Miscibility and phase diagrams of poly(phenyl acrylate) and poly(styrene-co-acrylonitrile) blends

D. Rana, B. M. Mandal* and S. N. Bhattacharyya*

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India
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The miscibility of blends of poly(phenyl acrylate) (PPA) and poly(styrene-co-acrylonitrile) (SAN) of different copolymer compositions has been studied by a film clarity test, T_g and cloud-point (T_p) studies. It was revealed that the miscibility of solvent-cast blends varies greatly from solvent to solvent. Careful annealing of solvent-cast blends below the cloud temperature and above the T_g removed the solvent effect on the lower AN content side of the miscibility window. On the higher AN content side of the miscibility window the solvent effect could not be removed by annealing at the highest permissible temperature $(< T_p \simeq 220°C)$. The phase diagrams of the blends were determined. The miscibility window at various temperatures has been constructed. It ranges between 11.5 and 32 wt% AN at 200°C. The various binary polymer segment interaction parameters have been evaluated using the composition of the miscibility window and the mean-field model.

INTRODUCTION

The phenomenon of greater miscibility in homopolymer–copolymer systems compared with that found in homopolymer–homopolymer systems is well established[1]. Miscibility in such systems has been attributed to the dilution of the strong repulsive interaction between the monomer residues in the copolymer by the monomer residues in the homopolymer, with which the repulsive interaction of the former is not as strong[2–4]. In the course of our systematic study[5–8] in the area of polymer blends, we came across a new miscible homopolymer–copolymer blend system, viz. that of poly(phenyl acrylate) (PPA) and poly(styrene-co-acrylonitrile) (SAN). PPA is miscible neither with polystyrene (PS) nor with poly(acrylonitrile) (PAN), but is miscible with their copolymers over a certain range of copolymer composition. A brief report on their miscibility was published by us[9]. The same miscible homopolymer–copolymer system was also independently reported by Sankarapandian and Kishore[10]. In our earlier communication[9] we reported that the copolymer composition region giving miscible blends varies from solvent to solvent. Examining blend films cast from solutions in a number of solvents by a film clarity test and T_g measurements, we found the miscibility window to range from 11.6 to 29.1 wt% of AN in SAN. Careful investigation now gives the miscibility window composition ranging from 11.5 to 32 wt% AN in SAN at 200°C. The miscibility window reported by Sankarapandian and Kishore[10] ranges from

15 to 35 wt% AN, which differs considerably from our value. In this paper we have discussed the cause of this discrepancy and also presented a detailed study of the solvent effect on the miscibility window, the phase diagrams, the values of the binary interaction parameters for the various polymer segments, etc.

EXPERIMENTAL

Poly(phenyl acrylate) (PPA) was a sample previously prepared and characterized in the laboratory[7]. Samples of SAN of different compositions were prepared by free-radical copolymerization of styrene and acrylonitrile at 60°C using azobisisobutyronitrile (AIBN) as initiator, keeping the conversion low, ca. 10%. The composition of the copolymers was determined from nitrogen analysis by a semi-micro Kjeldahl method[11,12]. The number-average molecular weights $(\bar{M}_n)$ of the copolymers were determined using a Hewlett–Packard 501 high-speed membrane osmometer and Schleicher and Schuell RC-51 membranes. The polydispersity index (PDI) of the polymers was determined by g.p.c. using polystyrene calibration standards. The characterization data of the polymer samples are given in *Table 1*. The solvents acetone (AC), ethylene dichloride (EDC), methylene chloride, tetrahydrofuran (THF) and chloroform were all reagent-grade chemicals and were used without further purification. The blends were prepared by the solution-casting method. Solutions of the blends were evaporated in an air oven at 50°C for 24 h and the blends were further dried in a vacuum oven at 120°C for 72 h.

The glass transition temperatures of the blends were determined using a Perkin–Elmer differential scanning

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* To whom correspondence should be addressed

calorimeter (DSC-7 with 3700 Data Station). The blends were annealed at 150°C in the d.s.c. apparatus for 20 min and then quenched. The samples were then scanned at a heating rate of 10°C min^{-1}. The T_g values reported in this paper were recorded at the half-height of the corresponding heat-capacity jump.

