Phase behaviour of blends of poly(tetrahydropyranyl-2-methyl methacrylate) with poly(styrene-*co*-acrylonitrile) and poly(*p*-methylstyrene-*co*-acrylonitrile)

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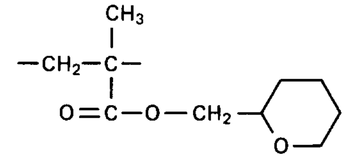
The miscibility of poly(tetrahydropyranyl-2-methyl methacrylate) (PTHPMA) with poly(styrene-*co*-acrylonitrile) (SAN) and poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN) has been studied by differential scanning calorimetry. PTHPMA is miscible with SAN having an acrylonitrile (AN) content between 0 wt% and 31 wt%, and with *p*MSAN having an AN content between 5 wt% and 29 wt%. Three segmental interaction parameters, $\chi_{\mathrm{THPMA/S}}$, $\chi_{\mathrm{THPMA/pMS}}$ and $\chi_{\mathrm{THPMA/AN}}$, were found to be −0.011, 0.019 and 0.64, respectively.

(Keywords: blends; phase behaviour; lower critical solution temperature; segmental interaction parameter; poly(tetrahydropyranyl-2-methyl methacrylate))

INTRODUCTION

A wide range of polymethacrylates, including poly(methyl methacrylate) (PMMA)[1–3], poly(ethyl methacrylate) (PEMA)[2], poly(n-propyl methacrylate) (PnPMA)[2], poly(chloromethyl methacrylate) (PCMMA)[4] and poly(tetrahydrofurfuryl methacrylate) (PTHFMA)[5], is known to be miscible with poly(styrene-*co*-acrylonitrile) (SAN) over a certain copolymer composition range. However, polymethacrylates with bulky alkyl pendent groups such as poly(isopropyl methacrylate) (PiPMA) and poly(n-butyl methacrylate) (PnBMA) are immiscible with SAN over the entire copolymer composition range[2]. Blends of some polymethacrylates with poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN) also exhibit miscibility windows[6,7].

We have earlier found that poly(tetrahydropyranyl-2-methyl methacrylate) (PTHPMA) is miscible with poly(α-methylstyrene) (PαMS) but immiscible with poly(*p*-methylstyrene) (P*p*MS). The miscibility of PTHPMA/polystyrene (PS) blends depends on their compositions[8]. PTHPMA/PS blends containing 20–30 wt% PS are immiscible but blends of other compositions are miscible. It is of interest to study how the miscibility behaviour of PTHPMA with styrenic polymers is being affected by the presence of acrylonitrile (AN) in the styrenic polymers. In this paper, we report the miscibility of PTHPMA with SAN and *p*MSAN, which enables us to evaluate three segmental interaction parameters.


PTHPMA

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EXPERIMENTAL

Materials

Tetrahydropyranyl-2-methyl methacrylate (THPMA) was obtained from Polysciences, Inc. and purified by fractional distillation at 83°C and 2 mmHg. (The monomer was sold as tetrahydropyranyl methacrylate. However, ^{1}H nuclear magnetic resonance analysis shows that the monomer is actually tetrahydropyranyl-2-methyl methacrylate.) PTHPMA was prepared by solution polymerization in 2-butanone at reflux temperature for 6 h, using 0.25 wt% azobisisobutyronitrile (AIBN) as initiator. The polymer was obtained by precipitation of the solution in excess of methanol. It was then dried *in vacuo* at 90°C for 48 h. The number average (M_n) and weight average (M_w) molecular weights (PS equivalent) of PTHPMA as determined by gel permeation chromatography are 44 000 and 65 000, respectively.

SAN with AN contents of 30 and 25 wt% were 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.

