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The effect of replacing the α-hydrogen with a methyl group on the miscibility of systems containing styrene, methacrylonitrile and methyl methacrylate

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Summary The phase boundaries as a function of copolymer composition have been established in one polymer/copolymer and two copolymer/copolymer blend systems involving the repeat unit methacrylonitrile. Using the critical conditions for miscibility according to the Flory-Huggins theory, and an overall blend interaction parameter (B_{blend}) expressed in terms of repeat unit interactions $B_{i\text{-}j}$, values of $B_{S\text{-}MAN}$ and $B_{MMA\text{-}MAN}$ have been determined. These are compared with the corresponding acrylonitrile interactions.

Introduction Miscible polymer blends are not restricted to systems containing specific interactions. A large number of blends are known in which at least one of the components is a copolymer and where miscibility is observed as a function of copolymer composition[1-5]. Miscibility occurs as a result of mutual repulsion between comonomer units and a mean field expression has been proposed to quantify the effect in terms of volume fraction weighted segmental interaction energy density parameters $B_{i\text{-}j}$. This takes the following general form and expresses the enthalpic contribution to the Flory-Huggins[6] free energy of mixing.

$$B_{blend} = \sum_{inter} \phi_i \phi_j B_{i\text{-}j} - \sum_{intra} \phi_i \phi_j B_{i\text{-}j} \qquad (1)$$

Phase boundaries are obtained as a function of composition from the critical condition $B_{blend} = B_{crit}$ with

$$B_{crit} = (RT/2)[V_1^{-0.5} + V_2^{-0.5}]^2 \qquad (2)$$

where V_1 and V_2 are the component (co)polymer molar volumes. Indexing a homopolymer-copolymer blend as $A + B_yC_{1-y}$ and a common-comonomer copolymer blend as $A_xB_{1-x} + C_yB_{1-y}$ (where the composition variables x and y are in volume fractions) equation (1) produces the two particular forms applicable to the systems studied in this contribution.

$$B_{blend} = yB_{AB} + (1\text{-}y)B_{AC} - y(1\text{-}y)B_{BC} \qquad (3)$$

$$B_{blend} = xyB_{AC} + (1\text{-}x)yB_{BC} + x(1\text{-}y)B_{AB} - x(1\text{-}x)B_{AB} - y(1\text{-}y)B_{BC} \qquad (4)$$

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The use of equations (4) or (5) has been described fully in previous papers[7,8]. Blends involving acrylonitrile (AN) units have been extensively examined, particularly blends of poly(styrene-*stat*-acrylonitrile) (S-AN) [4,7-14]. Here we explore the effect of replacing the nitrile α–hydrogen with a methyl group by examining the phase behaviour (i) of poly(methyl methacrylate) (PMMA) with poly(styrene-*stat*-methacrylonitrile) (S-MAN), (ii) of S-MAN with poly(methyl methacrylate-*stat*-methacrylonitrile) (MMA-MAN), and (iii) of S-MAN with poly(styrene-*stat*-methyl methacrylate) (S-MMA). These are of interest on two counts; comparison with similar structural variation in other systems[11,15,16], and because H-bonding by the nitrile α-hydrogen is proposed as contributing to the miscibility of acrylonitrile copolymers[17].

Experimental Monomers styrene, methacrylonitrile and methyl methacrylate (Aldrich) were washed three times with 10% aqueous sodium hydroxide and deionised water, dried over anhydrous magnesium sulphate and finally distilled under vacuum. The initiator α,α-azobisisobutyronitrile (AIBN) was purified by two recrystallizations from methanol. S-MAN, S-MMA and MMA-MAN copolymers were prepared by radical copolymerization in bulk in sealed evacuated flasks at 60°C using AIBN as initiator at 0.1 mol%. Monomer/initiator mixtures were degassed under vacuum and conversions were taken to approx. 10% to minimise composition drift. Copolymers were precipitated into methanol, dried and purified by reprecipitation from dichloromethane solution into methanol and finally dried in vacuum for 48 hours at 60°C.

Molecular weights were obtained using gel permeation chromatography in terms of polystyrene equivalents and copolymer compositions were established using elemental analysis. The corresponding copolymer molar volumes and volume fraction compositions were calculated using repeat unit molar volumes estimated by van Krevelen's group additivity scheme[18]. Copolymer details are contained in tables 1a, 1b and 1c.

Blends were prepared by codissolving 30 mg of each component in 1 cm^3 dichloromethane then precipitating into 10 cm^3 methanol. The solvent/ precipitant mixture was left to evaporate at room temperature, and the blends were dried in a vacuum oven at 60°C for 48 hours. Glass transition (Tg) values were measured by differential scanning calorimetry (dsc). Where the component Tgs were too close to resolve, the method of physical ageing[19] was adopted and the criterion of miscibility was the appearance of a single enthalpy relaxation peak.