The cloud points (T_p) of the blends were determined using an apparatus fabricated in our laboratory. The apparatus measures the relative intensity of light transmitted through a polymer film that is placed in a hot stage sandwiched between two microscope coverslips and kept under a N_2 atmosphere. The heating rate is manually controlled using a variable transformer. The temperature of the hot stage is measured by a chromel–alumel thermocouple placed in a hole drilled through the hot stage below the sample. A photodiode is used to measure the transmitted light. The outputs of the photodiode and of the thermocouple after amplification are fed into an $X-Y$ recorder. Near the cloud point the heating rate was kept at 1–2°C min^{-1}. The cloud point was taken as the onset temperature of the change in intensity of light. Each experiment was repeated four or five times using the same sample and cloud points were averaged.

The cloud temperatures were also determined by d.s.c. by annealing the blends at increasing temperatures followed by quenching and scanning. The first annealing temperature that gives rise to two T_g values was taken as the temperature of incipient phase separation and hence the cloud point.

Table 1 Characterization data of the polymer samples

Sample	AN (wt%)	$\bar{M}_n \times 10^4$	PDI
SAN 8	7.7	9.9	1.83
SAN 10	10.4	10.4	1.73
SAN 12	11.6	5.2	2.84
SAN 13	13.1	14.6	1.85
SAN 15	15.4	14.7	1.80
SAN 18	17.7	6.9	3.19
SAN 22	22.2	8.6	2.80
SAN 25	25.1	12.8	1.83
SAN 27	27.0	19.3	1.90
SAN 29	29.1	19.9	1.85
SAN 30	30.6	15.3	1.82
SAN 31	31.5	16.7	1.88
SAN 32	32.1	19.0	1.96
SAN 33	33.0	22.4	1.90
SAN 36	35.6	18.6	2.16
PPA	–	12.1	4.42

Thermogravimetric analysis (t.g.a.) was carried out using a Shimadzu DT 30 thermal analyser.

RESULTS AND DISCUSSION

The range of copolymer compositions giving clear films varied from solvent to solvent. Blend films cast from some solvents were clear but those cast from other solvents were opaque when the SAN compositions lie near the edges of the miscibility window. Thus the composition range of a copolymer that is miscible with PPA should not be established using any single film casting solvent. In our work we used five solvents to make polymer films, and the film clarity results are summarized in *Table 2*. In each case the film was annealed at 120°C for 72 h. These results establish that the copolymer compositions giving compatible blends with PPA at 120°C range between 11.6 and 31.5 wt% AN. This range was also established from d.s.c. studies to be described below. The results given in *Table 2* also include chloroform as the film casting solvent, which was used by Sankarapandian and Kishore[10] in the miscibility study of this same blend system by the T_g method. The data in *Table 2* show that chloroform is not an ideal solvent for casting blends for miscibility studies. This phenomenon, viz. the dependence of the clarity of the films of miscible polymer blends upon the nature of blend film casting solvent, has been reported by many workers[13–17]. This effect was attributed by Robard et al.[13] to a difference in the strengths of interaction of the solvent with the two polymers; the greater the difference, the higher is the chance that the blend film would be opaque.

D.s.c. traces of some of the blends for which the copolymer compositions in SAN lie near the edges of the compatible copolymer composition region as established from the film clarity results are shown in *Figure 1*. When the solvent used to cast the film gave clear films, the latter exhibited one T_g. Thus *Figure 1* shows that 1:1 (w/w) blends of PPA and SAN 13 cast from AC, THF, methylene chloride and chloroform exhibit two T_g values, while the one cast from EDC exhibits one T_g. In all cases the blends were annealed in the d.s.c. sample pan at 150°C for 20 min, quenched to 50°C and then scanned at a heating rate of 10°C min^{-1}. This annealing temperature was selected to be on the safe side so that the cloud temperatures were not exceeded. However, when higher annealing temperatures (e.g. 250°C) were used, all the above-mentioned blends exhibited one T_g. That this phenomenon is not a consequence of the

Table 2 Results of film clarity test for 1:1 (w/w) PPA–SAN blends cast from different solvents

SAN	AC	DCE	THF	Methylene chloride	Chloroform
SAN 8	opaque	opaque	opaque	opaque	opaque
SAN 10	opaque	opaque	opaque	opaque	opaque
SAN 12	clear	clear	opaque	opaque	opaque
SAN 13	clear	clear	nt[a]	nt	opaque
SAN 15	clear	clear	clear	clear	clear
SAN 22	clear	clear	clear	clear	clear
SAN 29	clear	clear	nt	nt	opaque
SAN 30	clear	opaque	nt	nt	opaque
SAN 31	clear	opaque	opaque	opaque	opaque
SAN 32	opaque	opaque	opaque	opaque	opaque
SAN 33	opaque	opaque	nt	nt	opaque
SAN 36	opaque	opaque	nt	nt	opaque

