Effect of copolymer composition on the miscibility of blends of styrene–acrylonitrile copolymers with poly(methyl methacrylate)

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The phase behaviour for blends of various polymethacrylates with styrene–acrylonitrile (SAN) copolymers has been examined as a function of the acrylonitrile content of the copolymer. Poly(methyl methacrylate), poly(ethyl methacrylate) and poly(n-propyl methacrylate) were found to be miscible with SANs over a limited window of acrylonitrile contents while no SANs appear to be miscible with poly(isopropyl methacrylate) or poly(n-butyl methacrylate). These conclusions were reached on the basis of lower critical solution temperature (*LCST*) and glass transition temperature behaviour. All miscible blends exhibited phase separation on heating, *LCST* behaviour, at temperatures which varied greatly with copolymer composition. An optimum acrylonitrile (AN) level ranging from about 10 to 14% by weight resulted in the highest temperatures for phase separation which has important implications for selection of SANs to produce homogeneous mixtures by melt processing. The basis for miscibility in these systems is evidently repulsion between styrene and acrylonitrile units in the copolymer as explained by recent models. The excess volumes for all blends are zero within experimental accuracy which suggests that the interactions for miscibility are relatively weak even for the optimum AN level. This interaction becomes smaller the larger or more bulky is the alkyl side group of the polymethacrylate.

(Keywords: blends; miscibility; polymethacrylates; styrene–acrylonitrile; copolymers; lower critical solution temperature)

INTRODUCTION

It has been known for more than a decade that poly(methyl methacrylate) (PMMA) forms miscible blends with copolymers of styrene and acrylonitrile (SAN) over a limited window of comonomer proportions[1,2] while PMMA is not miscible with homopolymers of styrene or acrylonitrile. Similar behaviour has been noted for other copolymer–homopolymer mixtures[3–9]. It is generally recognized that an exothermic heat of mixing between two polymers of high molecular weights is a requirement for their miscibility[10,11]. Recently, models have been developed[12–14] which strongly suggest that this exothermic mixing may arise in mixtures with copolymers when there is a strong intrachain repulsion between the comonomer units. In simple terms, the interaction parameter B for mixing two polymers A (homopolymer of monomer 3) and B (a random copolymer of monomers 1 and 2) which characterizes the heat of mixing per unit volume

$$\Delta H_{mix} = B\phi_A\phi_B \quad (1)$$

contains contributions from binary interactions between the three monomers involved:

$$B = B_{13}\phi_1' + B_{23}\phi_2' - B_{12}\phi_1'\phi_2' \quad (2)$$

appropriately weighted for copolymer composition, ϕ_i'. In the case of interest all three B_{ij} are positive, but B_{12} is considerably greater than the other two parameters. Recent calorimetry results for low molecular weight compounds that approximately simulate the PMMA–SAN system suggest that this is indeed the origin of the observed phase behaviour[15].

A number of papers[16–18] report a variety of types of physical studies on blends of PMMA with an SAN containing 28% by weight of acrylonitrile which is right at the upper limit of the composition range where miscibility occurs. For example, such mixtures exhibit phase separation on heating or lower critical solution temperature (*LCST*) behaviour[14,17] at relatively low temperatures. The narrow gap between the cloud point curve and the glass transition of these mixtures severely restricts the ability for melt processing to achieve single-phase mixtures, and this limits the utility of this system. These mixtures appear to exhibit ideal additivity of volume on mixing[18] which combined with other evidence[19] suggests a very weak net interaction or small negative B, for this pair. Based on the model and calorimetry results mentioned above, one would expect a stronger net interaction at acrylonitrile (AN) contents nearer the centre of the composition range of copolymer miscibility with PMMA.

Rather limited work has been reported for other polymethacrylates with SAN copolymers[20]. Poly(ethyl methacrylate) (PEMA) was found to be miscible with the SAN containing 28% AN while polymethacrylates with other alkyl pendant groups were judged not to be miscible[20].

Based on current understanding, we felt that a thorough re-examination of mixtures of SAN copolymers and polymethacrylates was in order and the results are reported here. The AN levels have been varied over a wide range and a series of polymethacrylates were considered. These mixtures were examined primarily for their glass transition behaviour and phase separation on heating; however, selected other physical properties were

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measured in some cases in an attempt to assess the strength of interactions involved.

MATERIALS AND EXPERIMENTAL PROCEDURES

Table 1 lists the various polymethacrylates used in this study along with abbreviations, the sources from which they were obtained, molecular weight information, where available, and their glass transition temperatures as determined by differential scanning calorimetry (d.s.c.). *Table 2* lists the wide range of styrene–acrylonitrile (SAN) copolymers used in this work, their sources, and molecular weight information, where available. This table also summarizes the phase behaviour of their blends with the various polymethacrylates which will be discussed later.

