Miscibility behaviour of polymethacrylates with poly(styrene-*co*-methacrylonitrile)

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The miscibility behaviour of various poly(styrene-*co*-methacrylonitrile) (SMAN)/polymethacrylate blends was studied using differential scanning calorimetry. SMAN is miscible with poly(ethyl methacrylate) (PEMA), poly(n-propyl methacrylate) (PnPMA) and poly(isopropyl methacrylate) (PiPMA) over certain copolymer composition ranges, but is immiscible with poly(n-butyl methacrylate) (PnBMA) and poly(isobutyl methacrylate) (PiBMA). The width of the miscibility window decreases with increasing size of the pendent ester group of the polymethacrylate, and is wider than that of the corresponding poly(styrene-*co*-acrylonitrile) blend system. Various segmental interaction parameters are calculated using a binary interaction model.

(Keywords: miscibility; poly(styrene-*co*-methacrylonitrile); polymethacrylates)

INTRODUCTION

The mixing of two polymers is accompanied by a negligible entropy change. As a result, the formation of a miscible polymer blend requires some specific interactions between the component polymers, giving rise to a negative enthalpy of mixing. However, if one of the two polymers is a copolymer, a miscible blend can be obtained over a certain copolymer composition range even in the absence of specific interactions. In this case, the favourable negative enthalpy of mixing arises from strong intramolecular interactions between the two different types of segments in the copolymer. Poly(alkyl methacrylate)s such as poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(n-propyl methacrylate) (PnPMA) are miscible with poly(styrene-*co*-acrylonitrile) (SAN)[1–4], poly(α-methylstyrene-*co*-acrylonitrile) (αMSAN)[5–7] and poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN)[8] over certain copolymer composition ranges, showing 'miscibility windows'. In addition, poly(n-butyl methacrylate) (PnBMA) is miscible with αMSAN[7] and *p*MSAN[8] over rather narrow copolymer composition ranges, but it is immiscible with SAN[2].

In a recent communication, we reported that PMMA is miscible with poly(styrene-*co*-methacrylonitrile) (SMAN)[9]. The miscibility window is wider than that of the PMMA/SAN system. We now report the miscibility of other poly(alkyl methacrylate)s with SMAN.

EXPERIMENTAL

Materials

Methacrylonitrile (Fluka) was purified by passing through a column packed with hydroquinone remover (Scientific Polymer Products). Styrene (Fluka) was fractionally distilled at 42°C and 15 mmHg (1 mmHg = 133.3 Pa). Ethyl methacrylate (Scientific Polymer Products), n-propyl methacrylate (Polysciences Inc.), n-butyl methacrylate (Scientific Polymer Products) and isopropyl methacrylate (Polysciences Inc.) were also purified by vacuum distillation at 50°C and 80 mmHg, 48°C and 20 mmHg, 48°C and 15 mmHg, and 55°C and 70 mmHg, respectively. SMAN copolymer samples were prepared by solution polymerization as described previously[9]. PEMA, PnPMA, PnBMA and PiPMA-1 were similarly prepared by free-radical polymerization in 2-butanone at 60°C for 5 h. Poly(isobutyl methacrylate) (PiBMA) and another PiPMA sample (designated as PiPMA-2) were obtained from Scientific Polymer Products Inc. *Table 1* shows the characteristics of the polymers.

Table 1 Characteristics of polymers

Polymer	T_g (°C)	M_n (kg mol^{-1})	M_w/M_n	Degree of polymerization, N
SMAN3.9[a]	97	24.3	1.78	240
SMAN5.6	96	22.0	1.68	220
SMAN10.3	96	14.7	1.70	150
SMAN13.2	96	22.1	1.98	230
SMAN17.1	96	16.9	1.58	180
SMAN20.4	97	17.0	1.54	180
SMAN25.5	98	21.4	1.99	235
SMAN27.3	97	18.0	2.33	200
SMAN30.5	101	25.0	2.10	280
SMAN35.4	103	21.3	2.22	245
SMAN40.1	105	17.9	2.33	210
SMAN46.6	106	18.7	2.15	225
SMAN53.0	107	15.7	2.03	195
SMAN57.8	108	15.4	1.80	195
PEMA	57	56.3	1.87	490
PnPMA	51	73.0	1.65	570
PiPMA-1	91	161.0	1.56	1260
PiPMA-2	82	41.6	1.80	325
PnBMA	36	61.0	1.98	430
PiBMA	56	144.5	1.68	1020

