Miscibility of Poly(aromatic acrylate)s and Methacrylates with Styrene/Acrylonitrile Copolymers

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ABSTRACT: Miscibilities of some poly[aromatic (meth)acrylate]s namely, poly(phenyl acrylate) (PPA), poly(phenyl methacrylate) (PPMA), poly(benzyl acrylate) (PBA), and poly(benzyl methacrylate) (PBMA)/polystyrene blends, have been studied through the so-called copolymer effect by incorporating acrylonitrile units in PS chains. In these systems, miscibility occurs on account of the strong repulsion between the acrylonitrile and styrene units in the copolymer. PBA and PBMA were blended with different styrene–acrylonitrile (SAN) copolymers. A miscibility window has been identified for the latter system, and from these limits, the binary interaction energy density parameters (B_{ij}'s) were calculated. Using these values, the miscibilities in other homopolymer–copolymer and copolymer–copolymer systems containing benzyl methacrylate, acrylonitrile, and styrene monomer units have been predicted and subsequently verified experimentally. The miscibility window limits in poly[aromatic (meth)acrylate]s/SAN copolymer blends have been compared. PBA does not exhibit a miscibility window with SAN copolymers, which has been explained by the weak intramolecular hydrogen bonding in PBA. The miscibility window in the PBMA/SAN copolymer system, as observed by DSC, shows a considerable narrowing in nonradiative energy transfer (NRET) measurements, as this technique is more sensitive.

Introduction

Due to an adverse entropy effect, polymers are generally not miscible. However, they become miscible if there is sufficient exothermic interaction between them.[1,2] Besides, exothermic mixing can also be achieved through the so-called "copolymer effect" which can be explained with the copolymer repulsion model.[3–5] According to this model, miscibility occurs in copolymer-containing blends if the intramolecular mutual repulsion between the dissimilar segments in the copolymer is sufficient to overcome the other interactions present in the mixture.

Generally, it is observed that polyacrylates and the corresponding polymethacrylates exhibit difference in the miscibility behavior in binary blends.[6–9] However, the miscibilities of polyacrylates and polymethacrylates are not much studied. In contrast to their aliphatic counterparts,[10–18] the blends of poly(aromatic acrylate)s and their polymethacrylates have not received much attention.[19–21] Studies on these blends would be interesting since phenyl rings in these esters offer the convenience of the introduction of the interacting sites for controlling the phase morphology. In the present investigation, we have studied blends of poly(aromatic acrylate)s and the corresponding methacrylates with SAN copolymers to compare the miscibility behavior of these esters, as well as the alkyl esters. Besides, detailed studies have also been carried out on the blends containing benzyl methacrylate-, styrene-, and acrylonitrile-containing polymers.

According to the Flory–Huggins theory,[1,2] the free energy of mixing at a given temperature is governed by the enthalpy of mixing and is described in terms of B_{blend}, the interaction energy density. At the limits of high molecular weights, miscibility is ensured when $B_{\text{blend}} < 0$. The B_{blend} is related to the interaction parameter "χ_{blend}" as follows:

$$\chi_{\text{blend}} = \frac{B_{\text{blend}}RT}{V_{\text{ref}}} \qquad (1)$$

where V_{ref} is the reference volume. Both B_{blend} and χ_{blend} terms are used in the literature for describing the polymer miscibility. However, since χ_{blend} involves V_{ref} data, it brings about serious error in comparing the miscibility in different systems.[13]

For copolymer-containing blends, the B_{blend} term is expressed as a linear combination of the individual binary interaction energy densities of the monomer pairs

$$B_{\text{blend}} = \sum_{i,j} C_{ij}B_{ij} \qquad (2)$$

where B_{ij} $(i \neq j)$ corresponds to each possible segmental interaction energy density in the given system and the coefficients C_{ij} are the functions of the copolymer compositions, $0 < C_{ij} < 1$. From the available values of B_{ij} or χ_{ij}, it is possible to predict the miscibility behavior in various copolymer-containing blends.[12–18,22–27] In the present investigation, the B_{ij}'s have been experimentally obtained from the studies on poly(aromatic acrylates) and their methacrylates with styrene–acrylonitrile (SAN) copolymer blends, and these values have been used to predict the miscibility of the combination of unknown blend systems containing these monomers. Subsequently, results have also been verified experimentally.

