BLENDS OF POLY(α-METHYLSTYRENE-*stat*-ACRYLONITRILE) WITH POLY(ALKYL ACRYLATE)S, POLY(ALKYL METHACRYLATE)S, POLY(DI-ALKYL ITACONATE)S AND ALKYL METHACRYLATE COPOLYMERS

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Abstract—The miscibility behaviour of the copolymer poly(α-methylstyrene-*stat*-acrylonitrile) (MSAN) with poly(alkyl acrylate)s, poly(alkyl methacrylate)s and poly(dialkyl itaconate)s has been investigated, where the alkyl groups were methyl, ethyl, n-propyl and n-butyl. Only in the poly(alkyl methacrylate) series were miscible blends obtained; no miscible systems were found for mixtures of MSAN with the other two sets of polymers. "Miscibility windows" were established for the MSAN–poly(alkyl methacrylate) blends and lower critical solution temperatures were also measured. From a knowledge of the phase boundaries, segmental interaction energy density parameters (B_{ij}) were calculated and used to make predictions about various copolymer–copolymer blends based on the appropriate monomers. These predictions were tested for blends of poly(α-methylstyrene-*stat*-acrylonitrile) and poly(methyl methacrylate-*stat*-acrylonitrile) and found to be very satisfactory.

INTRODUCTION

The existence of a so-called "miscibility window" in binary blends of some homopolymer/copolymer and copolymer/copolymer combinations is now well documented [1]. Several of these studies have shown that if the phase behaviour in these systems is established, the segmental interaction parameter (χ_{ij}) or alternatively the interaction energy density parameter (B_{ij}) may be derived and that these can then be used to predict the miscibility/immiscibility behaviour in other polymer mixtures [2]. Here $\chi_{ij} = (B_{ij}V_{ref}/RT)$ where V_{ref} is a reference volume normally chosen to be the approximate molar volume of all the monomer units considered. It has been observed that, in systems where "miscibility windows" have been located, one of the copolymers is constructed from dissimilar comonomer pairs, i.e. those with a large repulsive value of B_{ij}. Typical of these copolymers are poly(styrene-*stat*-acrylonitrile) (SAN) or poly-(butadiene-*stat*-acrylonitrile) (BAN) for which the B_{ij} values are 22.8 and 28.8 J cm⁻³ respectively [3, 4], and one or other of these are one of the components in a large number of miscible binary blends.

The reason for this can be understood from inspection of equation (1) which has been derived on the basis of the mean field theory [2(a)] and expresses the overall interaction parameter for the blend of two copolymers (A_xB_{1-x}) and (C_yD_{1-y}) as

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

Here x and y are the comonomer compositions expressed as the segment volume fractions. The equation shows that the intramolecular interaction parameters, B_{AB} and B_{CD}, are associated with negative terms and so if these are large and positive values, the overall B_{blend} may be negative and favour miscibility.

Conditions for miscibility are then

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

where V_i is the molar volume of polymer "i" and is related to r_i the degree of polymerization by $r_i = (V_i/V_{ref})$.

Only a few limited reports on the use of the copolymer poly(α-methylstyrene-*stat*-acrylonitrile) (MSAN) as a suitable blend component have appeared. Paul, Barlow and coworkers [5, 6] showed that a commercial MSAN sample with 30 wt% AN was miscible with poly(methyl methacrylate) (PMMA), while Goh and Siow [7] found that this sample was also miscible with copolymers of MMA with ethyl or butyl methacrylate. A more extensive study by Suess et al. [8] located a miscibility window for PMMA mixed with MSAN copolymers, whose compositions ranged from 18 to 42 wt% AN, when 40/60 blends were examined. A recent study [9] demonstrated that miscible blends of MSAN and chlorinated polyethylene could be prepared and that an ellipse of miscibility could be defined to encompass the miscible blends on a composition diagram.