Glass transition temperature (T_g) *measurements*

The T_gs of various samples were measured with a

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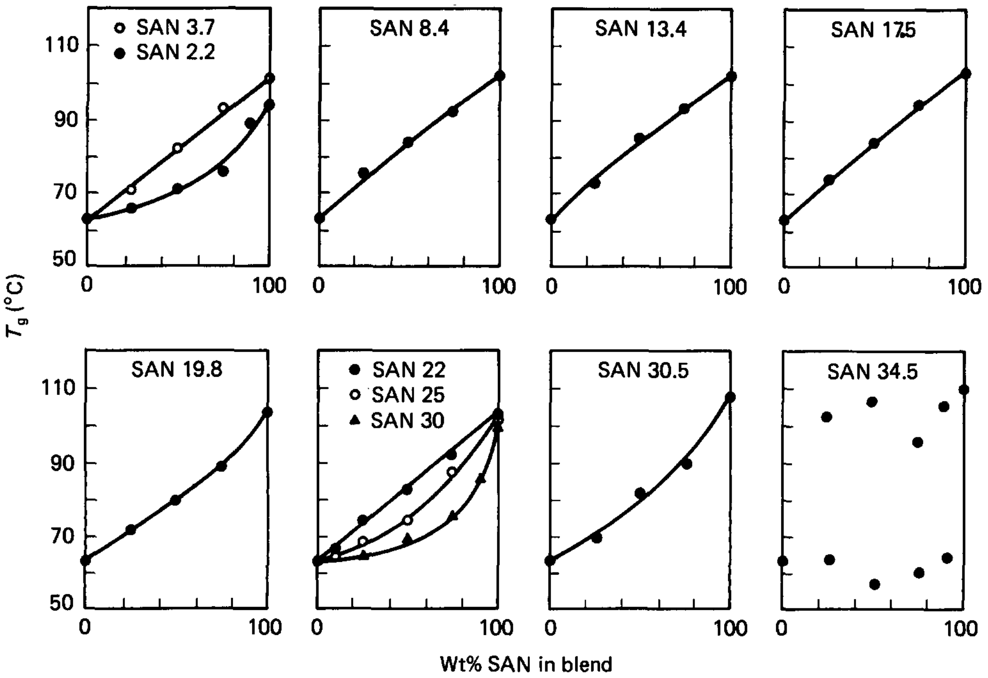

Figure 1 T_g-composition curves of various PTHPMA/SAN blends

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

Sample	M_w	M_n	T_g(°C)
SAN2.2 (4.2)	21 000	13 000	94
SAN3.7 (7.0)	23 000	14 000	101
SAN8.4 (15.3)	17 000	9 400	102
SAN9.8 (17.6)	31 000	20 000	103
SAN13.4 (23.3)	15 000	7 600	102
SAN17.5 (29.4)	27 000	20 000	103
SAN19.8 (32.6)	33 000	21 000	104
SAN22.0 (35.6)	116 000	51 000	103
SAN25.0 (39.5)	156 000	66 000	102
SAN30.0 (45.7)	125 000	61 000	100
SAN30.5 (46.3)	54 000	35 000	108
SAN34.5 (50.8)	29 000	21 000	110
*p*MSAN2.7 (5.8)	25 000	14 000	108
*p*MSAN4.6 (9.7)	50 000	25 000	108
*p*MSAN7.7 (15.7)	34 000	21 000	110
*p*MSAN13.6 (25.9)	42 000	21 000	108
*p*MSAN19.6 (35.2)	43 000	27 000	109
*p*MSAN21.3 (37.6)	52 000	28 000	110
*p*MSAN23.8 (41.0)	82 000	53 000	103
*p*MSAN26.5 (44.5)	44 000	27 000	105
*p*MSAN29.1 (47.7)	56 000	34 000	105
*p*MSAN32.3 (51.5)	62 000	38 000	104

The molar percentage of AN in the copolymer is given in parentheses

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 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-Johns 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

PTHPMA/SAN blends

Figure 1 shows the T_g–composition curves for various PTHPMA/SAN blends. Blends of PTHPMA with SAN containing AN levels ranging from 2.2 to 30.5 wt% were transparent and each exhibited a single, composition-dependent glass transition. However, PTHPMA/SAN34.5 blends were cloudy and each blend showed two glass transitions. Thus, SAN with AN content of 30.5 wt% or less is miscible with PTHPMA. It is interesting to note that the T_g for the majority of the miscible blends lies on or above the linear tie line connecting the pure component values. However, for the blends with SAN containing AN levels at the edges of the miscibility window, for example, SAN30.5, SAN30, SAN25 and SAN2.2, the T_gs lie below the tie line. The positive deviation of T_g is commonly taken as an indication of very strong intermolecular interactions which reduce the mobility of the polymer chain. Poorer miscibility was observed near the edges of the miscibility window, corresponding to a negative deviation in the T_g–composition curves.