Experimental Section

Poly(benzyl acrylate) (PBA) and poly(benzyl methacrylate) (PBMA) were prepared as reported earlier.[38] SAN copolymers, benzyl methacryalte–acrylonitrile (BAN) copolymers, and benzyl methacrylate–styrene (BS) copolymers were prepared by bulk polymerization at 60 °C using AIBN as the initiator. All the copolymerizations were carried out in a vacuum and the conversions were restricted to less than 10 mol % to limit the composition drift. Products were isolated by repeated

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Table 1. Characteristics of SAN, BS, and BAN Copolymers

sample	AN content mol %	AN content wt %	T_g (°C)	$[\eta]$,[a] dL/g
PS	0	0	100	0.431
SAN4	7.3	3.86	106	0.553
SAN8	14.3	7.84	107	0.796
SAN11	20.4	11.55	107	0.567
SAN15	25.1	14.59	109	0.759
SAN18	30.6	18.35	119	0.923
SAN21	33.8	20.65	111	1.163
SAN24	38.6	24.3	112	1.092
SAN27	41.5	26.55	113	1.347
SAN30	45.6	29.93	113	1.584
SAN34	49.8	34.1	113	1.563
SAN40	53.5	40	114	1.697

sample	BMA content mol %	BMA content wt %	T_g (°C)	η_{rel}[b]
BS6	3.43	5.67	105	0.76
BS18	11.62	18.20	102	0.83
BS28	18.41	27.63	96	0.64
BS41	29.36	41.29	89	0.55
BS48	35.21	47.91	84	0.84
BS59	45.82	58.87	83	0.59
BS68	55.16	67.55	81	0.93
BS72	60.09	71.81	79	1.12
BS83	73.72	82.6	79	1.04
BS91	85.36	90.8	74	0.93

sample	AN content mol %	AN content wt %	T_g (°C)	η_{rel}[c]
BAN3	10.41	3.38	70	1.24
BAN10	26.26	9.69	72	1.36
BAN14	34.54	13.71	78	1.04
BAN17	40.73	17.15	81	0.96

[a] Intrinsic viscosity in chloroform. [b] Relative viscosity of a 0.5 wt % solution in chloroform. [c] Relative viscosity of a 0.5 wt % solution in DMF.

reprecipitation of the chloroform or DMF solutions in excess methanol. The samples were vacuum dried to a constant weight. The compositions were determined by ^{1}H NMR. The characteristics of SAN, BS, and BAN copolymers are given in Table 1. The numerals of each copolymer indicate the copolymer composition in terms of the rounded off weight percent of the comonomer.

Respective blends of PBMA, PBA, and BS copolymers with SAN copolymers were prepared by gradual reprecipitation of chloroform solutions by adding methanol dropwise. Blends containing BAN copolymers were prepared by dissolving the components in DMF and reprecipitating in methanol. All the blends were dried at 70 °C in a vacuum to a constant weight; they were of 1:1 w/w compositions.

Glass transition temperature (T_g) measurements were carried out using a DuPont DSC-1090. A 10–20 mg portion of the blends were first heated to 160 °C and held at that temperature for 5 min to erase the sample history and to make good thermal contact. The samples were then cooled and scanned at 20 K min^{-1}. For blends, the criterion of miscibility was taken as the appearance of a single reproducible T_g.

Carbazolyl- and anthryl-labeled PBMA's were prepared by copolymerizing benzyl methacrylate with 2-(*N*-carbazolyl)ethyl methacrylate (CEMA)[10] and 9-anthrylmethyl methacrylate (AMMA),[10] respectively in THF at 60 °C using AIBN as the initiator. The concentration of these labels was found to be 0.61 and 0.51 mol %, rspectively by UV spectroscopy.[39]

Films of PBMA/SAN copolymer blends were cast from 2% chloroform solutions. The films were dried in a vacuum at 60 °C to a constant weight. Fluorescence spectra of the films were recorded with a RF 540 Shimadzu fluorometer with a band pass of 5 nm. The films were mounted between two quartz plates, with the exciting beam at 60° and observation of the emission at 30° to the sample surface.[40]

