Miscibility of blends of polymers based on styrene, acrylonitrile and methyl methacrylate

M. Nishimoto*, H. Keskkula and D. R. Paul†
Department of Chemical Engineering and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712, USA
(Received 22 August 1988; revised 21 October 1988; accepted 21 October 1988)

Miscibility of binary blends of homopolymers, copolymers and terpolymers based on styrene (S), methyl methacrylate (M) and acrylonitrile (AN) units was examined by optical clarity and lower critical solution temperature (LCST) behaviour. The blends were systematically classified into six groups according to the number of the monomers included. In each system, miscibility areas were calculated as a function of the monomer composition in the polymers using a binary interaction model and interaction parameters deduced from information available in the literature. Polymer pairs which were predicted to have some zone of miscibility are as follows: PMMA–SAN, PMMA–SMAN, SAN–MAN, SAN–SM, SAN–SMAN, MAN–SMAN, SMAN–SMAN. Experimental observations correspond well to the calculated miscibility zones. All miscible pairs show LCST behaviour. Cloud point curves for SAN–MAN blends and SAN–SMAN blends were determined as a function of AN wt% in the SAN copolymer.

(Keywords: blends; miscibility; styrene; methyl methacrylate; acrylonitrile)

INTRODUCTION

Over the years there has been a strong interest in miscibility of blends of copolymers with other polymers[1–27]. Simple models have emerged[28–36] that account for the important concept that interactions between units within copolymers may promote their miscibility. At the expense of additional complexity, these models have been conceptually extended to allow for any effects of sequence distribution within copolymer chains[33,37–39]. The simple models provide a useful framework for designing blends with controlled phase behaviour; however, an important step is quantification of the various binary interaction parameters needed.

A significant body of literature has become available on blends involving polymers based on the commodity monomers styrene (S), methyl methacrylate (M) and acrylonitrile (AN) and especially their copolymers[42–54]. The purpose here is to present some recent observations on blends involving certain homopolymers, copolymers and terpolymers made from these three monomers. The experimental results will be presented within the context of a simple binary interaction model for which the needed parameters have been estimated using various information in the literature. A main point that will emerge is the value of such a model for organizing a search for the many possible copolymer and terpolymer compositions that form miscible pairs.

BACKGROUND

The most simple, yet realistic, estimate of the free energy of mixing two polymers **A** and **B** (per unit volume of mixing) is provided by the Flory-Huggins theory[55]:

$$\Delta G_{\text{mix}} = RT\left(\frac{\phi_A \ln \phi_A}{\tilde{V}_A} + \frac{\phi_B \ln \phi_B}{\tilde{V}_B}\right) + B\phi_A\phi_B \qquad (1)$$

where ϕ_i is the volume fraction and $\tilde{V}_i$ is the molar volume of component **i**. In this model, the heat of mixing contribution is simply a van Laar-type expression characterized by an interaction energy density B. The combinatorial entropy term is frequently associated with a lattice model derivation and equation (1) is often expressed in terms of a reference volume V_r that stems from the notion of the volume of a lattice element[2]

$$\Delta G_{\text{mix}} = \frac{RT}{V_r}\left(\frac{\phi_A \ln \phi_A}{N_A} + \frac{\phi_B \ln \phi_B}{N_B} + \chi\phi_A\phi_B\right) \qquad (2)$$

where

$$N_A = \tilde{V}_A/V_r \quad \text{and} \quad N_B = \tilde{V}_B/V_r \qquad (3)$$

$$\chi = BV_r/RT \qquad (4)$$

The introduction of V_r is not necessary and does not offer any real convenience[2]. Its misuse is the source of considerable confusion in the comparison of interaction parameters from one situation to another[56,57] which deserves comment here since this problem was encountered repeatedly while extracting values from the literature for use in this paper. Many papers in this field begin with equation (2) (without ever explicitly stating the value of V_r to be used) and a statement that N_A and N_B are the degrees of polymerization of the two polymers. If degree of polymerization is taken literally as the number of monomers per chain, then as seen in equation (3), N_A and N_B can only be identified as such when the molar volumes of the monomers comprising polymers A and B are identical and V_r is taken to be this value. In reality, these values may differ considerably, e.g. the volume of a styrene unit is more than twice that of acrylonitrile,

---

* Permanent address: Asahi Chemical Industry Co. Ltd, 3-13 Ushio-dori, Kurashiki-shi 712, Japan
† To whom correspondence should be addressed

0032-3861/89/071279–08$03.00

and such issues become critical when we try to quantify interaction parameters and compare values from different techniques or sources. While the use of χ is very traditional in the polymer field, it must be remembered that the arbitrary reference volume V_r needs to be specified in order for χ values to have quantitative meaning (see equation (3)) and that, in general, both N_A and N_B cannot be equated to the degrees of polymerization of the components. Unfortunately, many papers reporting useful and carefully executed studies fail to mention what reference volume was used or, worse yet, fail to recognize that its specification is arbitrary. Simply stating that the mer volume was used is not adequate since in blends there must be two or more mers but there can only be one V_r. More care must be exercised in this area if quantitative use is going to be made of the wealth of information about interactions that is becoming available.

Owing to the relatively small contribution of the combinatorial entropy in equation (1) (because each $\tilde{V}_i$ is large), the value or sign of B (or χ) is the key to satisfying the thermodynamic conditions on ΔG_m required for miscibility. When **A** and **B** are multicomponent polymers, the net interaction parameter for their blends can be expressed in terms of B_{ij} parameters describing interactions between various **i** and **j** units in these polymers as described previously[28,56]. Using this binary interaction scheme, many different cases can be treated. Here, we begin with the general situation where **A** and **B** are terpolymers, whose content of monomers **1**, **2** and **3** are expressed in terms of volume fractions using ϕ_i' for **A** and ϕ_i'' for **B**. The interaction energy density for this case can be written as

$$B = B_{12}(\phi_1' - \phi_1'')(\phi_2'' - \phi_2') + B_{13}(\phi_1' - \phi_1'')(\phi_3'' - \phi_3') + B_{23}(\phi_2' - \phi_2'')(\phi_3'' - \phi_3') \tag{5}$$

The special cases involving various homopolymers and copolymers of interest later can be deduced from this general result.