[a] nt = not tested

Figure 1   D.s.c. thermograms of PPA and SAN 13 blends (1:1 w/w). Numbers refer to blends cast from (1) chloroform, (2) AC, (3) methylene chloride, (4) THF and (5) EDC. The blends were annealed at 150°C for 20 min before scanning

Figure 2   D.s.c. thermograms of PPA and SAN 13 blends (1:1 w/w) at two different annealing temperatures: (1) at 150°C for 20 min and (2) at 200°C for 30 min. The blends were cast from chloroform

Figure 3   D.s.c. thermograms of PPA and SAN 30 blends (1:1 w/w): blends cast from (1) AC and (2) EDC. The blends were annealed at 150°C for 20 min before scanning

existence of an upper cloud temperature was confirmed by annealing the blends again at 250°C and then cooling slowly to 50°C followed by scanning, whereupon a single T_g was again obtained. With chloroform as the blend casting solvent, annealing of the blends at 150°C for 20 min gave two T_g values, but annealing at higher temperature (ca. 200°C) for 30 min gave a single T_g. These results are shown in *Figure 2*. Thus the two T_g values initially found with blends cast from solvents other than EDC (*Figure 1*) are artifacts. It should be noted here that the blend film was clear for this copolymer composition only when cast from EDC. Films cast from the other solvents were opaque (*Table 2*). Fowler *et al.*[18] encountered this kind of pseudo-phase-separated system in a poly(methyl methacrylate) (PMMA)–SAN 9.5 blend cast from THF. The two T_g values vanished, giving rise to one T_g when the blends were properly annealed at temperatures above the glass transition temperature but below the lower cloud temperature. *Figure 3* similarly shows the d.s.c. traces of 1:1 (w/w) blends of PPA and SAN 30. The acetone-cast blend exhibited one T_g but the EDC-cast blend exhibited two T_g values. As the results in *Table 2* again show, blend films cast from EDC were opaque for this copolymer composition whereas those cast from AC were clear. In both cases the blends were annealed at 150°C for 20 min and then quenched before running the d.s.c. at a heating rate of 10°C min^{-1}. It should be noted that higher annealing temperatures and times (e.g. 8 h at 200°C or 210°C) for the blend containing SAN 30 and cast from either EDC or chloroform did not result in a single T_g. This is in sharp contrast to the blend system containing SAN 13 described above. The failure to mix the pseudo-phases in this case may indicate that the melt viscosities are still very high. Higher annealing temperatures could not be used lest the cloud temperatures (see later) are exceeded.

It has been stated in the introduction that the miscibility range found by us differed from the value reported by Sankarapandian and Kishore[10]. These workers used blends cast from chloroform solutions. We
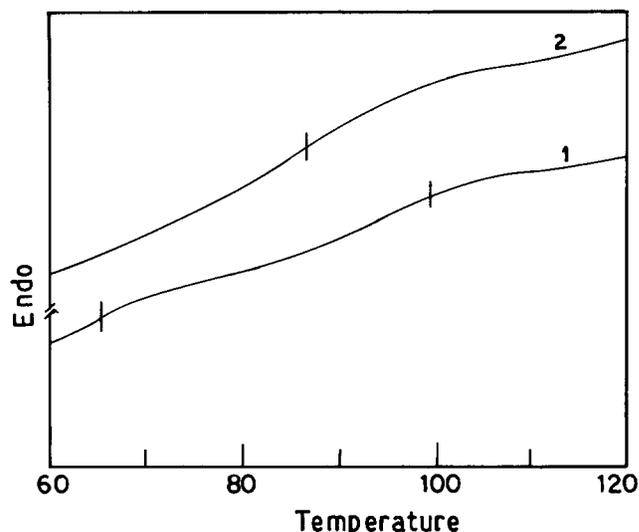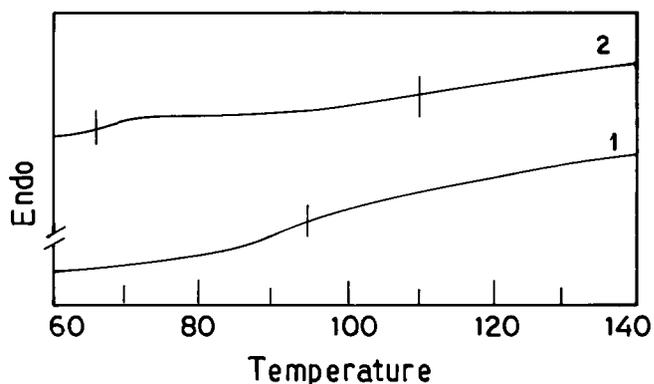
have concluded earlier in this paper that chloroform is not an ideal solvent for film casting. Thus, in order to establish miscibility by measuring T_g of chloroform-cast blends, these should be properly annealed. As we have established here for the blend with SAN 13, 30 min annealing at 150°C was not good enough; annealing at 200°C for 30 min ensured proper mixing in the melt. For the blends situated at the other side of the miscibility window, even annealing at 200°C for 8 h did not result in mixing of the pseudo-phases. Sankarapandian and Kishore[10] annealed their chloroform-cast blends at 140°C for 5 min and determined the miscibility by T_g measurements on blends so annealed. Therefore, the miscibility window reported by them is bound to be inaccurate.

