

# Blends containing tetramethyl bisphenol-A polycarbonate: 1. Styrenic polymers

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The phase behaviour of blends of tetramethyl bisphenol-A polycarbonate, MPC, with styrene copolymers and substituted styrene homopolymers was examined using d.s.c. and optical indications of phase separation on heating, i.e. lower critical solution temperature, *LCST*, behaviour. MPC was found to be miscible with styrene/acrylonitrile copolymers, SAN, having an AN content smaller than 13%, with a styrene/maleic anhydride copolymer, SMA, having an MA content equal to 8% and with oligomeric styrene/allyl alcohol copolymers, SAA, having an AA content less than 19.1%. MPC was also found to be miscible with an oligomeric poly( $\alpha$ -methyl styrene), P $\alpha$ MS, and a copolymer of  $\alpha$ -methyl styrene/acrylonitrile, P $\alpha$ MSAN. Some of the mixtures showed *LCST* behaviour and based on this and excess volume measurements, to the extent possible, qualitative conclusions were made concerning the relative strength of the interactions among the various blend pairs. It appears that small amounts of AN or MA in the copolymers apparently increases the strength of interactions relative to those observed in polystyrene blends with MPC, whereas the inclusion of a methyl group in the styrenic repeat unit has the opposite effect. The phase behaviour of MPC with styrene based copolymers appears to be influenced by intrachain repulsion between styrene and comonomer units. MPC was found to undergo thermal and solvent induced crystallization when blends were cast from tetrahydrofuran and toluene solutions, but no crystallinity was observed when methylene chloride was used as the solvent.

(Keywords: polycarbonate blends; crystallization; solution properties)

## INTRODUCTION

The phase behaviour of polymer blends is ultimately governed by the molecular structures of its components<sup>1</sup>. Thus, manipulation of structure is an effective means of fine tuning the degree of miscibility in blends<sup>2</sup>. In cases where two polymers are close to being miscible or show some partial miscibility, minor changes in structure of one or both components may enhance the interactions<sup>3</sup> sufficiently to render the system completely miscible. On the other hand, small changes in molecular structure may decrease the strength of the interactions and cause a miscible blend to phase separate.

An example of the above is provided by tetramethyl bisphenol-A polycarbonate (MPC), whose repeating unit differs from that of bisphenol-A polycarbonate (PC) by four methyl groups substituted on the backbone rings in the 2, 6, 2'- and 6'-positions. MPC is miscible with polystyrene, PS<sup>2,4-7</sup>, while PC is not<sup>8</sup>. The miscibility of PS with MPC was first reported by Shaw<sup>2</sup> who observed features which suggested lower critical solution temperature, *LCST*, behaviour. In a more extensive study, Casper and Morbitzer<sup>4</sup> constructed a complete phase diagram for this system. Glass transitions for the blends were determined by both d.s.c. and by thermal mechanical analysis. Lower critical solution temperature behaviour was noted, and a complete cloud point curve was established. In a more recent and extensive study, Yee and Maxwell<sup>6</sup> report results of d.s.c., density and dynamic mechanical measurements for MPC/PS blends.

The purpose here is to investigate the effect of changing the structure of styrenic polymers on miscibility with

MPC. The structural changes considered include modification of the repeating unit by a methyl group to give poly( $\alpha$ -methyl styrene) or poly(*p*-methyl styrene) and the incorporation with styrene of the comonomers acrylonitrile, maleic anhydride, and allyl alcohol in various amounts.

