Predictions of the miscibility behaviour of copolymer blends involving the monomers *N*-phenylitaconimide, methyl methacrylate, styrene and acrylonitrile

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Using the six segmental interaction parameters that characterize the pair interactions between the monomer units *N*-phenylitaconimide, methyl methacrylate, styrene and acrylonitrile, the theoretical miscibility ranges of several copolymer–copolymer combinations have been calculated. Comparison with the experimental phase behaviour has shown that acceptable predictions can be obtained, but also suggests that the adoption of uniquely valued interaction parameters may be inadequate to describe all situations, and the effects of polymer chain environment may have to be considered.

(Keywords: miscibility; copolymers; copolymer composition; segmental interaction)

INTRODUCTION

It is now well established that for high molar-mass polymers the entropic component of the free energy of mixing is vanishingly small, and thus if a homogeneous single-phase mixture is to be obtained the enthalpy term must necessarily be very small or negative. This situation pertains when specific interactions exist between the polymeric components, or when appropriate mixtures of copolymers are considered. In the latter type, miscibility may be observed between certain copolymer compositions and the necessary favourable enthalpy contribution arises from a strong intramolecular monomer–monomer antipathy between the comonomer pairs within the copolymers[1–3]. In a previous paper[4] we have considered an example of the most general case of a copolymer mixture, i.e. (A_xB_{1-x}) with (C_yD_{1-y}), where x and y are composition volume fractions, and showed that it is possible to predict the miscibility ranges if the relevant interaction parameters are known.

This has been achieved using the Flory–Huggins mean-field theory approach to mixing, where the enthalpy component may be described by an interaction term, χ_{blend}, which incorporates the various monomer (i)–monomer (j) interactions in the manner following Scott[5]:

$$\chi_{\text{blend}} = xy\chi_{\text{AC}} + (1-x)y\chi_{\text{BC}} + x(1-y)\chi_{\text{AD}} + (1-x)(1-y)\chi_{\text{BD}} - x(1-x)\chi_{\text{AB}} - y(1-y)\chi_{\text{CD}} \quad (1)$$

The criterion for miscibility is that $\chi_{\text{blend}} < \chi_{\text{crit}}$ where:

$$\chi_{\text{crit}} = 0.5(r_1^{-0.5} + r_2^{-0.5})^2 \quad (2)$$

with r_1 and r_2 the degrees of polymerization of the component copolymers in the mixture.

The specific system to which equation (1) has previously been successfully applied[4] comprised combinations of statistical copolymers of *N*-phenylitaconimide and methyl methacrylate (PIM–MMA) with statistical copolymers of styrene and acrylonitrile (S–AN). This is an example of a system requiring six interaction parameters to predict the phase behaviour.

Equation (1) also applies in simplified forms[4] to copolymer–copolymer mixtures with a common monomer unit and to homopolymer–copolymer systems. It can be shown that the general combination of four monomer units and two composition variables can give rise to 15 copolymer–copolymer blend combinations. Using the six χ_{ij} interaction parameters previously determined, which can predict the miscibility ranges in (PIM–MMA) plus (S–AN) blends, it is of interest to test the predictive ability of equation (1) in several related systems, having established the χ_{ij} parameters for the relevant interactions.

EXPERIMENTAL

The synthesis of *N*-phenylitaconimide (PIM) has been described previously[4]. Other monomers, styrene (S), acrylonitrile (AN) and methyl methacrylate (MMA), were obtained from commercial suppliers, freed from inhibitor and distilled prior to use.

Statistical copolymers of PIM and MMA were prepared as before[4]. The S–AN copolymers were kindly donated by D. Lath of the Slovak Academy of Sciences and their characterization has already been described[6]. Styrene–methyl methacrylate (S–MMA) copolymers were synthesized by conventional radical bulk copolymerization by W. K. Busfield of Griffith University, Queensland, Australia, and were characterized by n.m.r. spectroscopy. Statistical copolymers of PIM with S and of PIM with AN were prepared in tetrahydrofuran solution, while those of MMA with AN were prepared in bulk. In all cases the initiator α,α'-azobisisobutyronitrile was used at 333 K and conversions were kept to under

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10% to minimize composition drift. Copolymer compositions were determined by elemental or n.m.r. analyses and expressed in volume fractions using the molar volumes of the comonomer repeat units.

