Phase behaviour of blends of poly(cyclohexyl methacrylate) with poly(styrene-*co*-acrylonitrile) and poly(*p*-methylstyrene-*co*-acrylonitrile)

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The miscibility behaviour of poly(cyclohexyl methacrylate) (PCHMA) with poly(styrene-*co*-acrylonitrile) (SAN) and poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN) was investigated by differential scanning calorimetry. PCHMA was found to be miscible with SAN having acrylonitrile (AN) content up to 20 wt%, and with *p*MSAN having AN content up to 22 wt%. All miscible blends were examined for the lower critical solution temperature (*LCST*) behaviour and the results were used to construct the phase diagrams.

(Keywords: blends; phase behaviour; lower critical solution temperature; poly(cyclohexyl methacrylate))

INTRODUCTION

Several polymethacrylates, including poly(methyl methacrylate) (PMMA)[1,2], poly(ethyl methacrylate) (PEMA)[2], poly(n-propyl methacrylate) (PnPMA)[2] and poly(tetrahydrofurfuryl methacrylate) (PTHFMA)[3], are known to be miscible with poly(styrene-*co*-acrylonitrile) (SAN) over a limited range of copolymer compositions.However, polymethacrylates with bulky alkyl pendent groups such as poly(isopropyl methacrylate) (PiPMA)[2] and poly(n-butyl methacrylate) (PnBMA)[2] are immiscible with SAN over the entire copolymer composition range. Blends of some polymethacrylates also exhibit miscibility windows with poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN)[3,4].

Recently, we have reported that poly(tetrahydropyranyl-2-methyl methacrylate) (PTHPMA) is miscible with SAN and *p*MSAN over a certain copolymer composition range in spite of the bulkiness of the pendent tetrahydropyranyl groups[5]. It is interesting to have a similar study on poly(cyclohexyl methacrylate) (PCHMA), which has a bulky cyclohexyl group but without any other interacting functional moiety in its alkyl pendent group. An earlier report[6] has shown that PCHMA is completely miscible with both polystyrene (PS) and poly(*p*-methylstyrene) (P*p*MS). In this paper, we compare the miscibility behaviour of PCHMA with SAN as well as *p*MSAN with that of PTHPMA.

EXPERIMENTAL

Materials

PCHMA with a weight-average molecular weight (M_w) of 66000 was obtained from Scientific Polymer Products. SAN with acrylonitrile (AN) contents of 30 and 25 wt% was obtained from Scientific Polymer Products, Inc. while SAN with 22 wt% AN was provided by Monsanto. Other SAN and *p*MSAN samples were prepared by solution polymerization in 2-butanone at reflux temperature for 4 h using 0.30 wt% AIBN as initiator. The AN contents of the copolymers were determined by elemental analysis for nitrogen. In the following discussion, the number after SAN or *p*MSAN denotes the weight percentage of AN in the copolymer. The characteristics of the copolymers are shown in *Table 1*.

Preparation of blends

All blends were cast from tetrahydrofuran at room temperature. The blends were then dried *in vacuo* at 90°C for 3 days.

Table 1 T_g and molecular weight information of SAN and *p*MSAN

Sample	M_w	M_n	T_g (°C)
SAN3.7 (7.0)	23000	14000	101
SAN9.8 (17.6)	31000	20000	103
SAN13.4 (23.3)	15000	7600	102
SAN17.5 (29.4)	27000	20000	103
SAN19.8 (32.6)	33000	21000	104
SAN22.0 (35.6)	116000	51000	103
SAN25.0 (39.5)	156000	66000	102
SAN30.0 (45.7)	125000	61000	100
*p*MSAN2.7 (5.8)	25000	14000	108
*p*MSAN4.6 (9.7)	50000	25000	108
*p*MSAN7.7 (15.7)	34000	21000	110
*p*MSAN10.2 (20.2)	34000	28000	110
*p*MSAN13.6 (25.9)	42000	21000	108
*p*MSAN15.8 (29.5)	46000	28000	110
*p*MSAN19.6 (35.2)	43000	27000	109
*p*MSAN21.3 (37.6)	52000	28000	110
*p*MSAN23.8 (41.0)	82000	53000	103
*p*MSAN26.5 (44.5)	44000	27000	105
*p*MSAN29.1 (47.7)	56000	34000	105

Values in parentheses denote the molar percentage of AN in the copolymer

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Glass transition temperature (T_g) *measurements*

The T_g values of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter, using a heating rate of 20°C min^{-1}. The initial onset of the change of slope in the differential scanning calorimetry (d.s.c.) plot was taken as T_g. The reported T_g is the average value based on the second and subsequent runs.

