

A binary interaction model for miscibility of copolymers in blends

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Miscibility windows often exist in polymer blend systems when the chemical structure of one of the components is systematically varied, e.g. a random copolymer may be miscible with another polymer when neither limiting homopolymer is. A binary interaction model is developed which explains such behaviour. From this prediction, the general notion is advanced that many cases exist where the net exothermic heat of mixing required for miscibility of high molecular weight polymer mixtures may result from appropriate considerations of both intermolecular and intramolecular interactions of component units without an exothermic interaction existing between any individual pair of units. However, it is shown that for a net exothermic mixing the individual interaction parameters for the pairs of units must differ from those predicted by solubility parameter theory. Moreover, the departures from the geometric mean assumption of the solubility parameter theory need not be large to achieve conditions for miscibility. Several examples of the use of such a model are given including one where the homologous series of aliphatic polyesters is treated as 'copolymers' by considering their CH_x and COO constituents as the 'monomers'.

Keywords Blends; copolymers; interactions; thermodynamics; miscibility; heat of mixing

INTRODUCTION

Many examples of miscibility in polymer blends have been identified in the last decade¹⁻⁵, and it is generally agreed that the thermodynamic basis is an exothermic heat of mixing^{4,5} since entropic contributions are so small in such systems. An important objective of current research in the area is to understand, in terms of component molecular structures, the origin of these energetic interactions so that phase behaviour in technologically important multicomponent polymer systems may be better controlled or predicted.

A growing body of spectroscopic, calorimetric, and other experimental information suggests that specific intermolecular interactions are responsible for the exothermic heats of mixing and miscibility observed in many blend systems. There is little doubt that hydrogen bond formation, $n-\pi$ complex formation, and a variety of other specific interactions play an important role in determining polymer blend miscibility. On the other hand, the observed exothermic heats of mixing for many low and high molecular weight systems are quite small, and other mechanisms may be involved. The point of view developed here is that *intramolecular* interactions, in many cases, may be an important factor in realizing exothermic heats of mixing rather than specific *intermolecular* interactions as usually is assumed. To illustrate this concept a simple binary interaction model is applied to blends involving copolymers, and then it is suggested that similar thinking can be extended to blends involving homologous series of homopolymers by appropriate subdivision of the repeating units. The model appears to explain, at least qualitatively, numerous experimental

observations and may provide a framework for future quantification of the thermodynamics for some blend systems.

BACKGROUND

A necessary requirement for miscibility is that the free energy of mixing

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

be negative; however, this is not a sufficient condition, since stability considerations require in addition, for binary mixtures, that

$$\frac{\partial^2 \Delta G_m}{\partial \phi_i^2} > 0 \quad (2)$$

where ϕ_i is the volume fraction of either component—any suitable measure of concentration can be used. The simplest model for describing polymer-polymer mixtures is an extension of the results developed originally for polymer solutions by Flory and by Huggins which assumes the only contribution to the entropy of mixing is combinatorial in origin and is well-approximated by⁶

$$\Delta S_m = -R(V_A + V_B) \left[\frac{\phi_A \ln \phi_A}{\bar{V}_A} + \frac{\phi_B \ln \phi_B}{\bar{V}_B} \right] \quad (3)$$

where \bar{V}_i is the molar volume of component i and V_A and V_B are the actual volumes of these components comprising the mixture. This model further assumes the heat of mixing is described by a van Laar type expression

$$\Delta H_m = (V_A + V_B)B\phi_A\phi_B \quad (4)$$

where B is a binary interaction energy density. The latter is simply related to the more familiar chi parameters by

$$\frac{B}{RT} = \frac{\chi_A}{\bar{V}_A} = \frac{\chi_B}{\bar{V}_B} = \tilde{\chi}_{AB} \quad (5)$$

For present purposes, we prefer the use of B since its basis is always clearly a unit of mixture volume. The binary interaction model for the heat of mixing can be extended to multicomponent mixtures as follows⁶

$$\frac{\Delta H_m}{V} = \sum_{i>j} B_{ij}\phi_i\phi_j \quad (6)$$

where V = total volume of mixture = $\sum_i V_i$. The notation on the sum in equation (6) excludes terms with $i=j$ and double counting of terms with $i \neq j$ and of course, $B_{ij} = B_{ji}$.

While the sign of the combinatorial entropy always favors mixing, it is clear from equation (3) that its magnitude is greatly diminished for molecular weights (or molar volumes) of the order of those for most important polymers. Thus, in the limit of high molecular weights, the conditions for miscibility can only be satisfied by a negative interaction parameter leading to the conclusion that exothermic mixing is a requirement for miscibility in high molecular weight polymer-polymer blends.