Table 1a S-MAN copolymer details

Styrene (vol fn)	Tg (°C)	10^{-5} Mn ($gmol^{-1}$)	Mw/Mn
0.35	115	0.42	1.6
0.47	112	0.49	1.8
0.53	113	0.60	2.1
0.58	111	0.73	1.6
0.63	111	0.85	1.7
0.67	108	1.08	1.6
0.73	107	1.11	1.7
0.80	106	1.03	1.7
0.84	102	1.16	1.5
0.93	106	0.84	2.1
0.95	106	1.08	2.7

Table 1b S-MMA copolymer details

Styrene (vol fn)	Tg (°C)	10^{-5} Mn ($gmol^{-1}$)	Mw/Mn
0.00	113	0.63	2.4
0.19	118	1.72	1.8
0.30	112	1.63	1.9
0.39	109	1.21	2.0
0.48	107	1.09	2.0
0.52	106	1.24	1.9
0.58	103	1.07	1.8
0.64	102	1.07	1.8
0.72	103	1.01	1.7
0.85	105	0.84	1.8

Table 1c MMA-MAN copolymer details

MMA (vol fn)	Tg (°C)	10^{-5} Mn ($gmol^{-1}$)	Mw/Mn
0.19	112	0.18	1.5
0.32	111	0.27	1.6
0.40	111	0.26	1.7
0.49	111	0.37	1.7
0.58	111	0.47	1.5
0.67	112	0.46	2.2
0.74	114	0.39	2.3
0.82	116	0.53	2.3
0.90	120	1.23	1.6

Table 2 Miscibility of PMMA/S-MAN

Styrene (vol fn)	Enthlpy relaxation peak maxima (°C)
0.35	Immiscible. Aged for 1h at 115°C; peak at 135°C with distinct 'shoulder'.
0.47	Immiscible. Aged for 20h at 110°C; peaks at 125 &135°C
0.53	Miscible. Aged for 19h at 105°C; sharp peak at 128°C.
0.58	Miscible. Aged for 20h at 105°C; sharp peak at 126°C.
0.67	Miscible. Aged for 24h at 103°C; sharp peak at 125°C.
0.80	Miscible. Aged for 31h at 100°C; sharp peak at 123°C.
0.84	Immiscible. Tgs at 106 and 124°C (unaged).

Results and discussion The miscibility of blends of PMMA and S-MAN copolymers is shown in table 2. The two miscibility limits (y_1 and y_2) are the solutions to quadratic equation (3), and for this system they are located between samples with y = 0.47 and 0.53, and with y = 0.80 and 0.84 respectively. $B_{S\text{-}MMA}$

is known from previous work[11] (0.71 J cm^{-3}), B_{crit} = 0.083 J cm^{-3} was obtained from equation (2) in which an average of the copolymer molar volumes was used, and it follows that $B_{S\text{-}MAN}$ = 6.94 ± 1.37 and $B_{MMA\text{-}MAN}$ = 2.93 ± 0.85 J cm^{-3}. These values may now be employed to estimate the extent of any "miscibility windows" in the two copolymer blends, S-MAN with MMA-MAN and S-MAN with S-MMA, by solving equation (4) in x,y composition space. In both cases wedge-shaped regions of single-phase behaviour are predicted; the best-fits to the data are shown in figures 1 and 2 and were obtained with $B_{S\text{-}MAN}$ = 6.65 J cm^{-3} and $B_{MMA\text{-}MAN}$= 2.90 Jcm^{-3}. These are regarded as the values which best characterize the phase behaviour overall in the three systems.

Recently Goh et al. have presented data on the phase behaviour of tetrahydrofuran-cast PMMA/S-MAN blends from which they have estimated values of the Flory $\chi_{i\text{-}j}$ parameters for the system[20]. Although these cannot be compared directly with our results (two of the present authors[11], and others[4], have previously drawn attention to the deficiencies of quantifying segmental interactions in this manner), their data yield $B_{S\text{-}MAN}$ ~11 J cm^{-3} and $B_{MMA\text{-}MAN}$ ~ 4 J cm^{-3}. Their values are greater than ours and reflect the more extensive miscibility range experimentally realised by these authors.