This report presents an extended investigation of the miscibility of MSAN copolymers, ranging in composition from 8.6 to 47 vol% AN, with poly(alkyl acrylate)s, poly(alkyl methacrylate)s, poly(dialkyl itaconate)s and a second copolymer poly(methyl methacrylate-*stat*-acrylonitrile) (MMA–AN).

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Table 1. Characteristics of the MSAN copolymers used
for blend preparation

Sample code*	Volume fraction AN	$10^4 \bar{M}_n$	T_g (K)
MSAN 10	0.086	2.79	432
MSAN 12	0.109	3.65	431
MSAN 15	0.135	1.00	403
MSAN 16	0.144	1.25	401
MSAN 17	0.149	1.59	401
MSAN 20	0.164	1.56	400
MSAN 24	0.208	2.60	399
MSAN 27	0.243	4.87	398
MSAN 28	0.253	2.44	398
MSAN 33	0.290	7.88	397
MSAN 37	0.340	2.80	390
MSAN 46	0.423	6.07	388
MSAN 52	0.468	5.52	386

*The number in the sample code is the approximate wt%
AN in the sample.

EXPERIMENTAL PROCEDURES

Sample preparation

Copolymers MSAN were prepared and characterized as described elsewhere [9]. The compositions, glass transition temperatures (T_g) and the molecular weights of the samples used are listed in Table 1. These comonomers have a strong tendency to alternate making preparation of samples with either very low or very high AN contents difficult. The majority of samples were prepared by radical initiation in the bulk except for MSAN 10 and MSAN 12 which were synthesized by emulsion polymerization. Poly(methyl methacrylate-*stat*-acrylonitrile) copolymers were supplied by D. Lath [10] and the details of the sample characterization are shown in Table 2 together with the poly(alkyl methacrylate)s which were commercial samples. The poly(alkyl acrylate)s were also commercial samples but the poly(dialkyl itaconate)s were synthesized as described previously [11].

Blend preparation

All binary blends studied were (50/50) by weight and were prepared either by co-precipitation or by film casting from a common solvent. Methyl ethyl ketone (MEK) and tetra-hydrofuran were the favoured solvents and methanol or ethanol were the non-solvents. Co-precipitation was the preferred method of preparation when possible as it tends to reduce the effects of solvents often experienced when film casting is used. This procedure was used for the alkyl methacrylate blends but was not easily achieved with the acrylate or itaconate blends. All blends were vacuum dried for at least two days before use.

Characterization

T_gs were measured using a Perkin–Elmer DSC4 under a N_2 atmosphere and with a heating rate of 20 K min^{-1}. The T_g was taken as the extrapolated onset of the baseline shift and each value was the average of at least three successive scans. When blends were examined for which the difference between the component T_g values was less than 20 K, the physical ageing technique introduced by Bosma et al. [12] was used. As the criterion employed to establish miscibility

in these binary systems was the presence of a single T_g, ageing of these blends at a few degrees below the lower T_g gave a single enthalpy relaxation peak for a miscible blend and double enthalpy relaxation peaks when the blend was immiscible. Ageing times ranged from 15 to 80 hr. Number-average molecular weights, $\bar{M}_n$, were measured using a Knauer membrane osmometer with MEK as solvent.

Lower critical solution temperatures (LCST)

Phase separation of the blends on raising the temperature was observed using a Linkham PR 600 hot stage and microscope. The miscible blends were prepared for examination as clear films, and heated slowly at a constant rate. The onset of turbidity was taken to be the LCST of the blend.

