Prediction of the miscibility range in blends of poly(styrene-*co*-acrylonitrile) and poly(*N*-phenyl itaconimide-*co*-methyl methacrylate): a six-interaction-parameter system

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Miscibility in blends of two statistical copolymers of the type (A_xB_{1-x}) and (C_yD_{1-y}), namely poly(styrene-*co*-acrylonitrile) and poly(*N*-phenyl itaconimide-*co*-methyl methacrylate), has been studied using differential scanning calorimetry. Miscible blends of these copolymers were obtained over a wide composition range. Theoretical 'miscibility maps', i.e. miscibility boundaries as a function of copolymer composition, have been calculated for this system by a predictive mean-field treatment involving the six segmental interaction parameters (χ_{ij}). Excellent agreement between the predicted maps and experimental data is shown.

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

INTRODUCTION

There is considerable current interest, both academic and industrial, in the *prediction* of polymer–polymer miscibility, rather than simply to rationalize why a particular blend *is* miscible. Various approaches have been adopted, such as the matching of solubility parameters[1,2], calculations involving segmental polymer–polymer interaction parameters[3–6] and also through the maximization of potential specific interactions[7]. Much of the physical data required for the more complex theories of mixing are not readily available for the majority of systems and the simpler Flory–Huggins approach is still used.

Recently it has been demonstrated that systems consisting of a homopolymer and a copolymer[3,8], or two different copolymers[4,5], can be miscible over a range of copolymer compositions—the 'miscibility window'—even though the combinations of their corresponding homopolymers are immiscible. This would suggest that in systems of this type there are no effective specific interactions between the components and that the driving force for miscibility lies elsewhere. Such blend systems are of the general types $A_x+(C_yD_{1-y})$, $(A_xB_{1-x})+(C_yB_{1-y})$ or $(A_xB_{1-x})+(C_yD_{1-y})$, where x and y are the respective volume fractions of the monomer species in the copolymers.

The appearance of a miscibility window within certain copolymer compositions (without the presence of strong specific effects) is thought to arise from the presence of an unfavourable interaction between the monomer pair(s) comprising the copolymer(s)[8,9], which outweighs the aggregate effect of all the other interactions involved. This balance of segmental interactions can be formalized using a modification of the Flory–Huggins expression for the free energy of mixing (ΔG^M) in which the interaction parameter χ_{12} is replaced by an expandable term χ_{blend}, as in:

$$\Delta G^M/RT=[(\phi_1/r_1)\ln\phi_1+(\phi_2/r_2)\ln\phi_2]+\phi_1\phi_2\chi_{\text{blend}} \tag{1}$$

For the most general case of a blend of two statistical copolymers, (A_xB_{1-x}) and (C_yD_{1-y}), where x and y denote the copolymer compositions in terms of volume fractions, the χ_{blend} expression involves six composition-weighted segmental interaction parameters χ_{ij} for the monomer(i)–monomer(j) interactions relevant to the system, and this is given by:

$$\chi_{\text{blend}}=xy\chi_{AC}+(1-x)y\chi_{BC}+x(1-y)\chi_{AD}+(1-x)(1-y)\chi_{BD}-x(1-x)\chi_{AB}-y(1-y)\chi_{CD} \tag{2}$$

The first four terms on the right-hand side of equation (2) define additive interactions between the (non-bonded) component monomers of the mixture of the two copolymers, weighted according to the copolymer composition, whereas the remaining two terms define the intramolecular forces between the two different monomers comprising each of the copolymers. The form of equation (2) is similar to that proposed 40 years ago by Scott[10,11] for polymer–solvent interactions in ternary systems, and has been successfully applied to polymer–polymer blends by Krause *et al.*[12], Paul and Barlow[8], ten Brinke *et al.*[3] and Shiomi *et al.*[4].

Simplified expressions for χ_{blend} may be developed from composition-weighted χ_{ij} parameters. For a system comprising a homopolymer $(A_x, x=1)$ and a copolymer (C_yD_{1-y}), where only three χ_{ij} terms are involved, we have:

$$\chi_{\text{blend}}=y\chi_{AC}+(1-y)\chi_{AD}-y(1-y)\chi_{CD} \tag{3}$$

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Similarly, the χ_{blend} expression for the blend of two statistical copolymers with a common monomer unit, $(A_xB_{1-x})+(C_yB_{1-y})$, is given by a two-variable quadratic with three χ_{ij} parameters:

$$\chi_{blend}=\chi_{AB}x^2+(\chi_{AC}-\chi_{BC}-\chi_{AB})xy+\chi_{BC}y^2 \qquad (4)$$