[a] Number after SMAN denotes weight percentage of MAN in the copolymer

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Table 2 Characteristics of PEMA/SMAN (1:1) blends

Copolymer	Clarity of films	Number of glass transitions	*LCST* behaviour
SMAN3.9	Cloudy	2	–
SMAN5.6	Clear	1	Yes
SMAN10.3	Clear	1	No
SMAN17.1	Clear	1	No
SMAN27.3	Clear	1	No
SMAN35.4	Clear	1	Yes
SMAN40.1	Clear	1	Yes
SMAN46.6	Hazy	2	–
SMAN53.0	Cloudy	2	–
SMAN57.8	Cloudy	2	–

Preparation of blend

SMAN blends with various polymethacrylates in a weight ratio of 1:1 were prepared by solution casting from tetrahydrofuran. The solvent was allowed to evaporate slowly at room temperature. The blend films were dried *in vacuo* first at 60°C for a week and then at 90°C for another week.

Characterization

The miscibility behaviour of various blends was ascertained using the single glass transition temperature (T_g) criterion. T_gs of various blend samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter at a heating rate of 20°C min^{-1}. Since the differences in T_g values between PiPMA and SMAN samples are less than 20°C, the blends were subjected to an annealing process[10]. Each of the PiPMA/SMAN blends was first kept at 150°C for 5 min, and then annealed at 65°C for 2 weeks. The annealed sample was then scanned. A single enthalpy recovery peak indicates miscibility. All the clear films at room temperature were examined for lower critical solution temperature (*LCST*) behaviour using the method described previously[11]. The temperature at which the transparent film first showed cloudiness was taken as the cloud point.

RESULTS

The optical appearance of a blend often provides the first clue on miscibility. If the refractive indices of the two polymers are sufficiently different, a transparent blend indicates that the size of any heterogeneity present is much smaller than the wavelength of visible light. The refractive indices of PEMA, PnPMA, PiPMA, PnBMA and PiBMA are 1.485, 1.484, 1.552, 1.483 and 1.477, respectively, and those of SMAN samples are in the range 1.52–1.59[12]. Except for PiPMA, the refractive indices of the polymethacrylates are very different from those of SMAN samples. Thus, the optical clarity of blends other than those of PiPMA blends can be a good indication of miscibility.

PEMA/SMAN blends

Table 2 summarizes the optical appearance, the number of glass transitions and the *LCST* behaviour of PEMA/SMAN blends. Each of the blends of PEMA with SMAN having MAN contents between 5.6 and 40.1 wt% had a single T_g, indicating miscibility. However, the PEMA/SMAN3.9, PEMA/SMAN46.6 and PEMA/SMAN53.0 blends had two distinct T_gs, indicating that PEMA is immiscible with these SMAN samples. At room temperature, blends of PEMA with SMAN3.9, SMAN53.0 and SMAN57.8 were cloudy, but blends of PEMA with SMAN having MAN contents from 5.6 to 40.1 wt% were transparent. For these clear blends PEMA/SMAN5.6, PEMA/SMAN35.4 and PEMA/SMAN40.1 blends showed *LCST* behaviour and the others remained transparent up to 300°C, the highest temperature allowed by the apparatus. The phase diagram of this system is shown in *Figure 1*. The miscibility range of this system was found to be 4.5–44 wt% of MAN, much wider than that of PEMA/SAN blends[2].

PnPMA/SMAN blends

Table 3 summarizes the optical appearance, the number of glass transitions and the *LCST* behaviour of PnPMA/SMAN blends. PnPMA/SMAN35.4 and PnPMA/SMAN40.1 blends were cloudy and two T_gs were observed in each blend, indicating that PnPMA is immiscible with SMAN having MAN contents ≥35.4 wt%. Blends of PnPMA with SMAN having MAN contents from 3.9 to 30.5 wt% were clear at room temperature and each of them showed one T_g, indicating miscibility in this composition range. Since PnPMA is immiscible with polystyrene[2], the miscibility window of the PnPMA/SMAN system is then between 3 and 32 wt%