Figures 4 to *6* show the variation of glass transition temperature (T_g) with blend composition using the copolymers SAN 13, SAN 22 and SAN 30. Two of these copolymer compositions, SAN 13 and SAN 30, lie near the edges of the miscibility window, while SAN 22 is situated at about the middle of the window. The T_g values exhibit a positive deviation from the weighted average of the T_g values of the pure components. Fowler *et al.*[18] also reported such positive deviation for the T_g values of miscible blends of SAN and poly(ethyl methacrylate). Usually, positive deviation is characteristic of blend
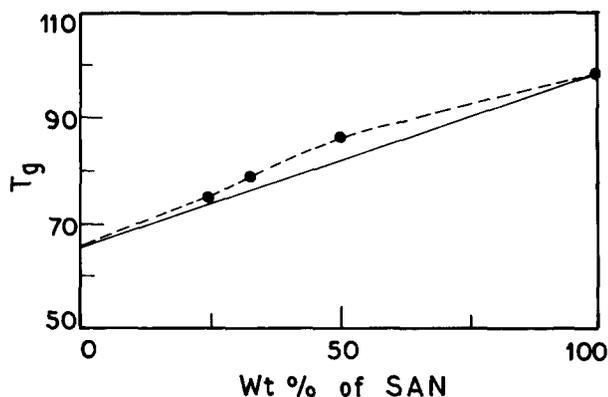
Figure 4 Plot of T_g vs. weight percentage of SAN 13 for the blends of PPA and SAN 13
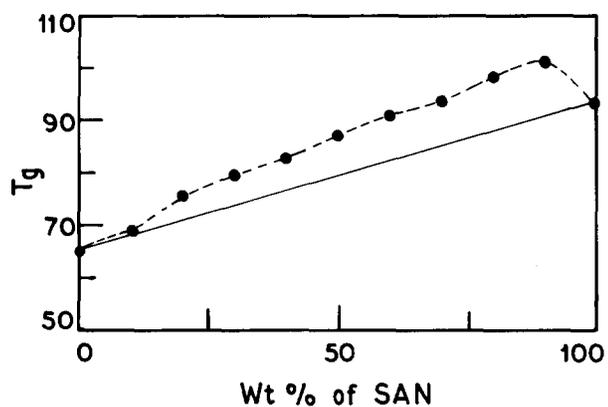
Figure 5 Plot of T_g vs. weight percentage of SAN 22 for the blends of PPA and SAN 22
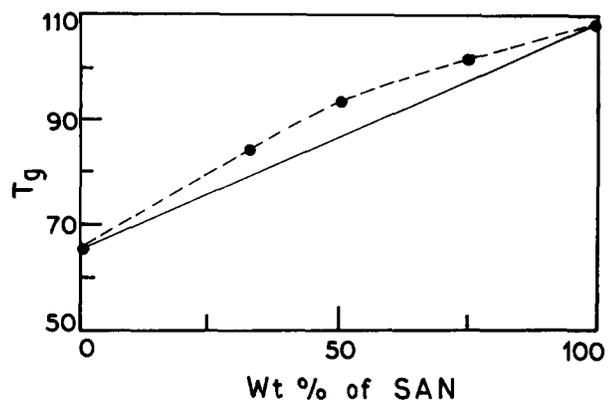
Figure 6 Plot of T_g vs. weight percentage of SAN 30 for the blends of PPA and SAN 30