All the miscible blends remained transparent upon heating to 300°C, except for the blends with SAN30.5, SAN30, SAN25, SAN22 and SAN2.2, which exhibit *LCST* behaviour. The cloud point curves are shown in *Figure 2*. At the edge of the miscibility window at the high AN content end, blends with higher AN content show lower cloud points. The *LCST* results were employed to construct the phase diagram of PTHPMA/SAN (50/50) blends as shown in *Figure 3*. It is noted that

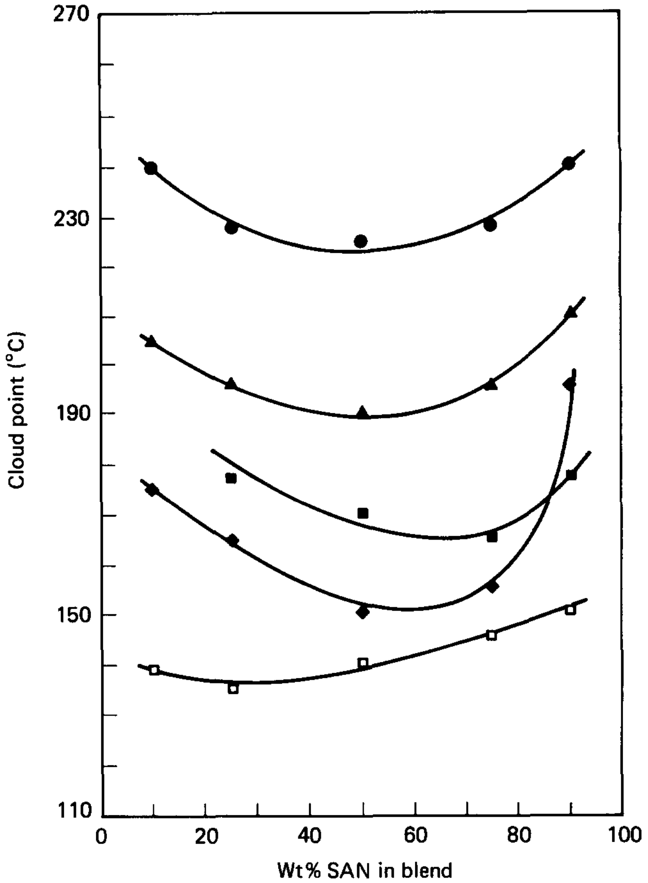

Figure 2 Cloud point curves of various miscible PTHPMA/SAN blends: (■) SAN2.2; (●) SAN22.0; (▲) SAN25.0; (◆) SAN30.0; (□) SAN30.5

the molecular weights of the three commercial samples SAN22, SAN25 and SAN30 are higher than those of the other SAN samples and, therefore, the cloud points for blends containing these three SAN samples may be different if these samples have similar molecular weights as the other SAN samples. Nishi and Kwei studied the effect of the molecular weight of PS on the cloud points of PS/poly(vinyl methyl ether) blends[9]. They observed that as the molecular weight of PS increased, the cloud point decreased but then increased when the molecular weight of PS was above 1.1×10^5. A similar study on the cloud points of PMMA/poly(α-methylstyrene-*co*-acrylonitrile) blends was reported by Goh *et al.*[10]. They also showed that the cloud point decreased as the molecular weight of PMMA increased up to 10^5 but further increase in the molecular weight of PMMA led to a higher cloud point. The reversal in the cloud point at higher molecular weight was attributed to kinetic effects in which chain entanglements hindered phase separation even though the separation was favoured thermodynamically.