Table 1 Polymethacrylates used in this study

Polymer	Abbreviation	Source	Molecular weight	T_g (°C)
Poly(methyl methacrylate)	PMMA	Rohm & Haas V(811)100	$M_n = 52\,900$ $M_w = 105\,400$	108
Poly(ethyl methacrylate)	PEMA	DuPont Elvacite 2042	$M_w = 438\,000$	67
Poly(n-propyl methacrylate)	PnPMA	Polysciences	na	46
Poly(isopropyl methacrylate)	PiPMA	Polysciences	na	87
Poly(n-butyl methacrylate	PnBMA	Scientific Polymer Products	na	21

na = not available

Table 2 Styrene–acrylonitrile copolymers used in this study and summary of their phase behaviour when blended with polymethacrylates

AN content (wt%)	Molecular weight	Observations for Blends With: PMMA T_g	PMMA Optical	PEMA T_g	PEMA Optical	PnPMA T_g	PnPMA Optical	PiPMA T_g	PiPMA Optical	PnBMA T_g	PnBMA Optical
0.0[a]	$M_n = 100\,000$ $M_w = 350\,000$	nt[b]	cloudy	2	cloudy	2	cloudy	2	cloudy	2	cloudy
2.0[c]	$M_n = 93\,500$ $M_w = 204\,000$	nt	cloudy	2	cloudy	1	clear	2	cloudy	2	cloudy
3.5[c]	$M_n = 96\,400$ $M_w = 211\,000$	nt	cloudy	2	cloudy	1	opaque	2	cloudy	2	cloudy
5.5[d]	$M_w = 270\,000$	nt	cloudy	1	clear	nt	nt	nt	nt	nt	nt
5.7[c]	$M_n = 87\,700$ $M_w = 212\,000$	nt	cloudy	1	clear	1	clear	2	cloudy	2	cloudy
6.3[d]	na[e]	nt	cloudy	nt	nt	nt	nt	nt	nt	nt	nt
9.5[c]	na	nt	clear	1	clear	1	clear	2	cloudy	2	cloudy
11.5[c]	na	nt	clear	1	clear	1	clear	2	cloudy	2	cloudy
13.5[c]	na	nt	clear	1	clear	1	clear	2	cloudy	2	cloudy
14.7[c]	$M_n = 82\,700$ $M_w = 181\,000$	nt	clear	1	clear	1	clear	2	cloudy	2	cloudy
15.5[c]	na	nt	clear	1	clear	1	clear	2	cloudy	2	cloudy
16.2[d]	$M_w = 197\,800$	nt	clear	1	clear	nt	nt	nt	nt	nt	nt
19.5[c]	na	nt	clear	1	clear	1	clear	2	cloudy	2	cloudy
20.5[d]	$M_w = 193\,800$	nt	clear	1	clear	nt	nt	nt	nt	nt	nt
24.0[f]	$M_n = 66\,700$ $M_w = 113\,000$	nt	clear	1	clear	nt	nt	nt	nt	nt	nt
24.8[f]	$M_n = 62\,900$ $M_w = 121\,000$	nt	clear	1	clear	nt	nt	nt	nt	nt	nt
25.0[c]	na	nt	clear	1	clear	1	opaque	2	cloudy	2	cloudy
25.0[d]	na	nt	clear	1	clear	nt	nt	nt	nt	nt	nt
26.9[f]	na	nt	clear	1	clear	nt	nt	nt	nt	nt	nt
28.0[g]	na	nt	clear	1	clear	2	cloudy	2	cloudy	2	cloudy
32.3[f]	$M_n = 50\,700$ $M_w = 75\,400$	nt	opaque	2	cloudy	nt	nt	nt	nt	nt	nt
33.0[d]	na	nt	cloudy								

[a] Cosden Oil and Chemical Co.
[b] nt = not tested
[c] Asahi Chemical Industry Co. Ltd
[d] Dow Chemical USA
[e] na = not available
[f] Monsanto Polymer Products Co.
[g] Union Carbide Corp.

Blends of the various SANs and the polymethacrylates were prepared by a solution casting method. The polymers were weighed and then simultaneously dissolved in tetrahydrofuran (THF) to give solutions containing approximately 3–5% by weight of total polymer. In every case, clear solutions were obtained which were poured into aluminium pans and covered with aluminium foil. Small holes were punched in the foil to retard the initial rate of solvent evaporation. Initial drying was done at room temperature under a hood for a minimum of three days. Further drying was done in a vacuum oven (3 days at 60°C and 3 days at 120°C) to ensure complete removal of solvent.

Thermal analysis was carried out using either a Perkin–Elmer DSC-2 or DSC-7 (both were equipped with a Thermal Analysis Data Station) at a heating rate of 20°C min^{-1} with samples weighing 5 to 15 mg. Glass transitions were computed by the onset method from second or subsequent heats. Heat capacities were obtained at 257°C using the procedure described previously[21] involving the use of a sapphire standard and subtraction of the contribution from the aluminium pan used.