Copolymer blends were prepared at 50/50 wt% by co-dissolution of the two components in a common solvent (tetrahydrofuran or chloroform), followed by co-precipitation into methanol. The glass transitions (T_g) of the blends were determined by d.s.c. The criterion of miscibility was taken as the appearance of a single reproducible T_g for the blend.

RESULTS AND DISCUSSION

Phase boundaries can be readily calculated by rearranging equation (1) and equating χ_{blend} to χ_{crit} to give:

$$0=y^2\chi_{CD}+y(Q+Rx)+(x^2\chi_{AB}+Px+\chi_{BD}-\chi_{\text{crit}}) \quad (3)$$

where

$$R=\chi_{AC}-\chi_{BC}-\chi_{AD}+\chi_{BD}$$
$$P=\chi_{AD}-\chi_{BD}-\chi_{AB}$$
$$Q=\chi_{BC}-\chi_{BD}-\chi_{CD}$$

For any given value of the volume fraction variable x in a copolymer A_xB_{1-x}, the roots of equation (3) provide the limiting composition of miscibility in terms of the volume fraction y in a copolymer C_yD_{1-y}, thereby allowing the construction of miscibility maps in two-dimensional space for $0<x,y<1$.

The various χ_{ij} in equation (3) are identified according to the system in question. For copolymer combinations with a common monomer unit, one χ_{ij} is of course set to zero and two other pairs are formally identical. For example, in the copolymer blend system $\text{PIM}_x\text{S}_{1-x}$ with $\text{S}_y\text{AN}_{1-y}$, $\chi_{AB}=\chi_{AC}=\chi_{\text{PIM-S}}$, $\chi_{BC}=\chi_{\text{S-S}}=0$ and $\chi_{BD}=\chi_{CD}=\chi_{\text{S-AN}}$. The values of the χ_{ij} interaction terms used are collected in *Table 1* and were derived by the various methods described elsewhere[4,6].

The calculated phase diagram for PIM–S and S–AN compares very favourably with experiment and is shown in *Figure 1*, where χ_{crit} is set equal to 0.0025 (which is based on the average of the copolymer molecular weights involved). Similar phase behaviour is predicted for the related combination of comonomers giving blends of copolymers of PIM–AN with S–AN, and this also conforms satisfactorily to the (more restricted) experimental data available as shown in *Figure 2*. The general shape of the miscibility regions displayed in *Figures 1* and *2* appears to be characteristic of systems in which there is a (relatively) large 'intramolecular' interaction, in this case that between S and AN.

The miscibility map for the combination of copolymers PIM–MMA blended with S–MMA is shown in *Figure 3*, where the predicted miscibility range is seen to be very much smaller. This system is distinct from the two previous ones in that comonomer pairings do not involve significant unfavourable intramolecular interactions (i.e. the χ_{AB} and χ_{CD} values are now much smaller). The theoretical prediction with the appropriate χ_{crit} value is a phase diagram with a very restricted range of miscibility located at high common monomer (MMA) concentrations.

Table 1 Values of the segmental interaction parameters χ_{ij} used

Monomer pair	χ_{ij}
PIM–MMA	0.047
PIM–S	0.16±0.05
PIM–AN	0.12±0.02
MMA–S	0.030
MMA–AN	0.46
S–AN	0.83

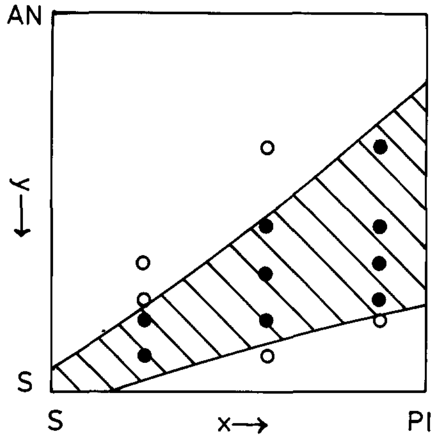

Figure 1 Miscibility map for the copolymer blend system PIM–S with S–AN; x and y are the volume fractions of PIM and S, respectively. The hatched area is the calculated miscibility range for $\chi_{\text{crit}}=0.0025$. Filled circles are one-phase blends, open circles are two-phase blends