Finally for a blend of two copolymers that differ only in composition, (A_xB_{1-x}) and (A_yB_{1-y}), equation (2) reduces to:

$$\chi_{blend}=(x-y)^2\chi_{AB} \qquad (5)$$

According to Flory–Huggins theory, a critical value (χ_{crit}) exists where the ΔG^M function exhibits an incipient double tangent, but now:

$$\chi_{blend}=\chi_{crit}=0.5(r_1^{-0.5}+r_2^{-0.5})^2 \qquad (6)$$

where r_i are the respective degrees of polymerization of the component copolymers. Thus χ_{crit} tends to zero for infinite molecular weight. Miscibility therefore corresponds to $\chi_{blend}<\chi_{crit}$ and immiscibility to $\chi_{blend}>\chi_{crit}$. The boundary between miscibility and immiscibility, where $\chi_{blend}=\chi_{crit}$, will be described by a function expressed in terms of x and y, i.e. equations (2)–(5) as appropriate, such that $\chi_{blend}=f(x,y)=\chi_{crit}$.

In this paper we report the presence of a miscibility window in blends of poly(styrene-*co*-acrylonitrile) (S-AN) and poly(*N*-phenyl itaconimide-*co*-methyl methacrylate) (PIM-MMA), an example of a copolymer blend $(A_xB_{1-x})+(C_yD_{1-y})$ where six intersegmental interaction parameters are needed to satisfy equation (2). This may be conveniently rearranged to give the general form of a conic section:

$$ax+2hxy+by+2ex+2fy+g=0 \qquad (7)$$

where

$$a=\chi_{AB}$$
$$h=0.5(\chi_{AC}+\chi_{BD}-\chi_{BC}-\chi_{AD})$$
$$b=\chi_{CD}$$
$$e=0.5(\chi_{AD}-\chi_{BD}-\chi_{AB})$$
$$f=0.5(\chi_{BC}-\chi_{BD}-\chi_{CD})$$
$$g=\chi_{BD}-\chi_{crit}$$

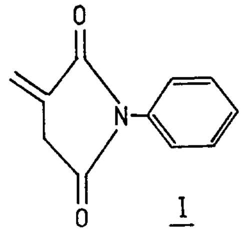
from which solutions can be readily obtained in the xy plane for any χ_{crit}.

These solutions represent slices through a three-dimensional boundary volume of χ_{crit}, x and y, and are displayed as contour maps in terms of x and y for any given χ_{crit} value, where $0<x,y<1$. The geometry of $f(x,y)$ is dependent on the sign and magnitude of the χ_{ij} parameters that appear in the appropriate χ_{blend} expression.

However, before the relevant χ_{ij} parameters are introduced for the PIM-MMA and S-AN blend system, there are several assumptions in the model that should be recognized: (a) the segmental interaction parameters χ_{ij} are assumed to be composition-independent; (b) both components are assumed to be mixed at the segmental level; and (c) any free-volume contributions to the mixing process are neglected in an explicit form (or at least are subsumed by the experimentally derived χ_{ij} parameters). Since, as will be seen, the calculation of the various χ_{ij} parameters combines the results of miscibility limits of different copolymer compositions, point (a) may be defended by considering them to be 'composition-averaged' values. Similarly, any free-volume contributions, which may be inherent in experimentally derived χ_{ij}, must also differ for different blend compositions. This too is 'averaged out'. Thus in the most general terms there is the underlying assumption that $\chi_{ij}=\chi_{ji}$, although this may not necessarily be valid.

EXPERIMENTAL PROCEDURES

N-Phenyl itaconimide (PIM, structure **I**) was synthesized from itaconic anhydride and aniline via the ring-opened α- and β-itaconamic acids followed by subsequent dehydration and cyclization at 343 K using acetic anhydride[13,14]. The crude imide was recrystallized from cyclohexane to give a pure product melting at 385–387 K. Methyl methacrylate (MMA), supplied by BDH, was freed from inhibitor and distilled prior to use.



I

Statistical copolymers of PIM and MMA (PIM-MMA) and PIM homopolymer (PPIM) were prepared in tetrahydrofuran solution under vacuum at 333 K using α,α'-azobisisobutyronitrile (AIBN) as initiator. Copolymer conversions were limited to less than 10% and the copolymers isolated by precipitation into methanol. Purification was effected by a further three reprecipitations from methyl ethyl ketone (MEK) or acetone solution into methanol and the samples were vacuum dried at 333 K. The copolymer compositions were determined by elemental analysis, and molecular weights were measured by membrane osmometry using MEK solutions.