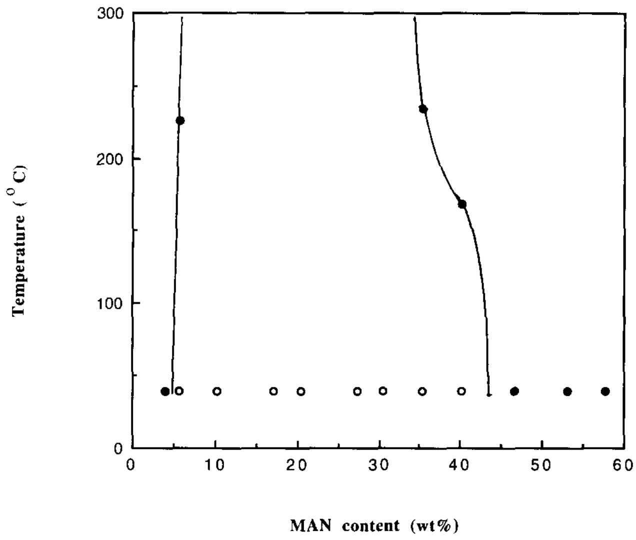

Figure 1 Phase diagram of PEMA/SMAN (1:1) blends: (○) miscible blend; (●) immiscible blend

Table 3 Characteristics of PnPMA/SMAN (1:1) blends

Copolymer	Clarity of films	Number of glass transitions	*LCST* behaviour
SMAN3.9	Clear	1	Yes
SMAN5.6	Clear	1	Yes
SMAN10.3	Clear	1	Yes
SMAN13.2	Clear	1	Yes
SMAN17.1	Clear	1	Yes
SMAN20.4	Clear	1	Yes
SMAN25.5	Clear	1	Yes
SMAN27.3	Clear	1	Yes
SMAN30.5	Clear	1	Yes
SMAN35.4	Cloudy	2	–
SMAN40.1	Cloudy	2	–

of MAN contents. All the miscible blends showed *LCST* behaviour and the phase diagram is shown in *Figure 2*.

PiPMA/SMAN blends

As mentioned earlier, the optical clarity of PiPMA/SMAN blends may not be taken as an indication of miscibility because of the matching in refractive indices of PiPMA and some SMAN samples. The d.s.c. curves of annealed PiPMA-1 blends are shown in *Figure 3*. The appearance of a single enthalpy recovery peak for some blends indicates miscibility. *Table 4* summarizes the glass transition behaviour of various blends. The results clearly demonstrate the effect of molecular weight on miscibility. PiPMA-1, which has a higher molecular weight, shows a narrower miscibility range than PiPMA-2.

Because of the matching refractive indices of PiPMA and SMAN, the *LCST* behaviour of the blends cannot be examined by the usual method. Instead, the technique of isothermal annealing was used. The sample was first annealed at an elevated temperature for 5 min, followed by annealing at 65°C for 2 weeks. The glass transition behaviour of the annealed blend was examined to find out whether annealing at that elevated temperature had induced phase separation. The phase diagrams of the two blend systems are shown in *Figures 4* and *5*. All the miscible blends undergo phase separation when annealed at sufficiently high temperatures.

PnBMA/SMAN and PiBMA/SMAN blends

All the blends were cloudy. Each of the blends had two glass transitions, indicating that SMAN is immiscible with PnBMA and PiBMA.

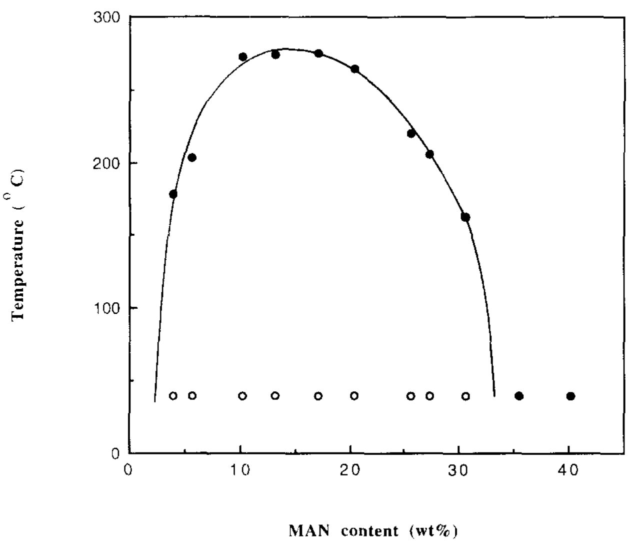

Figure 2 Phase diagram of PnPMA/SMAN (1:1) blends: (○) miscible blend; (●) immiscible blend

