The miscibility of copolymer blends involving the monomers itaconic anhydride, methyl methacrylate, styrene and acrylonitrile

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Isothermal phase boundaries for three separate copolymer blend systems, involving the monomers itaconic anhydride, methyl methacrylate, styrene and acrylonitrile, have been established as a function of copolymer composition. Analysis of these in terms of the Flory–Huggins approach and the isothermal blend interaction energy density parameter B_{blend} yields an estimate of the segmental interaction of itaconic anhydride with each of the other comonomers.

(Keywords: miscibility; copolymer blends; segmental interaction)

INTRODUCTION

In blends involving high-molar-mass polymers, the mixing entropy is negligible, and so, to obtain a homogeneous single phase, the mixing enthalpy must be close to zero, or indeed negative. This is fulfilled when specific interactions exist between components, and also when appropriate mixtures of copolymers are considered. In this latter case, miscibility is commonly composition-dependent, and such behaviour is successfully rationalized using simple Flory–Huggins theory with the extension of a compositionally dependent isothermal blend interaction parameter B_{blend}[1–3].

B_{blend} is formulated in terms of the individual segmental interactions and expresses the global effect of all the contact interactions in the mixture. In principle, any number of segmental components may be considered, though in practice the mathematics could become somewhat intractable. For the general case of a mixture of two statistical copolymers, A_xB_{1-x} with C_yD_{1-y}, six segmental interaction terms B_{ij} are required, so that:

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

where copolymer compositions are defined in volume fractions. Equation (1) can be re-expressed[4–6] more compactly in terms of the composition variables x and y as:

$$ax^2 + by^2 + cxy + dx + ey + f = 0 \quad (2)$$

with the coefficients a to f related to the B_{ij} through:

$$a = B_{\text{AB}}$$
$$b = B_{\text{CD}}$$
$$f = B_{\text{BD}} - B_{\text{blend}}$$
$$a + d + f = B_{\text{AD}} - B_{\text{blend}}$$
$$b + e + f = B_{\text{BC}} - B_{\text{blend}}$$
$$a + b + c + d + e + f = B_{\text{AC}} - B_{\text{blend}} \quad (3)$$

Equation (2) may be used to map out phase boundaries in x–y composition space for known values of the B_{ij} when it is solved under the critical condition $B_{\text{blend}} = B_{\text{crit}}$, where:

$$B_{\text{crit}} = (RT/2)(V_1^{-1/2} + V_2^{-1/2})^2 \quad (4)$$

is given in terms of the molar volumes (V_i/cm^3 mol^{-1}) of the blend components. Equation (2) obviously describes a conic section, so, for any observed phase diagram, a best-fit boundary in the form of a conic section should be selected to describe the data. The set of coefficients corresponding to this best fit may then be used to calculate the values of the system B_{ij} using equations (3) above, *provided* that the magnitude of B_{AB} is known from an independent experiment. This important last requirement is a consequence of the fact that a given set of conic coefficients may be scaled by any real number, and yet describe the same conic section. In effect B_{AB} is used to normalize equation (1) through $B_{\text{AB}} = a$, as discussed previously[5].

The experimental phase behaviour of three copolymer blends involving the repeat units styrene, acrylonitrile, methyl methacrylate and itaconic anhydride (2-methylene succinic anhydride) is examined in this contribution. From such a base set of four comonomers, it is possible, in principle, to prepare six copolymers, and pairing of these can give rise to 15 distinct copolymer blend systems. Here we restrict the investigation to blends of poly(styrene-*stat*-acrylonitrile) with poly(styrene-*stat*-itaconic anhydride) (S–AN + S–IA), poly(styrene-*stat*-acrylonitrile) with poly(methyl methacrylate-*stat*-itaconic

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anhydride) (S–AN + MMA–IA) and poly(methyl methacrylate-*stat*-acrylonitrile) with poly(methyl methacrylate-*stat*-itaconic anhydride) (MMA–AN + MMA–IA). B_{ij} values have been established[5,6] for the three pairings i–j = S–AN, S–MMA and MMA–AN. Although vinyl copolymers of itaconic anhydride have been prepared and characterized[7–9], as yet, miscibility behaviour involving this monomer unit has not been investigated.