RESULTS

Poly(alkyl methacrylate)s

(a) Blends of PMMA and MSAN were prepared as fine powders by coprecipitation from MEK solutions into methanol. As the difference between the T_g of PMMA and those of the MSAN copolymers was less than 20 K, the blends were aged at ~ 5 K below the lower T_g for periods of up to 80 hr. The samples were then quenched and the DSC scan, measured following this procedure, then showed one enthalpy relaxation peak when the system was miscible or two if immiscible. The data are represented schematically in Fig. 1(a) where the miscibility window is clearly delineated. It is predominantly in the low AN content composition region with no miscibility above 43 vol% AN in the copolymer. While there was no miscibility in blends of poly(α-methylstyrene) and PMMA using the method of preparation outlined above, it has been shown that a miscible blend of this pair can be forced by, for example, freeze-drying the mixture from benzene solution [13]. No such miscibility is observed when PMMA is mixed with polyacrylonitrile. In the present study, it is more realistic to regard the homopolymers as an immiscible pair but it does provide a reason for the asymmetry of the "window" on the composition scale. Because of the experimental difficulties in synthesizing MSAN copolymers with very low AN contents, the lower miscibility boundary had to be approximated and was assumed to lie midway between the miscible blend containing MSAN (8.6 vol% AN) and pure poly(α-methylstyrene). The upper boundary was treated in a similar fashion. While this procedure may introduce an error in the estimation of B_{ij}, the fact that these derived values can predict the miscibility of other systems with some accuracy (see for example the copolymer/copolymer blends in a later section) suggests that these errors may be small.

The segmental interaction energy densities calculated from these boundary conditions were scaled

Table 2. Characteristics of MMA–AN copolymers and poly(alkyl methacrylate)s used to blend with
MSAN

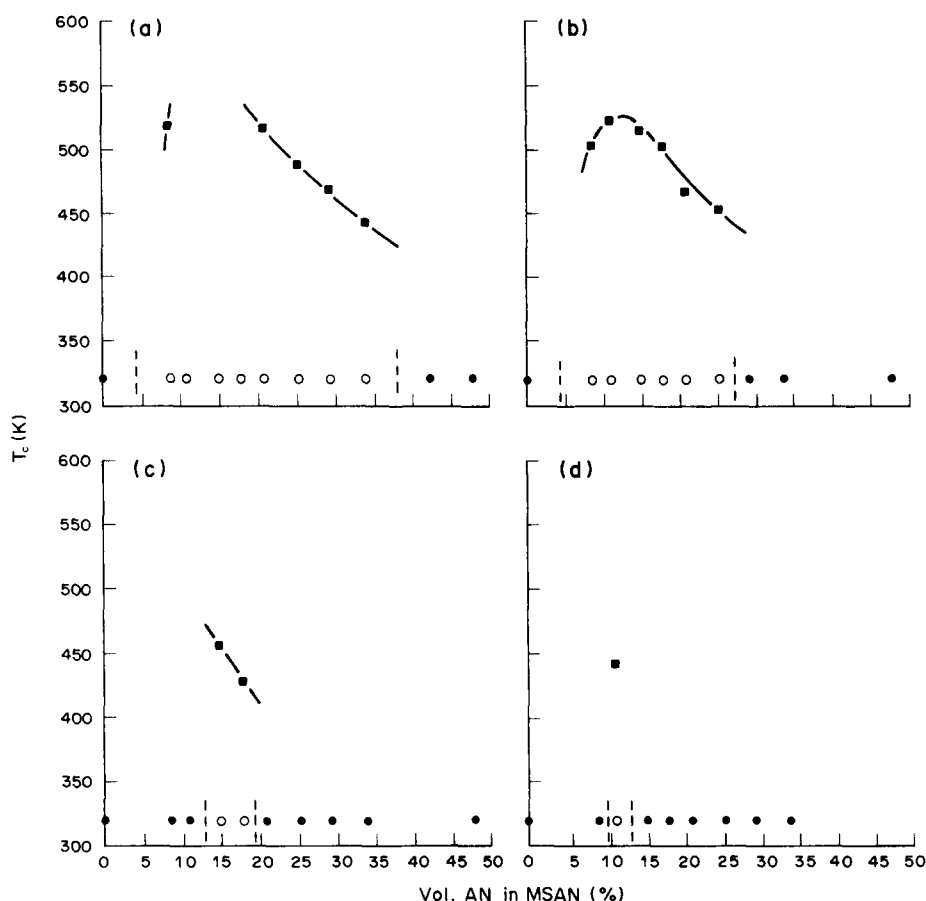| (MMA–AN) Sample wt% AN	$10^5 \bar{M}_n$	T_g (K)	Poly(alkyl methacrylate)	$10^5 \bar{M}_n$	T_g (K)
2.7	4.16	385	Methyl	1.54	384
10.3	5.32	369	Ethyl	3.40	338
20.8	5.27	363	Propyl	2.75	311
33.4	2.17	358	n-Butyl	3.20	291
48.8	1.85	353			