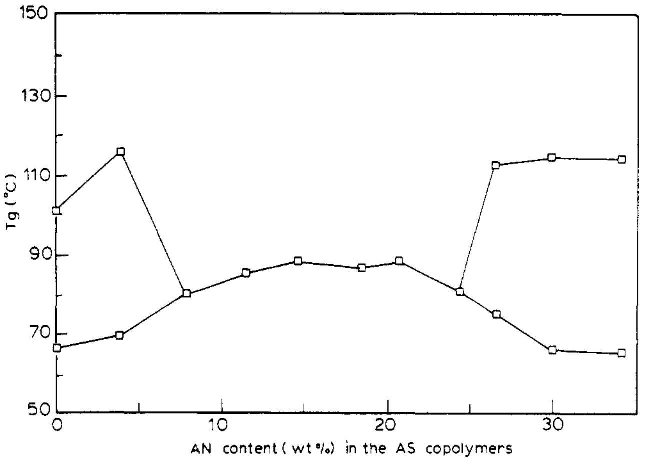

Figure 1. Dependence of T_g on AN content in PBMA/SAN copolymer blends (1:1 w/w).

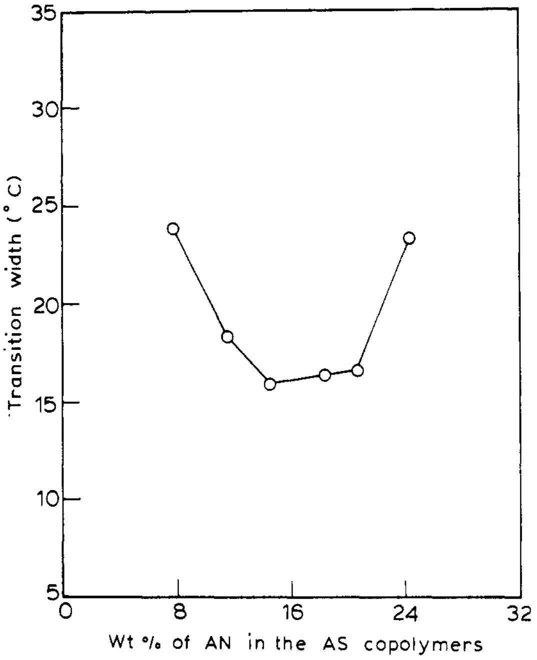

Figure 2. Dependence of glass transition width on the AN content in the PBMA/SAN copolymer miscible blends.

Results and Discussion

Miscibility of PBMA with SAN Copolymers. Thermal Studies. The miscibility in PBMA/SAN copolymer blends has been identified by T_g measurements. The T_g behavior of PBMA/SAN copolymer blends is shown in Figure 1. PBMA blends with SAN copolymers exhibit single T_g values between the acrylonitrile compositions of 7.8 and 24.3 wt % in the SAN copolymers. The width of the glass transition (TW)[41] is defined as the temperature interval between the onset and the completion of the heat capacity change at T_g. It is a measure of, heterogeneity in a miscible blend, and a plot of TW vs polymer composition is shown in Figure 2 for PBMA/SAN copolymer blends. It is clear from Figure 2 that the PBMA/SAN8 and PBMA/SAN24 blends exhibit much broader transitions, indicating that they lie at the limit of the miscibility window. Further decrease or increase of acrylonitrile content beyond these limits results in the further broadening of the transitions, eventually leading to a two-phase system. The T_g data of PBMA/SAN blends indicate that there exists a miscibility window in this system at 7.8 and 24.3 wt % of AN contents in the SAN copolymers.

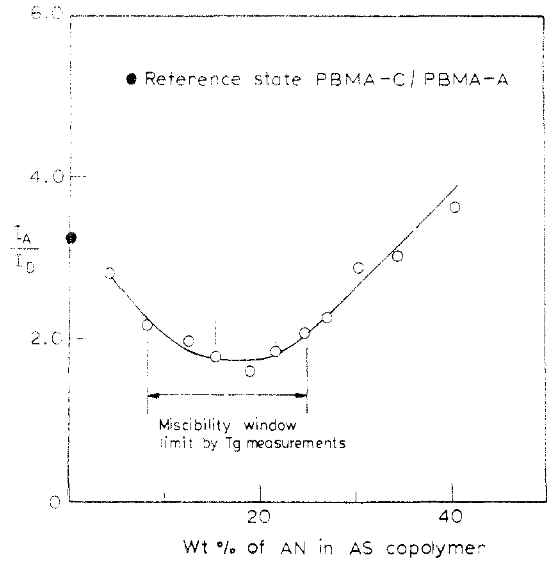

Figure 3. I_A/I_D values as a function of AN contents in SAN copolymers in PBMA/SAN blends.