Samples of S-AN copolymers with a range of compositions were kindly supplied by D. Lath of the Slovak Academy of Sciences. The preparation and characterization of these samples have been reported previously[6]. Two higher nitrile copolymers were synthesized by bulk copolymerization using AIBN at 333 K. These samples were isolated and characterized as before. A further sample was donated by DSM. The details of both the S-AN and the PIM-MMA copolymer systems are collected in *Tables 1* and *2*.

Blends were prepared by dropwise coprecipitation from 5% wt/vol MEK or acetone solutions of the blend components (at 50/50 wt%) into stirred methanol. The blends were collected as fine white powders and dried to constant weight in a vacuum oven.

The glass transition temperatures (T_g) of all copolymer samples and copolymer blends were determined using a Perkin–Elmer DSC-2 differential scanning calorimeter, scanning at 20 K min^{-1}. The values of T_g were estimated from the mid-point of the inflection in the heat capacity vs. temperature curve.

Blend miscibility was monitored using the criterion that a miscible blend exhibited one T_g whereas a phase-separated blend showed the T_g values for both components. All blends were first annealed at 20 K above the higher T_g component for 5 min prior to cooling at

Table 1 Composition, glass transition temperatures and molecular weights of the poly(styrene-*co*-acrylonitrile) samples used

Acrylonitrile (mol%)	Styrene (volume fraction)	T_g (K)	$10^{-3}M_n$
19.5	0.90	379	196
25.0	0.87	379	221
35.1	0.80	381	189
40.2	0.77	383	250
41.3[a]	0.76	383	53
42.7	0.75	383	144
45.1	0.73	385	262
50.5	0.69	385	138
53.5	0.66	386	400
58.6	0.61	387	240
53.6	0.56	388	142
80.4	0.35	386	200

[a] Donated by DSM

Table 2 Compositions, glass transition temperatures and molecular weights of the poly(*N*-phenyl itaconimide-*co*-methyl methacrylate) samples used

N-Phenyl itaconimide (mol%)	*N*-Phenyl itaconimide (volume fraction)	T_g (K)	$10^{-3}M_n$
10.3	0.16	407	190
20.6	0.31	415	45
28.7	0.41	423	50
35.0	0.48	426	50
41.2	0.55	439	144
49.7	0.63	449	237
55.6	0.68	459	80
79.4	0.87	493	283
100.0	1.00	505	20

180 K min^{-1}. Three subsequent scans were run to ensure reproducibility and stability of the blend. The boundary of miscibility was deemed to lie between a blend composition exhibiting one T_g and an adjacent composition exhibiting two T_g values.

RESULTS AND DISCUSSION

For the blend system $(\mathrm{PIM}_x\mathrm{MMA}_{1-x})+(\mathrm{S}_y\mathrm{AN}_{1-y})$, equation (2) can be presented more specifically as:

$$\chi_{\mathrm{blend}} = xy\chi_{\mathrm{PIM\text{-}S}} + (1-x)y\chi_{\mathrm{MMA\text{-}S}} + x(1-y)\chi_{\mathrm{PIM\text{-}AN}} + (1-x)(1-y)\chi_{\mathrm{MMA\text{-}AN}} - x(1-x)\chi_{\mathrm{PIM\text{-}MMA}} - y(1-y)\chi_{\mathrm{S\text{-}AN}} \tag{8}$$

Three of the above χ_{ij} parameters, namely $\chi_{\mathrm{MMA\text{-}S}}$, $\chi_{\mathrm{MMA\text{-}AN}}$ and $\chi_{\mathrm{S\text{-}AN}}$, have been determined by Cowie and Lath[6] from studies on the miscibility of S-AN copolymers with methyl methacrylate–acrylonitrile copolymers. Thus three χ_{ij} parameters remain to be established before χ_{blend} can be determined for the PIM-MMA plus S-AN system, namely the segmental interactions involving the PIM monomer.