Table 1 summarizes quantitative values, deduced from experimental data[58], for the three B_{ij} parameters appearing in equation (5) for the styrene (S)–methyl methacrylate (M)–acrylonitrile (AN) system. These parameters are all positive indicating endothermic mixing for each binary homopolymer pair; however, for certain copolymer and terpolymer situations the interaction energy, B, in equation (5) can be negative. We will use these parameters to compute these regions of exothermic mixing for comparison with miscibility observations on blends. The actual composition regions for blend miscibility will be somewhat greater than those for exothermic mixing, i.e. $B<0$, owing to the contributions from combinatorial entropy of mixing; however, since the polymers employed here have quite high molecular weights typical of commercial polymers, this effect is in general not very great. The parameters in *Table 1* have been assumed to be independent of temperature and composition since not enough experimental data of sufficient quality are available to accurately assess these second order effects; however, such information would be needed to compute phase diagrams showing LCST behaviour for comparison with blend results.

Table 1 Binary interaction parameters for styrene, methyl methacrylate and acrylonitrile units

Polymer pair	B_{ij} (cal cm^{-3})
S–AN	6.74[a]
S–MMA	0.181[b]
MMA–AN	4.11[a]

[a] Based on phase behaviour at ambient temperature
[b] At 30°C (see Fukuda *et al.*[63])

EXPERIMENTAL

In this work, the polymers obtained from various industrial sources described in *Table 2* were used as received. Experimental terpolymers and the methyl methacrylate–acrylonitrile copolymers were synthesized by solution polymerization in a coil reactor to reduce composition drift. The resulting polymers were recovered by standard methods and their compositions were determined by nitrogen and oxygen analysis. These data and molecular weights or solution viscosities are also listed in *Table 2*. Films of polymer blends were prepared by casting from 5% solutions of methylene chloride or methyl ethyl ketone with an initial slow drying at room temperature. To assure complete removal of the solvent, final drying was carried out for 4 days at 130°C (above the T_g of each component) in a vacuum oven. If cloudy films resulted, the solution casting temperature and the solvent were varied to see if other conditions would produce clear films. In general, methyl ethyl ketone gave clearer films in the cases of border-line miscibility. There was no indication that drying changed the state of mixing for the solvent cast blends; however, the phase behaviour reported here can be taken as representative of that at 130°C.

The determination of cloud points indicative of phase separation on heating of the miscible blends was carried out using a previously described method[42]. When the cloud point occurs at low temperature, heating rate effects can be significant. In these cases, samples were held at various temperatures near the expected cloud point for 10 min each to observe whether a slow phase separation occurred or not. Accurate cloud points were obtained in this way.

RESULTS AND DISCUSSION

The experimental results reported here consist of the determination of miscibility for binary blends based on optical appearance and phase separation on heating caused by LCST behaviour. These observations are compared with predictions made using the scheme outlined above. The results are organized in a hierarchy based on the number of monomers in the polymers blended.

Homopolymer–homopolymer blends

For pairs of homopolymers, equation (5) reduces to $B = B_{ij}$, so miscibility is governed simply by the pair interaction parameter. Considerable evidence is available to assert that in the high molecular weight limit homopolymers based on styrene, methyl methacrylate and acrylonitrile are not miscible with each other. This is reinforced by the value of the interaction parameters for each binary combination (see *Table 1*) estimated from various literature sources. Mixing is endothermic in each case. The most unfavourable interaction is for the

Table 2 Polymers used in this work

Polymer	Designation	Source and description	Molecular weight Solution Viscosity[a]
Polystyrene	PS	Dow, Styron 685D	$\bar{M}_w = 300\,000$ $\bar{M}_n = 132\,000$
Poly(methyl methacrylate)	PMMA	R&H, Plexiglas V811	$\bar{M}_w = 105\,400$ $\bar{M}_n = 52\,900$
Poly(styrene-co-acrylonitrile)	SAN9.5	Asahi Chemical, 9.5%AN	
Poly(styrene-co-acrylonitrile)	SAN14.7	Asahi Chemical, 14.7%AN	$\bar{M}_w = 182\,000$ $\bar{M}_n = 83\,000$
Poly(styrene-co-acrylonitrile)	SAN19.7	Asahi Chemical, 19.7%AN	
Poly(styrene-co-acrylonitrile)	SAN24.8	Monsanto, 24.8%AN	$\bar{M}_w = 121\,000$ $\bar{M}_n = 62\,400$
Poly(styrene-co-acrylonitrile)	SAN25	Dow, Tyril 1000, 25%AN	$\bar{M}_w = 152\,000$ $\bar{M}_n = 77\,000$
Poly(styrene-co-acrylonitrile)	SAN30	Dow, Tyril 880, 30%AN	$\bar{M}_w = 160\,000$ $\bar{M}_n = 81\,000$
Poly(styrene-co-acrylonitrile)	SAN32.3	Monsanto, 32.3%AN	
Poly(styrene-co-acrylonitrile)	SAN33	Monsanto, 33%AN	$\bar{M}_w = 146\,000$ $\bar{M}_n = 68\,000$
Poly(styrene-co-acrylonitrile)	SAN34	Asahi Chemical, 34%AN	$\bar{M}_w = 145\,000$ $\bar{M}_n = 73\,000$ Sol. Vis. = 12.0
Poly(styrene-co-acrylonitrile)	SAN40	Asahi Chemical, 40%AN	$\bar{M}_w = 122\,000$ $\bar{M}_n = 61\,000$ Sol. Vis. = 9.2
Poly(methyl methacrylate-co-acrylonitrile)	MAN12.3	Asahi Chemical, 12.3%AN	Sol. Vis. = 3.4
Poly(methyl methacrylate-co-acrylonitrile)	MAN26.4	Asahi Chemical, 26.4%AN	Sol. Vis. = 6.2
Poly(styrene-co-methyl methacrylate-co-acrylonitrile)	SMAN (21.0/57.4/21.6)	Asahi Chemical, 57.4%M, 21.6%AN	Sol. Vis. = 4.7
Poly(styrene-co-methyl methacrylate-co-acrylonitrile)	SMAN (40.0/39.1/20.9)	Asahi Chemical, 39.1%M, 20.9%AN	
Poly(styrene-co-methyl methacrylate-co-acrylonitrile)	SMAN (61.1/19.6/19.3)	Asahi Chemical, 19.6%M, 19.3%AN	Sol. Vis. = 6.8
Poly(styrene-co-methyl methacrylate-co-acrylonitrile)	SMAN (34.1/32.3/33.7)	Asahi Chemical, 32.2%M, 33.7%AN	Sol. Vis. = 5.3
Poly(styrene-co-methyl methacrylate-co-acrylonitrile)	SMAN (42.0/18.5/39.4)	Asahi Chemical, 18.5%M, 39.4%AN	