EXPERIMENTAL

Acrylonitrile, styrene and methyl methacrylate monomers were freed from inhibitor and then vacuum distilled. Itaconic anhydride was recrystallized twice from petroleum spirit to give a fraction free of acid (by infra-red spectroscopy). S–IA and MMA–AN copolymers were prepared by solution polymerization in vacuum with tetrahydrofuran as solvent at 333 K and using α,α'-azobisisobutyronitrile as initiator. Copolymerizations were limited to below 15% and the copolymers isolated by precipitation (twice) into cold methanol. Copolymer samples were vacuum dried for 24 h at 333 K and their compositions determined by elemental analysis. Molar masses were measured using g.p.c., which was calibrated using narrow molar-mass polystyrene standards.

The synthesis and characterization of S–AN and MMA–IA copolymers have been reported previously[6,9]. All copolymer details are noted in *Tables 1–4*. Molar volumes are calculated from the g.p.c.-determined molar masses using copolymer densities estimated from van Krevelen's group additivity scheme[10], and values of B_{crit} were calculated from the averaged copolymer molar volumes. In order to minimize possible effects from casting solvents, blends were prepared by codissolving samples in tetrahydrofuran at 50/50 wt% followed by precipitation into methanol. The blended samples were vacuum dried at 333 K and their glass transitions (T_g) determined using a Perkin–Elmer DSC-4. The criterion for a miscible blend was the appearance of a reproducible single T_g. Copolymer blends where the T_g values for each component were similar (within ca. 10 K) had to be thermally aged to discriminate between a one-phase or a two-phase blend, according to the method of Bosma *et al.*[11].

Table 1 Compositions, T_g values and molar masses of S–AN copolymers

Comonomer (mol%)			
S	AN	$10^4 M_n$ (g mol^{-1})	T_g (K)
20	80	20.0	387
38	62	14.2	385
43	57	21.5	387
55	45	19.0	385
64	36	20.0	381
71	29	18.3	380
77	23	17.5	371
89	11	12.4	378

Table 2 Compositions, T_g values and molar masses of S–IA copolymers

Comonomer (mol%)			
S	IA	$10^4 M_n$ (g mol^{-1})	T_g (K)
27	73	1.9	426
35	65	5.1	445
41	59	1.3	448
47	53	2.2	444
53	47	3.3	438
64	36	5.6	420
77	23	4.8	418

Table 3 Compositions, T_g values and molar masses of MMA–IA copolymers

Comonomer (mol%)			
MMA	IA	$10^4 M_n$ (g mol^{-1})	T_g (K)
12	88	–	428
54	46	3.5	410
67	33	8.6	399
75	25	6.0	404
86	14	12.9	396
96	4	7.7	398

Table 4 Compositions, T_g values and molar masses of MMA–AN copolymers

Comonomer (mol%)			
AN	IA	$10^4 M_n$ (g mol^{-1})	T_g (K)
10	90	3.5	352
11	89	3.9	357
15	85	4.1	361
19	81	3.3	358
30	70	4.3	368
34	66	3.2	352
37	63	3.0	352
45	55	3.0	355
72	28	1.4	349

RESULTS AND DISCUSSION

The experimental phase behaviour of the three systems S–AN + S–IA, S–AN + MMA–IA and MMA–AN + MMA–IA is depicted in *Figures 1–3*. The first and the last of these blends represent a particular case of the general blend, A_xB_{1-x} with C_yD_{1-y}, in which each copolymer contains a common comonomer. Since equation (1) implies a first-order approach to copolymer miscibility[1–3], i.e. each i–j contact is characterized by a single value of B_{ij}, which is independent of the nature of its intramolecular environment, it follows that we can set $B_{AB} = B_{AD}$, $B_{CD} = B_{BC}$ and $B_{BD} = 0$ in these two cases, and consequently a simpler form of equation (2) results, which describes an $A_xB_{1-x} + C_yB_{1-y}$ blend:

$$ax^2 + cyx + by^2 - B_{\text{crit}} = 0 \tag{5}$$

It is illustrative to consider the quadratic solutions to equation (5), when the composition variable y is held constant, and which has the discriminant $[(cy)^2 - 4a(by^2 - B_{\text{crit}})]$. With B_{crit} equal to zero, the discriminant is a constant, and so the predicted single-phase region is formed by two straight lines meeting at the origin, giving a wedge-shaped phase diagram such as that shown in *Figure 4*. For $B_{\text{crit}} > 0$, which is the case for all real polymer systems, the single-phase region is bounded by two shallow rectangular hyperbolae, but still centred on the origin. Also under this condition, and for appropriate values of a and b, the discriminant may be zero for some value of y ($0 < y \leqslant 1$) where equation (5) has only one

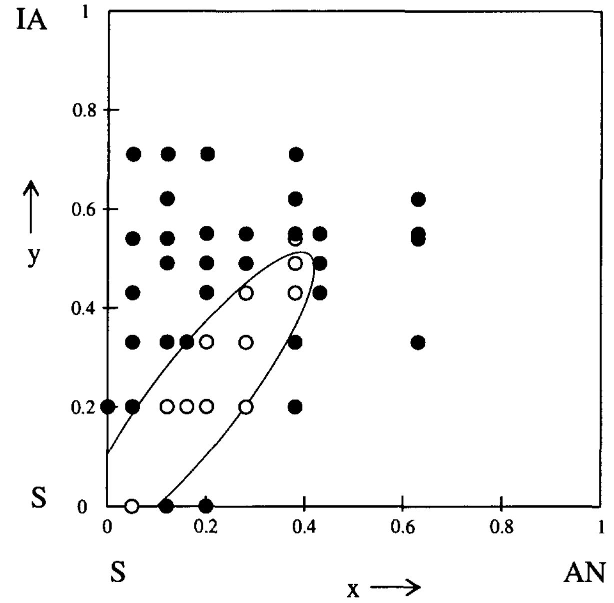


Figure 1 Miscibility behaviour of poly(styrene-*stat*-acrylonitrile) blended with poly(styrene-*stat*-itaconic anhydride). Open circles are single-T_g blends, filled circles are two-T_g blends. The system is indexed as $AN_xS_{1-x}+IA_yS_{1-y}$, where x is the volume fraction of AN and y is the volume fraction of IA. The contour is fitted as described in the text with $B_{crit}=0.08\ J\ cm^{-3}$

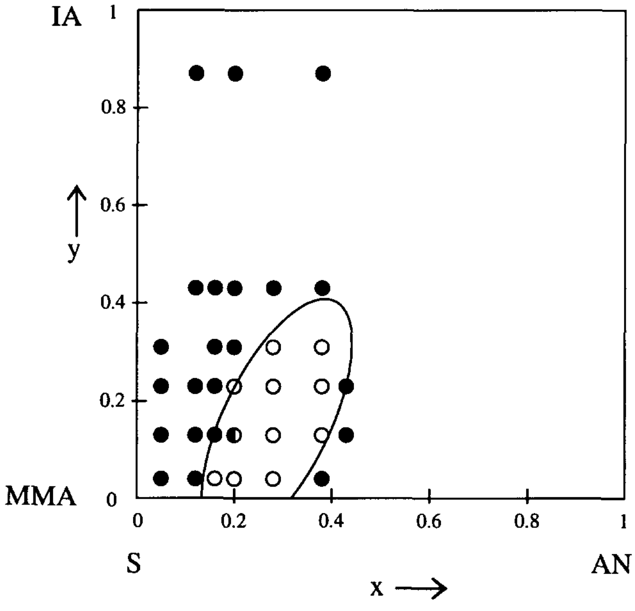


Figure 2 Miscibility behaviour of poly(styrene-*stat*-acrylonitrile) blended with poly(methyl methacrylate-*stat*-itaconic anhydride). Open circles are single-T_g blends, filled circles are two-T_g blends. The system is indexed as $AN_xS_{1-x}+IA_yMMA_{1-y}$, where x is the volume fraction of AN and y is the volume fraction of IA. The contour is fitted as described in the text with $B_{crit}=0.06\ J\ cm^{-3}$

root defining the vertex of an ellipse centred on the origin — and the limit of miscibility. The experimental S–AN + S–IA and MMA–AN + MMA–IA phase diagrams obviously accord with this latter state of affairs and so should exhibit semielliptical phase boundaries. As described in previous publications[4–6], we have used a computer-generated ellipse overlaid on the experimental data, variable in size, orientation and eccentricity, in real time, to allow choice of an appropriate boundary.

