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about 1 g/dL. A simple argument based on eq 5 and a critical chain length of 60 units for a polymer concentration of 2.119×10^{-3} g/g shows that the critical chain length is about 30 units in this case. Moreover, realizing that the apparent free energy of complexation decreases strongly for oligomers of decreasing molar mass (Figure 2), the real critical chain length is probably still smaller. The basic reason for this pronounced effect of the template concentration on the critical chain length is that complexation of an oligomer at higher template concentrations is accompanied by a smaller decrease in configurational entropy of the system because more places on the matrices are available to a particular oligomer. Although the real situation in the case of template polymerization is, due to growing chains jumping from one template to another, far more complicated, the increasing template effect as a function of template concentration is at least partly due to the reduced critical chain length.

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Experimental Simulation of the Effect of Intramolecular Repulsion on the Heat of Mixing for Polymer Blends

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ABSTRACT: Random copolymers are sometimes known to form miscible blends, over a certain window of comonomer contents, with other polymers even though neither limiting homopolymer does so. Binary interaction models that consider intramolecular interactions have been introduced, and these models predict that the necessary exothermic mixing can occur when the intramolecular interaction between comonomers is sufficiently repulsive relative to the repulsive intermolecular interactions. An experimental simulation of this effect is given here using low molecular weight liquids that approximately model the monomer residues in the blend system poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile). All three binary combinations exhibit endothermic mixing; however, exothermic behavior is observed when certain premixes of the analogues of styrene and acrylonitrile are mixed with the methyl methacrylate analogue. Agreement between experimental and calculated results is good.

Introduction

The equilibrium-phase behavior of polymer–polymer mixtures is governed primarily by the heat of mixing contribution to the free energy since the combinatorial entropy change is usually very small. In fact, in the limit of high molecular weights, typical of most commercial polymers, an exothermic heat of mixing is needed to satisfy the necessary and sufficient thermodynamic conditions for miscibility. Exothermic mixing is usually thought to result from some specific interaction between certain groups, e.g., OH and $\mathrm{C{=}O}$, in the two molecules being mixed, although the interactions among all other moieties contribute to the heat of mixing as well. Recently it has been recognized that *intramolecular* interactions among units within the molecules being mixed may also make an important contribution to the heat of mixing and can be the cause of exothermic mixing. This point of view has been incorporated into binary interaction models independently by Kambour, Bendler, and Bopp,[1] ten Brinke, Karasz, and MacKnight,[2] and Paul and Barlow.[3] This paper reports a direct experimental simulation, using low molecular weight compounds, which shows that because of repulsive

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intramolecular interactions exothermic mixing can occur when no single binary interaction for the system is exothermic.

Background

The models mentioned above[1-3] employ an interaction parameter, B, defined in analogy to the van Laar expression for the heat of mixing,

$$\Delta H_{\mathrm{mix}} = (V_{\mathrm{A}} + V_{\mathrm{B}}) B \phi_{\mathrm{A}} \phi_{\mathrm{B}} \qquad (1)$$

regardless of whether the remainder of the model is based on the conventional Flory–Huggins theory or the newer equation of state theories.[4] Here V_i and ϕ_i denote the volume and volume fraction that component i contributes to the mixture, and B is the interaction energy density of interest, which is, of course, simply related to the various χ parameters employed in the literature. The three papers mentioned[1-3] divide each polymer chain into arbitrary subunits and express the net interaction energy density, B, in terms of all of the pairwise interactions between the various subunits in the two chains by using binary interaction parameters, B_{ij}, and the volume fractions of these subunits in the chains.

This approach has been especially instructive in the consideration of the phase behavior of blends of random copolymers of various compositions with other polymers. Here, the subunits are logically taken as monomer residues in the chain. When the random copolymer is formed from monomers 1 and 2 and this material is mixed with a homopolymer comprised of monomer 3, the model predicts the net interaction energy density for the blend, in the notation of eq 1, to be

$$B = B_{13}\phi_1' + B_{23}\phi_2' - B_{12}\phi_1'\phi_2' \qquad (2)$$

where each B_{ij}, in this example, corresponds to the interaction energy density characteristic of mixing homopolymer i with homopolymer j and ϕ_i' is the volume fraction of i in the copolymer. This result offers an explanation for the observation that random copolymers are sometimes miscible with other polymers when their corresponding homopolymers are not.[2,3] A well-known example is blends formed from certain random copolymers of acrylonitrile and styrene and poly(methyl methacrylate) where we let AN = 1, S = 2, and MMA = 3. Polystyrene is not miscible with PMMA; hence $B_{23} > 0$. Likewise, polyacrylonitrile is not miscible with PMMA, so $B_{13} > 0$. Yet experimentally, it is known that SAN copolymers having AN contents in the range of approximately 9–30% w/w do form miscible blends with PMMA at typical melt-processing temperatures.[5] On the basis of the above discussion, B must be negative within this window of AN contents, i.e., ϕ_1', and positive outside this range. According to eq 2 this can occur if B_{12} has a sufficiently large positive value,[3] which in the current example would be the case if polystyrene and polyacrylonitrile were grossly immiscible. The latter is known to be true.[6]