[a] 10% solution viscosity in methyl ethyl ketone at 25°C

PS–PAN pair while the least unfavourable is for the PS–PMMA pair. In fact, blends of oligomers of styrene and of methyl methacrylate are miscible[59] because the combinatorial entropy contribution to the free energy can overcome the relatively weak unfavourable heat of mixing.

Ternary mixtures of PMMA and PS with a solvent have been extensively studied[60–62]. The interaction parameter shown in *Table 1* for PMMA–PS is an extrapolation to zero solvent content made by Fukuda and coworkers[63].

Homopolymer–copolymer blends

For blends of a copolymer consisting of monomer **1** and **2** with a homopolymer of **3**, equation (5) reduces to the familiar result

$$B = B_{13}\phi'_1 + B_{23}\phi'_2 - B_{12}\phi'_1\phi'_2 \qquad (6)$$

Based on this model, it is clear that B may become negative for a certain range of copolymer compositions even though all B_{ij} are positive. A well documented example of this behaviour is the miscibility of PMMA with SAN copolymer[42–45,49]. Using the copolymer composition limits for this system[42] and the interaction parameter for PMMA–PS mentioned earlier, the B_{ij} values for M–AN and S–AN shown in *Table 1* were computed[58]. These are somewhat larger than estimates made by Cowie and Lath[52,53].

Figure 1 shows for each of the three binary homopolymer–copolymer combinations the net interaction parameter, B, *versus* copolymer composition computed from equation (6) and the information in *Table 1*. The calculations reproduce the expected region of exothermic mixing for SAN blends with PMMA since these results were used to establish the parameters. The other pairs indicate only positive values of B (or immiscibility for high molecular weight) for PS with MAN copolymers and for PAN with SM copolymers. These predictions are consistent with a variety of experimental observations. In this work, 50/50 blends of MAN copolymer containing 3%, 12.3%, 26.4% by weight of AN proved to be immiscible with polystyrene. Based on the calculations in *Figure 2*, PS blends with MAN copolymers with small amounts of AN would have a better possibility for miscibility than any other candidates.

The appearance of a miscibility window for SAN copolymers with PMMA depends on the relative values of the B_{ij} parameters[28,42]. Strong repulsion within the copolymer coupled with weak interactions with the homopolymer favour this behaviour.

Homopolymer–terpolymer blends

For blends of a terpolymer of monomers **1**, **2** and **3** with homopolymer **3**, equation (5) reduces to

$$B = (1 - \phi'_3)[B_{13}\phi'_1 + B_{23}\phi'_2] - B_{12}\phi'_1\phi'_2 \qquad (7)$$

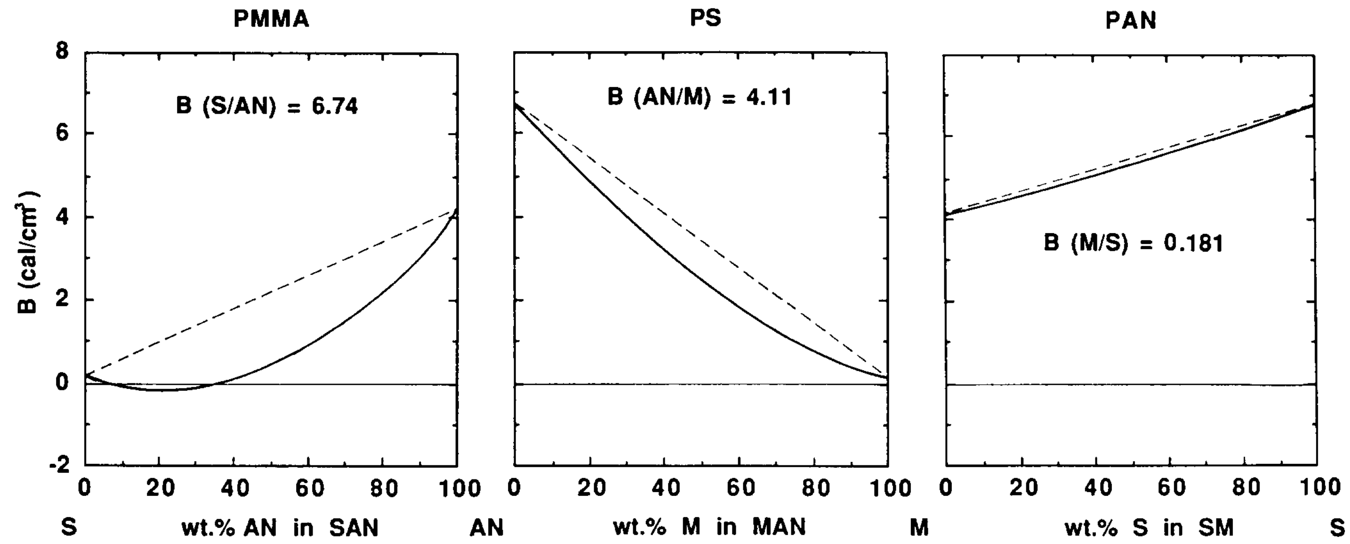

Figure 1 Calculated interaction parameters for blends of homopolymers and copolymers containing S, M, and AN as a function of copolymer composition