Figure 1 Miscibility window and experimental data for S-MAN/MMA-MAN

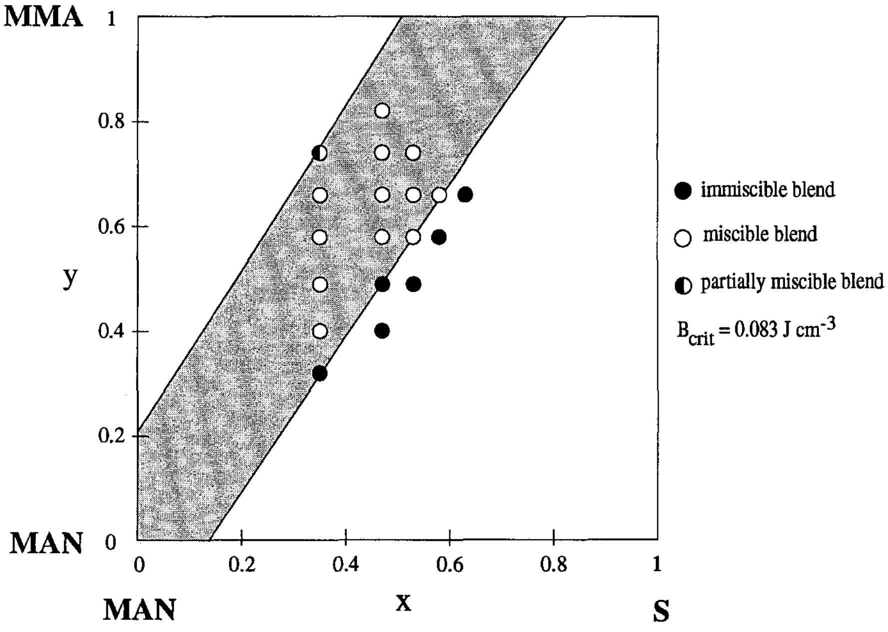
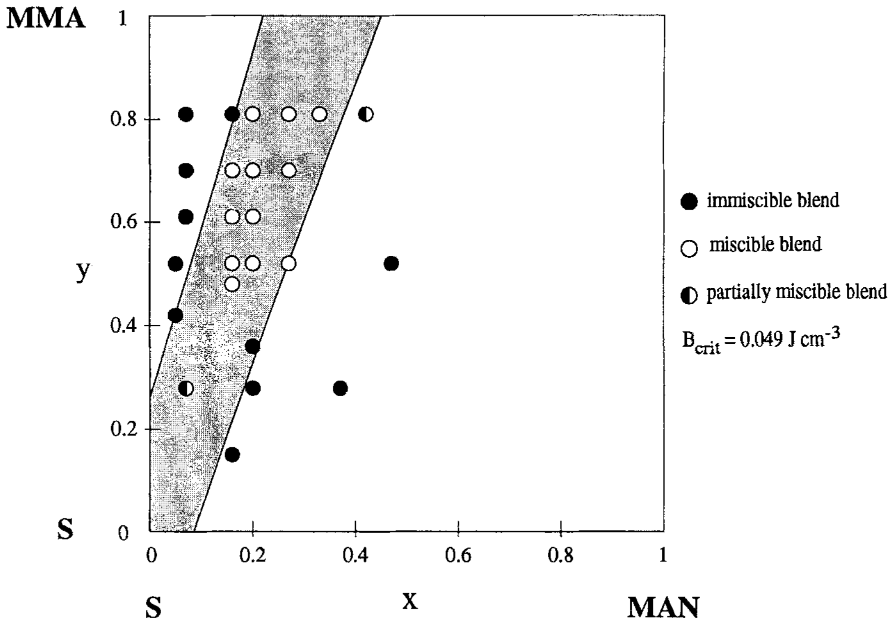


Figure 2 Miscibility window and experimental data for S-MAN/S-MMA



It is always open to question whether or not a solvent-cast mixture, or indeed a mixture formed by precipitation, is in a true equilibrium state. Our adoption of the latter form of blend preparation was cautioned by the highly polar nature of the nitrile unit and the possible trapping of ternary effects on solvent evaporation[21]. The remarks which follow are unaffected by the discrepancies between the two data sets and, in any case, pragmatically we offer our values as characteristic of the system as prepared.

The effect of the α-methyl group may be examined in the context of other $B_{i\text{-}j}$ values already established[11,15,22] and which are collected in table 3. Small values seem to characterize contacting units which differ only by this substituent, i.e. styrene-α-methyl styrene (S-MS), methyl methacrylate-methyl acrylate (MMA-MA), ethyl methacrylate-ethyl acrylate (EMA-EA), and a relatively minor change in the S-AN interaction is evident when styrene is replaced by MS[11]. On the other hand there is a substantial effect on replacement of the α-hydrogen on the nitrile backbone with methyl. The values of $B_{S\text{-}MAN}$ and $B_{MMA\text{-}MAN}$ obtained imply that these contacts are less unfavourable than the analagous contacts with AN.