Physically, exothermic mixing is possible even though all $B_{ij} > 0$ because of the decrease in the number of the strongly repulsive 1–2 contacts, relative to 1–3 and 2–3 contacts, made possible by having the random copolymer form a homogeneous mixture with homopolymer 3. A graphical visualization of this concept is shown in Figure 1 where enthalpy of a mixture of 1, 2, and 3 units, relative to the pure homopolymers of 1, 2, and 3, is shown by using a triangular composition diagram as the base. This enthalpy, H, surface is the sum of the three pairwise interactions

$$H = B_{12}\phi_1\phi_2 + B_{13}\phi_1\phi_3 + B_{23}\phi_2\phi_3 \qquad (3)$$

where the ϕ_i correspond to the volume fraction of i units in the mixture such that $\phi_1 + \phi_2 + \phi_3 = 1$ and the B_{ij} are the same quantities appearing in eq 2. The 1–2 leg corresponds to the various copolymers, and for the purpose of this illustration B_{12} has been taken to be much larger than B_{13} or B_{23} to exaggerate the point to be made. As expected, H is always positive since it is taken *relative* to pure homopolymers 1, 2, and 3. However, this is *not* the reference state to be used in computing the heat of mixing for a particular copolymer of 1 and 2, polymer A, with homopolymer 3, polymer B. The enthalpy, relative to the reference state used in Figure 1, for all copolymer–homopolymer 3 blends is given by the intersection of the enthalpy surface and a vertical plane passing through apex 3 that bisects the 1–2 axis at the copolymer composition. This can be conveniently viewed as a projection on a surface parallel to this plane as shown in Figure 1. This projection can have either positive or negative curvature depending on ϕ_1', and the relative values of the B_{ij} parameters—the example in Figure 1 was selected to be concave upward. The dotted tie line shown in the projection is the appropriate reference state for computing the heat of mixing of the copolymer, A, with homopolymer 3, B, i.e., eq 1. Since the enthalpy lies below this reference line in this example, the mixing is exothermic; however, in other situations it may lie above this reference line and, thus, be endothermic.

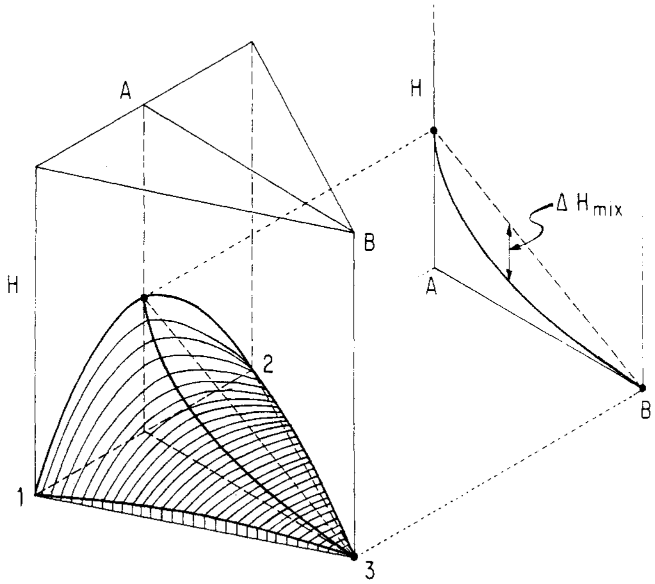

Figure 1. Three-dimensional enthalpy surface for mixtures of units 1, 2, and 3 relative to these pure components as calculated by binary interaction model (3). Projection at right shows heat of mixing of the pseudobinary comprised of a premix or copolymer of 1 and 2, component A, and species 3, component B.