PTHPMA/pMSAN blends

The T_g–composition curves for various PTHPMA/*p*MSAN blends are shown in *Figure 4*. Blends of PTHPMA with *p*MSAN containing 7.7–26.5 wt% AN were transparent, and each showed only one composition-dependent T_g, indicating complete miscibility within this range of AN contents. All the blends of PTHPMA with *p*MSAN2.7 and *p*MSAN32.3 were cloudy and two T_gs were observed in each blend, indicating their two-phase nature. Except for the (10/90) blend, all the PTHPMA/*p*MSAN4.6 blends were cloudy and each showed two T_gs. For the PTHPMA/*p*MSAN4.6 (10/90) blend, only one T_g was observed. This blend remained clear even on being heated to 280°C. PTHPMA/*p*MSAN29.1 blends containing 25 and 50 wt% of *p*MSAN29.1 were cloudy and each showed two distinct glass transitions. However, blends containing 10, 75 or 90 wt% *p*MSAN29.1 showed only a single glass transition and *LCST* behaviour was observed for all the miscible blends. Hence, the miscibility of PTHPMA/*p*MSAN29.1 blends depends on their compositions. Such a behaviour has been observed for other blends as well[11–14]. Blends of PTHPMA with *p*MSAN having AN contents of 7.7, 13.6, 19.6 and 21.3 wt% remained clear upon heating to 300°C. However, blends with *p*MSAN having AN contents of 23.8, 26.5 and 29.1 wt% underwent phase separation upon heating and the cloud point curves are shown in *Figure 5*. The present results indicate that blends containing *p*MSAN4.6 and *p*MSAN29.1 are near the verge of immiscibility in the phase diagram (*Figure 6*). PTHPMA is then concluded to be miscible with *p*MSAN having AN content between 5 wt% and 29 wt%.

Segmental interaction parameters

The miscibility behaviour of a homopolymer A/copolymer BC blend system is often explained by a simple binary interaction model[15–17]. The net interaction parameter χ_{blend} is related to various segmental interaction parameters by