Table 3 Some Collected Values of $B_{i\text{-}j}$

i-j	$B_{i\text{-}j}$ / Jcm^{-3}	Ref
S-MS	0.1	23
MMA-MA	1.2	15
EMA-EA	0.8	15
MS-AN	22.3	11
S-AN	22.8	11
S-MAN	6.6	this work
MMA-AN	13.3	11
MMA-MAN	2.9	this work

Table 4 Dispersive (d), polar (p) and H-bonding (h) components of the solubility parameter (δ / J$^{0.5}$ cm$^{-1.5}$)

Monomer	δ_d	δ_p	δ_h
S	18.1	1.0	0
MMA	16.5	5.7	9.0
AN	17.4	24.6	7.5
MAN	16.4	17.2	6.3

Although the first order approximation assumes $B_{i\text{-}j}$ to characterise uniquely enthalpic effects, it has been pointed out[15] that they could also reflect contributions from other (entropic/free volume) effects which are not quantified by the combinatorial term in the Flory-Huggins expression. Free volume and packing are related to the glass transition temperature but here, since the Tgs of AN and MAN homopolymers and copolymers are similar, it would not appear logical to ascribe the differences above to this origin and some other rationale should be sought. The experimental findings also contradict the concept of AN miscibility being driven, or part-driven, by H-bonding via the 'acidic' α-hydrogen. If this were the case then $B_{MMA\text{-}AN}$ might reasonably be expected to be less than $B_{MMA\text{-}MAN}$ since the former would be deemed to contain a (favourable) H-bonding component involving the ester function.

Although spectroscopic evidence for a possible weak H-bond interaction in low molecular weight model nitrile compounds was obtained, none was detected in polymer mixtures[23]. This, and the $B_{i\text{-}j}$ data above, suggests that such a picture is inappropriate. The explanation which we favour for the relative values of $B_{MMA\text{-}AN}$ and $B_{MMA\text{-}MAN}$ is quite straightforward and simply amounts to a 'dilution' of the the polar nitrile function contact area presented by the MAN unit compared with an AN unit. A semi-quantitative illustration of this can be drawn from the relative magnitudes of the polar contribution (δ_p) to the solubility parameter and table 4 shows calculated[18,24] values for the four repeat units involved here. The disparity between δ_p values in poly(nitrile)/PMMA mixtures is reduced by α-methyl substitution, and presumably a parallel advantage is retained in mixtures with styrene-nitrile copolymers. Interestingly, the nitrile δ_h values indicate similar (and minor) contributions from H-bonding and reinforces the idea that this effect is unimportant.

The concept of sub-dividing δ-parameters into different contributions and the idea that experimental B_{ij} values may similarly include contributions from more specific interactions than just simple dispersive forces can be brought together in a more formal sense. Since $B_{i\text{-}j} = (\delta_i - \delta_j)^2$ it follows, for example, that equation (3) may be reexpressed as

$$B_{crit} = \{\delta_A - [y\delta_B + (1-y)\delta_C]\}^2 \tag{5}$$

The terms within the square brackets give the solubility parameter (δ^*) of the copolymer as a function of volume fraction y (following directly the single liquid approximation of Scott[25]), and miscibility should occur when $(\delta_A - \delta^*)^2 \leq B_{crit}$ (quantifying the well-known solubility parameter matching concept[17,26,27]). An *a priori* prediction of the extent of miscibility is, in principle, possible from solubility parameter data; in practice the variability found in tabulated data, and the differences between various group additivity approaches[17,18,28,29], make this less than reliable. However the solubility parameter matching concept does provide a useful perspective as to the behaviour of the present system. The dispersive, polar and H-bonding contributions to the solubility parameter of S-MAN ($\delta^*_{d,p,h}$) match the corresponding contributions to δ_{PMMA} at volume fractions 0.05, 0.7 and 0.09 respectively. From table 2, miscibility occurs in the range $0.47 < y < 0.84$ and, although neither the dispersive nor the H-bonding components 'match' in this range, the polar components (and coincidentally the overall solubility parameters) do. The implication of this is that dispersive and H-bonding effects play a minor rôle in this system.

This picture contrasts with that given by Goh and his coworkers[20] who employ the "dispersive forces plus H-bonding" formalism of Painter and Coleman[17,26] to describe the miscibility of PMMA in S-MAN copolymers. We believe this approach has dubious merit here. Hydrogen-bonding is an extremely specific, and spectroscopically identifiable, contribution to mixing thermodynamics which does not have an obvious role in the present systems. The concept of the global minimisation of contact interactions as expressed through equation (1) seems a perfectly adequate description, though it must be admitted that the forces involved here are more polar than dispersive as is required by the original concepts of mean field theory[6,]

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