The model embodied in equations (3)–(6) is quite simplistic and cannot account for all of the issues of mixture thermodynamics. As a result, interaction parameters deduced from it using various phase behaviour information are often believed to include other effects than purely enthalpic ones. More modern theories which incorporate equation of state contributions into the terms for the enthalpy and entropy of mixing^{7–9} have been advanced to remove some of these short-comings of the simple model. These terms provide one mechanistic explanation for *LCST* (lower critical solution temperature) behaviour which is often observed in polymer blends and is not predicted by the model described above. However, the equation of state theories retain the concept of a binary interaction parameter, and the conclusion that this parameter must be negative to have miscibility in high molecular weight blends is not altered⁹ since the equation of state effects do not favor phase stability⁷. These theories simply refine the binary interaction parameter by removing extraneous effects, but they do not offer any insight into the sign or magnitude of this parameter which is, of course, the ultimate question for deciding whether blends of high molecular weight polymers are miscible or not. The sections which follow address one aspect of this important question, and the interaction parameters used are not limited to the simple Flory-Huggins framework but could be viewed as ones free of equation of state effects.

BLENDS OF COPOLYMERS WITH HOMOPOLYMERS

The potential role of intramolecular interactions as a factor in blend miscibility can be seen clearly by considering mixtures of copolymers with another polymer. There are numerous cases of miscibility involving copolymers when

their corresponding homopolymers are not similarly miscible. Several examples suffice to make this point. Styrene/acrylonitrile copolymers (SAN's) are miscible with poly(methyl methacrylate), PMMA¹⁰, and poly(ethyl methacrylate), PEMA¹¹, over a certain range of AN contents but neither polystyrene nor polyacrylonitrile is miscible with PMMA or PEMA. Ethylene/vinyl acetate copolymers (EVA's) are miscible with poly(vinyl chloride), PVC, over a certain range of VA contents¹² but neither polyethylene nor poly(vinyl acetate) is miscible with PVC. Similarly, butadiene/acrylonitrile copolymers over a limited composition range¹³ are miscible with PVC while the corresponding homopolymers are not. Likewise, α -methyl styrene/acrylonitrile copolymers are miscible with PMMA and PEMA¹⁴ but the homopolymers are not. Neither poly(*o*-chlorostyrene) nor poly(*p*-chlorostyrene) is miscible with poly(phenylene oxide), PPO¹⁵, but for a certain composition region random copolymers formed from these monomers are miscible with PPO. This system is especially interesting since these blends exhibit *LCST* behaviour and mixtures with a fixed amount of PPO have phase behaviour similar to that shown in *Figure 1* as the copolymer composition is varied. A similar relation probably exists for the other examples mentioned but the phase separation temperatures may exceed the thermal stability of one of the components over much of the composition range. Generally speaking, the higher the phase separation temperature, the more negative is the interaction parameter⁹.

The examples given above plus other observations^{16–19} lead us to believe that a 'miscibility window,' as schematically defined in *Figure 1*, may be a common feature when systematic structural variations are made in one component of a blend system. Random copolymers

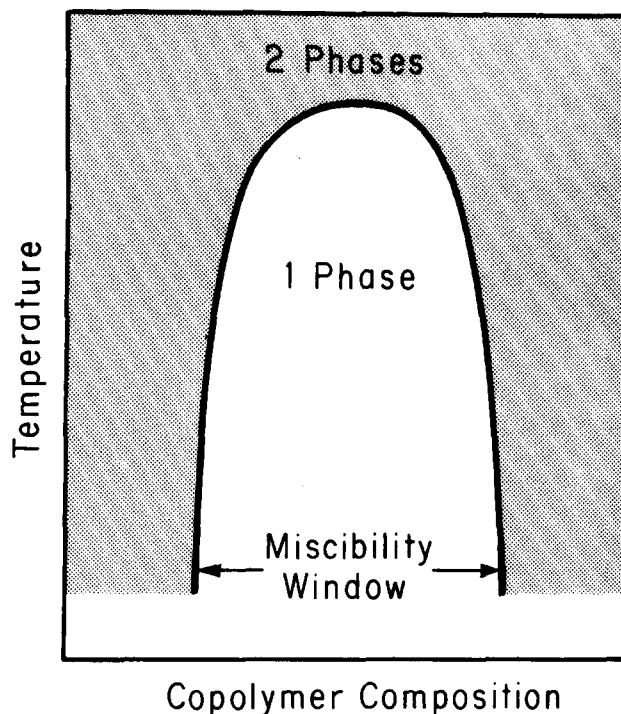


Figure 1 Diagram of phase behaviour for blends of a copolymer with another polymer showing *LCST* behaviour to illustrate the concept of a 'miscibility window'. The amount of the copolymer in the blend is held fixed while the composition of the copolymer, i.e. the relative proportions of its two monomers, is varied

offer a conceptually simple example of one way of making structural variations on a continuous scale. The simple binary interaction model developed below offers one possible explanation for such phenomena based on consideration of intramolecular interactions in addition to intermolecular ones. Obviously, such considerations are not limited to copolymer-type structural variations as suggested in detail in a later section.

