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Miscibility of blends of poly(styrene-*co*-methacrylonitrile) and methyl methacrylate based copolymers

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The phase behaviour of binary blends of styrene–methacrylonitrile (SMAN) copolymers and methyl methacrylate copolymers with cyclohexyl methacrylate and t-butyl methacrylate has been determined as a function of composition of each copolymer at 130, 150 and 180°C. These miscibility maps are compared with those of recently reported blends of styrene–acrylonitrile (SAN) copolymers with methacrylate copolymers. Blends of SMAN with methacrylate copolymers have a much wider miscibility area than the corresponding blends of SAN with methacrylate copolymers. From these miscibility maps, binary interaction energy densities, B_{ij}, have been calculated for various monomer unit pairs at each temperature. The approximate temperature dependence of B_{ij} for each monomer unit pair was also determined. The interaction of methacrylonitrile with styrene, cyclohexyl methacrylate and t-butyl methacrylate is repulsive (positive) but much less repulsive than that of acrylonitrile with the other monomer units. The results show that the α methyl group in the methacrylonitrile unit greatly affects the interaction energy density with other monomer units. Similar effects of the α methyl group have been reported recently by examining the miscibility of blends of poly(methyl methacrylate) with poly(methyl acrylate) or poly(ethyl acrylate). The effects of these issues on phase behaviour are discussed.

(Keywords: blends; miscibility; phase behaviour)

INTRODUCTION

There has been a strong interest in the miscibility of blends based on random copolymers or terpolymers[1–31]. These blends often have more interesting phase behaviour than those formed from corresponding homopolymers. Simple binary interaction models[29–31] have emerged and provide a simple way to rationalize these effects through the concept of intramolecular interactions within copolymers or terpolymers. The models also provide a useful framework for designing blends with controlled phase behaviour[27]. An important step towards accomplishing this is quantification of the various binary interaction parameters between the monomer units involved. A fruitful way of obtaining this information is to experimentally construct a map of the miscibility region as a function of copolymer composition which can be fitted to the model equation[27,28] to give the interaction energies.

Nishimoto *et al.*[27] demonstrated the usefulness of a quantitative interaction energy database in searching for miscible binary blends formed from homopolymers, copolymers or terpolymers made from the monomers styrene (S), acrylonitrile (AN) and methyl methacrylate (MMA). The interesting blends identified in that study stem from the basic fact that poly(methyl methacrylate) homopolymer forms miscible blends with styrene–acrylonitrile (SAN) copolymers over a certain range of AN contents. This general scheme was expanded on by examining the phase behaviour of SAN copolymers with some MMA-based copolymers[28]. In each case the new comonomer introduced was also a methacrylate. The interaction energy densities for every monomer unit were calculated by fitting the data to the model equations. The interactions of acrylonitrile with styrene, MMA and cyclohexyl methacrylate (CHMA) were found to be strongly repulsive (positive) in each case. The interaction of styrene with each methacrylate monomer unit was determined to be weakly repulsive except in the case of CHMA where it is very weakly negative, which means that polystyrene was miscible with poly(cyclohexyl methacrylate). In this paper, we expand further on this series of blends by examining the phase behaviour of styrene–methacrylonitrile (SMAN) copolymers with MMA-based copolymers. An interesting result is that these blends show a much wider miscibility area than corresponding blends of SAN copolymers with MMA-based copolymers. This result stems from the fact that interaction energy density values of methacrylonitrile

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(MAN) with the methacrylate monomer units are much smaller than those of acrylonitrile with the methacrylate monomer units.

BACKGROUND

The Flory–Huggins theory[32] provides a simple but realistic expression for the free energy of mixing two polymers A and B (per unit volume of mixing):

$$\Delta G_{mix} = RT\left(\frac{\phi_A \ln \phi_A}{V_A} + \frac{\phi_B \ln \phi_B}{V_B}\right) + B\phi_A\phi_B \quad (1)$$

where ϕ_i is the volume of component i. In this model the enthalpic contribution is simply a van-Laar-type expression characterized by an interaction energy density B. Two polymers are miscible if B is less than a critical value defined as:

$$B_{crit} = \frac{RT}{2}(V_A^{-1/2} + V_B^{-1/2})^2 \quad (2)$$

which is zero in the limit of high molecular weights. If B is temperature-independent, then this model does not predict the lower critical solution temperature (*LCST*) behaviour. However, if we consider B to be temperature-dependent, it is possible to predict *LCST* behaviour. In this paper, we focus on the miscibility of polymer blends as a function of both copolymer composition and temperature.