Cloud point measurements

All miscible blends were examined for the existence of lower critical solution temperature (*LCST*) behaviour. The film was sandwiched between two microscopic cover glasses and heated in a Fisher-Jones melting point apparatus with a heating rate of ~10°C min^{-1}. The optical appearance of the film was observed with a magnifying glass attached to the apparatus. A transparent film which turns cloudy upon heating indicates the existence of *LCST*. The temperature at which the film first showed cloudiness was taken as the cloud point. The reported cloud point is the average value of several measurements.

RESULTS AND DISCUSSION

PCHMA/SAN blends

The phase behaviour is often determined by calorimetric measurements using the well-known single composition-dependent T_g criterion. Clearly this method only works if the T_gs of the two component polymers are sufficiently far apart. If the T_gs of the two polymers are close to each other, it is necessary to anneal the blend under suitable conditions[7–9].

Since the T_g of PCHMA (95°C) is quite close to that of SAN (~100°C), all the blends were subjected to an annealing process and their enthalpy relaxation behaviour was examined[7,9]. All the PCHMA/SAN blends, except for the blends with SAN19.8 and SAN17.5, were first kept at 150°C for 5 min to eliminate the solvent effect and thermal history. They were then annealed at 90°C for 2 weeks. For comparison, PCHMA, SAN and two-phase PCHMA/SAN (50/50) mixtures were similarly annealed as the blends. Blends with SAN19.8 and SAN17.5 were first thermally treated at 120°C for 5 min in view of the *LCST* behaviour of these blends which will be discussed later.

Figure 1 shows some d.s.c. curves of annealed two-phase PCHMA/SAN (50/50) mixtures. Each annealed sample showed two peaks. *Figure 2* shows the d.s.c. curves of various annealed PCHMA/SAN (50/50) blends. A single enthalpy relaxation peak was observed for a blend containing SAN3.7, SAN9.8, SAN13.4, SAN17.5 or SAN19.8. Moreover, these blends were transparent. The refractive indices of PS and SAN25 are 1.591 and 1.570, respectively[10]. The refractive indices of various SAN samples are then significantly different from that of PCHMA (1.5057)[10]. The transparency of the blends does not arise from the matching of the refractive indices of PCHMA and SAN. Thus, the optical clarity and the glass transition behaviour show that PCHMA is miscible with SAN having AN content up to 20 wt%. In contrast, blends containing SAN22, SAN25 and SAN30 were cloudy. Each of these blends showed either two enthalpy relaxation peaks or a peak with noticeable shoulder, as shown in *Figure 2*. The results show that