The situation of interest here is easily visualized with the aid of the schematic shown in Figure 2. Polymer A is comprised of monomers 1 and 2 with volume fractions of each denoted by ϕ'_i . Polymer B is comprised entirely of a different monomer 3. There are thermodynamic interactions between the different monomer units in both the copolymer and the blend. To model this, it is convenient to think of either as a kind of molecular 'soup' disregarding chemical bonding between units; although, this mental convenience certainly is not retained in entropic considerations when A and B are mixed. In the blend of A and B, the volume fractions occupied by the various monomers are ϕ_1 , ϕ_2 and ϕ_3 while the volume fractions of A and B are ϕ_A and ϕ_B . Extending the concept of binary interactions given by equations (4) and (6) to individual monomer units leads to the following for the heat of mixing A and B

$$\Delta H_m = (V_A + B_B) \sum_{i>j}^3 B_{ij} \phi_i \phi_j - V_A B_{12} \phi'_1 \phi'_2 \quad (7)$$

The first term on the right is the enthalpy of the blend relative to the homopolymers formed from 1, 2, and 3 while the second term on the right is the enthalpy of copolymers A relative to homopolymer 1 and homopolymer 2, i.e., the 'heat of mixing' for the copolymer²⁰. Equation (7) can be greatly simplified and cast into the form of equation (4), i.e. an effective interaction parameter for mixing polymers A and B can be found. First, we note the following

$$\begin{aligned} \phi_1 &= \phi'_1 \phi_A \\ \phi_2 &= \phi'_2 \phi_A \\ \phi_3 &= \phi_B \\ \phi_A &= V_A / (V_A + V_B) \end{aligned} \quad (8)$$

which may be inserted into the expanded form of equation (7) to give

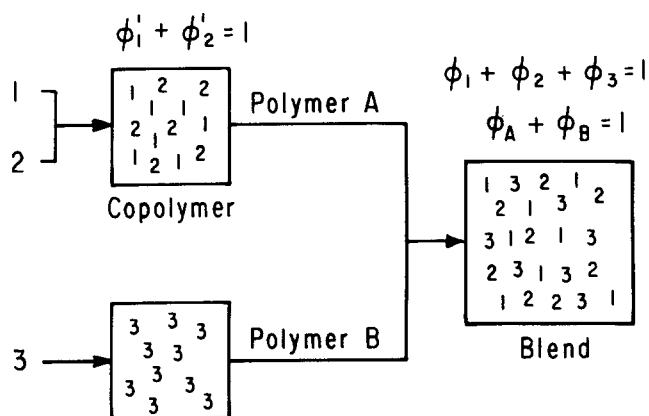


Figure 2 Schematic to illustrate the physical situation in the binary interaction model involving a copolymer

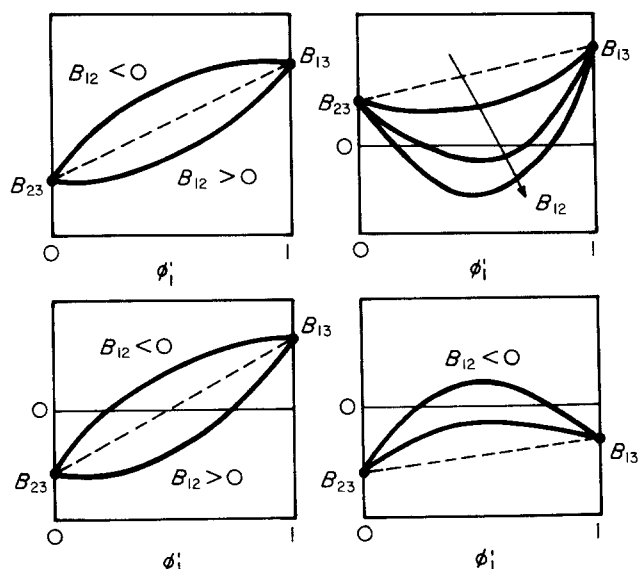


Figure 3 Illustrations of various ways the effective interaction parameter given in equation (10) may vary with copolymer composition. The broken line shows the additive case which results when $B_{12} = 0$

$$\begin{aligned} \frac{\Delta H_m}{V} &= B_{12}(\phi'_1 \phi_A)(\phi'_2 \phi_A) + B_{13}(\phi'_1 \phi_A)(\phi_B) \\ &+ B_{23}(\phi'_2 \phi_A)(\phi_B) - \phi_A B_{12} \phi'_1 \phi'_2 \\ &= [B_{13} \phi'_1 + B_{23} \phi'_2 - B_{12} \phi'_1 \phi'_2] \phi_A \phi_B \end{aligned} \quad (9)$$

In analogy to equation (4), we have the effective interaction parameter for mixing A with B

$$B = B_{13} \phi'_1 + B_{23} \phi'_2 - B_{12} \phi'_1 \phi'_2 \quad (10)$$

in terms of the interactions between the various units or monomers comprising the blend and the composition of the copolymer A—note that B does not depend on the proportions of the two polymers in the blend. The first two terms on the right in equation (10) define an additive interaction of polymer 3 with copolymer 1 + 2 weighted according to the copolymer's composition while the last term is the interaction between 1 and 2 in the copolymer. If B_{12} is positive, 1 and 2 don't 'like' each other and this repulsion makes B less than additive; whereas, if B_{12} is negative, B is greater than additive—see upper left illustration in Figure 3.