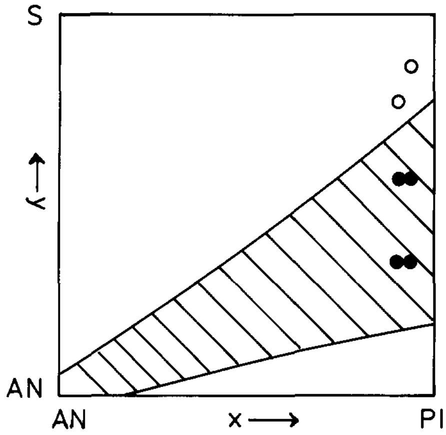

Figure 2 Miscibility map for the copolymer blend system PIM–AN with S–AN; x and y are the volume fractions of PIM and S, respectively. The hatched area is the calculated miscibility range for $\chi_{\text{crit}}=0.0025$. Filled circles are one-phase blends, open circles are two-phase blends

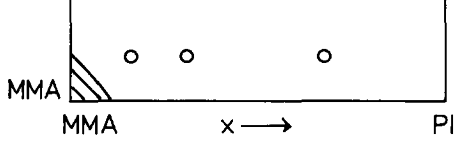

Figure 3 Miscibility map for the copolymer blend system PIM–MMA plus S–MMA; x and y are the volume fractions of PIM and S, respectively. The hatched area is the calculated miscibility range for $\chi_{\text{crit}}=0.0005$. Open circles are two-phase blends

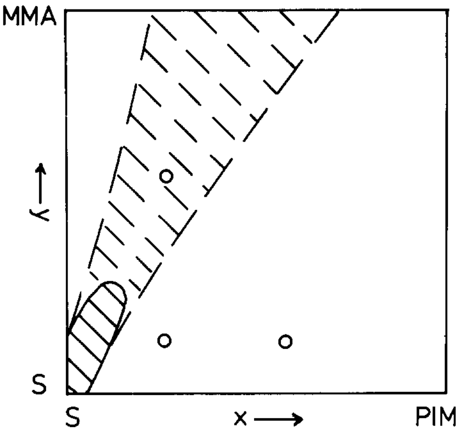

Figure 4 Miscibility map for the copolymer blend system PIM–S with MMA–S; x and y are the volume fractions of PIM and MMA, respectively. The hatched area (broken lines) is the calculated miscibility range with $\chi_{\mathrm{PIM-S}}=0.11$ and (full lines) the calculated miscibility range with $\chi_{\mathrm{PIM-S}}=0.20$, both at $\chi_{\mathrm{crit}}=0.0005$

Experimentally a large area of immiscibility is indeed confirmed; it is, however, difficult to probe the predicted miscible region using the single T_g criterion since the blend component copolymers are both nearly pure poly(methyl methacrylate) and the copolymer T_g values are essentially coincident.

Using the same three-monomer set, two other copolymer combinations are possible, PIM–S with MMA–S and PIM–S with PIM–MMA, and the results of a limited experimental investigation of the phase behaviour for the former are shown in *Figure 4*. The critical parameter determining the shape of the miscibility diagram appears to be $\chi_{\mathrm{PIM-S}}$ (here an intramolecular interaction), which was established with only limited reliability in the earlier study[4]. Predicted miscibility, based on the upper and lower error limits in $\chi_{\mathrm{PIM-S}}$ values shown in *Table 1*, ranges from a vanishingly small area, at high common monomer concentrations, to a narrow wedge extending to a limited range of PIM–S copolymers. Experimentally, immiscibility is observed for PIM–S compositions $\gtrsim 25$ vol% PIM and this conforms to prediction if $\chi_{\mathrm{PIM-S}}$ is set at only 10% less than the median value chosen previously[4]. It should be noted that all the other phase diagrams calculated here and in our previous work[4] are quite insensitive to the spread in $\chi_{\mathrm{PIM-S}}$ and in $\chi_{\mathrm{PIM-AN}}$ values, but the extent of the change, illustrated in *Figure 4*, does reflect the sensitivity of the predicted miscible regions on certain χ_{ij} parameters and the need to be able to determine accurate and reliable values for these interaction energies. The precise determination of $\chi_{\mathrm{PIM-S}}$ in the previous work[4] was not quite as critical because of the dominating effect of the $\chi_{\mathrm{S-AN}}$ value. In the presently studied system the $\chi_{\mathrm{PIM-S}}$ needs to be known more precisely and the experimental observations have allowed us to refine the value.