systems where strong hydrogen-bonding interactions exist, which was first reported by Ting et al.[19]. The recent work of Masson and Manley[20] provided further support to this view. These workers found positive deviation in T_g for blends of cellulose/poly(4-vinylpyridine) but negative deviation for methyl cellulose/poly(4-vinyl-pyridine). Thus, positive deviation is found for the former blend system where strong hydrogen-bonding interactions exist between cellulose OH and pyridine nitrogen in poly(4-vinylpyridine). However, recently Perrin and Prud'homme[21] showed that positive deviation can be accounted for with the help of the Gordon–Taylor equation[22], which relates T_g of blends with the T_g values

of the components and the difference in thermal expansion coefficients between glassy and liquid states of the polymers. The equation is as follows:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (1)$$

where w_i is the weight fraction of component i, T_{gi} is its glass transition temperature and k is the Gordon–Taylor coefficient, which is defined by:

$$k = v_2 \Delta \alpha_2 / v_1 \Delta \alpha_1 \qquad (2)$$

Here v_i is the specific volume of component i and $\Delta \alpha_1$ is the difference between its volume expansion coefficients in the liquid and glassy states. The equation yields a positive deviation when $k > 1$. Perrin and Prud'homme[21] estimated k for poly(vinyl chloride) (PVC) and many polymethacrylates, and found that for some of them $k > 1$ and they indeed exhibit positive deviation in T_g vs. composition curves. In the absence of $\Delta \alpha$ data in our system, it is not possible to comment whether the positive deviation in our system is due to this effect or to the net interaction in the present system being very strong, although no strong specific interactions like hydrogen bonding exist between any of the polymer segments in the present case.

The phase boundaries for the blend systems containing SAN of different AN contents as determined by optical cloud-point studies are shown in *Figure 7*. The incipient phase separation temperatures were difficult to determine accurately by d.s.c. For example, the 1:1 blend containing SAN 12 gave a single T_g after annealing at 175°C for 30 min but a double T_g when the annealing was done at 210°C. Annealing temperatures between 175 and 210°C gave broad transitions, from which the incipient phase separation temperature was difficult to discern. However,
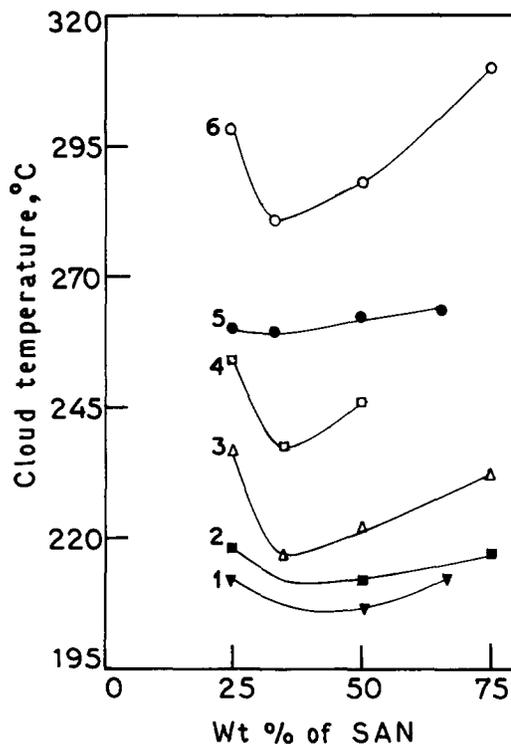
Figure 7 Cloud-temperature curves for blends of PPA and SAN of different copolymer compositions: (1) 11.6, (2) 31.5, (3) 30.6, (4) 29.1, (5) 13.1 and (6) 15.4 wt% of AN

the optical cloud-point studies gave the T_p for the same sample at 206°C. Hence the phase boundaries are constructed using T_p data. From the diagram it is clear that T_p increases as AN content in SAN increases from 11.6 to 13.1 to 15.4 wt% and decreases when AN content increases from 29.1 to 30.6 to 31.5 wt%. The T_p values for the blends containing SAN in the composition range 15.4 wt% < AN < 29.1 wt% could not be determined as these lay above the decomposition temperatures. Thermogravimetric analysis (t.g.a.) results revealed that the degradation temperatures of the blend systems for which the T_p values are reported in *Figure 7* lie above the latter. The lower critical solution temperature (*LCST*) data read from *Figure 7* as the minima of the cloud-point curves have been utilized in *Figure 8* to construct the miscibility window. It is evident from *Figure 8* that on the lower AN side of the miscibility window a steep change in T_p occurs with small change in AN content. On the other side the steepness is somewhat less. The results of the miscibility window may be utilized to calculate the binary interaction parameters involving the various monomer residues in the polymers. Thus, according to the mean-field model[2-4], the interaction parameter χ_{net} between a copolymer (1-2) and homopolymer (3) system can be expressed as follows:

$$\chi_{net} = \chi_{13}\phi_1 + \chi_{23}(1 - \phi_1) - \chi_{12}\phi_1(1 - \phi_1) \quad (3)$$

where each χ_{ij} corresponds to the interaction parameter characteristic of mixing homopolymer i with homopolymer j, and ϕ_i is the volume fraction of component i in the copolymer. At the *LCST*, χ_{net} is approximately equal to zero. Thus in the miscibility window diagram (*Figure 8*) there exist two values of ϕ_i at each temperature for which χ_{net} is zero. Putting these values of ϕ_i in equation (3), one gets two equations with three unknown χ_{ij} parameters. If one of them is known, the others may be evaluated[3]. In our present case the value for χ_{St-AN} at ambient temperature is available. Unfortunately, the miscibility window is known only at and above 200°C. However, since the edges of the window are rather steep and in view of the fact that this method of determination of χ_{ij} is not highly accurate, we may approximate the
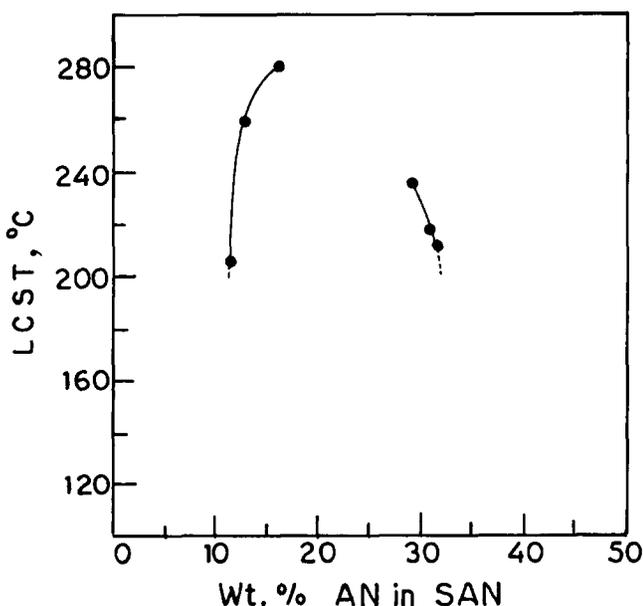
Figure 8 Miscibility window for 2:1 (w/w) blends of PPA and SAN

Table 3 Interaction parameter for the different segment pairs

χ_{St-AN}	χ_{St-PA}	χ_{AN-PA}
0.760	0.023	0.481
0.829	0.025	0.525

composition at the edges of the miscibility window at 200°C to be applicable at ambient temperature as well. Now regarding χ_{St-AN} we find in the literature that Cowie and Lath[23] determined a value of 0.829 at ambient temperature from the miscibility window studies of PMMA and SAN. They also calculated a value of 0.76 at 25°C from Molau's experimental data[24] on the miscibility of SAN of different compositions. On the other hand, Nishimoto et al.[25,26] arrived at a value of 6.74 cal cm^{-3} for B_{St-AN} from phase studies at ambient temperatures. These data give χ_{St-AN} = 0.76 at 25°C from the relation:

$$\chi_{St-AN} = \frac{V}{RT} B_{St-AN} \quad (4)$$

where V is the geometric mean of the molar volumes of the repeat units[27]. The values of the various χ parameters using these two different values of χ_{St-AN} (viz. 0.76 and 0.829) are given in *Table 3*.

These values may be compared with those derived by Sankarapandian and Kishore[10] (viz. χ_{St-PA} = 0.03 and χ_{AN-PA} = 0.48), who arrived at these values using χ_{St-AN} = 0.8 and their miscibility window compositions.

It should be noted, however, that the χ parameters determined by this method are deemed approximate since one uses the ambient temperature χ_{12} data in equation (3) but the values of ϕ_1 (miscibility window composition) at significantly higher temperatures (ca. 200°C). It is impossible to determine the miscibility window composition at ambient temperature since one cannot blend the polymers below their T_g values, and the T_g values of the present polymers are much above ambient temperature.

ACKNOWLEDGEMENT

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