The remaining three parts of Figure 3 show some interesting possibilities predicted by this model. The most intriguing is that in the upper right where all three component interactions are positive. In this case, polymer 3 is not miscible with either homopolymer 1 or homopolymer 2 in the high molecular limit; however, if B_{12} is a large enough positive value⁸

$$B_{12} > (\sqrt{B_{13}} + \sqrt{B_{23}})^2 \quad (11)$$

there will be a region of copolymer composition, ϕ'_1 , where B is negative and these copolymers will be miscible with 3 even in the high molecular limit. This simple result would appear to explain the 'miscibility window' mentioned earlier. Physically, it occurs because addition of polymer 3 to the copolymer dilutes the unfavourable

interactions between 1 and 2 leading to a net exothermic mixing condition even though no individual binary interaction is exothermic, i.e. no 'specific' intermolecular interactions are involved. We feel this is a profound conclusion with far reaching possibilities for understanding miscibility in polymer blend systems. Kambour *et al.*²¹ have employed a related model to interpret the thermodynamics of blends of the various brominated derivatives of polystyrene and poly(phenylene oxide). Also, Karasz *et al.*²² have been developing a similar line of reasoning to explain results from their laboratory.

The lower right part of Figure 3 considers the inverse possibility where all components B_{ij} 's are negative, i.e. any pair of the three homopolymers would be miscible. The model predicts that certain 1+2 copolymers could be immiscible with polymer 3 in the high molecular weight limit depending on the numerical values of B_{ij} . This would occur because dilution of more favourable 1-2 interactions with less favourable interactions of 3 with 1 and with 2 causes a net endothermic mixing condition. We are not familiar with any actual cases of this type of behaviour.

The lower left part of Figure 3 describes a somewhat more expected result predicted for the situation when homopolymers formed from 2 and 3 mix exothermically but those formed from 1 and 3 do not. As the amount of 1 in a 1+2 copolymer increases, a condition of endothermic mixing is eventually reached, but this point depends on the sign (and magnitude) of B_{12} as shown. In other words, there is a certain tolerance for 1 as a comonomer with 2 without precluding miscibility with polymer 3.

APPLICATION OF SOLUBILITY PARAMETER THEORY

One might wonder about the usefulness of solubility parameter theory for estimating B_{ij} since none of these terms must individually be negative to have miscibility according to equation (10). This exercise leads to some interesting insights so it is presented in detail here.

Applying the notions of Scatchard²³ and of Hildebrand and Scott²⁴, the individual binary interaction parameters are given by

$$B_{ij} = C_{ii} - 2C_{ij} + C_{jj} \quad (12)$$

where C_{ii} and C_{jj} are the cohesive energy densities of these pure component homopolymers and C_{ij} is a related term involving cohesive interactions between the unlike pairs. For nonpolar molecules, it is normally argued from suggestions of Berthelot²⁵ and the theories of London²⁶ that the latter is the geometric mean of the cohesive energy densities of the pure components

$$C_{ij} = \sqrt{C_{ii}C_{jj}} \quad (13)$$

Thus, introducing the solubility parameter defined as

$$\delta_i = \sqrt{C_{ii}} \quad (14)$$

permits combining equations (12) and (13) to obtain the familiar expression^{24,27-29}

$$B_{ij} = (\delta_i - \delta_j)^2 \quad (15)$$

Appropriate use of equation (15) for each term in equation (10) gives

$$B = (\delta_1 - \delta_3)^2 \phi'_1 + (\delta_2 - \delta_3)^2 \phi'_2 - (\delta_1 - \delta_2)^2 \phi'_1 \phi'_2 \quad (16)$$

which can be shown by simple algebraic manipulations to be equivalent to

$$B = [\bar{\delta} - \delta_3]^2 \quad (17)$$

where

$$\bar{\delta} = \delta_1 \phi'_1 + \delta_2 \phi'_2 \quad (18)$$

Simple inspection shows that the B predicted by equation (17) can never be negative, i.e. B_{ij} computed from solubility parameters will never lead to the condition for a 'miscibility window' given by equation (11). Additional comments are instructive.