Two further common monomer systems were studied by examining the combination of MMA–AN copolymers with PIM–MMA and PIM–AN copolymer samples, respectively. Wedge-shaped areas of miscibility are calculated for both of these systems, where χ_{ij} values of 0.047, 0.12 ± 0.02 and 0.46 were used for the PIM–MMA, the PIM–AN and the MMA–AN interactions, respectively, contrasting with the experimental evidence (*Figures 5* and *6*), which indicates that phase-separated blends exist within these same areas. Only by selecting a substantially lower value of $\chi_{\mathrm{CD}}=\chi_{\mathrm{MMA-AN}}=0.32$, rather than the 0.46 calculated previously[6] from the phase behaviour of PMMA homopolymer with S–AN copolymers, can the computed miscibility be reduced to a vanishingly small region at high PIM volume fractions, which would agree with the experimental observations. Since the value of $\chi_{\mathrm{BC}}=\chi_{\mathrm{MMA-AN}}=0.46$ is retained for the other interaction term involving AN and MMA, it appears that a distinction is necessary between the interaction energetics of two units that depends on their environment. In this case the distinction is between the *intramolecular* pairing of MMA and AN in the MMA–AN copolymer and the same pairing, but now an *intermolecular* one, involving MMA–AN and PIM–AN copolymer mixtures. This latter case is formally similar to the PMMA plus S–AN situation[6].

Differentiation of a pair interaction on the basis of environment is not without precedent. Cantow and Schulz[7,8] have elaborated a treatment of miscibility to take into account the configurational sequence distribution in a polymer, while Balazs *et al.*[9] and van Hunsel *et al.*[10] have considered the effect on the χ_{ij} values of the comonomer sequence distribution. These latter authors

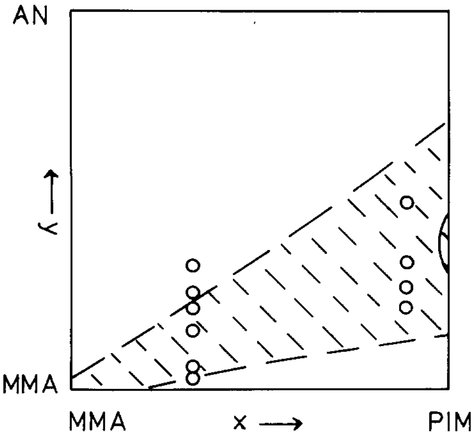

Figure 5 Miscibility map for the copolymer blend system PIM–MMA with AN–MMA; x and y are the volume fractions of PIM and AN, respectively. The hatched area (broken lines) is the calculated miscibility range with $\chi_{\mathrm{CD}}=\chi_{\mathrm{MMA-AN}}=0.46$ and (full lines) with $\chi_{\mathrm{CD}}=\chi_{\mathrm{MMA-AN}}=0.36$, both at $\chi_{\mathrm{crit}}=0.0005$