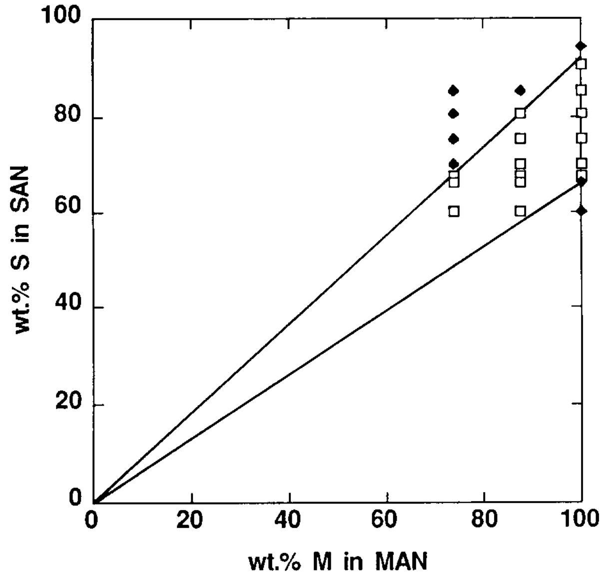

Figure 2 Phase behaviour of blends of SAN copolymers with MAN copolymers. The lines drawn bound the region of compositions where exothermic mixing is predicted. Points indicate experimental observations for blends: (□) miscible, (◆) immiscible

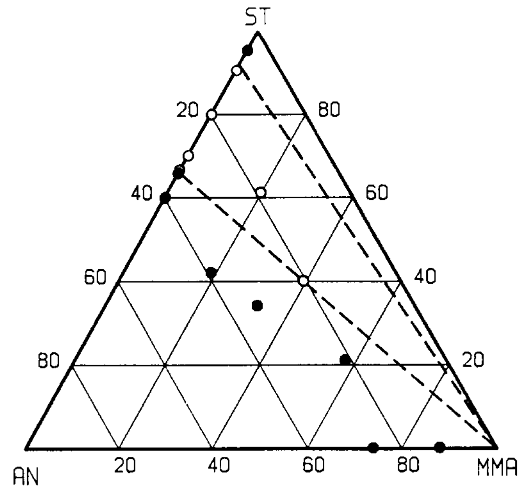

Figure 3 Phase behaviour of blends of SMAN terpolymers with PMMA. Terpolymers with compositions between dashed lines are predicted to mix exothermically with PMMA. Points indicate experimental observations for blends: (○) miscible, (●) immiscible

The consequence of this equation can be made more clear by expressing the content of monomers **1** and **2** in the terpolymer on a basis that excludes monomer **3**, which is common to the homopolymer, using

$$w_1 = 1 - w_2 = \phi'_1/(\phi'_1 + \phi'_2) \qquad (8)$$

With this change of variables, equation (7) becomes

$$B = (1-\phi'_3)^2[B_{13}w_1 + B_{23}w_2 - B_{12}w_1w_2] \qquad (9)$$

The term in the brackets is comparable to the right hand side of equation (6) which makes the following evident. If copolymers of **1** and **2** (i.e. limiting case of $\phi'_3 = 0$) do not have a region of exothermic mixing (miscibility window in the limit of high molecular weight) with homopolymer **3**, then no terpolymer compositions will mix exothermically with homopolymer **3** either. However, if the copolymer does have such a region, there will be a similar region for the terpolymer whose limits will be the same when expressed in terms of w_1 but the magnitude of B will be diminished by the dilution factor $(1-\phi'_3)^2$ as seen in equation (9).

From the above, it is clear that only PMMA should mix exothermically with styrene/methyl methacrylate/acrylonitrile terpolymer. On a triangular composition diagram, this region is defined by the miscibility window on the SAN copolymer boundary and the poly(methyl methacrylate) apex as shown in *Figure 3*. The lines represent the locus of points where $B=0$ as computed from equation (7) using the parameters in *Table 1*. Five terpolymers from *Table 2* were blended with PMMA. Three proved to be immiscible (solid points) while two were found to be miscible (open points). For these few examples, the agreement with the predicted value is excellent. Similar results have been reported recently by Ikawa and Hosoda[51].

Copolymer–copolymer blends

Blends of two different copolymers using monomers **1**, **2** and **3** can be divided into two types. First, there are three limiting cases where each copolymer contains monomers **i** and **j** but the two differ in composition, i.e. $\phi_i' \neq \phi_i''$. Equation (5) reduces to

$$B = B_{ij}(\phi_i' - \phi_i'')^2 \qquad (10)$$

for this situation as shown previously[54]. For copolymers based on the monomers of interest here, all B_{ij} are positive (see *Table 1*) and in the high molecular weight limit there is no miscibility unless the two copolymers are exactly of the same composition so that $B=0$. For finite molecular weights, the small combinatorial entropy term will allow miscibility when there is some finite mismatch of compositions. This mismatch can be estimated from

$$|\phi_i' - \phi_i''| = \sqrt{2\rho RT/B_{ij}M} \qquad (11)$$

when both polymers have the same density, ρ, and molecular weight, M. For $\rho = 1.1\,\mathrm{g\,cm^{-3}}$, $M = 10^5$, $T = 450°\mathrm{K}$, the critical composition difference calculated from the B_{ij} in *Table 1* are 5.4% for S/AN; 7.0% for MMA/AN; and 33.3% for S/MMA. The S/AN value agrees rather well with that measured by Molau[54]. Massa[59] found significant miscibility of polystyrene with styrene/methyl methacrylate copolymers, but his results are not extensive enough to draw any conclusions about the validity of this calculated result.