The net interaction energy for mixing a copolymer of monomers 1 and 2 with a copolymer of 3 and 4, according to the binary interaction model[29–31], can be written as:

$$B = (B_{13}\varphi_1 + B_{23}\varphi_2)\varphi_3 + (B_{14}\varphi_1 + B_{23}\varphi_2)\varphi_4 - B_{12}\varphi_1\varphi_2 - B_{34}\varphi_3\varphi_4 \quad (3)$$

where the B_{ij}s are parameters describing interactions between i and j monomer units and φ_i is the volume fraction of i monomer units in the copolymer. In this paper, we are interested in the case of blending two copolymers having no common monomer, i.e. copolymer 1+2 and copolymer 3+4, where 1 = styrene, 2 = MAN, 3 = MMA and 4 = CHMA or t-butyl methacrylate (tBMA). The approach to determine the interaction energy densities of monomer unit pairs is the same as that used previously[28]. The boundary dividing copolymer compositions that form miscible blends from immiscible ones, i.e. when $B = B_{crit}$, can be used to obtain information about the B_{ij}. In principle, these boundaries depend on temperature, so we determine the miscibility maps as a function of copolymer composition at three temperatures (130°C, 150°C and 180°C).

Table 1 shows B_{ij} values for binary pairs of styrene (S), MMA, AN and CHMA from the data of Nishimoto *et al.*[28]. Brannock *et al.*[24] determined B_{ij} values for styrene with methacrylate monomer units having various alkyl groups. These results reveal that the size and structure of the methacrylate alkyl group affects the interaction energy with other monomer units. Here, we are interested in the effect that a methyl group on the α position of AN has on such interaction energies (see *Table 1*), and in the difference between MAN and AN units.

EXPERIMENTAL

The SMAN copolymers, including polystyrene, used in this work are described in *Table 2*, while the MMA-based polymers are listed in *Table 3*. The former were synthesized in this laboratory while the latter are the same as used previously by Nishimoto *et al.* The SMAN copolymers were polymerized by emulsion polymerization with continuous monomer feed at 80°C using cumene hydroperoxide as initiator. The copolymer compositions shown in *Table 3* were determined by elemental analysis. Molecular weights of the copolymers were determined by gel permeation chromatography using polystyrene standards, with tetrahydrofuran as solvent.

Blends of the copolymer were prepared by solution casting from methyl ethyl ketone onto glass plates. The cast films were dried under a stream of dry nitrogen at ambient temperature for 1 day followed by further drying at 130°C for 4 days under vacuum.

The SMAN copolymers used here have glass transition temperatures (T_g)s that are not far enough separated from those of the methacrylate copolymers to make this a uniformly useful way of exploring phase behaviour for their blends. Fortunately, the refractive indices are

Table 1 Interaction energy density, B_{ij}, of various monomer pairs

	Interaction energy density (cal cm^{-3})				
		Data of ref. 28 recalculated at 130°C	This work		
Monomer pair	Ref. 28		130°C	150°C	180°C
S–AN	6.7	7.22			
S–MAN	–	–	1.20	2.02	2.15
MMA–AN	4.1	4.34	–	–	–
MMA–MAN	–	–	0.28	0.84	0.91
CHMA–AN	5.9	6.70	–	–	–
CHMA–MAN	–	–	1.40	2.65	2.11
S–MMA	0.18[a]	0.221[b]	0.221[b]	0.229[b]	0.242[b]
S–CHMA	−0.03	−0.12	−0.15	−0.43	−0.10
MMA–CHMA	0.8	0.80	0.75	0.64	0.50

[a] Data from ref. 35 determined at 30°C
[b] Data from ref. 34

Table 2 Styrene–methacrylonitrile copolymers used in this study

Polymer	Methacrylonitrile in polymer[a] (wt%)	Molecular weight[b] M_w	Molecular weight[b] M_n	Designation[c]
Polystyrene	0	350000	100000	PS
Poly(styrene-*co*-methacrylonitrile)	10.5	124300	67400	SMAN10.5
Poly(styrene-*co*-methacrylonitrile)	16.8	119000	63100	SMAN16.8
Poly(styrene-*co*-methacrylonitrile)	26.3	115600	63900	SMAN26.3
Poly(styrene-*co*-methacrylonitrile)	38.3	108600	59900	SMAN38.3
Poly(styrene-*co*-methacrylonitrile)	48.4	101000	52600	SMAN48.4
Poly(styrene-*co*-methacrylonitrile)	58.4	67900	36800	SMAN58.4
Poly(styrene-*co*-methacrylonitrile)	67.5	87700	46500	SMAN67.5
Poly(styrene-*co*-methacrylonitrile)	77.6	81800	45200	SMAN77.6

[a] From elemental analysis
[b] From g.p.c. calibrated using polystyrene standard
[c] PS was from Cosden; other copolymers were synthesized in this laboratory