The quantity $\bar{\delta}$ given by equation (18) is the rule generally suggested for calculating the solubility parameter of copolymers²⁷; hence, equation (17) is the same result that would be obtained in the usual application of solubility parameter theory to mixing polymers A and B. One might wonder why the rule of mixtures for copolymers ought to be additivity of solubility parameters rather than additivity of cohesive energy densities—the following shows why. By squaring equation (18), we obtain after some algebraic manipulations the following prediction for the copolymer's cohesive energy density, CED ,

$$CED = (\bar{\delta})^2 = C_{11} \phi'_1 + C_{22} \phi'_2 - [\delta_1 - \delta_2]^2 \phi'_1 \phi'_2 \quad (19)$$

Thus, we see that adding cohesive energy densities would neglect the 'heat of mixing' or 'self-energy' of the copolymer given by the third term which is appropriately considered by adding solubility parameters according to equation (18). Equation (19) can be generalized to cases where the heat of mixing 1 and 2 units is not described by equation (15) by writing²⁰

$$CED = C_{11} \phi'_1 + C_{22} \phi'_2 - B_{12} \phi'_1 \phi'_2 \quad (20)$$

Equation (13) is the restrictive assumption in the solubility parameter approach to the thermodynamics of mixtures, and it can be relaxed by defining a parameter k_{ij} as follows²⁹

$$C_{ij} = (1 - k_{ij}) \sqrt{C_{ii}C_{jj}} \quad (21)$$

Inserting this more general result into equation (12) gives

$$B_{ij} = (\delta_i - \delta_j)^2 + 2k_{ij} \delta_i \delta_j \quad (22)$$

which combined with equation (10) results in

$$B = (\bar{\delta} - \delta_3)^2 + 2k_{13} \delta_1 \delta_3 \phi'_1 + 2k_{23} \delta_2 \delta_3 \phi'_2 - 2k_{12} \delta_1 \delta_2 \phi'_1 \phi'_2 \quad (23)$$

as the replacement for equation (17). By way of example, we chose a case where $\delta_1 = 8$, $\delta_2 = 11$, and $\delta_3 = 9$ (cal cm^{-3})^{1/2} and $\phi'_1 = \phi'_2 = 0.5$. In this case, equation (23) predicts exothermic mixing, i.e. $B < 0$, would occur if $k_{13} = k_{23} = 0$ and $k_{12} > 1/176$. Thus, we see that only very slight departures from equation (13) are needed to realize blend miscibility.

BLENDS OF TWO COPOLYMERS HAVING A COMMON MONOMER

The binary interaction model developed earlier can be extended to another interesting case in which A is a

copolymer of 1 and 2 and B is a copolymer of 1 and 3. The heat of mixing in this case is given by

$$\Delta H_m = (V_A + V_B) \sum_{i>j} B_{ij} \phi_i \phi_j - V_A B_{12} \phi'_1 \phi'_2 - V_B B_{13} \phi''_1 \phi''_3 \quad (24)$$

where the first term on the right gives the heat of mixing for the blend relative to the three homopolymers and the other two terms are the 'heats of mixing' of the two copolymers, A and B, relative to this same basis. Thus as before, the difference is the heat of mixing of the two copolymers. The ϕ'_i give the composition of A and the ϕ''_i give the composition of B. We may eliminate the ϕ_i from equation (24) by recognizing that

$$\begin{aligned} \phi_1 &= \phi'_1 \phi_A + \phi''_1 \phi_B \\ \phi_2 &= \phi'_2 \phi_A \\ \phi_3 &= \phi''_3 \phi_B \end{aligned} \quad (25)$$

to obtain the effective interaction parameter for mixing of A and B

$$\frac{\Delta H_m}{\phi_A \phi_B V} = B = B_{12} \phi'_2 (\phi'_2 - \phi''_3) + B_{13} \phi''_3 (\phi''_3 - \phi'_2) + B_{23} \phi'_2 \phi''_3 \quad (26)$$

after algebraic rearrangement.

Interest in this case is stimulated by a recent paper³⁰ which reported that copolymers of styrene and acrylonitrile are miscible with copolymers of styrene and maleic anhydride over certain ranges of composition for the two copolymers—for analysis let S=1, AN=2, and MA=3. The reported data are reproduced on the right in Figure 4. The region of miscibility on this map of copolymer composition lies roughly about the 45° line or in the region where $\phi'_2 \approx \phi''_3 \equiv \phi$. Substituting these conditions into equation (26) gives the following simplification

$$B = B_{23} \phi^2 \quad (27)$$

From equation (27), we see that in the limit of high molecular weights miscibility can only occur if $B_{23} < 0$. In other words, AN units must interact exothermically with MA to achieve these results. It should be possible to test this conclusion using appropriate experiments.