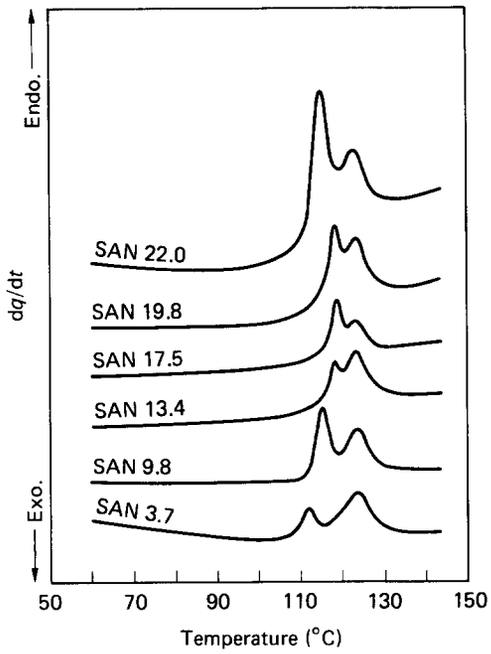

Figure 1 D.s.c. curves of annealed two-phase physical PCHMA/SAN (50/50) mixtures

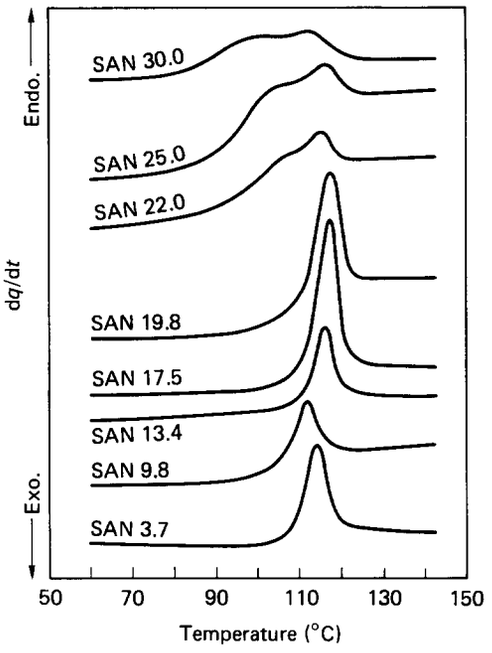

Figure 2 D.s.c. curves of annealed PCHMA/SAN (50/50) blends

PCHMA is immiscible with these three SAN samples. Blends containing SAN3.7, SAN9.8 remained transparent upon heating to 300°C but those containing SAN13.4, SAN17.5 and SAN19.8 turned cloudy upon heating, showing *LCST* behaviour. The cloud point curves for the three miscible blend systems are shown in *Figure 3*. Based on the miscibility behaviour and the cloud point results, the phase diagram for PCHMA/SAN (50/50) blend is shown in *Figure 4*.

PCHMA/pMSAN blends

All the blends of PCHMA with *p*MSAN containing 2.7, 4.6, 7.7, 10.2, 13.6, 15.8, 19.6 and 21.3 wt% of AN

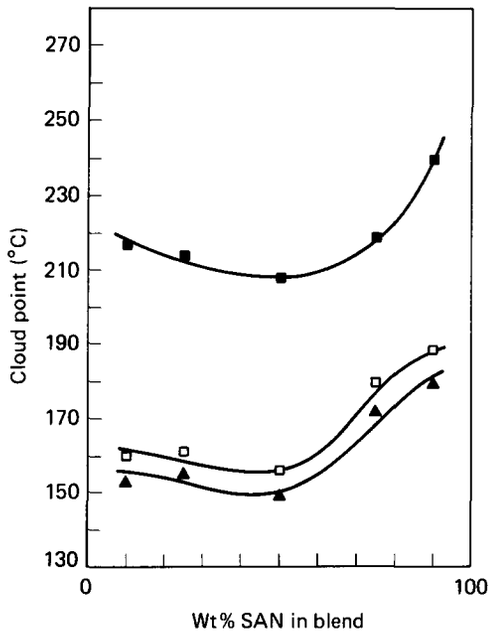

Figure 3 Cloud point curves for blends of PCHMA with SAN13.4 (■), SAN17.5 (□) and SAN19.8 (▲)