Nonradiative Energy Transfer (NRET) Studies. The NRET method employed in the present investigation is similar to the one followed by Prudhomme et al.,[40] where only one of the components of the blend is labeled with donor and acceptor separately. The labeled chains of a given component, in equal proportions, are mixed in small concentrations with the unlabeled chains of the same component. This labeled component is then mixed with the second component of the blend. In the event of complete miscibility, the donor and acceptor groups are separated due to dispersion. The immiscibility, on the other hand, will not affect the average distance between the donor and acceptor. Hence, the variation of the average distance between the donor and acceptor groups, which is characterized by the efficiency of the energy transfer, is a measure of the miscibility. The energy transfer efficiency is described by the ratio I_A/I_D, where I_A and I_D are the emission intensities of the acceptor and donor groups, respectively. The I_A/I_D of the labeled unblended component is taken as the reference value, which will be high due to the maximum energy transfer from the donor to the acceptor. In the blend, with the increase in the extent of the miscibility of the two components, I_A/I_D decreases due to the random dispersion of the chains. For carbazole donor and anthracene acceptor groups, Amrani and co-workers[39] have shown that NRET is efficient to detect the miscibility over distances up to 2.8 nm.

PBMA chains were labeled separately with carbazolyl donor (PBMA-C) and anthryl acceptor (PBMA-A) groups. SAN copolymers were mixed with the labeled PBMA's and were diluted with unlabeled PBMA component until the concentration of the labels was 4×10^{-3} mol L^{-1} in the blends. The PBMA/SAN copolymer blends were of 60/40 w/w composition. In the blend films, the carbazolyl donor was excited at 297 nm and the emission intensities were measured for carbazolyl groups (I_D) at 347 nm, and for anthryl groups (I_A) at 415 nm. The variation of I_A/I_D with the copolymer composition, in the PBMA/SAN copolymer blends, is shown in Figure 3. The I_A/I_D decreases and acquires a minimum value when the AN content in the SAN copolymers is between 15 and 21 wt % (the plateau region of the minima), indicating the random dispersion of the blend at a level of 2.8 nm. Compared to the miscibility window limit of 15–21 wt % of AN contents in SAN copolymers, which corresponds to a 2.8 nm level of miscibility, the corresponding miscibility window limit, from T_g measurements, is 8–24 wt % of AN units in the SAN copolymers, which corresponds to about an 8 nm level of miscibility. This is indeed very close to the detection level (~10 nm) of the T_g measurements. The NRET measurements detect the miscibility to a higher resolution level as compared to the thermal measurements.

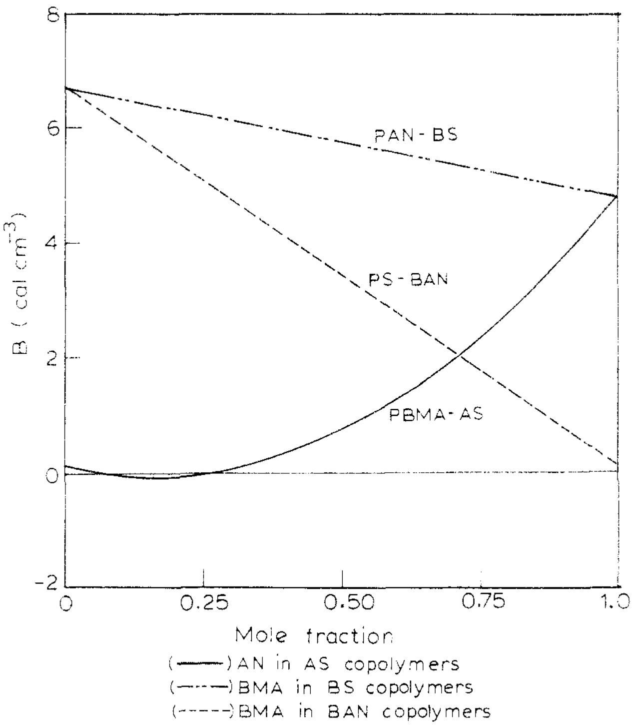

Figure 4. Calculated B_{blend} values for the blends of homopolymer–copolymers containing BMA, AN, and St units as a function of the copolymer compositions.