The temperature at which phase separation occurred on heating (cloud point) for blends exhibiting lower critical solution temperature (*LCST*) behaviour was obtained as follows. A small piece of film was sandwiched between two glass slides and placed on a hot plate device described previously[17]. The upper surface of this device is an aluminium block with a thermocouple embedded just below the sample. A temperature controller was used to obtain a heating rate in the range of 2 to 5°C min^{-1}. The cloud point, judged by eye, was taken as the temperature where the first indication of cloudiness developed. When the cloud point occurred at rather high temperatures where cumulative heat history might lead to serious problems of depolymerization or degradation, another approach was used. The temperature of the hot plate was preset near the expected cloud point. The sample was then placed on the heated surface and observed for a time long enough to cause phase separation but short relative to severe decomposition. The lowest temperature, taken in 5°C increments, at which cloudiness developed was designated as the cloud point. Similar experiments described later were used to judge the effect of the finite heating rate on the cloud point which can be important in some cases because of the kinetics of phase separation.

Densities were determined at 30°C using a density gradient column based on aqueous calcium nitrate solutions. By this method, densities could be measured to within 0.0003 g cm^{-3}. An average of at least three determinations on separate samples are reported.

RESULTS AND DISCUSSION

Glass transition behaviour

The glass transition behaviour for SAN–PMMA blends was not examined in this study for two reasons. First, the glass transition temperature (T_g) values for pure SAN and PMMA are so close that resolution of separate T_g values for a blend is rather difficult[1]. Secondly, a substantial body of evidence is already available[1,16–18] establishing conclusively that blends of PMMA with certain SANs, but not all, are indeed miscible and the range of AN levels where miscibility occurs is relatively well established[1].

The glass transition behaviour for blends of PEMA with the various SANs was examined in detail since the component T_g values are sufficiently separated for conclusive resolution and such information has not been reported previously. *Figure 1* shows typical results for selected SANs with a wide range of AN levels while *Table 2* summarizes whether one or two T_g values were noted for all of the SANs examined. Blends of PEMA with SANs containing 5.5 to 28.0% AN by weight exhibit a single, composition-dependent glass transition which indicates complete miscibility within this window of AN contents. For 3.5% AN or less, two T_g values are seen; however, significant partial miscibility with PEMA is evident even at the low AN contents of 2.0 and 3.5%. These blends show rather complex dependence of the two T_g values observed on blend composition, which probably relates to the details of the preparation for each sample. The important point is that a single T_g is not obtained when the SAN contains 3.5% AN or less. Blends with polystyrene show little evidence of even partial miscibility. Blends based on an SAN containing 32.3% AN also showed two glass transitions; however, the SAN phase evidently contains some PEMA.

It is interesting to note that the glass transition temperature for the miscible blends lies above the linear tie line connecting the pure component values. For many miscible systems, the T_g falls below the tie line. The T_g data for each miscible blend was statistically fitted to the Gordon–Taylor equation[22]:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) \quad (3)$$

to obtain a value for the parameter k. The values of k so obtained did not conform to any decisive trend with the percentage of AN of the copolymer, so no further discussion of these results is warranted.

In the interest of time and available material, a more limited examination was made of the glass transition behaviour for blends of the various SANs with poly(n-propyl methacrylate) (PnPMA), poly(isopropyl methacrylate) (PiPMA) and poly(n-butyl methacrylate) (PnBMA). For these systems, only the 50/50 blend was examined with the results summarized in *Table 2*. When two T_g values were observed, they were rather close to the values for the pure components, indicating immiscibility. When one T_g was observed, this value was near that expected for a miscible blend. On this basis, PnPMA was judged to be miscible with SANs whose AN levels were in the range of 2 to 25% by weight. More evidence for miscibility in this range is given later. PiPMA and PnBMA gave two T_g values when blended with all of the SANs.

Optical observations

Many miscible blend systems exhibit phase separation on heating caused by the existence of a lower critical solution temperature[16,20]. Such behaviour has been noted several times in the past[16,17] for blends of PMMA with an SAN containing 28.0% AN. The lowest curve in *Figure 2* demonstrates this once again, and the cloud point curve obtained generally agrees with previous reports when allowance is made for the differences in grades of PMMA used in the various studies. *Figure 2* also shows cloud point curves for selected other SANs with lower amounts of AN, and interestingly those curves all lie above that for the SAN with 28.0% AN. Similar observations are noted in *Figure 3* for SAN blends with