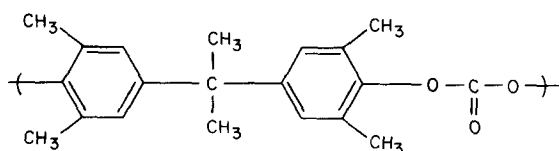
Bisphenol-A polycarbonate was previously shown to be immiscible with PS<sup>8</sup>; however, it showed some partial miscibility when blended with styrene/acrylonitrile copolymers, SANs<sup>9</sup>. The extent of miscibility was observed to be greatest when the AN content of the copolymer was about 25 to 27% by weight. Since MPC is miscible with PS, the above results suggest that MPC may also show one phase behaviour when blended with SANs over some range of AN contents. Although MPC was previously found to be immiscible with a styrene/acrylonitrile copolymer containing about 25% by weight of acrylonitrile<sup>5</sup>, to our knowledge no reports have been published about the miscibility of MPC with SANs containing smaller amounts of acrylonitrile. On the other hand, it is interesting to note that poly(2,6-dimethyl-1,4-phenylene oxide), PPO, whose repeating unit is structurally similar to that of MPC and is also miscible with PS, was reported to be miscible with a styrene/maleic anhydride copolymer, SMA, containing about 8% maleic anhydride, MA, but immiscible with copolymers containing about 14% MA<sup>10</sup>. Furthermore, several patents exist<sup>11-13</sup> claiming the miscibility of PPO with poly( $\alpha$ -methyl styrene)<sup>14</sup>. This clearly suggests that MPC may show the same kind of phase behaviour when blended with these copolymers and homopolymer.

Styrene/allyl alcohol copolymers have also been used in this study as well as an  $\alpha$ -methyl styrene/acrylonitrile copolymer. Results for MPC/PS blends have been duplicated here for comparison purposes.

This paper constitutes the first part of a series dealing with blends containing MPC. The second part will deal with the phase behaviour of blends of MPC with a series of aliphatic polyesters.

## MATERIALS AND PROCEDURES

The materials used in this work, their properties and origin are listed in Table 1. Tetramethyl bisphenol-A polycarbonate, MPC, was supplied by Bayer AG through the courtesy of Drs V. Serini and L. Bottenbruch. This polymer is a thermoplastic with a rather high glass transition temperature having the following structure:



Due to the presence of the methyl groups on the rings, MPC is highly resistant to hydrolysis. The styrenic polymers used in this study all had molecular weights in the range 1 to  $3 \times 10^5$  except for the styrene/allyl alcohol copolymers and the poly( $\alpha$ -methylstyrene) which have very low molecular weights and should be regarded as oligomers. The acrylonitrile, AN, and maleic anhydride, MA, content for the copolymers are also shown in Table 1. The numerical value included as part of the code for these copolymers indicates the nominal per cent by weight in AN or MA. The styrene/allyl alcohol copolymers, SAAs, are also designated with a number indicating the nominal level of their OH content.

Toluene was used initially to cast blends of MPC and PS from solution. This procedure was subsequently abandoned due to development of MPC crystallinity during the evaporation of the solvent. Methylene chloride,  $\text{MeCl}_2$ , was used instead to cast films of MPC with PS and with other styrene containing copolymers. Tetrahydrofuran, THF, was used to cast blends of MPC with the styrene copolymer containing 4.4% allyl alcohol. The polymer solutions were left in aluminium pans at room temperature until most of the solvent evaporated.