The regular change in the I_A/I_D ratio in both the flanks of the miscibility window (Figure 3) may be accounted for by the interfacial diffusion of the components into each other, resulting in a thick interface. Such interface in the blends of PMMA/SAN copolymers has been observed by ellipsometric studies.[42]

Calculation of Binary Interaction Energy Densities in PBMA/SAN Blends. For the PBMA/SAN copolymers, the interaction energy density can be written from eq 2 as

$$B_{blend} = f(y) = yB_{BMA/AN} + (1 - y)B_{BMA/St} - y(1 - y)B_{St/AN} \quad (3)$$

where BMA, AN and St correspond to benzyl methacrylate, acrylonitrile, and styrene monomer units, respectively. At the limit of the miscibility window, i.e., when y_1 and y_2 correspond to 0.07 and 0.223 volume fractions of AN units in SAN copolymers (obtained from T_g measurements), $B_{blend} = 0$. Using the reported value[14] of $B_{St/AN} = 28.03$ J cm^{-3}, the quadratic equation (3) was solved to obtain the other two B_{ij} values: $B_{BMA/AN} = 20.25$ J cm^{-3} and $B_{BMA/St} = 0.44$ J cm^{-3}. Comparison of these B_{ij} values indicate that they follow the order $B_{St/AN} > B_{BMA/AN} > B_{BMA/St}$. The magnitude of these values closely matches the situation in other PMMA/SAN copolymer blends[14] and poly(phenyl acrylate)/SAN copolymer blends.[20]

The B_{ij} values thus obtained from PBMA/SAN copolymer blends were used to calculate the interaction parameters in homopolymer–copolymer blends containing BMA, St, and AN monomer units, like PBMA/SAN, PS/BAN, and PAN/BS blends. In Figure 4 the varia-

Table 2. DSC Results for PS/BAN and PBA/SAN Blends

blends (1:1 w/w)	T_g values (°C)	blends (1:1 w/w)	T_g values (°C)
PS + BAN3	70, 102	PBA + PS	12, 101
PS + BAN10	72, 103	PBA + SAN4	13, 103
PS + BAN14	78, 104	PBA + SAN11	12, 109
PS + BAN17	70, 103	PBA + SAN18	13, 110
		PBA + SAN27	13, 110
		PBA + SAN34	12, 110

tions of the interaction energy density with the copolymer compositions, in the above blends, are indicated. In Figure 4 the situation closely resembles that in methyl methacrylate St and AN monomers containing homopolymer–copolymer blends on account of the close match of B_{ij} values with the BMA counterparts. The positive values of B_{blend} obtained for PS/BAN and PAN/BS blends indicate that these blends are immiscible at all the compositions of the copolymers at the limit of high molecular weights. The T_g measurements were made for some PS/BAN blends of 1:1 w/w compositions (Table 2). The PS/BAN blends exhibit two T_g's, indicating immiscibility. The appearance of miscibility window in PBMA/SAN copolymer blends is a result of the strong repulsion within the SAN polymer coupled with the weak interactions with the homopolymer units.

The B_{ij} values were also used to predict the miscibility in copolymer–copolymer blends comprising of these three monomers.

Miscibility Behavior in BS/SAN, BAN/SAN, and BS/BAN copolymer–copolymer blends. The three B_{ij} values obtained from the study of PBMA/SAN copolymer blends were substituted in the following equations for predicting the phase behavior in BS-SAN, BAN-SAN, and BS-Ban copolymer–copolymer blends, respectively:

$$B_{\text{blend}} = x^2B_{\text{BMA/St}} + xy(B_{\text{BMA/AN}} - B_{\text{BMA/St}} - B_{\text{St/AN}}) + y^2B_{\text{St/AN}} \quad (4)$$

$$B_{\text{blend}} = x^2B_{\text{BMA/AN}} + xy(B_{\text{BMA/St}} - B_{\text{BMA/AN}} - B_{\text{St/AN}}) + y^2B_{\text{St/AN}} \quad (5)$$

$$B_{\text{blend}} = x^2B_{\text{BMA/St}} + xy(B_{\text{St/AN}} - B_{\text{BMA/AN}} - B_{\text{BMA/St}}) + y^2B_{\text{BMA/AN}} \quad (6)$$

In the above equations, the x and y values for which $B_{\text{blend}} \leq 0$ were identified by substituting the corresponding B_{ij} values, and the predicted miscibility map for these systems are represented as the hatched area in Figures 5 and 6. For BS/BAN blends, the B_{blend} is positive at all the copolymer compositions, and hence there is no miscibility map for this system, i.e. no hatched area in Figure 7. The prediction of miscibilty/immiscibility in these blends are supported by T_g measurements.