There are three cases to be considered here where one copolymer contains monomers **1** and **2** and the other copolymer contains monomers **1** and **3**, i.e. monomer **1** is common to both polymers. Equation (5) reduces to

$$B = B_{12}\phi_2'(\phi_2' - \phi_3'') + B_{13}\phi_3''(\phi_3'' - \phi_2') + B_{23}\phi_2'\phi_3'' \qquad (12)$$

as shown previously[31]. Since B depends only on two composition variables, ϕ_2' and ϕ_3'', regions of negative B can be mapped on two dimensional plots like *Figure 2* where acrylonitrile is the common monomer. The experimental points agree well with lines $B=0$ calculated from equation (12) using the parameters from *Table 1*. Cowie and Lath[52] have published an equivalent mapping with substantially similar results. Note that the region of exothermic mixing does not include the diagonal line (using volume fractions) as this would require $B_{23} < 0$[14,28]. There is a miscibility region similar to that seen in *Figure 2* for the case where the common monomer is styrene, i.e. blends of SAN and SM copolymers, as described by Cowie and Lath[52]. However, when methyl methacrylate is the common monomer, there is no region of exothermic mixing of the blends for these copolymers, i.e. SM and MAN.

Blends of SAN and MAN copolymers phase separate on heating, i.e. show LCST behaviour, as illustrated by the cloud point curves seen in *Figure 4*. It is instructive to examine how the cloud point for a 50/50 blend varies with AN content of the SAN copolymer. This is illustrated in *Figure 5* for MAN copolymers containing 0, 12.6 and 26.4% by weight of acrylonitrile. Each curve is believed to exhibit a maximum that is at a temperature too high to be measured. The results for PMMA agree with those reported earlier[42]. As AN is incorporated into the acrylic polymer, the peak shifts to a higher level of AN in the SAN and the range of miscibility narrows as may be expected from *Figure 2*.

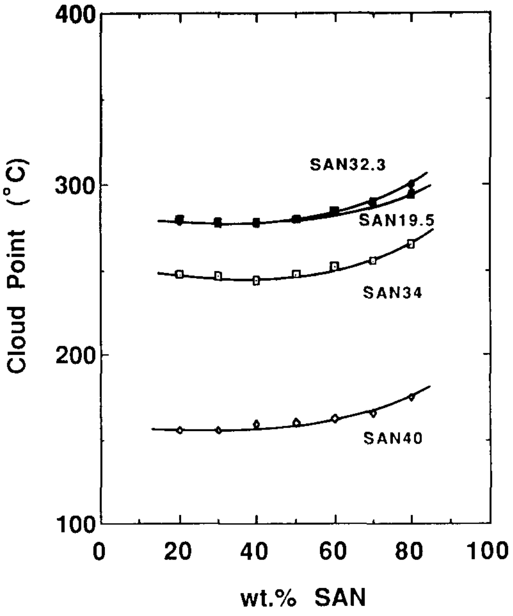

Figure 4 Cloud point curves for blends of various SAN copolymers with a MAN copolymer containing 12.3% by weight of AN

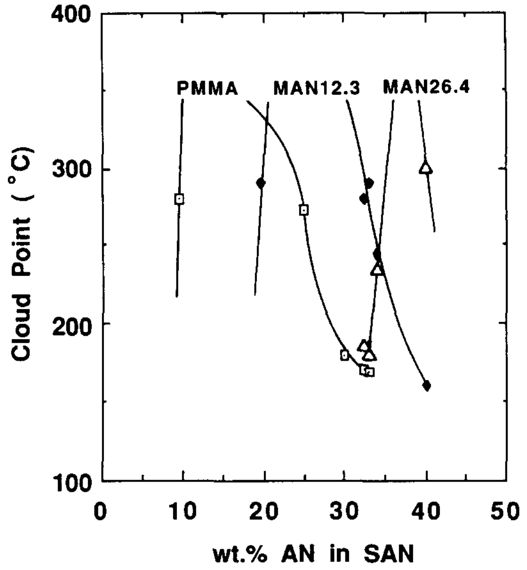

Figure 5 Cloud points of 50/50 blends of SAN/MAN copolymers *versus* AN content of SAN copolymer for three MAN copolymers: (□) 0% AN (PMMA=Rohm & Haas Plexiglas V811); (◆) 12.3% AN; (△) 26.4% AN

It should be noted that blends of typical commercial SAN copolymers (24 to 30 wt% AN) with PMMA have relatively low cloud points, and that such blends are sometimes opaque after injection moulding because the temperature during processing exceeds the cloud point. These results suggest that incorporation of a small amount of AN into the acrylic polymer can raise the cloud point for blends with a commercial SAN to a level where this is no longer a problem.

Copolymer–terpolymer blends

For this case, equation (5) does not reduce to a form that provides ready physical interpretation. As a result, we will illustrate by example the type of behaviour that can occur when various copolymers are blended with terpolymers of styrene, methyl methacrylate and acrylonitrile by showing the zones of exothermic mixing on the triangular composition diagram of the terpolymer. Again

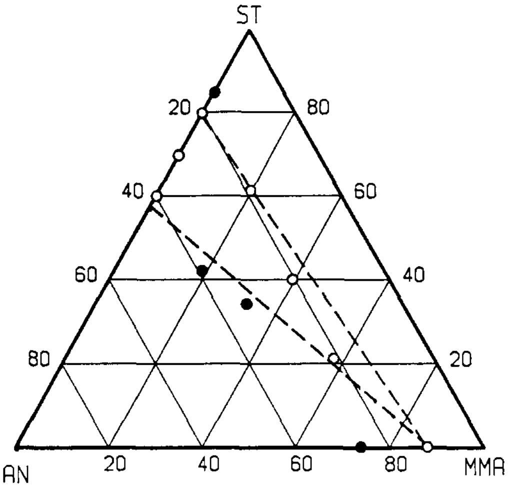

Figure 6 Phase behaviour of SMAN terpolymers with a MAN copolymer containing 12.3% AN. See *Figure 3* for key to lines and symbols

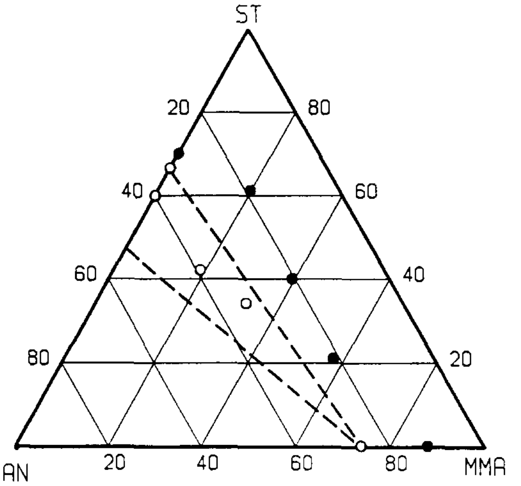

Figure 7 Phase behaviour of SMAN terpolymers with a MAN copolymer containing 26.4% AN. See *Figure 3* for key to lines and symbols

the dashed lines shown in these diagrams are compositions where $B=0$ as computed from the parameters in *Table 1*.

