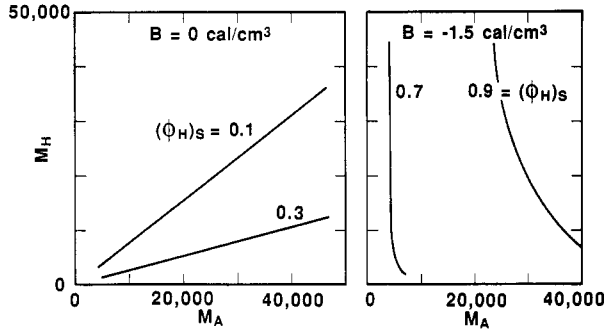

Figure 11. Maps of homopolymer and copolymer segment molecular weights that give constant $(\phi_H)_s$ lines for athermal (left) and exothermic (right) mixing.

indicate that significant amounts of homopolymer can only be incorporated into A domains when $M_H < M_A$. Rearrangement of eq 16 for this case at equilibrium yields

$$\left(\frac{M_A}{M_H}\right)[\ln (\phi_H)_s + 1 - (\phi_H)_s] + \frac{\rho_A}{6\rho_H}\{2[1 - (\phi_H)_s]^{1/3} - 1 + (\phi_H)_s\} - \left(\frac{M_A}{M_H}\right)\left[\ln K - \left(\frac{1}{3}\right)(\phi_H)_s\left(\frac{d \ln K}{d \ln x}\right)\right] = 0 \quad (18)$$

Since K is a function of M_H/M_A through the ratio R_G/a, it is then evident that $(\phi_H)_s$ is a function only of the ratio M_H/M_A for a specified system. We compare the results of this model with that of Meier[15] in Figure 12 where the equilibrium ratio of homopolymer volume solubilized per volume of A segments, $(\phi_H)_s/[1 - (\phi_H)_s]$, is plotted against the molecular weight ratio M_H/M_A. To make this comparison, we have set b_H in eq 7 equal to $C_A/6^{1/2}$ (see eq 13), as required when A and H are identical. Our simple model gives results that parallel those computed by Meier but we predict higher levels of solubilization. At $M_H/M_A = 1$, the current model predicts about 2.5 times more solubilization than predicted by Meier.

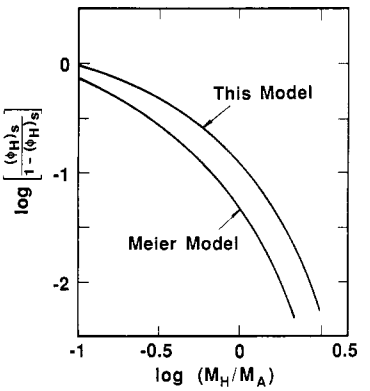

Figure 12. Comparison of relative volume of homopolymer solubilized as a function of molecular weight ratio (homopolymer to block of copolymer) for Meier's model and this model.

For the calculations shown in Figures 8–11, b_H in eq 7 has been set to the value appropriate for PPO so the results in these figures for $B = 0$ are not the same as those shown in Figure 12.

Figures 8–10 show that $(\phi_H)_s$ increases dramatically from that for the athermal case as exothermic interactions are introduced. For all finite values of B and molecular weights, $(\phi_H)_s$ is always less than one, implying that a separate homopolymer phase always forms when enough of this component is added to the copolymer. At first sight this would seem to be a necessary limitation introduced by the artificial device of having the A segments spanning the mixed domain as shown on the right in Figure 1. The fact is that the $\Delta S_H^{(e)}$ term is normally much larger in magnitude than $\Delta S_A^{(e)}$ as shown in Figure 4, and $(\phi_H)_s < 1$ is predicted even when the $\Delta S_A^{(e)}$ term is set equal to zero in our model. The limit on solubility is actually the result of assuming a lamellar morphology exists for all values of ϕ_H. For real blends at high ϕ_H, the mixed phase will become the continuous one with B domains (having convex surfaces) dispersed in it. This will provide significant relaxation of the conformational constraints inherent in the lamellar morphology as ϕ_H approaches unity. Modeling this situation would be very complex and is beyond the scope of the current investigation. Intuitively, we see no reason why for certain values of B, M_H, and M_A, $(\phi_H)_s$ could not approach unity as experimental data suggest.[6,10,11] The present model does offer some useful insight about the behavior of real systems when appropriate recognition is made of this inherent limitation imposed by the assumed morphology.