Table 3 Methyl methacrylate copolymers used in this study

Polymer	Description	Solution viscosity[a]	Designation
Poly(methyl methacrylate)	Plexiglas V811[b]	3.3	PMMA
Poly(MMA-*co*-CHMA)	6.1% CHMA	10.3	MCH6.1
Poly(MMA-*co*-CHMA)	11.2% CHMA	7.5	MCH11.2
Poly(MMA-*co*-CHMA)	14.7% CHMA	5.3	MCH14.7
Poly(MMA-*co*-CHMA)	21.1% CHMA	4.0	MCH21.1
Poly(MMA-*co*-CHMA)	28.5% CHMA	3.8	MCH28.5
Poly(MMA-*co*-CHMA)	34.4% CHMA	3.0	MCH34.4
Poly(MMA-*co*-CHMA)	43.8% CHMA	3.7	MCH43.8
Poly(MMA-*co*-CHMA)	56.7% CHMA	3.2	MCH56.7
Poly(MMA-*co*-CHMA)	64.1% CHMA	2.5	MCH64.1
Poly(MMA-*co*-CHMA)	80.7% CHMA	2.1	MCH80.7
Poly(MMA-*co*-CHMA)	83.4% CHMA	3.0	MCH83.4
Poly(MMA-*co*-CHMA)	86.8% CHMA	4.2	MCH86.8
Poly(MMA-*co*-CHMA)	91.4% CHMA	4.0	MCH91.4
Poly(cyclohexyl methacrylate)		5.1	PCHMA
Poly(MMA-*co*-tBMA)	10.6% BMA	16.8	MtB10.6
Poly(MMA-*co*-tBMA)	21.9% BMA	31.2	MtB21.9
Poly(MMA-*co*-tBMA)	33.8% BMA	28.7	MtB33.8
Poly(MMA-*co*-tBMA)	45.0% BMA	16.9	MtB45.0

[a] Viscosity of 10 wt% solution in methyl ethyl ketone (cP)
[b] Commercial product from Rohm and Haas Co.

different enough in most cases for optical methods to yield equivalent information. Depending on the composition of the copolymers, films cast from their blends proved to be essentially transparent or opaque after the thermal treatment at each temperature. Films which became opaque were judged as phase-separated blends. Cloud point temperatures caused by *LCST* behaviour were determined using isothermal annealing in order to minimize artifacts caused by slow phase-separation kinetics that may occur when the cloud point temperature is close to T_g (ref. 33). Annealing of various blends was carried out by bringing the sample to a desired temperature for a specified time period, i.e. for 4 days at 130°C, 24 h at 140°C, 150°C and 160°C, and 3 h at 180°C and 200°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

SMAN/PMMA

SMAN copolymers are miscible with PMMA over a certain range of MAN compositions which is quite wide compared with similar blends of SAN/PMMA. SAN is miscible with PMMA when the AN content is larger than 9% and lower than 34% at 130°C (ref. 22); on the other hand, SMAN is miscible with PMMA when the MAN content in SMAN is 38.3%, 48.4%, 58.4% and 67.5% at 130°C. *Figure 1* illustrates phase diagrams for the blends of SMAN48.4/PMMA. *Figure 2* shows how the cloud points for blends containing 50% PMMA vary with the composition of the SMAN copolymer. Compared with the well known miscibility window of the blend of

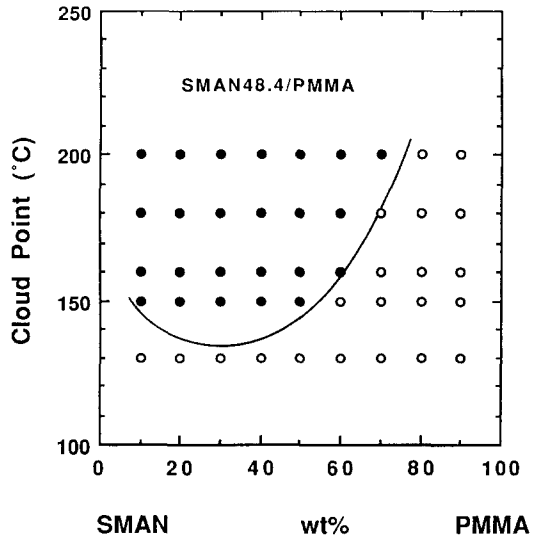

Figure 1 Cloud point curve for blends of PMMA/SMAN copolymer with 48.4% MAN: ○, clear; ●, cloudy. Blends annealed for 4 days at 130°C, for 24 h at 140°C, 150°C and 160°C, and for 3 h at 180°C and 200°C

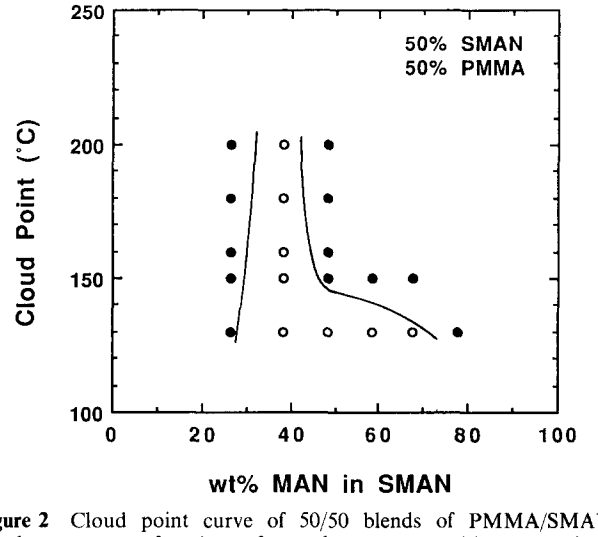

Figure 2 Cloud point curve of 50/50 blends of PMMA/SMAN copolymers as a function of copolymer composition: ○, clear; ●, cloudy. Blends annealed for 4 days at 130°C, for 24 h at 140°C, 150°C and 160°C, and for 3 h at 180°C and 200°C