Fig. 1. "Miscibility windows" and LCSTs for blends of MSAN with poly(alkyl methacrylate)s: (a) poly(methyl methacrylate), (b) poly(ethyl methacrylate), (c) poly(propyl methacrylate), (d) poly(butyl methacrylate), miscible blends (○), immiscible blends (●) and LCST (■).

using the value derived elsewhere [9] for the acrylonitrile–methyl methacrylate interaction $B_{AN-MMA} = 13.3\,J\,cm^{-3}$. A value for B_{crit} was estimated from equation (2) using the average molar volumes of the copolymer samples closest to the miscibility boundaries. The estimated B_{ij} values for these systems are listed in Table 3.

This analysis leads to an estimated value for the acrylonitrile–α-methylstyrene interaction of $B_{AN-MS} = 22.3\,J\,cm^{-3}$. It is large and close to that for the acrylonitrile–styrene interaction, viz. $B_{AN-S} = 22.8\,J\,cm^{-3}$, which is not unreasonable as the heat of mixing of polystyrene and poly(α-methylstyrene) is small and close to being athermal [14]. Thus their interaction with AN is likely to be similar. The miscibility of these blends is recorded at ambient temperatures but the thermal stability can be measured by locating the LCST, if present, as the blends are heated. These values are also plotted in

Table 3. Segmental interaction parameters derived from the phase boundaries of MSAN/poly(alkyl methacrylate) blends

ij	B_{ij} (J cm^{-3})	ij	B_{ij} (J cm^{-3})
AN–MMA	13.3	MS–MMA	0.437
AN–EMA	15.6	MS–EMA	0.324
AN–PMA	15.8	MS–PMA	0.681
AN–BMA	16.3	MS–BMA	0.534

Fig. 1(a) but blends prepared from MSAN samples with compositions between 10.0 and 16.0 vol% AN did not phase separate on heating up to temperatures where decomposition began. These blends are consequently the most miscible and the data recorded in Fig. 1(a) are comparable to those reported by Suess et al. [8] who used film clarity and opacity as an indication of miscibility. They did not, however, derive any interaction parameters from their measurements.

(b) Blends of MSAN with poly(ethyl methacrylate) (PEMA), poly(n-propyl methacrylate) (PPMA), and poly(n-butyl methacrylate) (PBMA) were prepared by co-precipitation and their room temperature miscibility established on the basis of the existence of either one or two T_gs. No ageing of these blends was required as the component T_gs are sufficiently different. The LCSTs were also established for the miscible blends and the data are summarized in Fig. 1(b), (c) and (d). It can be seen that there is a narrowing of the miscibility window as the length of the side chain increases until for MSAN/PBMA only the sample MSAN 17 was miscible with PBMA. This change in miscibility is also evident in the LCST values, i.e. for blends with MSAN 17, the LCST decreases progressively from a very miscible system with PMMA, where no LCST could be detected, down to an LCST = 443 K for the PBMA blend. Naturally,

this change should be reflected in the values of B_{ij} calculated for each system which are listed in Table 3; they show an increase in the acrylonitrile–alkyl methacrylate interaction parameters with increasing side chain length but no discernible trend in the α-methyl-styrene–alkyl methacrylate values. However, the latter are smaller, suggesting these segments show a greater tendency towards miscibility and the lack of an obvious progression in the values may be a consequence of the uncertainties in establishing the miscibility boundaries.