When B has nonzero values, eq 18 has the additional term

$$\frac{BM_A}{(\rho_A RT)}[1 - (\phi_H)_s]^2 \quad (19)$$

on the left-hand side so that $(\phi_H)_s$ is no longer simply a function of M_H/M_A as in the athermal case. The differences between the exothermic and athermal case are evident in Figures 8–11. As mixing becomes exothermic, $(\phi_H)_s$ gets larger as M_A increases with M_H constant (Figure 8) because both conformational terms contribute relatively less to the total free energy. As M_H increases when M_A is held fixed (Figure 9), $(\phi_H)_s$ decreases for mildly exothermic mixing and actually increases when the interaction is stronger. For the former, the entropy of mixing is a significant part of the driving force and it decreases as M_H increases, while for the latter this effect is unimportant and the increase in $(\phi_H)_s$ stems from the decrease in magnitude of the $\Delta S_H^{(e)}$ term as shown in Figure 5. When $M_H = M_A$ (Figure 10), the dominant issue is the increase

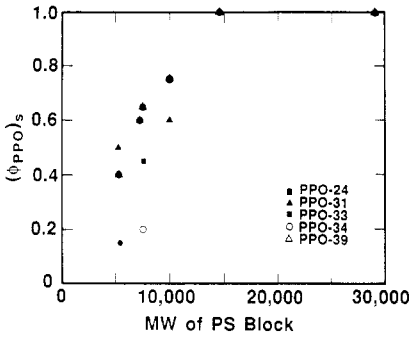

Figure 13. Experimentally determined saturation concentration of PPO in PS microphase as a function of the molecular weight of the PS block of the copolymer. Numbers following PPO in the legend correspond to the nominal weight-average molecular weight of the homopolymer in thousands. Data were determined from glass transition behavior of blends as described in companion paper.

in M_A, so these results parallel those of Figure 8.

The effects of both M_H and M_A can be easily seen by showing lines of constant $(\phi_H)_s$ on maps of M_H versus M_A as done in Figure 11. As expected, these reduce to lines of the form M_H/M_A = a constant when $B = 0$, as shown on the left. An important conclusion from this model is that M_H plays a relatively minor role compared to M_A in the phase behavior when mixing is significantly exothermic (see eq 19). This is illustrated on the right side of Figure 11 for the M_A versus M_H map when $B = -1.5$ cal/cm^3 (a probably value for PPO–PS). First, the $(\phi_H)_s$ values are much larger at comparable molecular weights than when $B = 0$ (left side of Figure 11). Second, the effect of M_H is either nil or the opposite of that when B is zero.

Comparison with Experiment. The companion paper[11] has shown that the extent of PPO solubilization in the polystyrene microphase is essentially independent of the PPO homopolymer molecular weight over the range studied. As seen above, this is what the current model predicts when the interaction parameter, B, has negative values in the range expected for PPO–PS blends. However, the experimental results[11] show that $(\phi_H)_s$, as estimated by glass transition behavior, does depend on the PS block molecular weight as seen in Figure 13. The trend of these data is remarkably similar to the model predictions shown in Figure 8 when B has values like those expected for the PPO–PS system. An important distinction is that experimentally we estimate that $(\phi_H)_s$ is approximately unity at high enough block molecular weights. As pointed out earlier, the inherent structure of the model precludes this possibility. Also because of the way the copolymer is modeled, the molecular weight of the PS blocks in these copolymers cannot be simply equated to M_A in the model; however, they are very similar. In spite of these limitations, the model predictions parallel the experimental observations rather closely, suggesting that the essential physical issues have been captured.