SAN/PMMA[22], the SMAN/PMMA window is wider and shifts to a higher level of nitrile content. The shape of the miscibility window described in *Figure 2* is somewhat similar to that of SAN/PMMA blends. The left-hand edge (lower level of nitrile content) of the miscibility window is quite steep but the right-hand edge has a more gentle slope, at least at low temperature. This must stem from the temperature dependence of B_{ij} of each monomer unit pair, which is calculated and discussed later in this paper. As seen in *Figure 2*, the data points are too sparse to determine accurately the edges of the miscibility window. However, we will be able to estimate this more accurately using data from blends of SMAN copolymers with P(MMA–CHMA) copolymers. From that estimation, SMAN copolymers are miscible with PMMA at 130°C from 27.3 to 68.2 wt% MAN. The B_{ij} values used to make this estimation will be described later in this paper.

SMAN/P(MMA–CHMA)

Figure 3 illustrates how the miscibility of blends of SMAN and P(MMA–CHMA) copolymers depends on the composition of the two copolymers at 130°C. The miscibility boundary for blends of SAN and P(MMA–CHMA) copolymers described by Nishimoto *et al.*[28] is also shown in *Figure 3* for comparison. The miscible area for SMAN/P(MMA–CHMA) blends is much wider than that for SAN/P(MMA–CHMA) blends. According to equation (3), the shape of the miscibility boundary should be part of an ellipse. *Figure 3* includes the SMAN/PMMA blend results, along the 0% CHMA axis, described above. The miscibility window for P(MMA–CHMA) copolymers with PS is observed along the 0% MAN axis as described by Nishimoto *et al.*[28].

There are six B_{ij} parameters for the four monomers identified as 1 = styrene, 2 = MAN, 3 = MMA and 4 = CHMA. These six B_{ij} values at 130°C are estimated by fitting equations (2) and (3) to the miscibility boundaries observed for blends of SMAN copolymers with P(MMA–CHMA) copolymers, and the results are listed in *Table 1*. The blend composition used in this study to calculate B_{ij} values is 50/50 (w/w) for SMAN/MMA-based copolymers. This condition should be adopted for

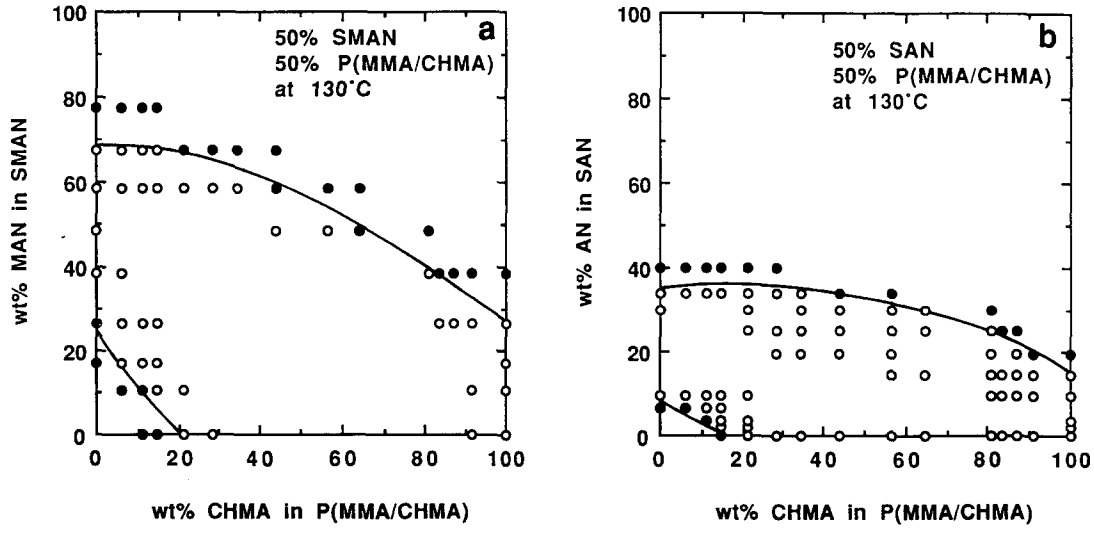

Figure 3 Miscibility map of 50/50 blends of MMA–CHMA copolymer with SMAN copolymer (a) and SAN copolymer (b) at 130°C. Lines represent the position where $B = 0$, calculated by using B_{ij} in *Table 1*: ○, clear; ●, cloudy