The final choice of a best-fit boundary involves some degree of subjectivity, but following the first-order approximation noted above there are constraints on this exercise: common interactions should have the same B_{ij} value in each of the three systems; intracopolymer and intercopolymer B_{ij} should be equal-valued; and i–i contacts have zero interaction. The phase boundaries shown in *Figures 1–3* represent our chosen best fit obtained over all three systems following those conditions, and the resulting B_{ij} values have been summarized in *Table 5*. $B_{S\text{-}AN}=22.8\ J\ cm^{-3}$, established

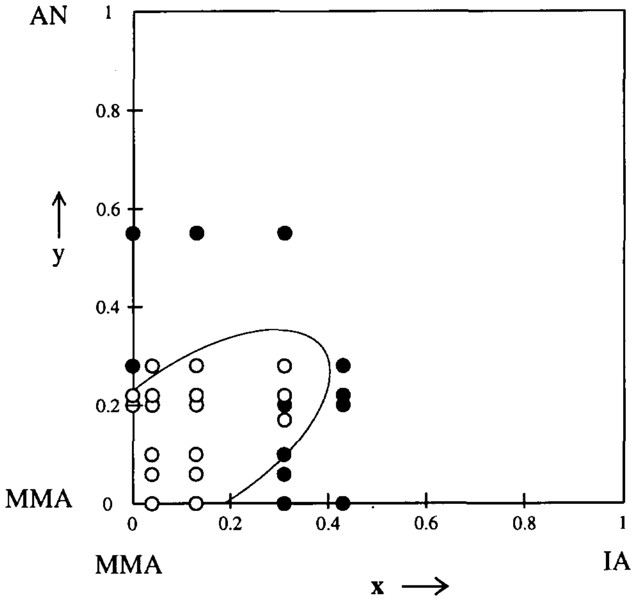


Figure 3 Miscibility behaviour of poly(methyl methacrylate-*stat*-itaconic anhydride) blended with poly(methyl methacrylate-*stat*-acrylonitrile). Open circles are single-T_g blends, filled circles are two-T_g blends. The system is indexed as $IA_xMMA_{1-x}+AN_yMMA_{1-y}$, where x is the volume fraction of IA and y is the volume fraction of AN. The contour is fitted as described in the text with $B_{crit}=0.14\ J\ cm^{-3}$