Miscibility of Poly(phenyl acrylate) with SAN Copolymers. The presence of a miscibility window in PPA/SAN copolymer blends has been reported earlier[20,21] which corresponds to 14.6 and 34.1 wt % of acrylonitrile in SAN copolymers. The B_{ij} values in the system are calculated using the reported value[14] of $B_{\text{St/AN}} = 28.03$ J cm^{-3} and the resultant values are $B_{\text{PA/St}} = 1.17$ J cm^{-3} and $B_{\text{PA/AN}} = 16.65$ J cm^{-3}.

Miscibility of Poly(phenyl methacrylate) with SAN Copolymers. Recently Nishimoto et al.[14] reported the presence of the miscibility window for this system as determined by optical clarity and phase separation studies. The window limit corresponds to 9.5 and 34 wt % of AN contents in the SAN copolymers. The B_{ij} values for this system, by using the value of $B_{\text{St/AN}} = 28.03$ J cm^{-3} were calculated[14] and they correspond to $B_{\text{PMA/St}}$ 0.84 J cm^{-3} and $B_{\text{PMA/AN}} = 16.74$ J cm^{-3}.

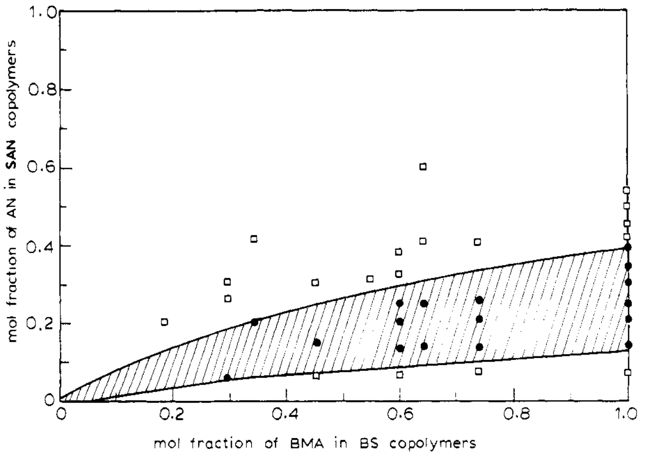

Figure 5. Miscibility behavior of BS/SAN copolymer–copolymer blends: hatched area, the miscibility range; ●, miscible blends; □, immiscible blends.

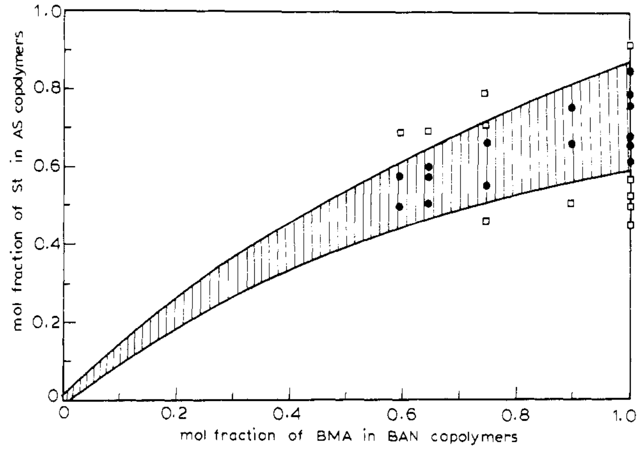

Figure 6. Miscibility behavior in BAN/SAN copolymer–copolymer blends: hatched area, calculated miscibility map; ●, miscible blends; □, immiscible blends.