the blend of two polymers having the same molecular weight without any distribution. However, as shown in previous papers[27,28], the 50/50 (w/w) blend presents reasonable results in this series of studies using a binary interaction model, if the B_{crit} value is small enough compared to the B_{ij} value. That is the case in this study. B_{ij} values listed in *Table 1* are calculated using the condition $B_{crit}=0$ cal cm^{-3}, although the real B_{crit} values are in the range of around 0.01 to 0.02 cal cm^{-3}, estimated using equation (2). Because the absolute values of B_{crit} are small enough compared with those of B_{ij} in this study, the differences between the B_{ij} values calculated as $B_{crit}=0$ cal cm^{-3} and as $B_{crit}=0.02$ cal cm^{-3} are small, as listed in *Table 4*. Because equation (3) is the elliptic function and provides only five independent equations to estimate B_{ij} values, we need at least one B_{ij} parameter from another source and then the other five parameters can be estimated by the curve-fitting method. Among the six parameters listed, the styrene–MMA interaction ($B_{13}=0.221$ cal cm^{-3}) is from the work of Callaghan and Paul[34]. Nishimoto *et al.* used a value for this pair from the work of Fukuda *et al.*[35] to calculate interaction parameters for the binary pairs of four monomers: styrene, AN, MMA and CHMA. Fukuda *et al.*'s value was determined from concentrated ternary solution measurements at 30°C. Higashida *et al.*[36] have pointed out that calculation of these parameters should be carried out using the data obtained at the same temperature. Callaghan and Paul[34] determined the interaction parameter of the binary pair of styrene and MMA by the critical molecular weight method and estimated the temperature dependence of styrene/MMA interaction. The six interaction parameters for styrene, MMA, AN and CHMA at 130°C are recalculated using the B_{13} data of Callaghan and Paul and miscibility boundary data of the blend of SAN copolymers with P(MMA-*co*-CHMA) copolymers determined by Nishimoto *et al.*[28]. These recalculated data are also listed in *Table 1*. The following procedure is taken to determine the parameters. The ellipses (miscibility border) are drawn by computer using the appropriate B_{ij} values and the discrepancy between calculated miscibility border and experimental result are shown, then the B_{ij} values are readjusted finely to minimize the discrepancy. It is hard to place meaningful error limits on parameters obtained by fitting the model to the experimental data; however, a perturbation analysis that varies one parameter at a time showed that relatively small changes led to unacceptable fits of the data.

Table 4 Interaction energy density, B_{ij}, of various monomer pairs

Monomer pair	Interaction energy density (cal cm^{-3})	
	Calculated as $B_{crit}=0$ cal cm^{-3}	Calculated as $B_{crit}=0.02$ cal cm^{-3}
S–MAN	1.20	1.12
MMA–MAN	0.28	0.28
CHMA–MAN	1.40	1.40
S–MMA	0.221[a]	0.221[a]
S–CHMA	−0.15	−0.15
MMA–CHMA	0.75	0.75

[a] Data from ref. 34

The interaction parameter for MAN with styrene (B_{12}) is 1.20 cal cm^{-3} at 130°C and is quite small compared with the AN/styrene interaction which is 7.22 cal cm^{-3}, recalculated using the data of Nishimoto *et al.* (*Table 1*). The interaction parameters for MAN with other monomer units listed in *Table 1* are also smaller than those of AN with other monomer units. This large difference between AN and MAN must be due to the methyl group in MAN. At this point, there are some interesting questions about how the methyl group in MAN affects the interaction energy with other units. A methyl group at the α position may affect the electron donation or withdrawal from the side chain group also attached to the α carbon. Cowie *et al.*[37] showed that poly(methyl acrylate) ($M_w=8000$) was immiscible with poly(methyl methacrylate) ($M_w=6860$) even though the molecular weights of both polymers are quite low. On the other hand, Callaghan and Paul[34] demonstrated that polystyrene ($M_w=52\,000$) was miscible with poly(α-methylstyrene) ($M_w=55\,000$). Qualitatively, the α methyl group may have more effect on monomer units which have electron-attracting side chains, such as

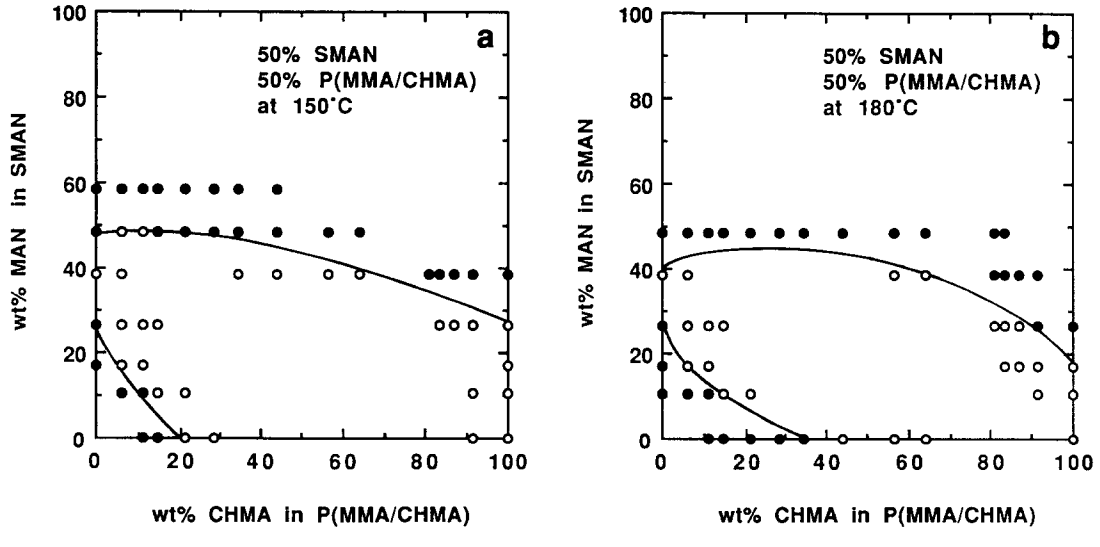

Figure 4 Miscibility map of 50/50 blends of MMA–CHMA copolymer with SMAN copolymer at 150°C (a) and 180°C (b). Lines represent the position where $B=0$, calculated by using B_{ij} in *Table 1*: ○, clear; ●, cloudy