As illustrated by example in *Figures 6* and *7*, MAN copolymers mix exothermically with terpolymers falling within the type of triangular region shown. The copolymer composition, on the AN–MMA axis, defines one apex of this triangle since this copolymer will mix endothermically with all other MAN copolymers other than itself. One side of the triangle lies on the AN–S axis and its composition limits are defined by the zone mapped in *Figure 2*. Thus, as the copolymer becomes rich in AN, the side on the AN–S axis becomes shorter and moves towards the AN apex. The data in *Figures 6* and *7*, although sparse, agree quite well with the predictions.

For SM copolymers, there is a similar triangular region with an apex on the S–MMA axis. As the styrene content increases the side on the AN–S axis becomes shorter and moves towards the styrene apex in accordance with a S/AN–S/MMA diagram similar to *Figure 2*. For diagrams like *Figures 6* and *7* and corresponding ones for SM copolymers, the longest side on the AN–S axis occurs for blends with PMMA (see *Figure 3*).

Figures 8 and *9* illustrate the kind of exothermic regions that exist for mixing SAN copolymers with terpolymers. At high AN levels, this triangle has a side located on the AN–MMA axis whose limits are defined by *Figure 2*. For AN levels where the copolymer is miscible with PMMA (see *Figures 1* to *3*), the zone for exothermic mixing with terpolymers will include the PMMA apex as illustrated in *Figure 9*, and documented previously by Ikawa and Hosoda[51]. At lower AN levels, this zone will have a side located on the S–MMA axis with limits defined by the diagram analogous to *Figure 2* for styrene being the common monomer of the two copolymers. Again the data in *Figures 8* and *9* support the predictions.

Figure 10 shows some limited data and the expected trends for cloud points of 50/50 blends of three terpolymers with AN content of SAN copolymers.

Terpolymer–terpolymer blends

Particular terpolymers of styrene, methyl methacrylate and acrylonitrile are predicted to mix exothermically with other terpolymers over regions of compositions like those illustrated in *Figures 11* to *13*. The lines defining these

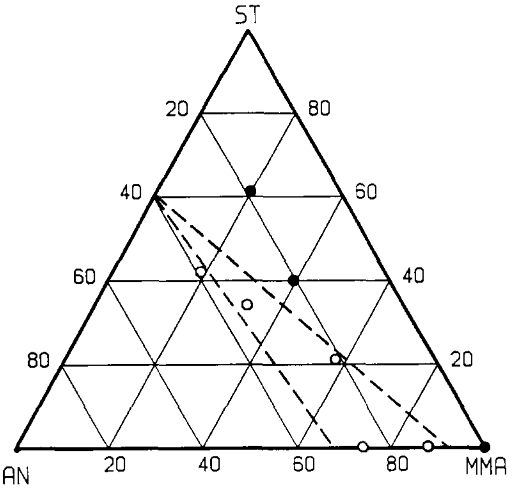

Figure 8 Phase behaviour of SMAN terpolymers with an SAN copolymer containing 40% AN. See *Figure 3* for key to lines and symbols

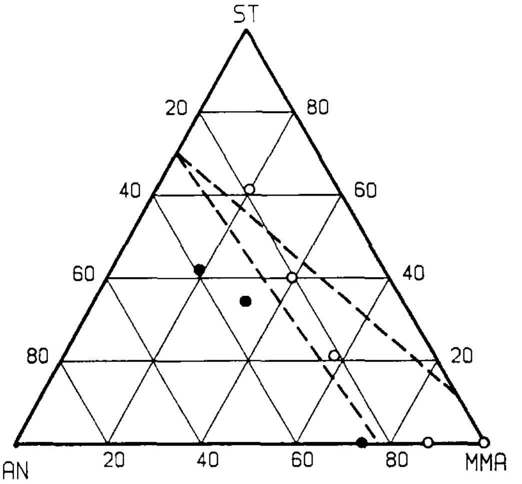

Figure 9 Phase behaviour of SMAN terpolymers with an SAN copolymer containing 30% AN. See *Figure 3* for key to lines and symbols

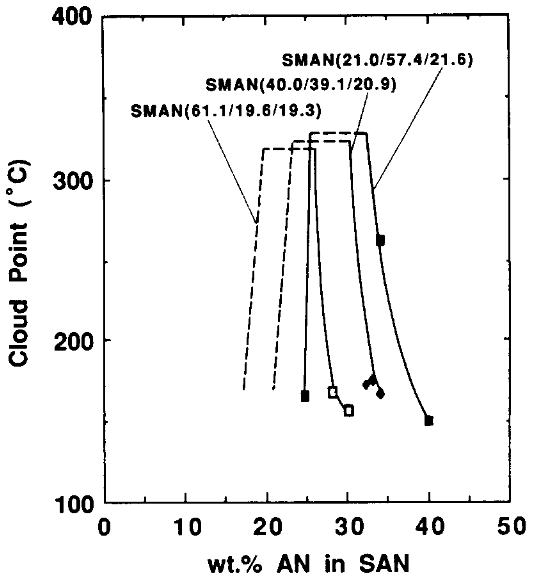

Figure 10 Cloud points of 50/50 blends of SAN with (■) SMAN (21.0/57.4/21.6), (◆) SMAN (40.0/39.1/20.9) and (□) SMAN (61.1/19.6/19.3) *versus* AN content of the copolymer