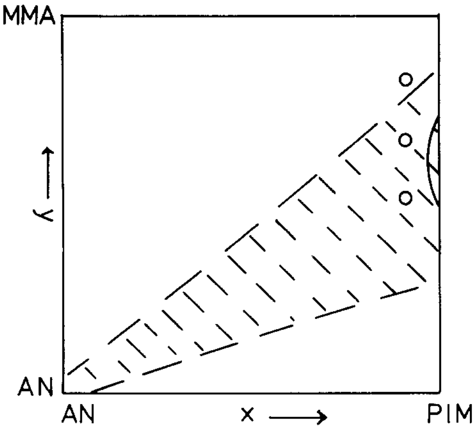

Figure 6 Miscibility map for the copolymer blend system PIM–AN with MMA–AN; x and y are the volume fractions of PIM and MMA, respectively. The hatched area (broken lines) is the calculated miscibility range with $\chi_{\mathrm{CD}}=\chi_{\mathrm{MMA-AN}}=0.46$ and (full lines) with $\chi_{\mathrm{AD}}=\chi_{\mathrm{PIM-MMA}}=0.36$, both at $\chi_{\mathrm{crit}}=0.0005$

developed the idea that the energy of, for example, an A–C pair interaction depends on the chemical sequence defining the A-containing triad, e.g. BAB or AAA. Similarly Ellis[11] has concluded, from miscibility studies on nylons, that the site of a methylene unit, whether mid-chain or otherwise, can affect the magnitude of its interaction with other groups. From a realistic standpoint the idea that any pair interaction can have a unique and environment-independent value can only be an approximation; however, it is one that permits tractable calculations of copolymer–copolymer miscibility.

In the experimental determination[6] of $\chi_{\mathrm{MMA-AN}}$, the MMA and the AN units were not components of a common copolymer; i.e. $\chi_{\mathrm{MMA-AN}}=0.46$ represents an 'inter' interaction value, whereas a value of 0.32 is required to describe adequately the observed 'intra' interaction behaviour of the present two systems. In a real sense a distinction between inter and intra interactions is the most obvious case of sequence effects in copolymers. Confirmation, in part, for such a distinction in the χ_{ij} comes from the observation that in the six χ_{ij} combination PIM–S with MMA–AN, a value of $\chi_{\mathrm{MMA-AN}}=0.46$ predicts areas of miscibility; in contrast a value of 0.32 is sufficient just to collapse the area of miscibility to zero. This latter condition agrees with the fact that no miscible combinations could be found in this blend system.

The question of the absolute value of an interaction parameter has been addressed recently by Nishimoto *et al.*[12] in another sense. These workers restate that χ_{ij} in terms of the Flory–Huggins theory is not an interaction energy density, but a dimensionless parameter related to the energy density (B_{ij}) via $\chi_{ij}=B_{ij}V_r/RT$. As such, the absolute value of χ_{ij} depends upon the reference volume V_r chosen to define the Flory–Huggins lattice site. It is common practice, but strictly wrong, to use χ_{ij} values without regard to a defined V_r. In the present case χ_{ij} values are derived from the phase boundaries of polymer and copolymer mixtures, involving several monomer units of different molar volumes. Although any V_r can be chosen, the definition of χ_{crit} (equation (2)) requires that the degree of polymerization be in turn defined by $r_i=V_i/V_r$, where V_i is the molar volume of the (co)polymer. In this and the previous paper[4] we have chosen to leave V_r undefined – which in turn introduces the approximation that the molar volumes of all monomers involved have identical values. Our calculations show that this has not introduced any serious errors in the present case where the χ_{ij} values refer to an internally consistent monomer set.

We are aware of the limitations that possible concentration and temperature dependence of any of the χ_{ij} parameters has been neglected in these calculations, and this could also have some effect on the values. It should be noted that many of the χ_{ij} parameters have been derived from measurements of phase boundaries, and these cannot always be defined with great precision. This emphasizes the importance of having an internally consistent data set.

CONCLUSIONS

In summary, it has been shown that the interaction parameter data set previously derived[4] can be used in a predictive manner (with minor refinements) with reasonable success, despite all the shortcomings of an elementary Flory–Huggins approach. However, there does seem a need for precise assignment of the values of such parameters since, in certain cases, the calculated phase behaviour is extremely sensitive to small numerical changes, especially in combinations without at least one significantly large interaction value. Also the original premise[4], that χ_{ij} may be equated to χ_{ji} or more generally that the χ_{ij} parameters are uniquely valued, seems to require some qualification. Different parameter values may be required to describe the same pair interaction in an intramolecular as opposed to an intermolecular environment.

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