nitrile or carbonyl (corresponding to acrylonitrile or methyl acrylate, respectively), than ones which have electron-donating side chains such as a phenyl group (corresponding to styrene). However, for a more general discussion of the effect of the methyl group at the α position of vinyl monomers, a more systematic B_{ij} database for other monomers which do and do not contain α methyl groups is needed.

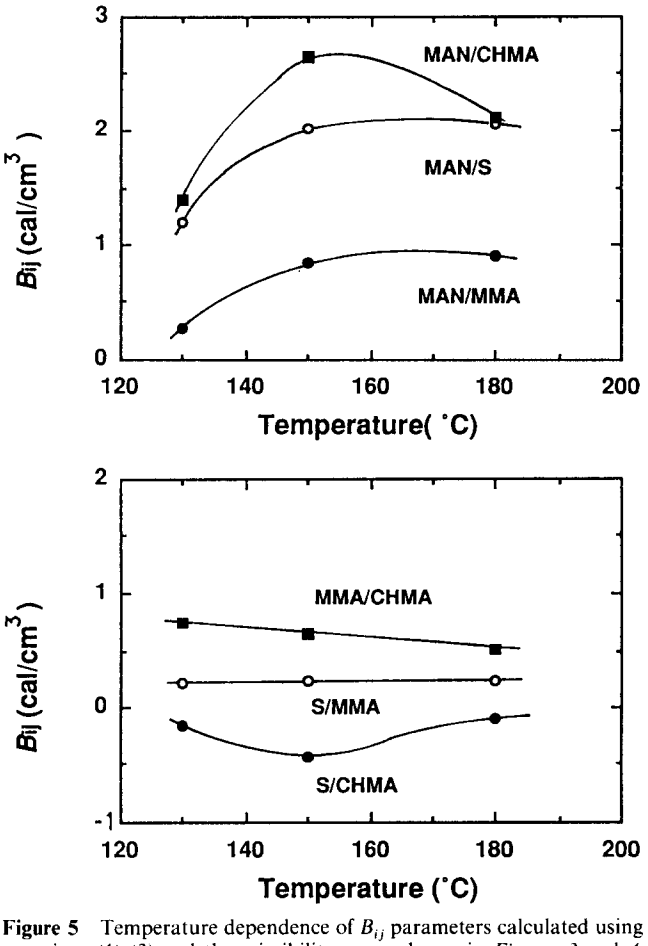

Figure 5 Temperature dependence of B_{ij} parameters calculated using equations (1)–(3) and the miscibility maps shown in *Figures 3* and *4*. Data for the S/MMA pair are from ref. 34

Figure 4 illustrates the miscibility boundaries observed for blends of SMAN copolymers with P(MMA–CHMA) copolymers at 150°C and 180°C. The six interaction parameters at these temperatures were calculated by the curve-fitting method, as mentioned earlier, and are listed in *Table 1*, where interaction parameters for styrene with MMA at these two temperatures are also from the work of Callaghan and Paul[34]. The miscibility region shrinks as temperature increases; in particular, the upper border of the miscibility region at 130°C moves downwards by a considerable amount, while the lower border moves slightly upwards at elevated temperature (*Figure 3a* and *Figure 4*). The temperature dependence of the six B_{ij} parameters is plotted in *Figure 5*. The interaction between styrene and CHMA increases as the temperature increases when the temperature is higher than 150°C. This suggests that the blend of PS with PCHMA shows *LCST* behaviour, which was found experimentally by Nishimoto *et al.*[28]. The interactions of the pairs of MMA/CHMA and MAN/CHMA decrease as the temperature increases when the temperature is higher than 150°C. However, these parameters may not reach low enough values for the blends of corresponding homopolymer pairs to exhibit upper critical solution temperature (*UCST*) behaviour at observable temperatures.

SMAN/P(MMA–tBMA)

Figure 6 illustrates how the miscibility of the blends of SMAN and P(MMA–tBMA) copolymers depends on the composition of the two copolymers at 130°C. The miscibility boundary of the blends of SAN and P(MMA–tBMA) copolymers described by Nishimoto *et al.*[28] is also shown in *Figure 6* for comparison. The miscibility region of the blends of SMAN with P(MMA/tBMA) is wider than that of the blends of SAN with P(MMA–tBMA). Six B_{ij} parameters for four monomer units are calculated by curve fitting and are listed in *Table 5*. The interactions of tBMA and of CHMA with other monomer units are almost the same except for styrene. The B_{ij} between tBMA and styrene is 0.34 cal cm^{-3} (positive, i.e. repulsive), while the B_{ij} of CHMA with styrene is -0.15 cal cm^{-3} (negative, i.e. attractive).