Blends of PIM-MMA

The interaction parameter $\chi_{\mathrm{PIM\text{-}MMA}}$ can be determined from blends of various samples of PIM-MMA that differ only in copolymer composition, i.e. from blends of the type $(\mathrm{PIM}_x\mathrm{MMA}_{1-x})$ and $(\mathrm{PIM}_y\mathrm{MMA}_{1-y})$. In this case equation (5) becomes:

$$\chi_{\mathrm{blend}} = (x-y)^2\chi_{\mathrm{PIM\text{-}MMA}} = \chi_{\mathrm{crit}} \tag{9}$$

which can be solved for $\chi_{\mathrm{PIM\text{-}MMA}}$ in terms of the range of y copolymer composition (δy) with which a given copolymer of composition x is miscible, viz. $\chi_{\mathrm{PIM\text{-}MMA}} = 4\chi_{\mathrm{crit}}/(\delta y)^2$.

The range of mutual miscibility of the PIM-MMA samples is shown in *Figure 1* where the abscissa represents the $(\mathrm{PIM}_x\mathrm{MMA}_{1-x})$ copolymer and the ordinate the $(\mathrm{PIM}_y\mathrm{MMA}_{1-y})$ copolymer, with x and y the volume fraction of PIM in the copolymer pairs blended. *Figure 1* is obviously a miscibility map with a symmetry element since PIM-MMA copolymers with $x=y$ must be miscible with each other, as indicated by the diagonal broken line. Any blend on one side of the diagonal is formally identical with its mirror image on the other side. The full lines drawn on *Figure 1* represent the estimated phase boundaries between miscible and immiscible blends, where the vertical separation gives $\delta y = 0.53$.

The value of χ_{crit} was calculated (from the molecular weights of the miscible copolymer pair nearest to the phase boundary) as 0.0033 and, using the estimated δy above, $\chi_{\mathrm{PIM\text{-}MMA}}$ is found to be 0.047. This relatively small χ_{ij} value may be contrasted with $\chi_{\mathrm{S\text{-}AN}} = 0.83$ found by Cowie and Lath[6] for S-AN blends. This latter system has a much smaller miscibility window, reflecting the fact that styrene and acrylonitrile comonomers are highly incompatible with each other.

Blends of S-AN with PPIM

The remaining two interaction parameters were obtained from the miscibility limits measured for PPIM (homopolymer) mixed with $(\mathrm{S}_y\mathrm{AN}_{1-y})$ using equation (3) with the appropriate indices for the analysis. With the boundary condition of $\chi_{\mathrm{crit}} = \chi_{\mathrm{blend}}$ set, this can be expanded and common terms collected to give a quadratic in y:

$$0 = y^2 - y[(\chi_{\mathrm{PIM\text{-}AN}} + \chi_{\mathrm{S\text{-}AN}} - \chi_{\mathrm{PIM\text{-}S}})/\chi_{\mathrm{S\text{-}AN}}] + (\chi_{\mathrm{PIM\text{-}AN}} - \chi_{\mathrm{crit}})/\chi_{\mathrm{S\text{-}AN}} \tag{10}$$

This may be solved by analogy with the general form of a quadratic in y, y_1, and y_2, where y_1 and y_2 are the solutions to (10) in volume fraction styrene. That is, if y_1 and y_2 are the roots of $(y-y_1)(y-y_2)=0$ then it is readily shown that:

$$(\chi_{\mathrm{PIM\text{-}AN}} + \chi_{\mathrm{S\text{-}AN}} - \chi_{\mathrm{PIM\text{-}S}})/\chi_{\mathrm{S\text{-}AN}} = y_1 + y_2 \tag{11}$$

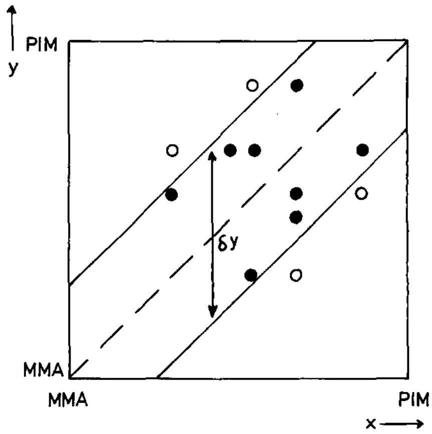


Figure 1 The mutual miscibility of poly(*N*-phenyl itaconimide-*co*-methyl methacrylate) blends: (●) miscible blend; (○) immiscible blend. x and y are the volume fractions of *N*-phenyl itaconimide in the copolymer pairs blended. Full lines are estimated phase boundaries

Table 3 Miscibility data for poly(*N*-phenyl itaconimide) mixed with poly(styrene-*co*-acrylonitrile)

Volume fraction styrene in SAN	T_g (K)	Miscibility[a]
0.90	381, 505	im
0.80	389, 505	im
0.76	399	m
0.73	407	m
0.69	414	m
0.66	415	m
0.61	420	m
0.56	418	m
0.35	416	m