As might be expected, the data suggest there is some tolerance in the match of AN and MA contents of the two copolymers. The extent of the mismatch allowed can be analysed simply in terms of equation (26) if we make the reasonable assumption of near symmetry, i.e. $B_{12} \sim B_{13}$ (both are known to be positive), and define the new coordinates θ and ϕ as shown on the left in Figure 4. Using the latter, point P is described as follows

$$\phi'_2 = \phi(1 + \tan \theta) \quad (28)$$

$$\phi''_3 = \phi(1 - \tan \theta)$$

Using these new coordinates and the symmetry assumption, equation (26) can be rewritten as

$$B = B_{12} \phi^2 \left[4 \tan^2 \theta + \frac{B_{23}}{B_{12}} (1 - \tan^2 \theta) \right] \quad (29)$$

Thus, $B=0$ along the lines given by

$$\tan \theta = \pm \sqrt{\frac{-B_{23}}{4B_{12} - B_{23}}} \quad (30)$$

The value of B is negative inside the region defined by these lines and is positive outside it. The dashed lines drawn in the diagram on the right in Figure 4 define such a symmetrical region which describes the limited data reasonably well. From the angle these lines make with the 45°, we estimate that $B_{23} \sim -0.07B_{12}$. Relaxation of the assumption of symmetry is straightforward but does not seem justified in view of the limited data available.

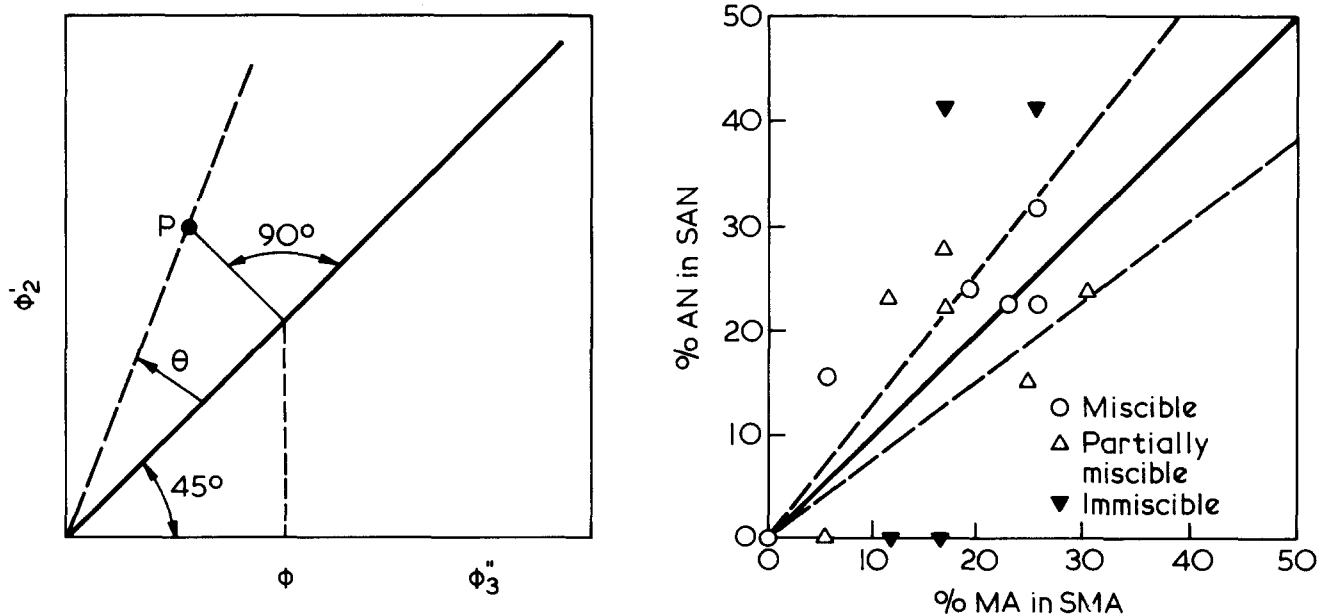


Figure 4 Two dimensional composition maps for blends of copolymers having one monomer in common. Diagram on left defines coordinate system used in the analysis while the one on the right displays observations on phase behaviour of blends of styrene/acrylonitrile copolymers with styrene/maleic anhydride copolymers. Broken lines suggest region of miscibility. Note 1=S, 2=AN and 3=MA

BLENDS OF TWO COPOLYMERS DIFFERING IN COMPOSITION

Two copolymers which differ in composition of the monomers comprising them may or may not be miscible. We can analyse this case by reducing equation (26) to the situation where 2 and 3 are the same component (hence $B_{23} = 0$), viz.

$$B = B_{12}\phi'_2(\phi'_2 - \phi''_2) + B_{12}\phi''_2(\phi''_2 - \phi'_2) \\ = B_{12}(\phi'_2 - \phi''_2)^2 \quad (31)$$