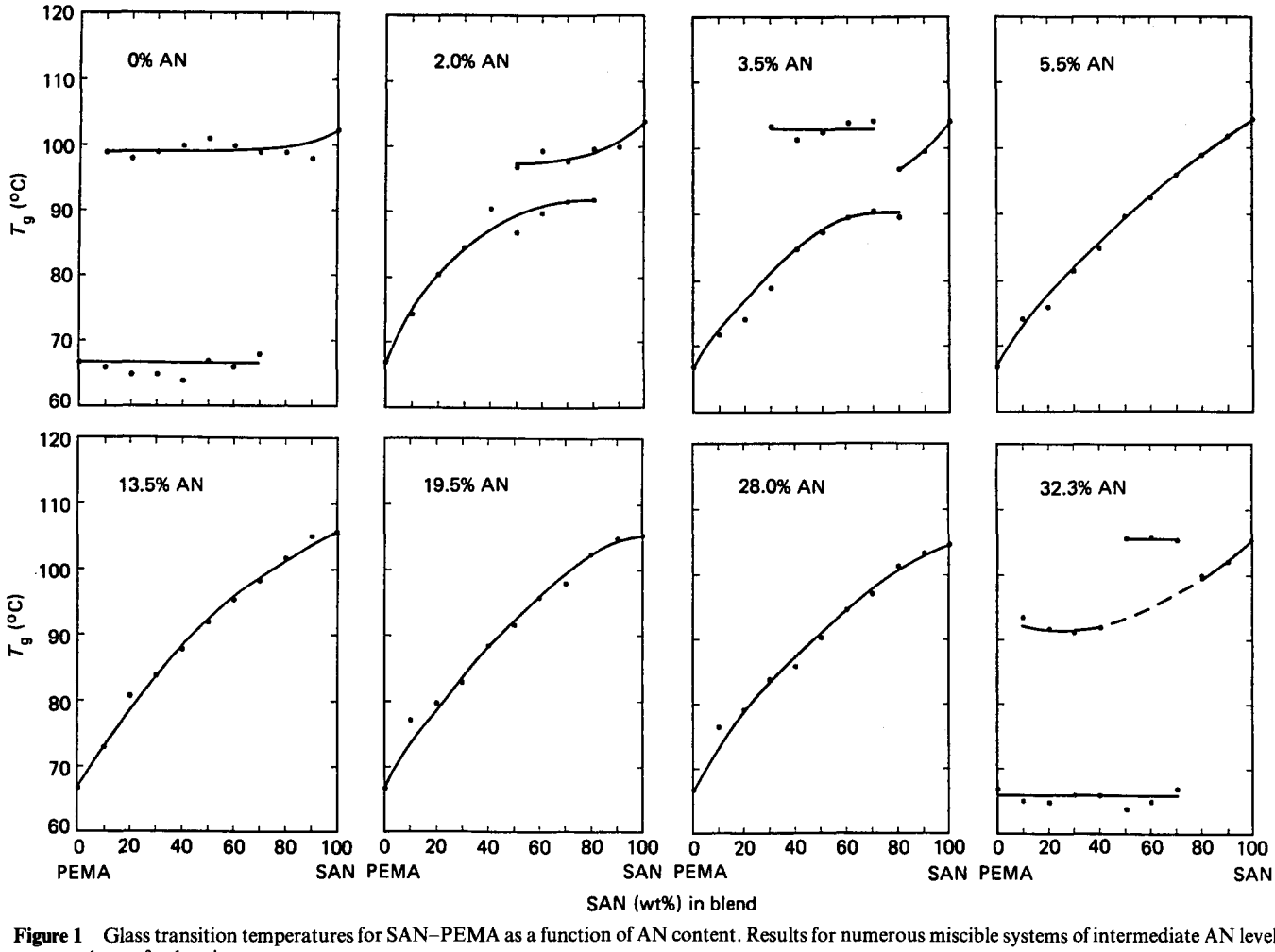

Figure 1 Glass transition temperatures for SAN–PEMA as a function of AN content. Results for numerous miscible systems of intermediate AN level are not shown for brevity

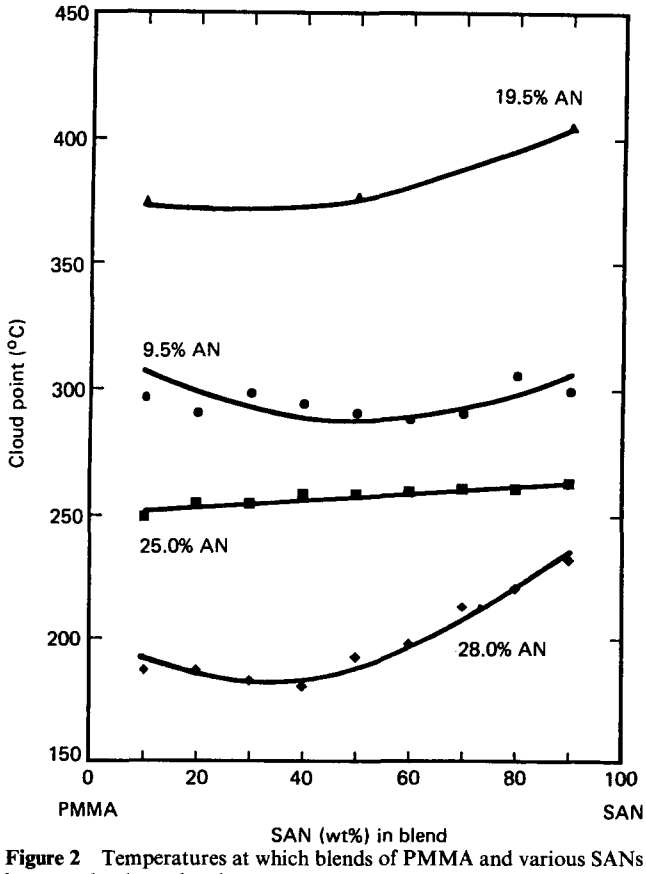

Figure 2 Temperatures at which blends of PMMA and various SANs become cloudy on heating