The role of intramolecular repulsion as a factor in the phase behavior of blends involving copolymers has far-reaching consequences, and it would be instructive to develop a direct experimental demonstration of this effect. This is done here by calorimetric measurement of the heat of mixing for low molecular weight liquids, which may serve to some approximation as analogues of units in polymer chains. To see the utility of this approach it is necessary to recognize that the binary interaction model assumes to a first approximation that the enthalpy computed by eq 3 is not affected by the presence of covalent bonds between the units 1, 2, and 3. Consequently, eq 2 would allow one to estimate the heat of mixing of low molecular weight species 3 with a binary mixture of low molecular weight species 1 and 2 having a composition ϕ_1'. Thus, an important demonstration would be whether, for

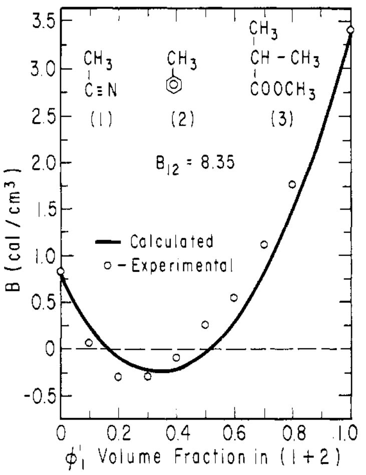

Figure 2. Interaction energy densities as defined by eq 1 for mixing species 3 with a premix of 1 and 2 having composition ϕ_1'. Circles are experimental values while the solid line was computed from eq 2 by using B_{12}, B_{13} (B at $\phi_1' = 1$), and B_{23} (B at $\phi_1' = 0$) shown.

an appropriate choice of 1, 2, and 3 where each binary mixes endothermically, mixing of 3 with a premix of 1 and 2 could ever give off heat, i.e., exothermic mixing, or have $B < 0$.

Experimental Section

A simple calorimeter described in previous publications[7,8] was used to measure the enthalpy change on mixing equal volumes of two liquids at room temperature. From this single observation an interaction energy density was computed via eq 1. Possible departures from the parabolic assumption of the van Laar equation were not considered. Three liquids were selected for this study: 1, methyl cyanide; 2, toluene; and 3, methyl isobutyrate.

Mixing all combinations of binary pairs of these three pure components gave values for B_{12}, B_{13}, and B_{23}. In a separate series of experiments, components 1 and 2 were premixed to various values of the volume fraction ϕ_1'. Equal volumes of these premixes and component 3 were mixed in the calorimeter, and the net interaction energy density, B, was computed as before from the observed heat of mixing of this pseudobinary system. All of the experimental results are summarized in Figure 2.

Results and Discussion

As seen in Figure 2, all three binary interaction parameters for this choice of compounds are positive, i.e., all binaries mix endothermically, with B_{12} being considerably larger than the other two. The solid line in Figure 2 was computed from eq 2 by using the three experimental B_{ij} values. Interestingly, a window in the ϕ_1' range for which mixing of 3 with premixes of 1 and 2 will be exothermic is predicted. The open circles are the experimental data obtained in the manner described earlier. The measured and predicted results agree rather well but not perfectly, and the existence of a window for exothermic mixing is confirmed experimentally. Thus, we have a simple and direct experimental illustration using this model system that exothermic mixing can occur when three molecular units are combined in an appropriate way even though all pairwise combinations of these units mix endothermically. There is every reason to believe that a similar response applies to mixing homopolymers with random copolymers, thus confirming the importance of intramolecular interactions as proposed earlier.[1-3] Several further comments are in order.

It is no accident that the low molecular weight compounds chosen for this study are strikingly similar to but not identical with the saturated residues of three monomers comprising the blend system SAN–PMMA. It is interesting that the region of negative B's in Figure 2 corresponds rather closely to the AN composition window over which SAN copolymers are miscible with PMMA. This agreement is partly fortuitous since the heats of mixing observed are sensitive to the detailed molecular structures of the three components. However, it is very important to note that the principal conclusion from this study expressed in the previous paragraph is in no way limited to whether these compounds are perfect analogues for the SAN–PMMA system or not. That is, these results confirm experimentally that the so-called repulsion effect can lead to exothermic mixing.

A casual consideration of these ideas might lead one to wonder whether ternary blends formed from appropriate combinations of homopolymers 1, 2, and 3 would be miscible, since we have reasoned that exothermic mixing leads to miscibility in polymer blends and that the enthalpic response depicted in Figure 1 is to a first approximation independent of how units 1, 2 or 3 may or may not be bonded together. A more careful analysis of this proposition reveals that such a homogeneous mixture cannot be attained as a equilibrium state. A ternary combination of low molecular weight compounds such as the one employed here can form a thermodynamically stable mixture in spite of a strong repulsion between the 1–2 pair because of the considerable contribution of combinatorial entropy to the free energy of mixing. However, since the latter is such a small factor for blends of high molecular weight polymers,[9] the 1–2 energetic repulsion would preclude miscibility for the high molecular weight version of the same ternary; however, to demonstrate this rigorously would require a complex thermodynamic analysis beyond the scope of the present discussion.[1,10] Physically, this may be easily understood by the implicit requirement for a homogeneous phase of the premix or copolymer comprised of 1 and 2 units that is to be mixed subsequently with 3. Chemical bonds force this condition in the random copolymer while combinatorial entropy does it in the corresponding low molecular weight case. However, the 1–2 repulsion would preclude this condition for homopolymers or even block copolymers of high enough molecular weights.[11]