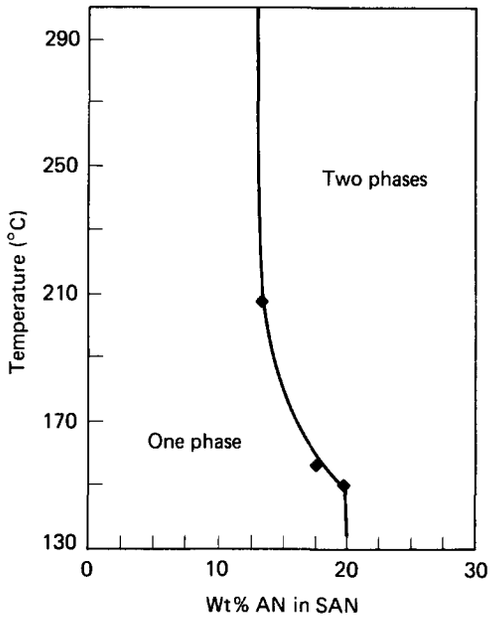

Figure 4 Phase diagram of PCHMA/SAN (50/50) blends

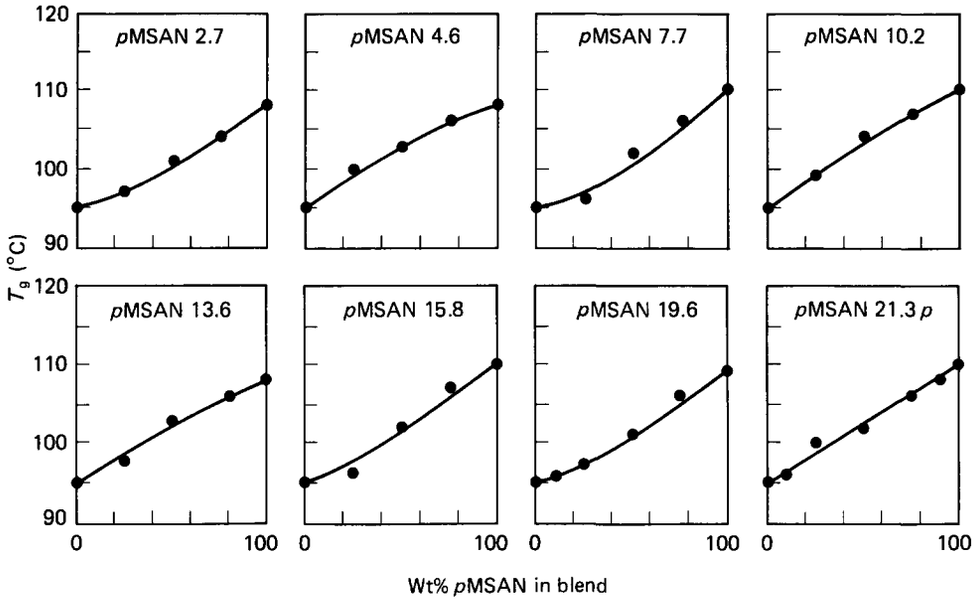

Figure 5 T_g–composition curves for miscible PCHMA/*p*MSAN blends

were transparent and each of the blends showed only one composition-dependent T_g. Therefore, PCHMA is miscible with these *p*MSAN samples. The T_g–composition curves of the eight miscible blend systems are shown in *Figure 5*. Except for PCHMA/*p*MSAN15.8, PCHMA/*p*MSAN19.6 and PCHMA/*p*MSAN21.3 blends which showed *LCST* behaviour, the other miscible blends remained transparent upon heating to 300°C. The cloud point curves are shown in *Figure 6*. Blends of PCHMA with *p*MSAN23.8, *p*MSAN26.5 and *p*MSAN29.1 were cloudy and the glass transitions were broad. To ascertain the immiscibility of these blends, they were kept at 150°C for 5 min before being annealed at 90°C for 5 days. The d.s.c. curves of the annealed (50/50) blend samples are shown in *Figure 7*. Two glass transitions were observed in each of the annealed samples. This obviously indicates that PCHMA is immiscible with all these *p*MSAN. Therefore, PCHMA is miscible with *p*MSAN having AN content up to 22 wt% and the phase diagram is shown in *Figure 8*.

Miscibility behaviour

The miscibility behaviour of a homopolymer A/copolymer BC blend system is often explained by a simple binary interaction model[11–13], which takes into consideration various segmental interactions. The net interaction parameter χ_{blend} is expressed by the equation

$$\chi_{blend} = y\chi_{A/C} + (1-y)\chi_{A/B} - y(1-y)\chi_{B/C} \quad (1)$$

where y is the volume fraction of C in the copolymer.

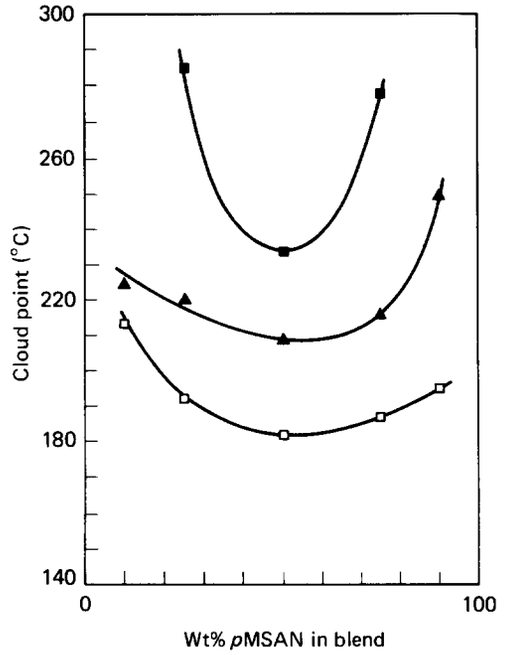

Figure 6 Cloud point curves for blends of PCHMA with *p*MSAN15.8 (■); *p*MSAN19.6 (▲) and *p*MSAN21.3 (□)

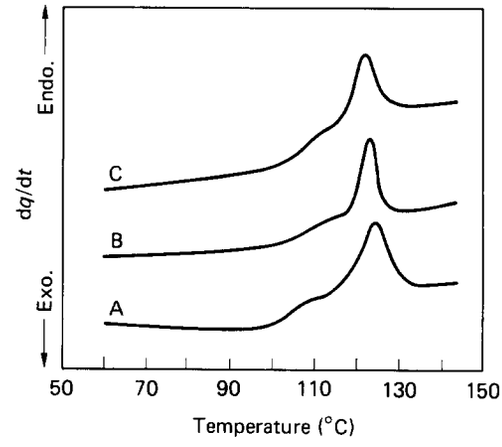

Figure 7 D.s.c. curves for annealed (50/50) blends of PCHMA with *p*MSAN23.8 (A), *p*MSAN26.5 (B) and *p*MSAN29.1 (C)