If B_{12} is positive, then B is always positive, and in the limit of very high molecular weights, miscibility will not be obtained if there is any mismatch in composition of the two copolymers. Of course, the neutral case of $B = 0$ is achieved when the two copolymers are identical in composition. However, for finite molecular weights where there is still a contribution to the free energy from the combinatorial entropy, some finite mismatch in copolymer composition can be tolerated. Using the stability conditions and the simple model described in the Background, we find²⁸ the critical condition to be

$$B = 2\rho RT/M \quad (32)$$

for the case where $\rho_A = \rho_B = \rho$ and $M_A = M_B = M$. Combining equations (31) and (32) gives

$$B_{12}(\phi'_2 - \phi''_2)^2 = \frac{2\rho RT}{M} \quad (33)$$

which defines the critical composition difference between the two copolymers for miscibility. This result says that the critical difference is independent of the absolute composition of the copolymers which is exactly what was found by Molau³¹ in his studies on blends of different SAN's. Using polymers with $\bar{M}_n \sim 10^5$, he found the critical composition difference to be 3.5 to 4.5% by weight. This result may be compared with equation (33) by using equation (15) to estimate B_{12} . We will use $\rho = 1.1 \text{ g cm}^{-3}$, $T = 450 \text{ K}$, and values of the solubility parameters of $9.1 \text{ (cal cm}^{-3})^{1/2}$ for polystyrene and $12.7 \text{ (cal cm}^{-3})^{1/2}$ for polyacrylonitrile³². With these values, equation (33) gives $|\phi'_2 - \phi''_2|$ to be 4% which compares very well with the experimental results from Molau.

AN EXAMPLE OF TREATING A HOMOLOGOUS SERIES OF HOMOPOLYMERS AS COPOLYMERS

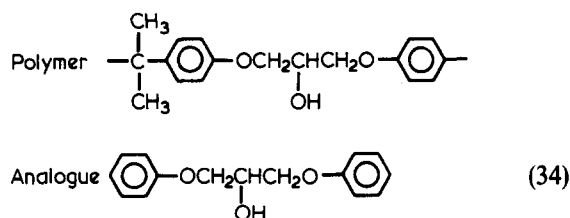
In our investigations of the relationships between polymer molecular structure and blend miscibility, we have seen trends caused by systematic variation in the structure of one component that is not a copolymer which we feel may be explained by an extension of the reasoning advanced here. Specifically, we refer to results obtained for blends of the homologous series of aliphatic polyesters with polycarbonate¹⁹, poly(vinyl chloride)¹⁸, styrene-allyl alcohol copolymers¹⁷, polyepichlorohydrin³³, poly(vinylidene chloride-co-vinyl chloride)³⁴, and the polyhydroxyether of bisphenol-A¹⁶. The latter serves as an excellent example, and recent results for this set of systems will be used as an illustration here³⁵. Table 1 shows the various polyesters which have been blended with this polymer and the conclusions about

Table 1 Phase behaviour observed for blends of the polyhydroxy ether of bisphenol-A with various polyesters

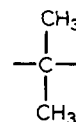
			$\frac{\text{CH}_x}{\text{COO}}$
PES	$-(\text{CH}_2)_2-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_2-\text{C}(=\text{O})-\text{O}-$	Immiscible	2
PEA	$-(\text{CH}_2)_2-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{O}-$	Miscible	3
PBA	$-(\text{CH}_2)_4-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{O}-$	Miscible	4
PCL	$-(\text{CH}_2)_5-\text{C}(=\text{O})-\text{O}-$	Miscible	5
PCDS	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_2-\text{C}(=\text{O})-\text{O}-$	Miscible	(5)
PHS	$-(\text{CH}_2)_6-\text{O}-\text{C}(=\text{O})-(\text{CH}_2)_8-\text{C}(=\text{O})-\text{O}-$	Immiscible	7

miscibility as deduced from glass transition observations. Clearly, as the structure of the polyester is varied, a 'miscibility window' is observed—the ratio of aliphatic carbons per ester group in the polyester is used as the 'composition' variable in Table 1.

To apply the model developed above to the present case we think of the polyesters as a series of 'copolymers' consisting of CH_x (unit 1) and COO (unit 2). The volume fractions of each of these units can be computed from the increments each add to the molar volume³⁶. Interaction parameters for blends of the polyesters with the polyhydroxy ether of bisphenol-A have been estimated using both melting point depression¹⁶ and a vapour sorption probe technique³⁶. In addition, direct calorimetry using low molecular weight analogues of the various polymers has been used to measure the heats of mixing^{35,36}. Analogues for the polyesters were the same as used in another study¹⁹. Diphenoxypropanol was used as the analogue for the polyhydroxy ether of bisphenol-A whose structures are compared below.



To emphasize the similarity of these two compounds, the repeat unit of the polymer is not written as it would be done normally—the two differ only by the



unit in the polymer which is probably not very significant to the observations.

The estimates of the interaction parameter, B , determined by the three methods mentioned are plotted in Figure 5 versus the CH_x volume fraction in the polyester or its analogue. While there is some scatter, the values

from the three techniques agree rather well, and a trend somewhat like that shown in the upper right of Figure 2 is suggested. Equation (10) has been fitted by regression analysis to these results (treating either structure in equation (34) as component 3). The resulting parameters (see box in Figure 5) were used with equation (10) to compute the solid line in Figure 5. This line does an adequate job of describing the trend of the data. Interestingly, all the parameters deduced from this fit are positive. Because of the sparsity and scatter of the data, considerable variations in the parameters would produce similarly acceptable fits. At the present time, there is no good way to ascertain whether the magnitudes of these parameters are reasonable or not. It is important to note that within the limits of accuracy of this presentation, one does expect poly(ethylene succinate), PES, and poly(hexamethylene sebacate), PHS, to be miscible, as observed¹⁶, since they lie outside the miscibility window.