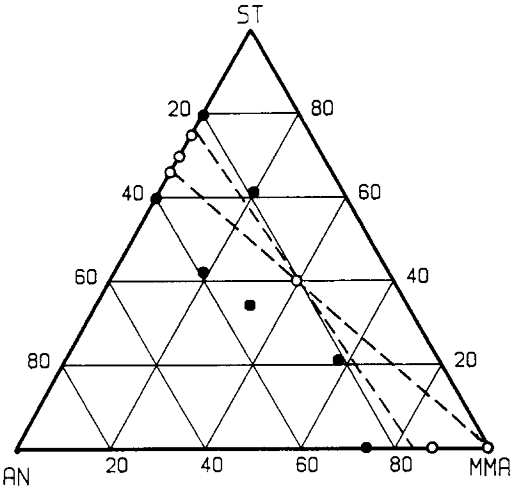

Figure 11 Phase behaviour of blends of SMAN terpolymers with another SMAN terpolymer containing 40% S, 39.1% M, and 20.9% AN. Regions enclosed by dashed lines are terpolymer compositions predicted to mix exothermically with this particular terpolymer (point of intersection of dashed lines). Points indicate experimental observations for blends: (○) miscible, (●) immiscible

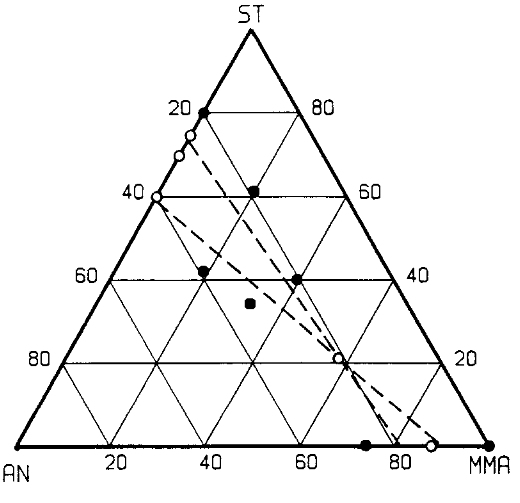

Figure 12 Phase behaviour of blends of SMAN terpolymers with another SMAN terpolymer containing 21.0% S, 57.4% M, and 21.6% AN. See *Figure 11* for key to lines and symbols

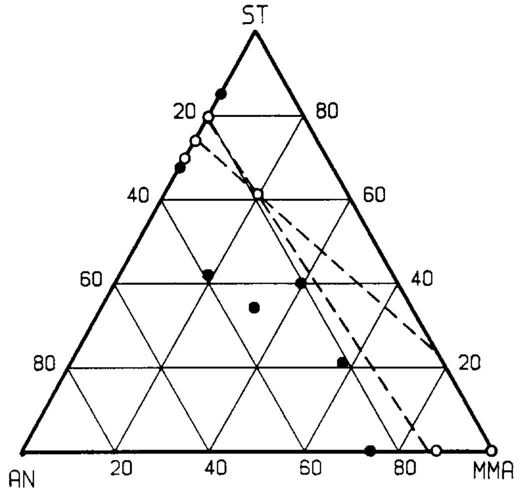

Figure 13 Phase behaviour of blends of SMAN terpolymers with another SMAN terpolymer containing 61.1% S, 19.6% M, and 19.3% AN. See *Figure 11* for key to lines and symbols

zones intersect at the composition of the particular terpolymer since when it is blended with itself mixing is athermal. The data shown in these figures all agree with the predictions, but the points are too sparse to defend the locations of these zones on experimental grounds for none of the available terpolymers happened to fall in the predicted miscible zones.

Based on calculations using the B_{ij} values in *Table 1*, any terpolymer, regardless of its composition, will have some zone of exothermic mixing with other terpolymers.

SUMMARY

The results shown here illustrate a rich array of possible phase behaviour patterns for binary blends of various combinations of homopolymers, copolymers and terpolymers based on styrene, methyl methacrylate and acrylonitrile. Parts of the picture described here have been the subjects of other recent investigations[51–53], and, in general, there is good agreement about the results. The important point to be emphasized is that none of the corresponding homopolymers are miscible with each other; however, if at least one component is a copolymer or a terpolymer, then many possibilities for miscibility emerge. However, similar behaviour is not assured for any choice of three monomers. It is, therefore, easy to see the need for a theory to guide the design of such polymers for achieving miscibility. The binary interaction model used seems to provide an adequate framework in this case, and its parameters seem to be known well enough for these monomers to give satisfactory predictive capability. It should be emphasized that it has not been practical to prepare enough compositions of copolymers and terpolymers to definitively map the phase behaviour of every type mentioned here. Furthermore, for simplicity we have calculated the regions of $B>0$ or $B<0$ for comparison with blends results. This is satisfactory to a point, but one must remember that other issues such as combinatorial entropy, equation of state contributions, temperature dependence of interaction parameters, etc. must be included for a more refined picture.

ACKNOWLEDGEMENTS

Financial support of this work has been provided by the

National Science Foundation Grant No. DMR-86-03131. The authors wish to thank Asahi Chemical for providing polymer samples and financial support of M. Nishimoto.