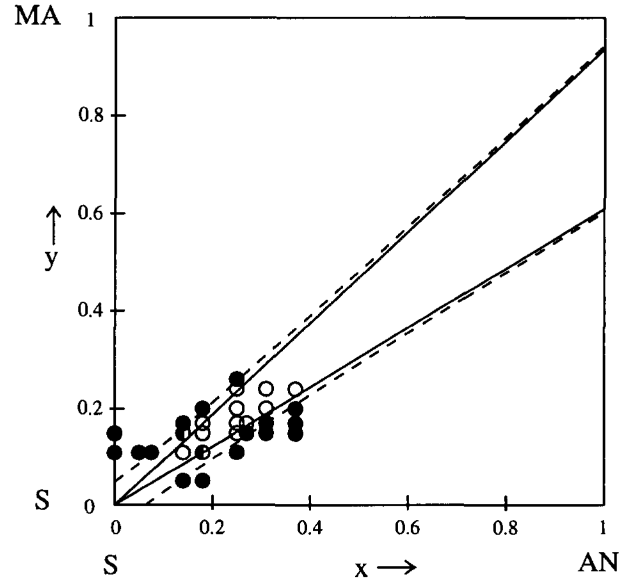


Figure 4 Miscibility behaviour of poly(styrene-*stat*-acrylonitrile) plus poly(styrene-*stat*-maleic anhydride) blends, redrawn from ref. 19. Open circles are single-phase blends, filled circles are two-phase blends. The system is indexed as $AN_xS_{1-x}+MA_yS_{1-y}$, where x is the volume fraction of AN and y is the volume fraction of MA. Full lines are calculated for $B_{crit}=0\ J\ cm^{-3}$ and broken lines for $B_{crit}=0.09\ J\ cm^{-3}$, both with $B_{S\text{-}MA}=40\ J\ cm^{-3}$, $B_{AN\text{-}MA}=1\ J\ cm^{-3}$ and $B_{S\text{-}AN}=22.8\ J\ cm^{-3}$

Table 5 Best sets of interaction parameters obtained from all three copolymer systems

i–j (type)	B_{ij} (J cm^{-3})		
	S–AN + S–IA	S–AN + MMA–IA	MMA–AN + MMA–IA
S–AN			
inter	19.8		
intra	22.8[a]	22.2[a]	
S–IA			
inter	11.9	11.8	
intra	12.8		
AN–IA			
inter	6.2	6.6	6.6
MMA–IA			
inter			8.1
intra		8.5	8.2
MMA–S			
inter		1.0	
MMA–AN			
inter		13.2	11.1
intra			13.4[a]

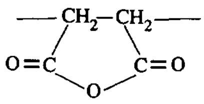
[a] Normalizing values taken from refs. 5 and 12

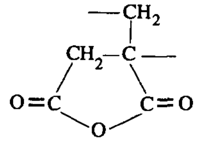
previously[5,12], was used to normalize the coefficient sets of S–AN + S–IA and of S–AN + MMA–IA, though this was reduced marginally in the latter to obtain better agreement between the common interactions. Similarly, a slightly changed value for $B_{\mathrm{MMA-AN}}$ was found more appropriate in MMA–AN + MMA–IA. Thus, although there is good agreement between the common B_{ij} values, there is not absolute agreement. The phase boundaries obtained by constraining the fitting exercise to generate absolute parameter agreement provided inadequate descriptions of the experimental data, and some comments on this situation seem appropriate.

Contours predicted on the basis of equation (5) are semi-ellipses centred at the origin, whereas that chosen to best represent the S–AN + S–IA blends in *Figure 1* is obviously not origin-centred and so follows from equation (2). The algebraic consequences of this are non-identical values of $B_{\mathrm{S-AN}}$ for the intercopolymer and intracopolymer contacts. Such a differentiation, on the basis of contour fitting, has been found previously[6,13,14], and in this respect the present system has particularly close parallels with blends of S–AN and poly(butadiene-*stat*-acrylonitrile) (B–AN), where a slightly smaller intercopolymer contact value for $B_{\mathrm{S-AN}} = 21.6$ J cm^{-3} was required to describe the data. The phase behaviour in *Figure 3* is less well defined; even so, a reasonable theoretical description can only be obtained using a non-origin-centred ellipse, so inter- and intracopolymer contacts take different values here also.

Variations in the local segmental environment are suggested as the reason for observed deviations from first-order behaviour[15–17], and a theoretical approach to this effect has been particularly well elaborated in the case of blends of different compositions of the same copolymer by Zhikuan *et al.*[18]. These form a limiting case for $A_xB_{1-x} + C_yB_{1-y}$ blends where the value of B_{AB} approaches that of B_{BC} (while $B_{\mathrm{AC}} \to 0$). The appropriate conic section is an ellipse of infinite eccentricity, i.e. the miscibility–immiscibility boundaries are a pair of parallel lines each equidistant from the diagonal of *x*, *y* composition space. Deviations from this simple pattern are accommodated by postulating differentiated diad[17] or even triad[18] interactions, and, since the distinction between intercopolymer and intracopolymer contacts is sensibly an extreme case of sequence effects, similar arguments could be applied here. Such a refinement results in extreme algebraic complexity[18], and indeed it seems that numerical values of individual triad parameters are not accessible. Realistically, the idea that any pair interaction can have a unique value can only be an approximation; however, noting that the experimental variations in the values of the B_{ij} notionally common to the three systems and those between intra- and intercopolymer contacts are of similar magnitude, we suggest that it is better to retain a pragmatic approach and to obtain reasonable estimates for a mathematically tractable first-order theory — which in the end has wider application.