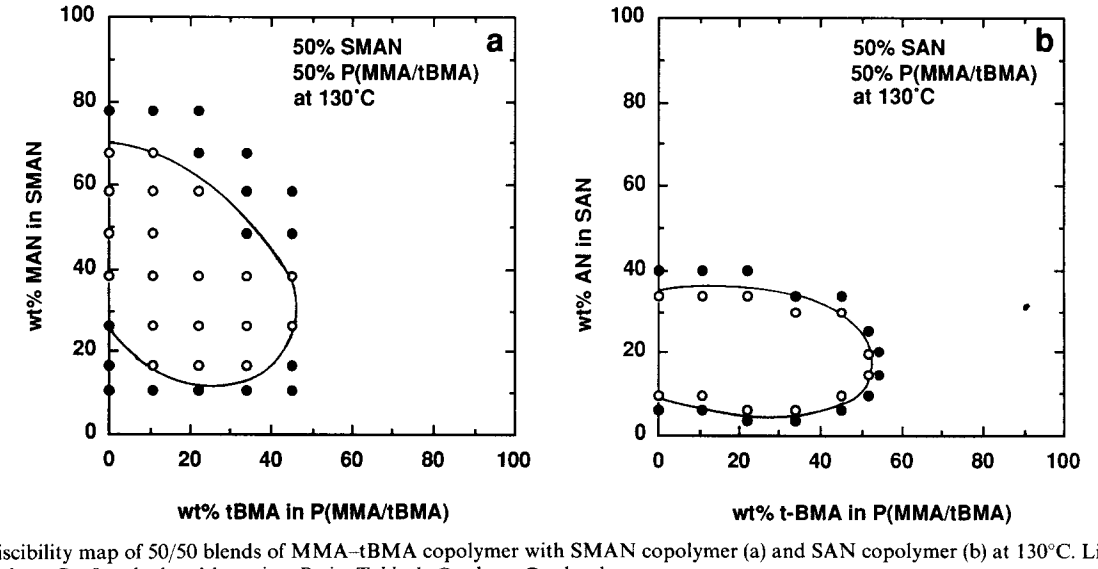

Figure 6 Miscibility map of 50/50 blends of MMA–tBMA copolymer with SMAN copolymer (a) and SAN copolymer (b) at 130°C. Lines represent the position where $B=0$, calculated by using B_{ij} in *Table 1*: ○, clear; ●, cloudy

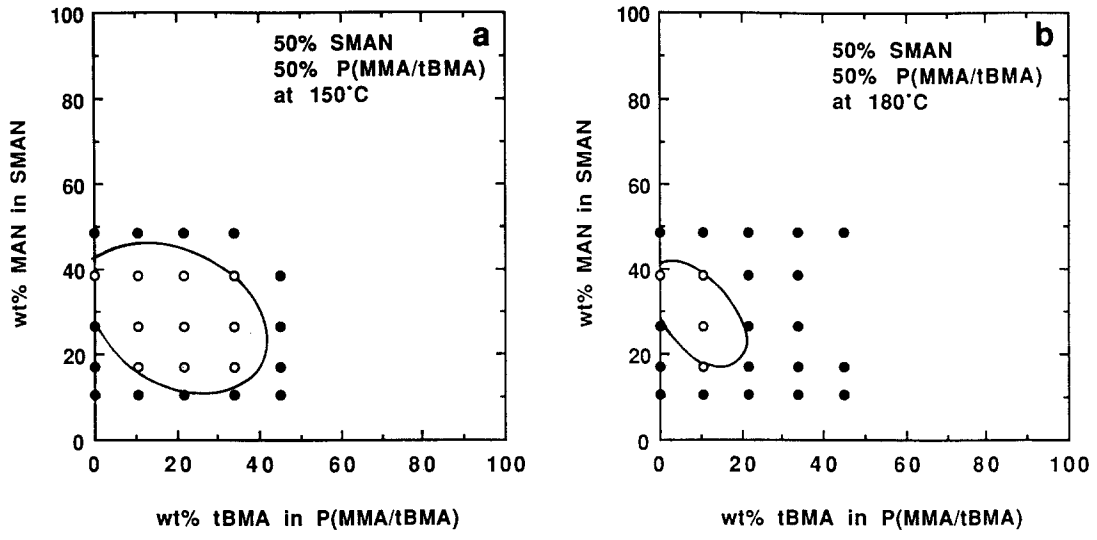

Figure 7 Miscibility map of 50/50 blends of MMA–tBMA copolymer with SMAN copolymer at 150°C (a) and 180°C (b). Lines represent the position where $B=0$, calculated by using B_{ij} in *Table 1*: ○, clear; ●, cloudy