Blends of MSAN with poly(alkyl acrylate)s and poly-(dialkyl itaconate)s

Blends were prepared (by casting from MEK solutions) from the range of MSAN copolymers available with the methyl, ethyl, propyl and butyl esters of the acrylates and itaconates but in no case was a miscible blend observed. All the mixtures exhibited two T_gs, equivalent to the parent components of the blends. These observations agree with limited data reported by Goh et al. [6] for poly(alkyl acrylate)s mixed with one sample of MSAN containing 30 wt% AN, which were also immiscible.

Blends of two copolymers

Poly(methyl methacrylate-stat-acrylonitrile) (MMA–AN) is known to form a range of miscible blends with SAN [9] and, while SAN and MSAN are themselves only miscible in a restricted composition range [15], it is nevertheless likely that MMA–AN and MSAN can also form miscible blends. The miscibility behaviour of these and related copolymer blends can be predicted from a knowledge of the appropriate B_{ij} values, and for blends of copolymers with a common monomer equation (1) reduces to

$$B_{\text{blend}} = x^2 B_{AB} + xy(B_{AC} - B_{AB} - B_{BC}) + y^2 B_{BC}. \quad (3)$$

Solution of equation (3) requires knowledge of only three interaction parameters and for blends of MMA–AN and MSAN the miscibility map can be calculated using $B_{\text{MS-AN}}$, $B_{\text{MMA-AN}}$ and $B_{\text{MS-MMA}}$, all of which are known. These three interaction parameters will predict all the miscibility maps for different copolymer combinations involving these three monomers, i.e. blends of (MSAN)/(MMA–MS) or (MMA–AN)/(MMA–MS). Similarly three such copolymer pairs are possible for each of the other monomers EMA, PMA and BMA in combination with MS and AN. As all the appropriate values of B_{ij} have been estimated here, the theoretical miscibility maps for all 12 possible blend combinations are shown in Fig. 2 where the shaded area represents the miscible region and the rest corresponds to areas of immiscibility. These diagrams are calculated for $B_{\text{crit}} = 0.068$ which is the best average representation of molecular weight for the samples used here.

Some general trends are obvious. In each set of three blends, i.e. each row in Fig. 2 corresponding to the change in alkyl methacrylate used in the copolymers, the copolymer combinations in which the alkyl methacrylate is the common monomer (third column in Fig. 2) are essentially immiscible displaying only very small regions of miscibility. All the remaining groups show substantial areas of miscibility but these

decrease as the length of the ester side chain increases. This finding is consistent with the corresponding narrowing of the miscibility window with increasing length of the n-alkyl side chain.

For both the MMA and EMA containing blends, the miscibility ranges depicted in columns one and two are derived for infinitely large molecular weights. When the blends containing PMA and EMA are considered, the miscibility ranges are now strongly dependent on the component molecular weight and shrink as the molecular weight increases until they disappear for very long chains. In the case of the blends represented in the third column, the limited miscibility is only evident for finite molecular weights.

The predictions were tested for one copolymer blend combination, (MSAN)/(MMA–AN), and the data are shown in Fig. 3. The open circles represent miscible blends and the closed circles the immiscible ones; the agreement is remarkably good and suggests that the other predicted miscibility maps will be reasonably accurate. This predictive aspect has also been demonstrated for other blend combinations and shown to be quite reliable [16].