[a] m, miscible; im, immiscible

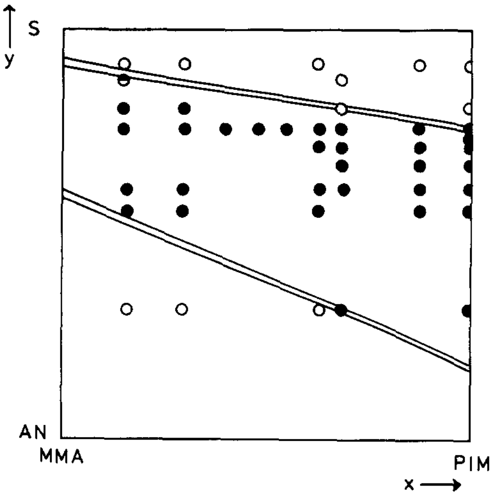


Figure 2 Miscibility of poly(*N*-phenyl itaconimide-*co*-methyl methacrylate) with poly(styrene-*co*-acrylonitrile): (●) miscible blend; (○) immiscible blend; (◓) partially miscible blend. Full lines represent phase boundaries calculated as described in text: inner boundary lines for molecular weight 50000 g mol^{-1}; outer boundary lines for infinite molecular weight

and

$$(\chi_{\text{PIM-AN}} - \chi_{\text{crit}})/\chi_{\text{S-AN}} = y_1 y_2 \qquad (12)$$

The miscibility data for PPIM in S-AN is shown in *Table 3*. The lower limit (y_1) of PPIM miscibility in (S-AN) occurs at 0.78 volume fraction styrene. The upper boundary lies between the miscible blend of the S-AN copolymer with 0.65 volume fraction acrylonitrile and the immiscible combination of PPIM with acrylonitrile homopolymer. A median value of $y_2 = 0.17$ volume fraction styrene was estimated in this case. The χ_{crit} parameter was defined by the molecular weights of PPIM and the miscible S-AN copolymer closest to y_1 and found to be 0.0093. The value $\chi_{\text{S-AN}} = 0.83$ was used to allow calculation of $\chi_{\text{PIM-AN}} = 0.12$ from equation (12) and $\chi_{\text{PIM-S}} = 0.16$ from equation (11).

Miscibility of PIM-MMA and S-AN blends

The six χ_{ij} parameters of the PIM-MMA plus S-AN blend system are collected below:

$\chi_{\text{PIM-MMA}} = 0.047$ $\quad \chi_{\text{PIM-S}} = 0.16$ $\quad \chi_{\text{PIM-AN}} = 0.12$
$\chi_{\text{MMA-S}} = 0.030$ $\quad \chi_{\text{MMA-AN}} = 0.46$ $\quad \chi_{\text{S-AN}} = 0.83$

Using these, equation (9) was solved for $\chi_{\text{crit}} = 0.005$ and $\chi_{\text{crit}} = 0$, corresponding to molecular weight 50×10^3 g mol^{-1} and infinite molecular weight, respectively. The contours representing the boundaries between miscible and immiscible blends for these two conditions are shown on *Figure 2*; the outer boundary represents $\chi_{\text{crit}} = 0$ and the inner $\chi_{\text{crit}} = 0.005$. It is apparent that, for this system, there is very little molecular-weight dependence.

Figure 2 also contains the results of blending studies on a large number of copolymer combinations where the filled circles represent single-T_g, one-phase, blends and the open circles two-phase blends. The agreement between the calculated and experimental regions of miscibility is remarkably good considering the assumptions made and the relative inaccuracies in determining the χ_{ij} parameters.

CONCLUSIONS

The miscibility in several blends of homopolymers with copolymers has been predicted using the simple mean-field approach and an expanded form of the interaction parameter involving three χ_{ij} values. In the system reported here we have shown that it can also be used to define the miscibility region in blends of copolymers where six interaction parameters are now required to solve the equations. Successful application of the approach rests to a large extent on the validity of the values determined for each χ_{ij} and some variation in these values for the same comonomer pair has been noted. For example Molau[15] reported $\chi_{\text{S-AN}} = 0.76$, whereas the value used here is $\chi_{\text{S-AN}} = 0.83$. The utility of the χ_{ij} set reported in this work can only be judged if they can be used to predict miscibility in other related systems, and in a forthcoming publication this will be tested for a number of homopolymer–copolymer blends.

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