In our earlier paper[3] we pointed out that a window of exothermic mixing like that demonstrated in Figure 2 cannot exist if the B_{ij} values are accurately given by the solubility parameter theory of Hildebrand:[13]

$$B_{ij} = (\delta_i - \delta_j)^2 \tag{4}$$

The latter result assumes that the i–j interaction energy is simply the geometric mean of the i–i and j–j interactions or the so-called Berthelot condition.[14] Simple dispersive forces are expected to adhere to the latter rather well, but there is no reason to expect this to apply for interactions between complex polar units. So any case of exothermic mixing implies that subunits of the molecules being mixed do not follow the additivity rules implicit in eq 4. In extreme cases for some so-called "specific" interactions, the B_{ij} may be negative; however, it is quite limiting to think only in these terms for interactions to drive blend miscibility, since positive B_{ij}, which differ significantly from the prediction of eq 4, can be as useful for this purpose. Clearly, there are examples of systems with subunits that by conventional thinking are expected to interact specifically, but yet the net heat of mixing is not exothermic owing to domination by interactions between other subunits.

Basically the approach employed here is an attempt to break the net heat of mixing into contributions from subunits of the molecules being mixed. The choice of monomer units for this purpose is an appealing and useful one as described earlier;[1–3] however, there may be even greater utility by selecting smaller subunits like CH_2, COO, etc., as done recently.[12] In its present form, the model represents a mean-field approach and does not include sequence order or steric placement of groups and, therefore, cannot account for the importance of spatially specific issues on mixture phase behavior.

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Kinetics of the Conformational Transition of Poly(methacrylic acid) after Changes of Its Degree of Ionization

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ABSTRACT: The kinetics of the conformational transition of poly(methacrylic acid) after a pH jump was followed in a stopped-flow apparatus by monitoring changes in the emission intensity of a dansyl label attached to the polymer chain. Part of the process was too fast to be followed, but the subsequent approach to equilibrium exhibited to a first approximation biphasic kinetics. The rate constants for chain expansion increased sharply with increasing pH. In the contraction of the chain, the final approach to equilibrium took place almost at a constant rate in the pH range 4.11–5.11. A drift in pH, monitored by the absorbance of methyl red, took place over a similar time as the change in the fluorescence of the dansyl label.

Introduction

Phenomena accompanying the ionization of poly(methacrylic acid) (PMA) have features suggesting cohesive forces that oppose the expansion of the chain molecule due to the repulsion between the ionized carboxyls. Katchalsky[2] was first to draw attention to the fact that the viscosity of PMA solutions remains almost constant before a critical degree of ionization, α, is reached; at this point the viscosity increases dramatically, indicating a sudden expansion of the chain molecule. Significantly, the pK of the carboxyl groups, which rises steeply with an increasing polymer charge in the initial stages of the ionization, enters a plateau region at the point at which the viscometric data indicate rapid chain expansion, as would be expected from the dispersion of the electrostatic charge over a much larger volume. Katchalsky believed that the resistance to the chain expansion was due to hydrogen bonding between carboxyl groups, but this interpretation ceased to be plausible when Arnold[3] showed that both the solution viscosity and the pK of poly(acrylic acid) (PAA) increase smoothly with an increasing α. Arnold wrote that the reason for the difference in behavior of the two poly(carboxylic acids) "remains obscure although it could be connected to the greater flexibility of the poly(acrylic acid) molecule".

Leyte and Mandel[4a] suggested that the behavior of PMA may be understood as reflecting an equilibrium between a contracted and an expanded form so that the plateau in the plot of pK against α is analogous to a phase transition. They formulated a procedure for deriving the free energy change for the transition between the two forms and Leyte[4b] concluded from such data that the cooperative chain length contains 30 monomer residues. Various arguments were advanced for and against hydrogen bonding as the origin of the resistance to chain expansion. Anufrieva et al.[5] found that addition of methanol to aqueous PMA solutions produces a smooth increase of viscosity with increasing α, so that the resistance to the chain expansion is eliminated. They concluded that this resistance observed in water solution must be due to hydrophobic bonding. Crescenzi et al.[6] studied the ionization of PMA and PAA by calorimetry and found that while the enthalpy of ionization was a smooth function of α for PAA, the plot for PMA exhibited a striking endothermic peak in the region in which viscosimetry and titration data indicated a rapid transition from a contracted to an expanded form. They noted that the dissociation of hydrophobic bonds would have been expected to be exothermic. Nevertheless, since the enthalpy of the transition from the contracted to the expanded form was found to have a positive tem-

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