REFERENCES

1 Paul, D. R., Barlow, J. W. and Keskkula, H. 'Encyclopedia of Polymer Science and Eng.' John Wiley and Sons, New York, 1988, **12**, 399

2 Krause, S. 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978, Ch. 2

3 Fried, J. R., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1978, **11**, 150

4 Vuković, R., Karasz, F. E. and MacKnight, W. J. *Polymer* 1983, **24**, 529

5 Vuković, R., Karasz, F. E. and MacKnight, W. J. *J. Appl. Polym. Sci.* 1983, **28**, 219

6 Vuković, R., Kurešević, V., Karasz, F. E. and MacKnight, W. J. *J. Appl. Polym. Sci.* 1985, **30**, 317

7 Vuković, R., Kurešević, V., Šegudović, N., Karasz, F. E. and MacKnight, W. J. *J. Appl. Polym. Sci.* 1983, **28**, 1379

8 Alexandrovich, P., Karasz, F. E. and MacKnight, W. J. *Polymer* 1977, **18**, 1022

9 Maeda, Y., Karasz, F. E. and MacKnight, W. J. *J. Appl. Polym. Sci.* 1986, **32**, 4423

10 Kressler, J. and Kammer, H. W. *Acta Polymerica* 1987, **38**, 600

11 Keskkula, H. and Paul, D. R. *J. Appl. Polym. Sci.* 1986, **31**, 1189

12 Kressler, J., Kammer, H. W., Schmidt-Naake, G. and Herzog, K. *Polymer* 1988, **29**, 686

13 Aoki, Y. *Macromolecules* 1988, **21**, 1277

14 Kim, J. H., Barlow, J. W. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 223

15 Chiu, S. C. and Smith, T. G. *J. Appl. Polym. Sci.* 1984, **29**, 1781

16 Chiu, S. C. and Smith, T. G. *J. Appl. Polym. Sci.* 1984, **29**, 1797

17 Jo, W. H., Cruz, C. A. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn.* in press

18 Kim, J. H., Barlow, J. W. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn.* in press

19 Kim, J. H., Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* in press

20 Zakrzewski, G. A. *Polymer* 1973, **14**, 347

21 Shiomi, T., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1986, **19**, 2644

22 Kenney, J. F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 123

23 Min, K. E. and Paul, D. R. *Macromolecules* 1987, **20**, 2828

24 Min, K. E. and Paul, D. R. *J. Appl. Polym. Sci.* 1989, **37**, 1153

25 Min, K. E. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 2257

26 Goh, S. H., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1982, **22**, 34

27 Suess, M., Kressler, J., Kammer, H. W. and Heinemann, K. *Polymer Bulletin* 1986, **16**, 371

28 Paul, D. R. and Barlow, J. W. *Polymer* 1984, **25**, 487

29 Kambour, R. P., Bendler, J. T. and Bopp, R. C. *Macromolecules* 1983, **16**, 753

30 ten Brinke, G., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1983, **16**, 1827

31 Shiomi, T., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1986, **19**, 2274

32 ten Brinke, G., Rubinstein, E., Karasz, F. E., MacKnight, W. J. and Vukovic, R. *J. Appl. Phys.* 1984, **56**, 2440

33 Balazs, A. C., Sanchez, I. C., Epstein, I. R., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1985, **18**, 2188

34 Karasz, F. E. in 'Polymer Blends and Mixtures' (Eds. D. J. Walch, J. S. Higgins and A. Maconnachie), NATO ASI Series, Martinus Nijhoff Publishers, 1985, Series E: No. 89, 25

35 Karasz, F. E. and MacKnight, W. J. *Adv. Chem. Ser.* 1986, **211**, 67

36 Kang, H. S., MacKnight, W. J. and Karasz, F. E. *Am. Chem. Soc., Polym. Prepr.* 1987, **28**(2), 134

37 Hunsel, J. V., Balazs, A. C., Koningsveld, R. and MacKnight, W. J. *Macromolecules* 1988, **21**, 1528

38 Balazs, A. C., Karasz, F. E., MacKnight, W. J., Ueda, H. and Sanchez, I. C. *Macromolecules* 1985, **18**, 2784

39 Cantow, H. J. and Schulz, O. *Polymer Bulletin* 1986, **15**, 449

40 Pfennig, J. L. G., Keskkula, H., Barlow, J. W. and Paul, D. R. *Macromolecules* 1985, **18**, 1937

41 Kammer, H. W. *Acta Polymerica* 1986, **37**, 1

42 Fowler, M. E., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 1177

43 Stein, V. D. J., Jung, R. H., Illers, K. H. and Hendus, H. *Angew. Makromol. Chem.* 1974, **36**, 89

44 Suess, M., Kressler, J. and Kammer, H. W. *Polymer* 1987, **28**, 957

45 Schmitt, B. J., Kirste, R. G. and Jelenic, J. *Makromol. Chem.* 1980, **181**, 1655

46 McBrierty, V. J., Douglass, D. C. and Kwei, T. K. *Macromolecules* 1978, **11**, 1265

47 Naito, K., Johnson, G. E., Allara, D. L. and Kwei, T. K. *Macromolecules* 1978, **11**, 1260

48 Kruse, W. A., Kirste, R. G., Haas, J., Schmitt, B. J. and Stein, D. J. *Makromol. Chem.* 1976, **177**, 1145

49 Kressler, J., Kammer, H. W. and Klostermann, K. *Polym. Bulletin* 1986, **15**, 113

50 Fowler, M. E., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 2145

51 Ikawa, K. and Hosoda, S. *Polym. Prepr. Japan* 1988, **27Q**, 1a49

52 Cowie, J. M. G. and Lath, D. *Makromol. Chem., Macromol. Symp.* 1988, **16**, 103

53 Cowie, J. M. G. and Lath, D. *Polym. Commun.* 1987, **28**, 300

54 Molau, G. E. *J. Polym. Sci., Polym. Lett. Edn.* 1965, **3**, 1007

55 Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, New York, 1953

56 Roe, R. J. and Rigby, D. *Adv. Polym. Sci.* 1987, **82**, 103

57 Cruz-Ramos, C. A. and Paul, D. R. *Macromolecules* in press

58 Brannock, G. R., Ph.D. Dissertation, University of Texas, 1989

59 Massa, D. J. *Adv. Chem. Ser.* 1979, **176**, 433

60 Parent, R. R. and Thompson, E. V. *Am. Chem. Soc., Polym. Prepr.* 1977, **18**, 507

61 Fukuda, T. and Inagaki, H. *Pure Appl. Chem.* 1983, **55**, 1541

62 Fukuda, T., Nagata, M. and Inagaki, H. *Macromolecules* 1984, **17**, 548

63 Fukuda, T., Nagata, M. and Inagaki, H. *Macromolecules* 1986, **19**, 1411