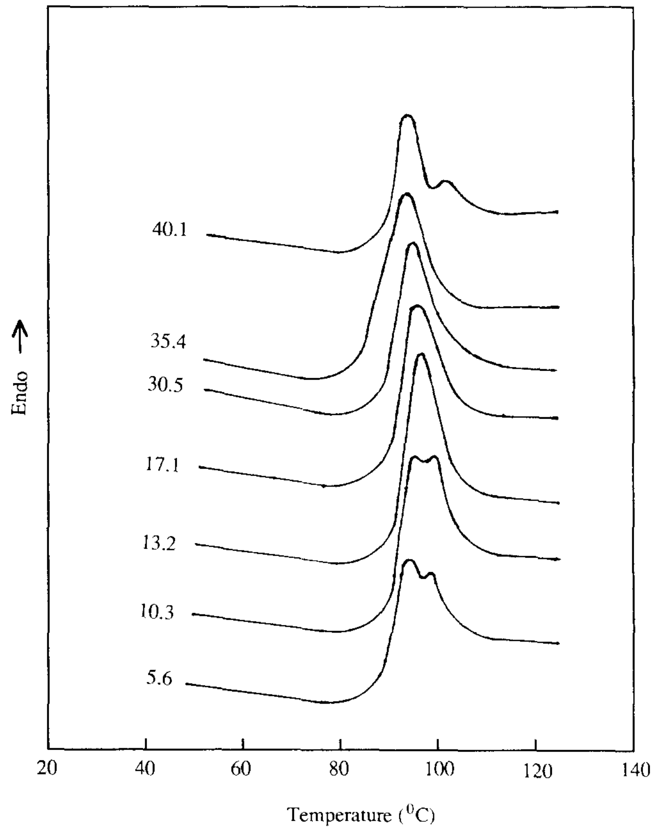

Figure 3 D.s.c. curves of annealed PiPMA-1/SMAN (1:1) blends (number denotes wt% of MAN in the copolymer)

Table 4 Characteristics of PiPMA/SMAN (1:1) blends

	PiPMA-1/SMAN blend system		PiPMA-2/SMAN blend system	
Copolymer	Clarity of blend	Number of glass transitions	Clarity of blend	Number of glass transitions
SMAN3.9	Hazy	2	Hazy	2
SMAN5.6	Hazy	2	Clear	2
SMAN10.3	Clear	2	Clear	1
SMAN13.2	Clear	1	Clear	1
SMAN17.1	Clear	1	Clear	1
SMAN20.4	Clear	1	Clear	1
SMAN25.5	Clear	1	Clear	1
SMAN27.3	Clear	1	Clear	1
SMAN30.5	Hazy	1	Clear	1
SMAN35.4	Hazy	1	Clear	1
SMAN40.1	Hazy	2	Hazy	1
SMAN46.6			Cloudy	2
SMAN53.0			Cloudy	2

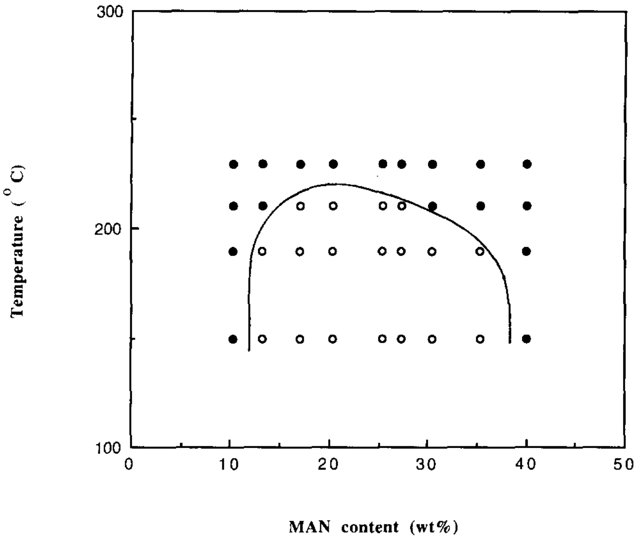

Figure 4 Phase diagram of PiPMA-1/SMAN (1:1) blends: (○) miscible blend; (●) immiscible blend