DISCUSSION

Copolymers of MSAN form miscible blends with poly(alkyl methacrylate)s over restricted composition ranges when the alkyl side chain is no longer than an n-butyl group; no such miscibility could be detected when blended with the structurally similar acrylates and itaconates. This result was somewhat unexpected and it is difficult to find a satisfactory explanation for the observations. It has been suggested that, in copolymer/homopolymer blends, the "miscibility window" may represent a matching of the solubility parameters (δ) for the two components and, while it is recognized that the calculation of δ for polymers can be unreliable, internally consistent group additivity schemes [17, 18] can be used to estimate these quantities for comparison purposes. Use of several of these schemes always produced the same conclusion, that whereas the δ values increased in the order methacrylates < acrylates < itaconates, there was a better match of δ parameters for the latter two groups with the MSAN copolymers than with the miscible methacrylates. If the δ values are calculated using the carefully optimized group additivity scheme proposed by Coleman et al. [18], then the range for the MSAN copolymers lies between $\delta = 9.0$–13.8 (cal cm^{-3})$^{0.5}$. The corresponding values for methyl to n-butyl for the alkyl methacrylates are $\delta = 9.0$, 8.9, 8.8 and 8.7 (cal cm^{-3})$^{0.5}$ for the alkyl acrylates, $\delta = 9.6$, 9.3, 9.1 and 8.9 (cal cm^{-3})$^{0.5}$, and for the dialkyl itaconates, $\delta = 9.9$, 9.5, 9.2 and 9.0 (cal cm^{-3})$^{0.5}$. Even if possible specific interactions are allowed for, this approach appears not to explain why there are differences in miscibility among these structurally related groups. It should be noted that the alkyl acrylate and itaconate blends were film cast from MEK as satisfactory co-precipitation samples could not be prepared. Thus the miscibility could be affected by the solvent used to prepare the film, and this possibility may be worth exploring. Differences in free volume is another possible factor that may
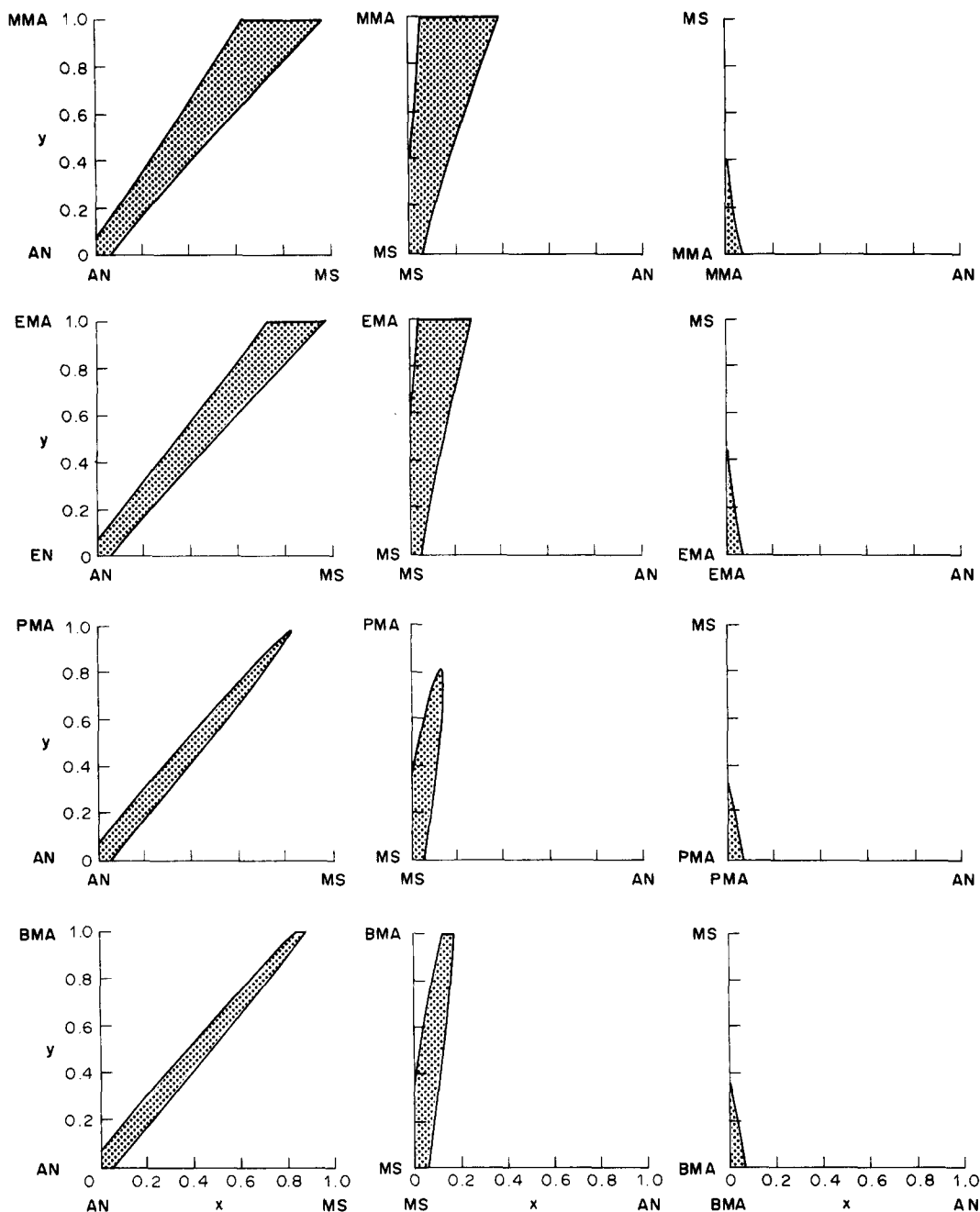
Fig. 2. Miscibility maps predicted for various copolymer blend combinations, involving copolymers prepared from the monomers, acrylonitrile (AN), α-methylstyrene (MS), methyl methacrylate (MMA), ethyl methacrylate (EMA), propyl methacrylate (PMA) and butyl methacrylate (BMA). The maps are plotted in terms of the volume fractions, x and y of monomers in the copolymer using the interaction parameters quoted in the text. In the left hand column, x is the volume fraction of MS and y the volume fraction of the alkyl methacrylate. In the centre column, x is the AN content and y that for the alkyl methacrylate; in the right hand column, x is the AN content and y is the MS composition.