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

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

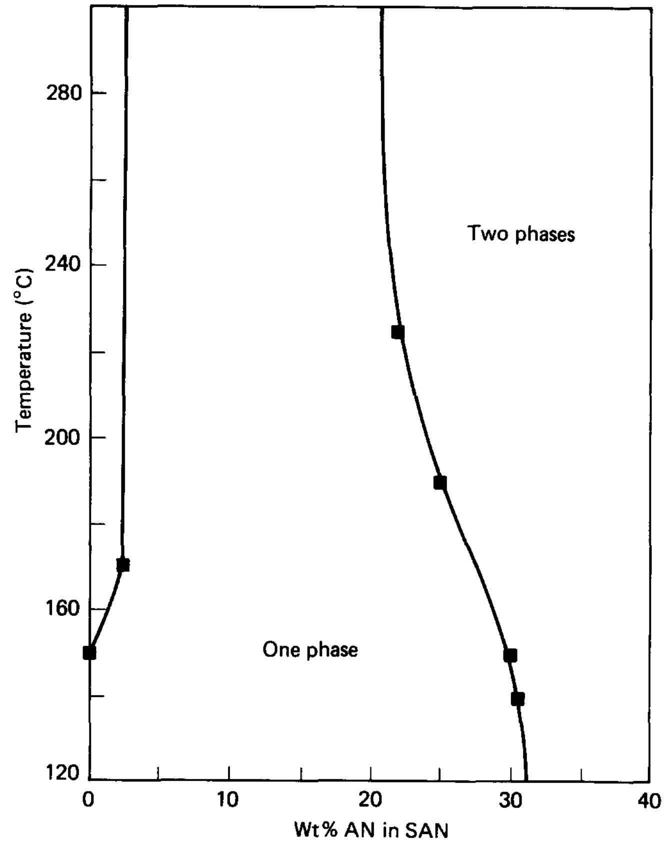

Figure 3 Phase diagram of PTHPMA/SAN (50/50) blends

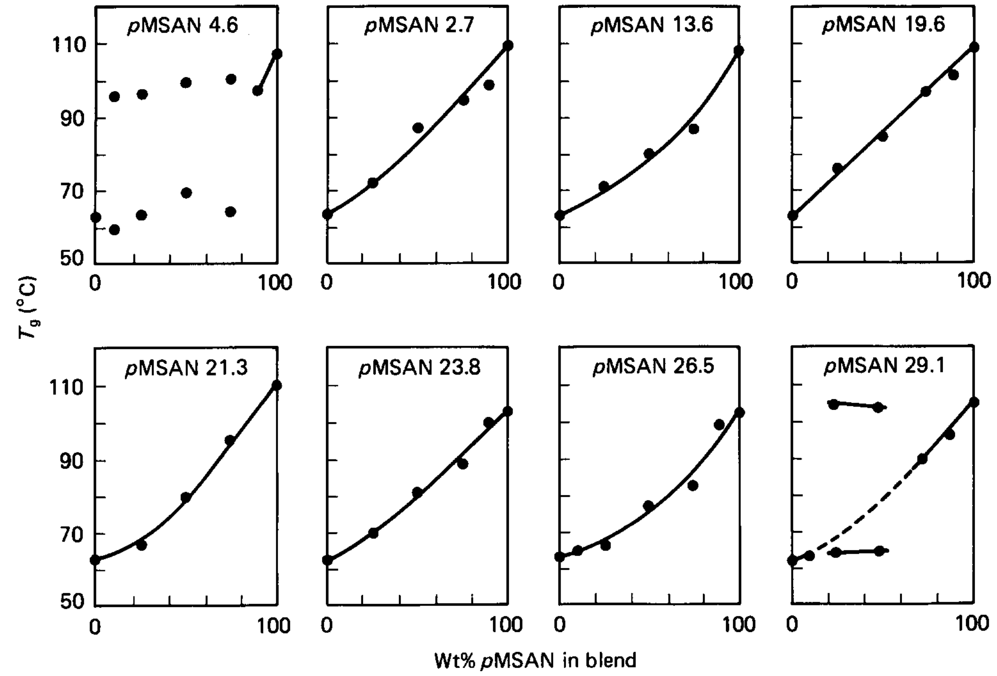

Figure 4 T_g-composition curves of various PTHPMA/*p*MSAN blends

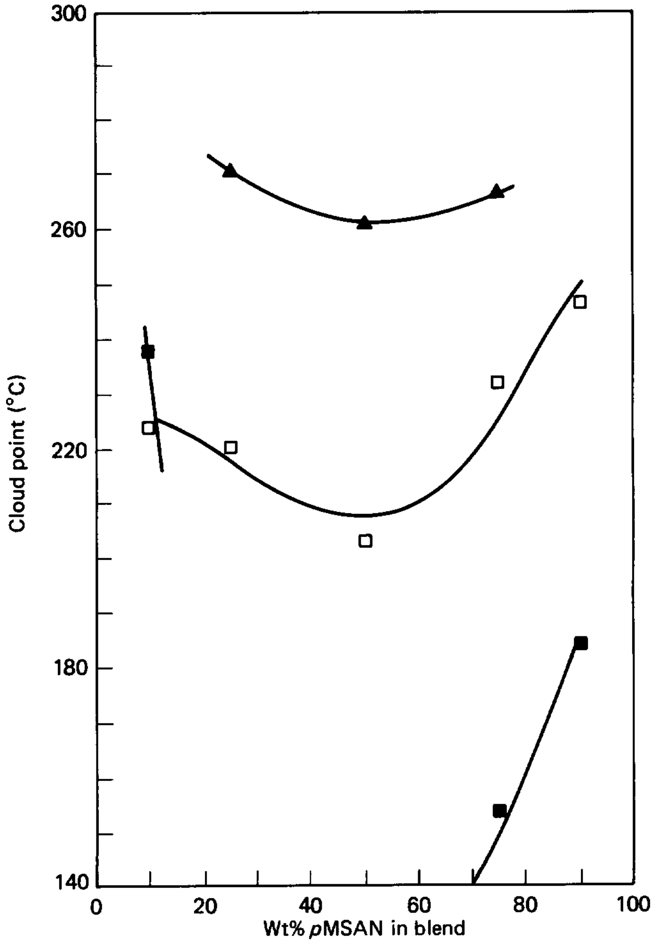

Figure 5 Cloud point curves of various miscible PTHPMA/*p*MSAN blends: (▲) *p*MSAN23.8; (□) *p*MSAN26.5; (■) *p*MSAN29.1

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

$$\chi_{\text{crit}} = 1/2[N_1^{-1/2} + N_2^{-1/2}]^2$$

with N_1 and N_2 the degrees of polymerization of A and BC. χ_{crit} depends more on the smaller N value and it approaches zero when both N_1 and N_2 are sufficiently large. The miscibility behaviour of a homopolymer/copolymer blend system enables the evaluation of various segmental interaction parameters. On the other hand, a knowledge of these interaction parameters enables the prediction of the phase behaviour of a blend system[18,19].