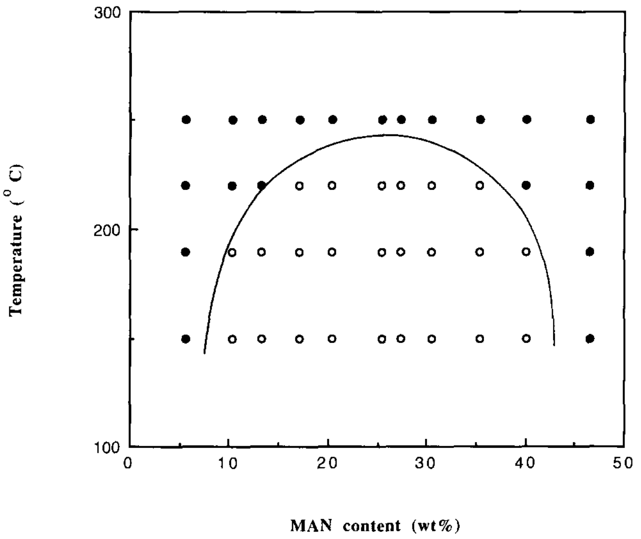

Figure 5 Phase diagram of PiPMA-2/SMAN (1:1) blends: (○) miscible blend; (●) immiscible blend

DISCUSSION

The miscibility behaviour of various polymethacrylates with SMAN and SAN is summarized in *Table 5*. For both systems, the width of the miscibility range decreases with increasing size of the pendent alkyl group of polymethacrylate. Similar trends were also observed for polymethacrylates with αMSAN[7] and *p*MSAN[8]. The polymethacrylate/SMAN blend systems have wider miscibility ranges than the corresponding SAN systems. Another interesting point is that PiPMA is miscible with SMAN over a rather wide copolymer composition range, but it is immiscible with SAN and *p*MSAN.

Segmental interaction parameters

The miscibility of homopolymer A/copolymer B_yC_{1-y} blend is commonly explained using a binary interaction model[13–15]. Based on the model, the interaction parameter (χ_{blend}) for a blend system is related to three segmental interaction parameters by the following equation

$$\chi_{blend} = y\chi_{AB} + (1-y)\chi_{AC} - y(1-y)\chi_{BC} \qquad (1)$$

where y is the volume fraction of segment 'B' in the copolymer BC.

For SMAN/polymethacrylate blends, χ_{blend} is expressed by the equation

$$\chi_{blend} = y\chi_{MA/MAN} + (1-y)\chi_{S/MA} - y(1-y)\chi_{S/MAN} \qquad (2)$$

where y represents the volume fraction of MAN in SMAN copolymers and subscripts MA, MAN and S denote methacrylate, methacrylonitrile and styrene segments, respectively. At the miscibility–immiscibility boundary, χ_{blend} equals χ_{crit}, which is given by the following equation:

$$\chi_{crit} = \tfrac{1}{2}(N_1^{-1/2} + N_2^{-1/2})^2 \qquad (3)$$

where N_1 and N_2 are the degrees of polymerization for the two polymers. In the present work, a value of N of 220 for SMAN is used to calculate χ_{crit} as most of the copolymer have N values close to this value. For the PEMA/SMAN system, χ_{crit} is taken to be 0.0063 based on the N values of 220 and 490 for SMAN and PEMA, respectively, and $\chi_{S/MAN} = 0.52$ (ref. 9). The miscibility window is considered at 4.5 and 44 wt% of MAN, corresponding to y values of 0.043 and 0.43. $\chi_{S/EMA}$ and $\chi_{EMA/MAN}$ are calculated to be 0.016 and 0.29, respectively. For the PnPMA/SMAN blend system, χ_{crit} is 0.0060 and y values are 0.029 and 0.31. $\chi_{nPMA/MAN}$ and $\chi_{nPMA/S}$ are then 0.35 and 0.011, respectively. For PiPMA-1/SMAN blends, χ_{crit} is 0.0049 and y values are 0.115 and 0.37. $\chi_{iPMA/S}$ and $\chi_{iPMA/MAN}$ are then 0.027 and 0.29, respectively. For the PiPMA-2/SMAN blend system, y values are 0.077 and 0.42, and χ_{crit} is 0.0076. $\chi_{iPMA/S}$ and $\chi_{iPMA/MAN}$ are found to be 0.025 and 0.29, respectively, which are in excellent agreement with those obtained from the PiPMA-1 system.