account for this change in miscibility but at present we have insufficient data to test this hypothesis.

Clearly the appropriate values of the B_{ij} are unfavourable for the alkyl acrylates and alkyl itaconates and work is now in progress to attempt to estimate these values. The efficacy of these interaction parameters in the prediction of miscibility in new blend compositions is demonstrated in Fig. 2 and makes

their estimation worthwhile but the need to have these B_{ij} (or χ_{ij}) values scaled to a common reference point is essential when making these predictions. Thus the parameters used should be internally consistent in this respect.

A recent study by Goh et al. [19] on the miscibility of poly(p-methylstyrene-stat-acrylonitrile) with poly(alkyl methacrylate)s makes an interesting
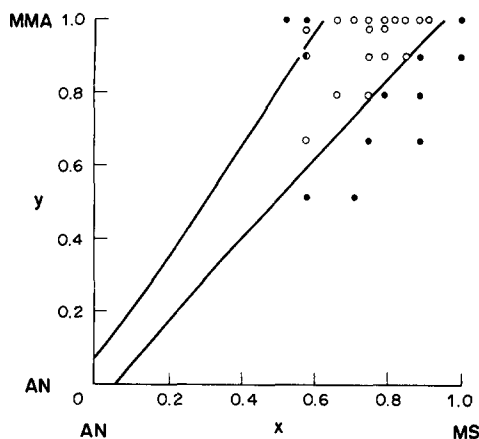
Fig. 3. Experimental confirmation of the predicted miscibility map for blends of (MSAN) with (MMA–AN). Miscible blends (O), partially miscible (◑), immiscible (●).

comparison with the present work. The miscibility windows are of comparable width but the phase stability as reflected in the LCST values is better in the p-methyl substituted copolymers. However, the values of χ_{ij} obtained by Goh *et al.* which are common to the study here, are smaller than ours but show similar trends with the length of the methacrylate side chain.

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