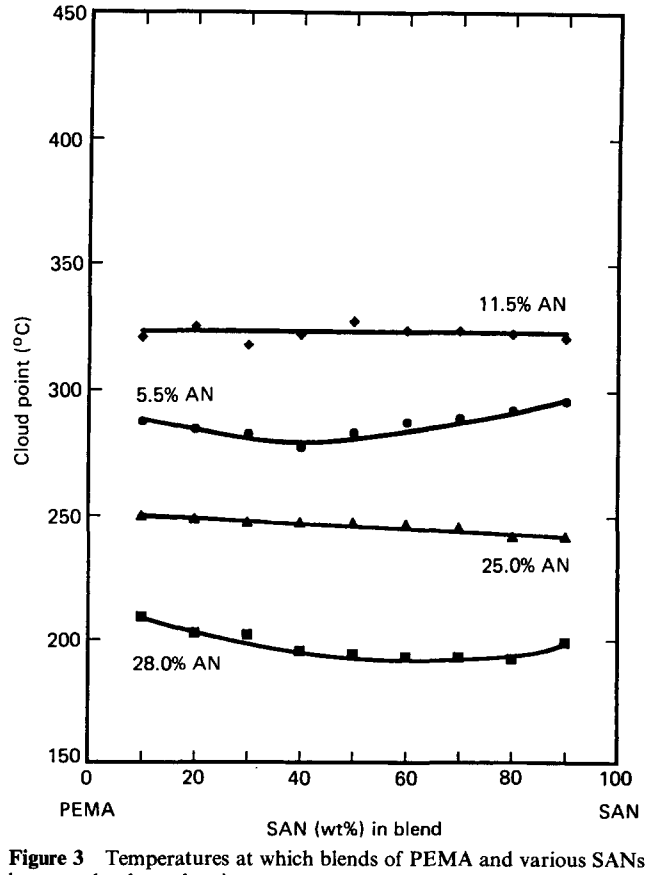

Figure 3 Temperatures at which blends of PEMA and various SANs become cloudy on heating

PEMA. In all cases, the samples which became cloudy on heating could be reversed to clear samples given a sufficiently slow cooling rate.

A more revealing representation of the effect of percentage of AN on the cloud point behaviour is shown in *Figure 4* where the temperature at which 50/50 blends of PMMA, PEMA and PnPMA with SANs became cloudy on heating is plotted *versus* the amount of AN in the copolymer. All three systems exhibit a maximum in the cloud point at an intermediate percentage of AN. This clearly demonstrates the window in AN content where SANs are miscible with these polymers. Similar behaviour has been noted for other homopolymer–copolymer blends[8] which can be qualitatively understood in terms of equation (1). In general, one expects a higher value of the cloud point or the *LCST* the more exothermic the heat of mixing or the more negative the interaction parameter[23]. For compolymers which are miscible with other polymers owing to the intramolecular repulsion effect, which is obviously the basis for the behaviour of the present systems, one learns from equation (2) that a certain copolymer composition produces a minimum, or most negative, value of the interaction parameter. Qualitatively, this corresponds to the maximum in the cloud point values *versus* copolymer composition as shown in *Figure 4*. The cloud point occurs at lower temperatures on either side of this composition because the interaction parameters are less negative on either side of this optimum composition. For SANs containing 13.5 and 16.2% AN, no cloud points could be observed for blends with PMMA since they evidently are at temperatures higher than where extremely rapid decomposition occurs. Thus, the maximum for the PMMA blends falls somewhere in the vicinity of 13 to 14% AN. The window in AN contents for SAN miscibility with PMMA appears to be somewhat more narrow than for PEMA and PnPMA. However, the values of the cloud point decrease as the length of the alkyl group in the polymethacrylates increases and this most likely reflects the order, PMMA > PEM-A > PnPMA, for the strength of the net interactions responsible for miscibility with SANs. Blends with PiPMA and PnBMA were cloudy at all temperatures, which confirms their immiscibility with all SANs. The maxima in *Figure 4* appear to shift slightly towards lower AN levels as one goes from PMMA to PEMA to PnPMA.