The various segmental interaction parameters are summarized in *Table 6*. For comparison purposes, the χ values for the corresponding SAN blends are also shown in *Table 6*. The χ values for various methacrylates with styrene obtained from SMAN and SAN systems are in good agreement. These values are small and positive, indicating that the interactions are weakly repulsive. The interaction decreases slightly in magnitude with increasing size of the pendent group of the polymethacrylate from methyl to n-propyl. On the other hand, the χ values for various methacrylates with MAN are large, indicating strong repulsive interactions. The interaction becomes more intense when the pendent group changes from methyl to n-propyl. Nevertheless, these χ values are smaller than those corresponding methacrylate/AN interaction parameters. The χ values obtained from the PiPMA/SMAN blend system reveal some interesting

Table 5 Miscibility windows of some binary blends

	SMAN (wt% of MAN)	SAN (wt% of AN)
PMMA	8–63[9]	9–35[1] 8–30[2] 9–39[3]
PEMA	4.5–44	5–30[2]
PnPMA	2–32	5.5–20[2]
PiPMA-1	12–38	Immiscible
PiPMA-2	8–43	
PnBMA	Immiscible	Immiscible

Table 6 Segmental interaction parameters for SMAN and SAN blends

Polymer blend system	SMAN system	SAN system[8]
PMMA	$\chi_{MMA/S}=0.03$	$\chi_{MMA/S}=0.03$
	$\chi_{MMA/MAN}=0.19$	$\chi_{MMA/AN}=0.46$
	$\chi_{S/MAN}=0.52$	$\chi_{S/AN}=0.829$
PEMA	$\chi_{EMA/S}=0.016$	$\chi_{EMA/S}=0.016$
	$\chi_{EMA/MAN}=0.29$	$\chi_{EMA/AN}=0.57$
PnPMA	$\chi_{nPMA/S}=0.011$	$\chi_{nPMA/S}=0.013$
	$\chi_{nPMA/MAN}=0.35$	$\chi_{nPMA/AN}=0.65$
PiPMA-1	$\chi_{iPMA/S}=0.027$	
	$\chi_{iPMA/MAN}=0.29$	
PiPMA-2	$\chi_{iPMA/S}=0.025$	
	$\chi_{iPMA/MAN}=0.29$	

Table 7 Miscibility ranges predicted by the δ approach[17]

	Miscibility range (wt% MAN)	
	Predicted	Observed
PMMA	2–60	8–63
PEMA	3–50	4.5–44
PnPMA	6–42	2–32
PnBMA	9–34	Immiscible
PiPMA	Immiscible	12–38; 8–43
PiBMA	Immiscible	Immiscible

points. By changing the pendent group from n-propyl to isopropyl, the interaction between the methacrylate and the styrene becomes more intense, but that between the methacrylate and the methacrylonitrile becomes less intense. However, since PiPMA is immiscible with SAN and *p*MSAN, $\chi_{iPMA/AN}$ cannot be evaluated to examine whether $\chi_{iPMA/AN}$ is also smaller than $\chi_{nPMA/AN}$.

Based on the binary interaction model, the width of the miscibility range of a homopolymer/copolymer blend system depends on the signs and magnitudes of the three segmental interaction parameters. When all the χ values are positive as in the present systems, a wider miscibility range results when the intramolecular χ value is large and the two intermolecular χ values are small. The weaker interaction between styrene and methacrylonitrile as compared with that between styrene and acrylonitrile would narrow the miscibility range. However, the interaction between methacrylate and methacrylonitrile is less intense than that between methacrylate and acrylonitrile, and this reduction is more than enough to compensate for the weaker intramolecular interaction in SMAN, giving rise to a wider miscibility range.

Coleman *et al.*[16,17] suggested that the miscibility range of a homopolymer/copolymer blend system can be predicted using a non-hydrogen-bonded solubility parameter (δ) approach. Since the δ value of a copolymer varies with its composition, there will be a range of copolymer compositions over which their δ values are closely matched to that of the homopolymer, giving rise to miscibility. We have earlier found that the miscibility window for PMMA/SMAN blend system predicted by the δ approach is in good agreement with our experimentally observed range[9]. The δ values of SMAN are in the range 19.4–24.3 $J^{1/2}\,cm^{-3/2}$, and those of PEMA, PnPMA, PiPMA, PnBMA and PiBMA are 18.2, 17.9, 17.4, 17.8 and 17.4 $J^{1/2}\,cm^{-3/2}$, respectively. The miscibility ranges for various methacrylate/SMAN blend systems can then be predicted using computer software developed by Coleman *et al.* and assuming a moderate hydrogen-bonding interaction. The results are summarized in *Table 7*. The predicted miscibility ranges for blends of SMAN with PEMA and PnPMA are in fairly good agreement with our observed results. The δ approach predicts that SMAN is miscible with PnBMA and immiscible with PiPMA. However, these predictions contradict our experimental results.

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