The miscibility behaviour of S–AN and S–IA contrasts with that of S–AN and copolymers of styrene and maleic anhydride (S–MA), a system whose phase behaviour has been studied by Aoki[19] (see *Figure 4*) and by Martura *et al.*[20]. Parallels might be expected between S–IA and S–MA copolymers since both contain the same five-membered anhydride ring* and both have a tendency to form alternating sequences with styrene†. The data for S–AN + S–MA have been analysed as conforming to a wedge-shaped single-phase region rather than a closed-off ellipse, and the contact interactions have been calculated in terms of the Flory χ parameter[19]. These


MA


IA

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* Molecular models indicate a close similarity in orientation and accessibility of the anhydride ring in both S–MA–S and S–IA–S triads, despite the extra methyl group in the latter

† Our own composition data give the following reactivity ratios: $r_{\mathrm{S}} = 0.34$ and $r_{\mathrm{IA}} = 0.075$

may be transformed to give $B_{S\text{-}MA} \simeq 40\,\mathrm{J\,cm^{-3}}$ and $B_{AN\text{-}MA} \simeq 1\,\mathrm{J\,cm^{-3}}$, which compare with the corresponding (itaconic anhydride) interactions $B_{S\text{-}IA} \simeq 12\,\mathrm{J\,cm^{-3}}$ and $B_{AN\text{-}IA} \simeq 6.5\,\mathrm{J\,cm^{-3}}$ obtained here. This somewhat unexpected divergence of agreement for a notionally similar pair of structural units cautions in favour of B_{ij} data being regarded as strictly experimentally based parameters. However, it is also important to take account of the experimental base from which any value has been extracted. The data in *Figure 4* are restricted to MA volume fractions less than ca. 0.28 (presumably due to the practical difficulties of synthesizing copolymers beyond equimolar compositions), and so an unambiguous delineation of the S–AN + S–MA phase diagram has not been achieved. Thus, since the full extent of miscibility in this blend is in question, the B_{ij} values above cannot be regarded as finalized. Nevertheless, accepting things as they stand, and also that contributions to B_{ij} include both free-volume and orientation contributions in addition to enthalpic effects[21], it would appear that the 'pendent' incorporation of the anhydride ring in S–IA, rather than as part of the backbone, does have a significant effect on the interaction value.

Returning to the 15 possible copolymer blend systems from the four comonomers S, AN, MMA and IA, predictive calculations, based on the values of the interaction parameters summarized in *Table 5*, indicate that the remaining two four-comonomer systems (S–IA + MMA–AN and S-MMA + AN–IA) should exhibit no miscibility whatsoever, and that only common-monomer blends should show one-phase behaviour. Apart from the common-monomer blends studied here (*Figures 1* and *3*) and the S–AN + MMA–AN and S–AN + S–MMA combinations examined and found miscible by Cowie and Lath[12], the remainder are calculated to have vanishingly small regions in which one-phase behaviour occurs and these are limited to compositions very close to the origin.

CONCLUSION

To conclude, the phase behaviour of the present systems provides estimates of three further B_{ij} (i = IA; j = S, AN, MMA) to add to the growing body of literature in this area. By their very definition B_{ij} are segment-specific, first-order approximations to the enthalpic component to the free energy of mixing. Their utility, and that of the simple extended Flory–Huggins model, is that they allow a search for possible copolymer or terpolymer[22] binary mixtures (and indeed ternary mixtures[23]) that will form miscible systems. Comparison of structural variations as above may show some general trends. However, given their slightly 'impure' enthalpic nature, any future value as a possible base on which to construct a group contribution scheme from submonomer units is somewhat doubtful.

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