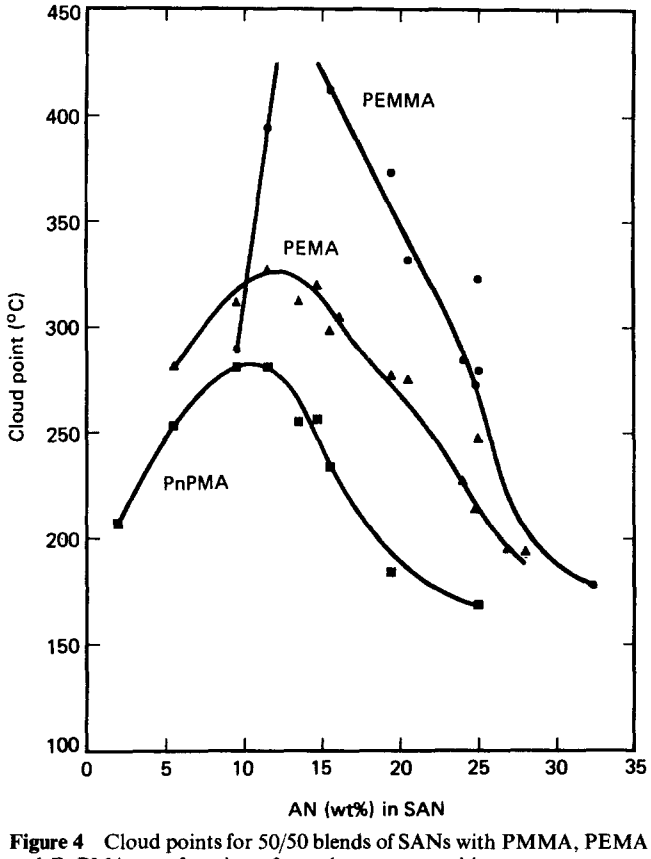

Figure 4 Cloud points for 50/50 blends of SANs with PMMA, PEMA and PnPMA as a function of copolymer composition

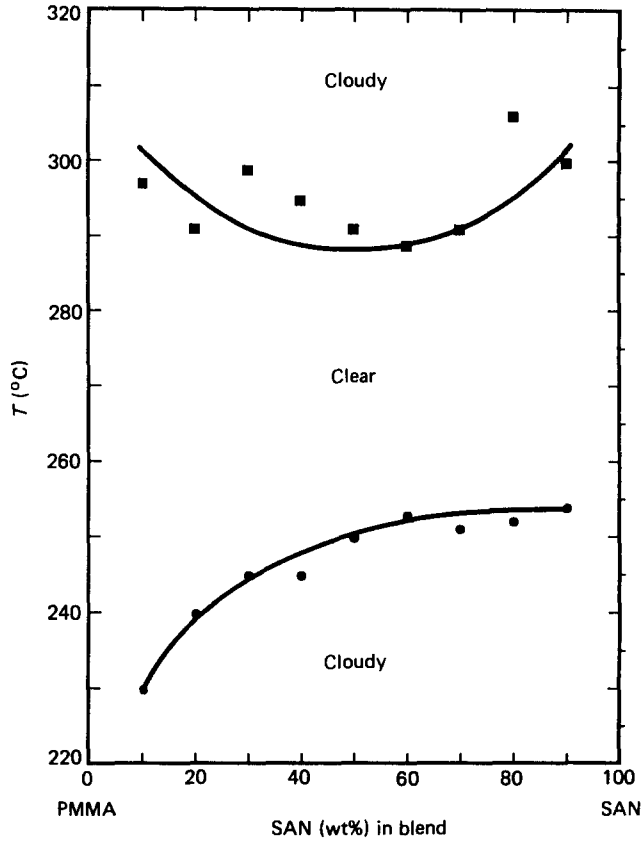

Figure 5 Optical behaviour for blends of PMMA with an SAN containing 9.5% AN as cast from THF. Note the lower curve is an artifact of the blend preparation method as described in the text

It is important to stress the kinetic nature of the phase separation process which may result in cloud points measured at the finite heating rates of 2–5°C min^{-1} being somewhat higher than the true equilibrium values. To demonstrate this, several blends were held isothermally for 30 min at temperatures 10 to 20°C below the values obtained with a finite heating rate[24]. Many of these mixtures became cloudy on holding in this manner at about 10°C lower than the cloud points observed while heating. The isothermal values approach the kinetically determined ones when phase separation occurred at rather high temperatures since temperature affects the rate at which this process can take place.

Blends of PMMA with an SAN containing 9.5% AN were cloudy as cast from THF – note that 9.5% AN is on the left edge of the SAN copolymer composition window for miscibility with PMMA. On heating these blends became clear at temperatures defined by the lower curve in *Figure 5* which is suggestive of upper critical solution

temperature (*UCST*) behaviour. On further heating these same blends became cloudy again (upper curve in *Figure 5*) because of *LCST* behaviour. Thus, this seemed to be a system with both a *UCST* and an *LCST* as discussed in some recent reports[25,26]. However, more careful examination proved the apparent *UCST* was an artifact of the blend preparation process. Similar blends cast from methylene chloride were found to be completely clear, as were blends prepared by melt mixing in a Brabender Plasticorder at temperatures below the lower curve in *Figure 5*. Blends made by the latter two methods exhibited cloud points on heating at the same temperatures given by the upper curve in *Figure 5*. We conclude that phase separation occurred during casting from THF which has been repeatedly demonstrated to happen with some solvents for miscible systems that interact weakly[27–35]. Evidently, on heating, the THF cast blends gained enough mobility to diffuse into the homogeneous equilibrium state. We describe these results simply as a caution to others about this type of possibility for reaching erroneous conclusions.

It is interesting to note that many commercial SANs contain about 25 to 28% AN since this is the azeotropic copolymer composition range[36]. Blends of such SANs with the polymethacrylates phase separate on heating at rather low temperatures which makes melt processing difficult if homogeneous mixtures are desired. These results show that this restriction is greatly relaxed by going to lower AN levels as this dramatically elevates the temperature at which phase separation occurs, thus opening a broader range of temperature for processing.