Summary

The companion paper[11] considered the extent to which PPO homopolymer can be incorporated into styrene-based block copolymers to give a single mixed hard phase of PPO and PS segments as indicated experimentally by glass transition behavior. As shown there and in Figure 13, the PPO appears to be completely miscible in the PS domains, $(\phi_H)_s = 1$, so long as the PS end blocks have a molecular weight of about 14 000 or above. Below this limit there is a finite saturation concentration which appears to be only slightly affected, if at all, by the PPO molecular weight over the range examined. These trends are in marked contrast to that repeatedly observed[38,40-44] for blends of PS homopolymer with styrene-based block copolymers. We believe these differences were related to the exothermic mixing of PPO–PS segments in the former as compared to the athermal mixing of styrene units of the PS homopolymer and copolymer blocks in the latter since the simple model developed here predicts trends comparable to the experimental observations. Obviously, if the interaction with the styrene blocks and the homopolymer were endothermic, as found for most polymer blends, solubilization would be even less than seen for polystyrene homopolymer.

The model follows conceptually along the lines used by Meier except for the following differences. A finite enthalpic interaction between the homopolymer and copolymer segments has been added. The copolymer segments are considered to be connected to both boundaries of the lamellar domain in order to simplify the treatment of how these segments are distributed there. This simplification eliminates the possibility for concentration gradients of the A and H chains in the mixed phase which are likely to exist in reality. Finally, we assume the domain interface is sharp and does not contribute to the free energy. Despite these simplifications, our model predictions for the athermal case, $B = 0$, closely parallel those of the Meier model.[15]

Our model assumes monodisperse homopolymer chains and block segments. The latter is well approximated by the materials used. This is not the case for PPO; however, the lack of any significant effect of molecular weight per se suggests that polydispersity of the PPO homopolymer should not be an important factor.

The lamellar morphology assumed is reasonable for low homopolymer contents. However, the conformational changes associated with this geometry naturally lead to a finite saturation concentration of homopolymer. This limit may not exist in actual systems because morphological rearrangements can occur to reduce the barriers to the solubilization process. A system whose mixed phase is continuous rather than lamellar would be rather difficult to model by the approach used here. It would be ideal to have available the predictions of the mean-field-type theories used by Noolandi et al.[12,13] and Sanchez and de la Cruz[16] applied to the current problem, as they can be more general and rich in the details of spatial variations. Usually the main focus of such theories is to predict entire phase diagrams including the completely homogeneous mixed state (H, A, and B units). The copolymers considered in our experimental program and most such materials of practical interest in this connection never reach this state at any experimentally accessible temperature. Thus, the experimental observations of the type reported in the companion paper[11] give no information about this region of the phase diagram for comparison with theory.

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Comparative Study of the Modulus and Orientation of the Dipole Moments Associated to the Side Groups of Poly(chlorophenyl acrylates)

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ABSTRACT: The dipole moments of model compounds of the repeating unit of phenyl and substituted phenyl acrylate polymers (phenyl propionate and its halogenated derivatives *o*-chlorophenyl propionate, *m*-chlorophenyl propionate, and *p*-chlorophenyl propionate) were measured in solutions of the compounds in benzene and cyclohexane at several temperatures. The polarity of the halophenyl propionates is extremely dependent on the location of the chlorine atom in the phenyl group in the sense that the value of the dipole moment increases from 1.77 ± 0.03 D at 20 °C for *o*-chlorophenyl propionate to 2.59 ± 0.03 D at the same temperature for *p*-chlorophenyl propionate. Comparison of the dipole moment of phenyl and *p*-chlorophenyl propionates suggests that inductive effects do not account for the difference of their polarity. The critical analysis of the dipole moment of *m*-chlorophenyl propionate and *o*-chlorophenyl propionate indicates that the rotational angles about Ph–O bond are ±60° and ±120° for the former compound and only ±75° for the latter.

Introduction

Although the kinetic phenomena involved in the free radical addition of halogenated phenyl acrylate monomers have been the subject of several investigations,[1-4] no study has been carried out, to our knowledge, focused on the analysis of the configuration-dependent properties of the resulting polymers. It is evident that the substitution of a methoxy group for a phenoxy or a halophenoxy group will alter both the structural geometry and the potentials affecting the torsional rotations of the side groups and the main chain and will have a great incidence in the values of the spatioconfigurational properties such as dipole moments and unperturbed dimensions. Among these properties, the dipole moments should be the most sensitive not only to the halogenation of the phenyl group but also the location of the substitution.

A preliminary step in the investigation of the polarity of poly(halophenyl acrylate)s is to determine the dipole moment associated to the repeating units of the chains. The dipole moment modulus and orientation within esters

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