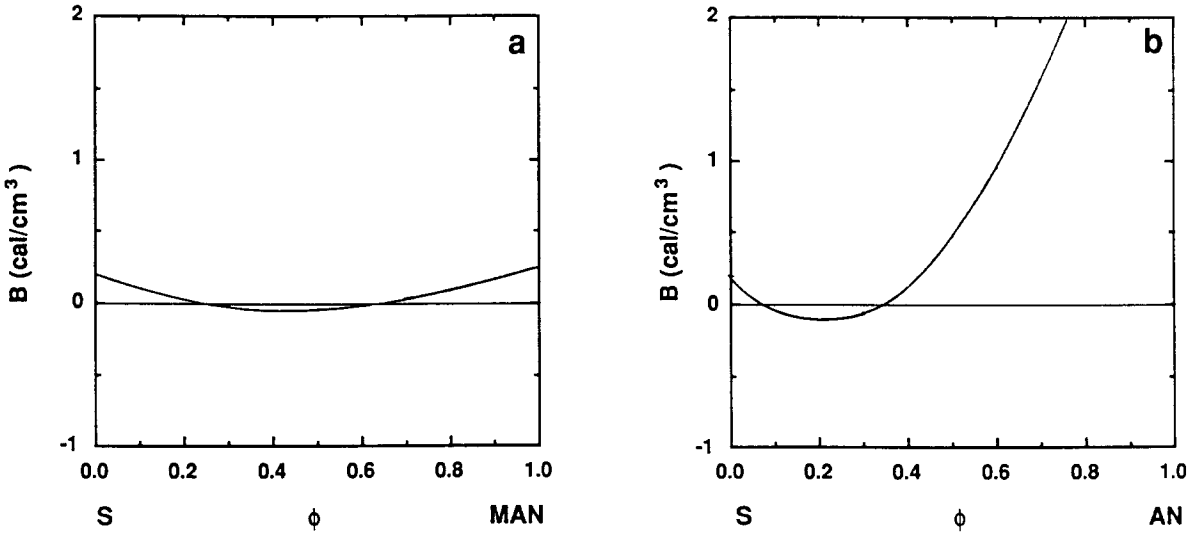

Figure 8 Net interaction energy, B, of PMMA and SMAN copolymer pair (a) and PMMA and SAN copolymer pair (b) as a function of copolymer composition. Calculated from equation (3) using B_{ij} values from *Table 1*

Figure 7 illustrates the miscibility boundaries observed for blends of SMAN with P(MMA–tBMA) at 150°C and 180°C. The miscibility region shrinks as the temperature increases (*Figures 6* and *7*), in a similar manner to the blends of SMAN with P(MMA–CHMA). The six interaction parameters at each temperature were calculated from these miscibility data and are listed in *Table 5*. There are not enough data points to determine accurate interaction parameters at these two temperatures. More data points near the miscibility border are needed to reach quantitative conclusions about the temperature dependence of the interaction parameter.

SUMMARY

It is shown that SMAN copolymer is miscible with PMMA, P(MMA–CHMA) and P(MMA–tBMA) at a certain range of MAN content. Similar results were obtained recently for blends of SAN copolymer with PMMA and methacrylate copolymers[28]. However, the miscibility window of blends of SMAN copolymers with PMMA is much wider (27.3–68.2 wt% MAN in SMAN) than that of blends of SAN with PMMA (9–34 wt% AN in SAN). This stems from the fact that the interaction parameter of MAN with MMA (0.28 cal cm^{-3}) is much smaller than that of AN with MMA (4.34 cal cm^{-3}). Net interaction of these blends can be calculated by using

Table 5 Interaction energy density, B_{ij}, of tBMA with other monomers

	Interaction energy density (cal cm^{-3})		
Monomer pair	130°C	150°C	180°C
tBMA–S	0.34	0.50	3.03
tBMA–MAN	1.47	2.29	7.40
tBMA–MMA	0.76	1.00	4.37

equation (3) and appropriate parameters from *Table 1*. The results of this calculation are shown in *Figure 8*.

The miscibility region for the blends of SMAN with P(MMA–CHMA) or P(MMA–tBMA) is also strikingly wider than that of SAN with P(MMA–CHMA) or P(MMA–tBMA) blends. At this time, we cannot discuss this large difference between AN and MAN quantitatively. However, it is clear that the α methyl group in the MAN unit greatly affects the interaction energy density with other monomer units.

The temperature dependence of B_{ij} was determined for the monomer unit pairs: S/MMA, S/MAN, S/CHMA, MMA/MAN, MMA/CHMA and MAN/CHMA. The interaction between S and CHMA (negative at 130°C) increases as temperature increases. This suggests that blends of PS with PCHMA shows *LCST* behaviour, which was confirmed experimentally by Nishimoto *et al.*

It should be recognized that B is governed by two effects: the enthalpic term leading to smaller B values with increasing temperature in the case where there are no specific interactions, i.e. positive B, and the free volume term leading to higher B values with increasing temperature. It is very complex to discuss the net interaction parameter of copolymer/copolymer blends using the binary interaction model considering B as a function of the two parameters above, because each B_{ij} includes both the enthalpic term and the free volume term. In this paper, we did not make any attempt to divide the parameter into an enthalpic term and a free volume term. However, a better understanding of the general phase behaviour of copolymer/copolymer blends could be achieved if complete sets of pressure–volume–temperature data were available for all components.

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