Volumetric properties

Density results for the various SAN copolymers are plotted in *Figure 6* as specific volume *versus* AN content. The data are well represented by the linear relation

$$V = 0.9548 - 9.423 \times 10^{-4} \text{ (wt\% AN)} \qquad (4)$$

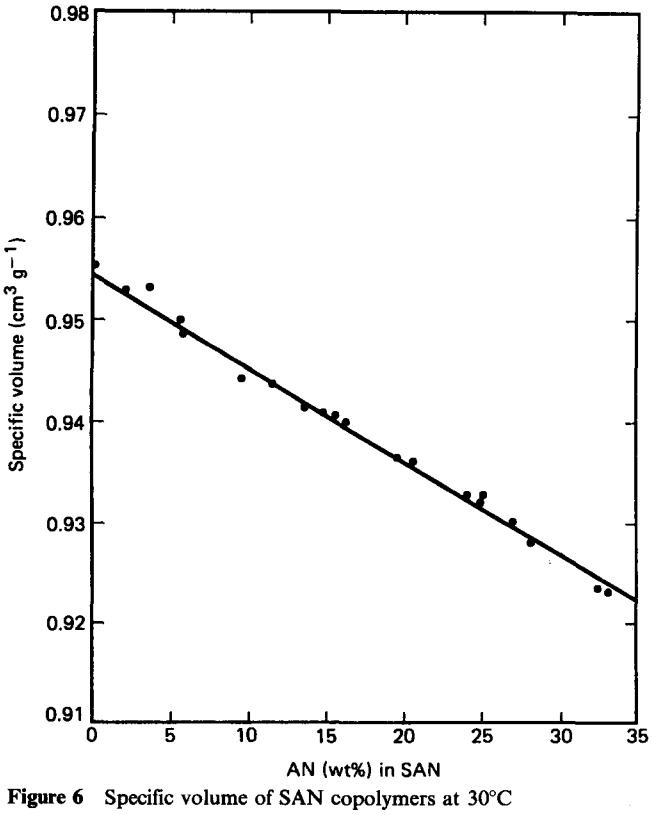

Figure 6 Specific volume of SAN copolymers at 30°C

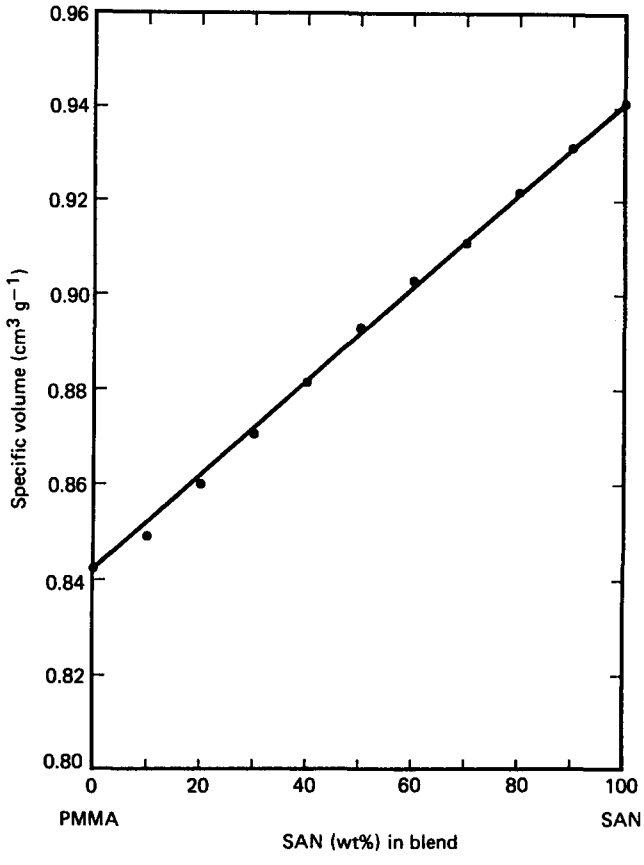

Figure 7 Specific volume for PMMA blends with an SAN containing 13.5% AN

determined by regression analysis and shown in *Figure 6* by the full line. When extrapolated to 100% AN, a specific volume corresponding to a density of 1.16 g cm^{-3} is obtained. This compares well with the value of 1.17 g cm^{-3} reported for pure polyacrylonitrile[37] and suggests that SAN copolymers exhibit essentially volume additivity.

As noted earlier, PMMA blends with an SAN containing 28.0% AN (near the right edge of the miscibility window) exhibit volume additivity[18] within experimental accuracy. One might expect some negative departure from additivity for AN levels nearer the optimum value for miscibility owing to the expected stronger interactions between the polymethacrylates and SANs in this region. *Figures 7* and *8* show specific volume data for blends of PMMA and for blends of PEMA with an SAN containing 13.5% AN. Within experimental accuracy, these blends exhibit volume additivity which was also found for blends with SANs having AN levels spanning the entire miscibility window. Based on this indirect evidence, we conclude that the absolute level of the net interaction of SANs with the polymethacrylates, PMMA and PEMA, must be rather weak, even at the optimum AN level, since no measurable excess volume can be detected.