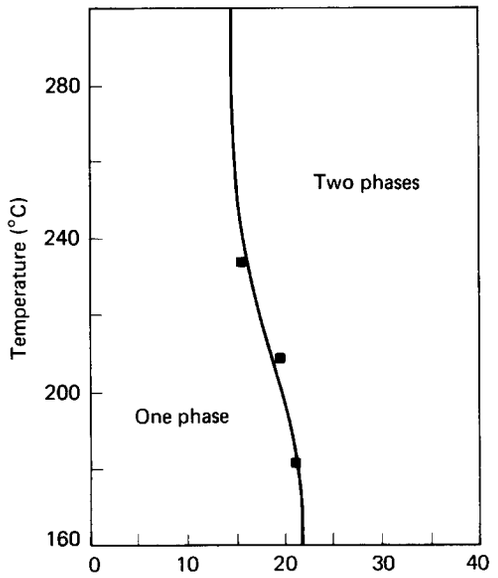

Figure 8 Phase diagram of PCHMA/*p*MSAN (50/50) blends

The criterion for miscibility is that $\chi_{blend} < \chi_{crit}$ where

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

with N_1 and N_2 the degrees of polymerization of A and BC. For the present two blend systems, the y values are 0.18 and 0.19 for PCHMA/SAN and PCHMA/*p*MSAN, respectively. By applying equations (1) and (2), the following two equations are obtained:

$$\chi_{crit} = 0.18\chi_{CHMA/AN} + 0.82\chi_{CHMA/S} - (0.18)(0.82)\chi_{S/AN} \quad (3)$$

$$\chi_{crit} = 0.19\chi_{CHMA/AN} + 0.81\chi_{CHMA/pMS} - (0.19)(0.81)\chi_{pMS/AN} \quad (4)$$

where $\chi_{S/AN}$ and $\chi_{pMS/AN}$ are 0.829 (ref. 14) and 0.91 (ref. 15), respectively. The other three segmental interaction parameters cannot be quantitatively determined from the two equations. However, we attempt the three χ values as outlined below. We have earlier reported that PTHPMA is miscible with SAN having AN contents between 0 wt% and 31 wt% and with *p*MSAN having AN contents between 5 wt% and 29 wt%[5]. The segmental interaction parameters $\chi_{THPMA/S}$, $\chi_{THPMA/pMS}$ and $\chi_{THPMA/AN}$ are −0.011, 0.019 and 0.64, respectively[5]. The present work shows that PCHMA/SAN and PCHMA/*p*MSAN blends have narrower miscibility windows than those of PTHPMA/SAN and PTHPMA/*p*MSAN blends. We have also noted[6] that PCHMA has a better miscibility with PS and P*p*MS than that of PTHPMA, indicating that $\chi_{CHMA/S}$ and $\chi_{CHMA/pMS}$ are more negative than $\chi_{THPMA/S}$ and $\chi_{THPMA/pMS}$, respectively. The narrower miscibility windows for PCHMA/SAN and PCHMA/*p*MSAN blends then imply that $\chi_{CHMA/AN}$ must be significantly more positive than $\chi_{THPMA/AN}$. If we assume a value of −0.02 for $\chi_{CHMA/S}$, application of equations (3) and (4) gives 0.80 and −0.007 for $\chi_{CHMA/AN}$ and $\chi_{CHMA/pMS}$, respectively. The estimated $\chi_{CHMA/pMS}$ is less negative than $\chi_{CHMA/S}$. It has been observed that the segmental interaction parameter between the *p*-methylstyrene segment and the other segment is always more positive or less negative than that between the styrene segment and the same reference segment[5,16–19]. The estimated values of $\chi_{CHMA/pMS}$ and $\chi_{CHMA/S}$ are also consistent with the observed trend.

Nishimoto and co-workers[20] recently reported the miscibility of SAN with poly(methyl methacrylate-*co*-cyclohexyl methacrylate). From the phase behaviour, the interaction energy densities B were found to be −0.13 and 24.72 J cm^{-3} for $B_{CHMA/S}$ and $B_{CHMA/AN}$, respectively. It is interesting to note that our estimated χ values are in fairly good agreement with those reported by Nishimoto and co-workers[20].

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