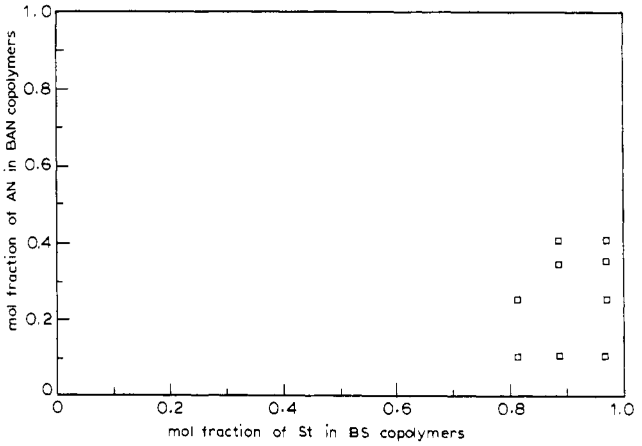

Figure 7. Miscibility behavior in BS/BAN copolymer–copolymer blends: □, immiscible blends.

Miscibility of Poly(benzyl acrylate) with SAN Copolymers. The DSC results of the PBA/SAN copolymer blends of 1:1 w/w compositions are given in Table 2 and suggest that PBA is immiscible with PS and SAN copolymers as shown by two T_g's in these blends. Thus, contrary to the results for PPA, PPMA, and PBMA homopolymers, no miscibility window was obtained for PBA/SAN copolymer blends.

Table 3. Miscibility Window Limits in Poly(alkyl methacrylate), Poly(aryl methacrylate)s, and PPA with SAN Copolymer Blends

	wt % of AN		
poly(meth)acrylate	lower limit	upper limit	ref
PMMA	8.9–9.4	34.4–36.9	16
	8.0–12.9	37.0–39.3	15
	6.3–9.5	>32.3	10
PEMA	0.0	28.0–30.0	10
PnPMA	0.0	25.0–28.0	10
PPMA	6.3–9.5	34–40	14
PBMA	3.9–7.8	24.3–26.6	this work
PPA	11.6–14.6	34.1–40.0	this work
PBA	no miscibility window		this work

Table 4. B_{ij} Values for Systems Containing Aromatic Acrylates, Methacrylates, Styrene, and Acrylonitrile Containing Polymers ($B_{St/AN}$ = 28.03 J cm^{-3}, ref 14)

$B_{meth(acrylate)-AN}$ (J cm^{-3})	$B_{meth(acrylate)-St}$ (J cm^{-3})
$B_{PA/AN} = 16.65$	$B_{PA/St} = 1.17$
$B_{PMA/AN} = 16.74$	$B_{PMA/St} = 0.84$
$B_{BMA/AN} = 20.25$	$B_{BMA/St} = 0.44$

Comparison of Polyacrylates and Polymethacrylates with SAN Copolymers. The miscibility window limits for several poly(alkyl methacrylate)/SAN copolymer blends have been tabulated by Brannock et al.[9] Table 3 comprises the miscibility window limits for the polyacrylates and methacrylates identified so far.

The immiscibility of polyacrylates with SAN copolymers is noteworthy. This difference in the miscibility behavior between the polyacrylates and polymethacrylates may be attributed to the presence of weak intramolecular hydrogen bonding between the carbonyl group of the esters and the α-hydrogen of the polyacrylates. A similar explanation has been offered for the difference in the miscibility behavior of polyacrylates with polymethacrylates with PVC and chlorinated polyethylenes.[6] The existence of a miscibility window in PPA/SAN copolymer blends could not be explained on the same line. It should be noted that PPA happens to be the only polyacrylate to show a miscibility window with the SAN copolymers.

The B_{ij} values of poly(aromatic acrylate) and their methacrylates blends with SAN copolymers are given in Table 4. Comparison of the above values reveals that the binary interaction energy densities of (meth)acrylate–AN pairs are similar and so are those for the (meth)acrylate–styrene pairs. This is the consequence of similar miscibility window limits present in these systems as indicated in Table 4. These B_{ij} values are comparable with the corresponding alkyl methacrylate pairs reported elsewhere.[14]

Conclusion

PPA, PPMA, and PBMA homopolymers exhibit windows with SAN copolymers which have been accounted for the dominant repulsion between the St and AN units in SAN copolymers compared to other interactions in the blends. PBA does not show a miscibility window due to the possible intramolecular hydrogen bonding. The level of miscibility in PBMA/SAN copolymer blends was verified by NRET studies, it shows considerable narrowing of the miscibility window limits compared to that obtained from T_g measurements. From the miscibility window limits the B_{ij} values were calculated and compared among the poly(aromatic acrylates) and their methacrylates blends with SAN copolymers. The predicted miscibility/immiscibility were verified by experiments.

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