Excess heat capacities

In a recent paper[21], we reported the excess heat capacities for two miscible blend systems and discussed the potential value of such information as an aid to understanding the thermodynamics of miscible blends. The observed excess heat capacities were all positive and had values of the order of 0.01 to 0.02 cal g^{-1} K^{-1} at their

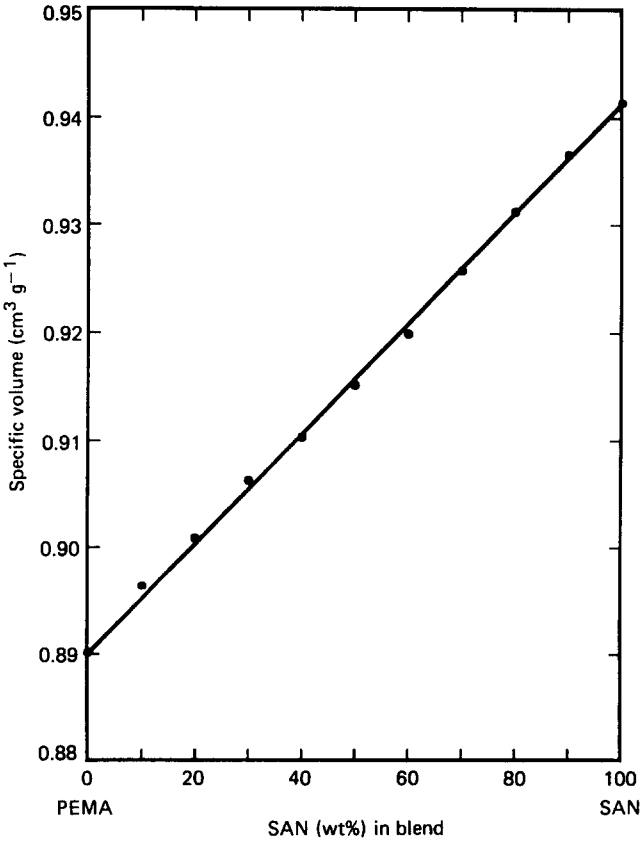

Figure 8 Specific volume for PEMA blends with an SAN containing 13.5% AN

maxima. Similar experiments were done for PMMA blends with SANs of varying AN levels at a temperature of 257°C, and the detailed results are described elsewhere[38]. Out of seven blend systems examined, two showed slightly negative excess heat capacities while five showed positive values which were nearly an order of magnitude less than those reported previously. Because of the experimental uncertainty of measuring such small values, further discussion of these results does not seem warranted.

SUMMARY

The results of this study indicate that three polymethacrylates, PMMA, PEMA and PnPMA, form miscible blends with styrene–acrylonitrile copolymers over a limited range of copolymer compositions specific to each while the polymethacrylates, PiPMA and PnBMA, do not appear to be miscible with any SANs. The result for PMMA is well known[1]; however, the present study includes an extensive examination of the effect of AN level on the temperature at which phase separation occurs on heating, which has not been described previously.

The conclusions about the PEMA–SAN systems are based on extensive examinations of glass transition temperature (T_g) and *LCST* behaviour. Morawetz[2] has also studied blends of PEMA with SANs as a function of AN level using a non-radiative energy transfer approach and concluded these mixtures are never completely miscible; although he did identify an AN range for optimum energy transfer that corresponds closely with the window of compositions for miscibility found here. Based on the classical evidence of glass transition and *LCST* behaviour, we conclude that these blends form one-phase mixtures within the identified range of AN contents; however, the net interactions responsible for this may not be very large.

Our conclusion of miscibility for PnPMA–SAN blends is based on a limited examination of T_g behaviour, but the *LCST* behaviour noted fully justifies this conclusion. Blends of PiPMA and PnBMA were judged to be immiscible with all SANs since their blends were always cloudy.

The basis for the miscibility of SAN copolymers with PMMA, PEMA and PnPMA seems to be a relatively strong repulsion of styrene and acrylonitrile units within the copolymer[15]. This effect is explained, at least qualitatively, by recent models[12–14] and accounts for the frequent observation of miscibility with certain copolymers when their corresponding homopolymers are not miscible. These models predict a window of copolymer compositions where interactions with other polymers may be exothermic and an optimum composition where the interaction is strongest. This situation is believed to be responsible for the maximum seen in the temperature at which blends phase separate on heating as the SAN composition is varied. Nevertheless, all evidence available suggests that even at the optimum the absolute net interaction energy is relatively weak. The strength of this net interaction with SAN appears to follow the order PMMA > PEMA > PnPMA or to grow weaker as the alkyl side chain becomes longer or bulkier such that PiPMA and PnBMA are not miscible with SANs at all.

An important consequence of the above is that optimizing the AN level can lead to blends with polymethacrylates which are more amenable to melt processing. Many commercial SANs have AN levels in the range of 25 to 28% by weight which is right on the edge of the miscibility region for all polymethacrylates and as a consequence these blends phase separate at relative low temperatures on heating. SANs with a lower content of acrylonitrile phase separate at considerably higher temperatures to provide a broader range of temperatures for melt processing blends which are homogeneous.

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