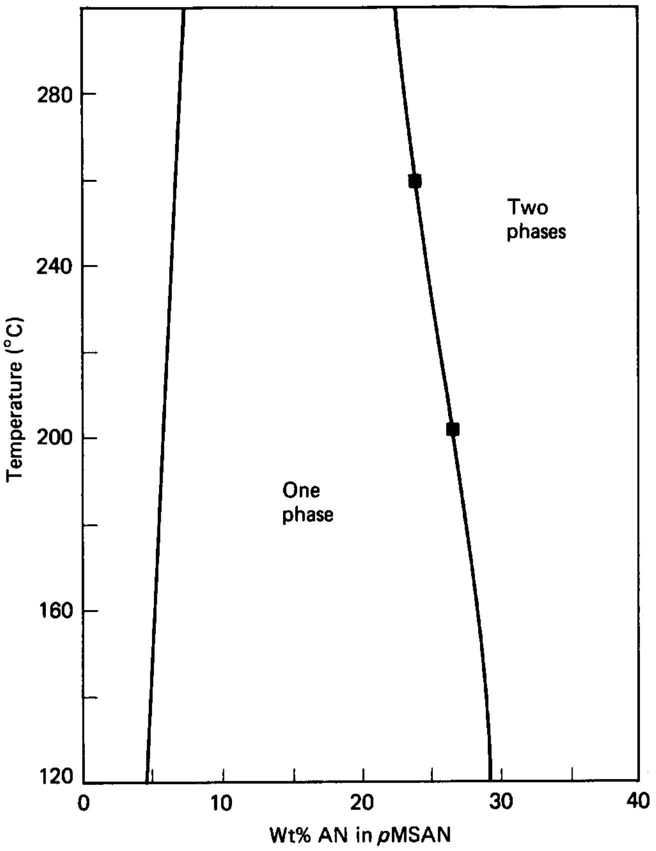

Figure 6 Phase diagram of PTHPMA/*p*MSAN (50/50) blends

For the present two blend systems, $\chi_{S/AN}$ and $\chi_{pMS/AN}$ are 0.829 and 0.91, respectively[3,7]. The other three interaction parameters can be evaluated from equation (1). For the PTHPMA/*p*MSAN blend system, the miscibility boundaries are at 5 and 29 wt% AN, corresponding to *y* values of 0.045 and 0.27. χ_{crit} values of 0.0083 and 0.0077 were obtained using the degrees of polymerization of PTHPMA and *p*MSAN nearest to the phase boundaries. Application of equation (1) leads to values of 0.019 and 0.64 for $\chi_{THPMA/pMS}$ and $\chi_{THPMA/AN}$, respectively. For the PTHPMA/SAN blends, the boundary is at 30.5 wt% AN, corresponding to a *y* value of 0.29. Using the value of $\chi_{THPMA/AN}$ just obtained and χ_{crit} of 0.0063, $\chi_{THPMA/S}$ was found to be -0.011. The small negative value of $\chi_{THPMA/S}$ suggests that PTHPMA/PS blends are miscible. This is supported by our earlier work[8] that PTHPMA is miscible with PS yet the miscibility is composition-dependent. It is also noted that $\chi_{THPMA/pMS}$ is larger than $\chi_{THPMA/S}$. This is consistent with other reports that the segmental interaction parameter between *p*-methylstyrene (*p*MS) and other segments is larger than that between styrene and the same reference segment[7,20–22]. The favourable interaction between THPMA and styrene segments leads to a wider miscibility range for the PTHPMA/SAN blend system. The relatively small value of $\chi_{THPMA/pMS}$ and the strong repulsive intramolecular interaction between *p*MS and AN segments are responsible for the miscibility of PTHPMA/*p*MSAN blends. Despite the presence of bulky alkyl pendent groups, PTHPMA is miscible with SAN over a certain copolymer composition range but PiPMA and PnBMA are immiscible with SAN over the entire copolymer composition range[2]. Apparently, the presence of the ether oxygen atom and other factors such as the ring size may affect the miscibility behaviour. Further work on PTHPMA is in progress and the miscibility of poly(cyclohexyl methacrylate) (PCHMA) with SAN and *p*MSAN is discussed in an accompanying paper[23].

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