The central point here is not to give a definitive quantitative treatment of the thermodynamics for these systems but to suggest that the origin of the exothermic mixing responsible for the cases of miscibility may result from appropriate consideration of both intermolecular and intramolecular interactions rather than some specific intermolecular interaction mechanism. For the present systems, one might instinctively think of hydrogen bonding between the hydroxyl in component 3 and the carbonyl of the ester as the mechanism responsible for miscibility. While this point of view is entirely reasonable, we point to the fact that our analogue calorimetry experiments also gave exothermic mixing of esters with a compound quite similar to that in equation (34) but not having the hydroxyl group³⁵ viz. diphenoxyethane. The thermodynamics of the systems listed in Table 1 and their analogues may involve several interaction mechanisms; however, this model introduces a possibility that must be given serious consideration.

Another potentially possible way of rationalizing the type of miscibility window referred to above is by use of the modified solubility parameter model that replaces equation (13) with equation (21). Suppose polymer 1 is a homologous series like the aliphatic polyesters and polymer 3 is not varied. The interaction parameter in this case is given by

$$B = (\delta_1 - \delta_3)^2 + 2k_{13}\delta_1\delta_3 \quad (35)$$

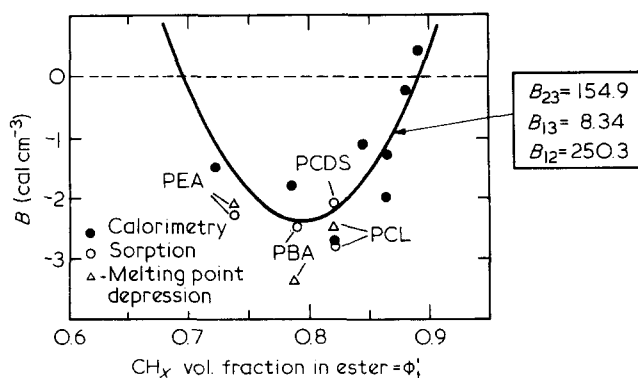


Figure 5 Interaction parameters for blends of aliphatic polyesters with the polyhydroxy ether of bisphenol-A and their low molecular weight analogues treating the polyesters as 'copolymers'. Solid line was computed from equation (10) using parameters in box. Note: 1 = CH_x, 2 = COO and 3 = structures given by equation (34)

where $\delta_1 = f(\text{CH}_x/\text{COO})$ whose range may traverse the value of δ_3 . If k_{13} is a negative number and essentially constant, then a 'miscibility window' would result, i.e. B would be negative when δ_1 is not too different from δ_3 but B would be positive when δ_1 is sufficiently larger or smaller than δ_3 .

SUMMARY

The literature contains many examples of 'miscibility windows' in polymer blend systems as the molecular structure of one of the components is systematically varied. The most well recognized cases involve random copolymers, but similar behaviour may be seen using a homologous series of homopolymers. A simple binary interaction model that considers both intermolecular and intramolecular interactions was presented as one simple way of understanding such phenomenon at least in a quantitative sense. The most profound conclusion is that a net exothermic heat of mixing for driving miscibility can exist when none of the interaction parameters between individual units is negative. This means that specific interactions between two component polymers is not a requirement for their miscibility. We are not suggesting that such specific interactions do not exist in some cases, but apparently miscibility can occur in many cases where such a strong interaction mechanism does not exist. However, it was pointed out that even in the latter cases, the interaction between individual units must depart from the predictions of simple solubility parameter theory in order to achieve the needed net exothermic heat of mixing required for miscibility in blends when both components have high molecular weights. However, it was shown that only rather small departures from the geometric mean assumption inherent in this theory are sufficient to cause miscibility.

The utility of the model developed was illustrated by several examples involving blends of copolymers. One case presented showed how similar intramolecular considerations may be applied to homopolymers by appropriate subdivision of the repeating units.

Clearly, the theory of physical interactions between different small molecules or different moieties of larger molecules is one of the unsolved problems of physical chemistry, and the failure to break the net interaction for mixing two different types of molecules into its component parts has hampered the reduction of experimental observations into a tabulation of more useful information. The approach given here is a simple but arbitrary means of handling the latter issues. An in-depth understanding of the thermodynamics of polymer blends will require extensive theoretical and experimental advances in these areas. The ultimate goal is to develop a suitable formalism and a data base so that interaction parameters between any two unlike chemical moieties can be tabulated in a way similar to the UNIFAC method³⁷ currently being developed for prediction of phase behaviour in low molecular weight systems.

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