Table 1 Polymers used in this study

Abbreviation	Polymer	Copolymer composition (wt %)	Density ( $\text{g cm}^{-3}$ )	$T_g$ ( $^{\circ}\text{C}$ )	Molecular weight information	Source/ (Designation)
MPC	Tetramethyl bisphenol-A polycarbonate	—	1.0824 <sup>a</sup>	193.5 <sup>a</sup>	$\eta_{\text{rel}} = 1.29^e$	Bayer AG
PS	Polystyrene	—	1.0483 <sup>a</sup>	103 <sup>a</sup>	—	Cosden Oil and Chem. Co. (Cosden 550)
SAN 2	Styrene/acrylonitrile copolymer	2% AN	1.0487 <sup>a</sup>	103 <sup>a</sup>	$\eta = 0.7 \text{ cp}^d$ $\bar{M}_w = 204\,000$ $\bar{M}_n = 93\,500$	Asahi Chemical Industry Co., Ltd.
SAN 5	Styrene/acrylonitrile copolymer	5.5% AN	1.0507 <sup>a</sup>	107 <sup>a</sup>	$\bar{M}_w \sim 270\,000$	Dow Chemical Company
SAN 9	Styrene/acrylonitrile copolymer	9.5% AN	1.0568 <sup>a</sup>	102 <sup>a</sup>	$\eta = 8.5 \text{ cp}^d$	Asahi Chemical Industry Co., Ltd.
SAN 11	Styrene/acrylonitrile copolymer	11.5% AN	1.0587 <sup>a</sup>	104 <sup>a</sup>	$\eta = 8.4 \text{ cp}^d$	Asahi Chemical Industry Co., Ltd.
SAN 13	Styrene/acrylonitrile copolymer	13% AN	1.0652 <sup>b</sup>	109 <sup>a</sup>	$\bar{M}_n = 56\,300$ $\bar{M}_w = 149\,000$ $\bar{M}_z = 293\,000$	Borg-Warner (Resin 21082-73)
SAN 16	Styrene/acrylonitrile copolymer	16.2% AN	1.0636 <sup>b</sup>	108 <sup>a</sup>	$\bar{M}_w = 197\,800$	Dow Chemical Company
SAN 25	Styrene/acrylonitrile copolymer	25% AN	1.0775 <sup>b</sup>	109 <sup>a</sup>	—	Dow Chemical Company (Tyril 860)
SAN 70	Styrene/acrylonitrile copolymer	69.7% AN	—	108 <sup>a</sup>	$[\eta] = 0.80^f$	Monsanto Co.
SMA 8	Styrene/maleic anhydride copolymer	8% MA	1.0755 <sup>a</sup>	118 <sup>a</sup>	$\sim \bar{M}_w = 200\,000$ $\sim \bar{M}_n = 100\,000$	Arco Chem. Co. (Dylark 232)
SMA 14	Styrene/maleic anhydride copolymer	14% MA	—	128 <sup>a</sup>	$\bar{M}_w = 180\,000$ $\bar{M}_n = 90\,000$	Arco Chem. Co. (Dylark 332)
SAA 1	Styrene/allyl alcohol copolymer	4.4% AA or 1.3% OH	1.05 <sup>c</sup>	44 <sup>a</sup>	$\bar{M}_w = 2\,100$	Monsanto Co.
SAA 2	Styrene/allyl alcohol copolymer	8.4% AA or 2.5% OH	1.05 <sup>c</sup>	41 <sup>a</sup>	$\bar{M}_w = 1\,420$	FRP Company
SAA 5	Styrene/allyl alcohol copolymer	19.1% AA or 5.7% OH	1.06 <sup>c</sup>	60 <sup>a</sup>	$\bar{M}_w = 2\,340$	Monsanto Co.
SAA 7	Styrene/allyl alcohol copolymer	25.8% AA or 7.7% OH	1.09 <sup>c</sup>	45 <sup>a</sup>	$\bar{M}_w = 1\,700$	Monsanto Co.
P $\alpha$ MS	Poly( $\alpha$ -methyl styrene)	—	1.0765 <sup>a</sup>	68 <sup>a</sup>	$\bar{M}_n = 940$	Amoco Chemicals Corp. (Resin 18-290)
P $\alpha$ MSAN	$\alpha$ -Methyl styrene acrylonitrile copolymer	30% AN	—	119 <sup>a</sup>	$\bar{M}_w = 160\,000$	BASF (Luran KR 2556 U)
PpMS	Poly(para-methyl styrene)	—	—	112 <sup>a</sup>	$\bar{M}_w = 357\,000$	Mobil Chemical Company

<sup>a</sup> This work

<sup>b</sup> Ref. 36

<sup>c</sup> Ref. 37

<sup>d</sup> 10% solution viscosity in MEK

<sup>e</sup> In methylene chloride ( $c = 5\text{g}/1$ ) at temperature  $T = 25^{\circ}\text{C}$

<sup>f</sup> Measured at  $25^{\circ}\text{C}$  in dimethyl formamide (ref. 9)

The resulting films were then placed in a vacuum oven for three days at 80°C or 110°C for the blends cast with toluene.

A Perkin-Elmer DSC-2 equipped with a computerized data station was used to measure the thermal behaviour of these blends. The glass transitions were recorded during the second heat, using a heating rate of 20°C/min, after the samples had been quenched, at 320°C/min, from 317°C to 7°C. In some cases, a slightly different procedure had to be used as noted in subsequent sections. The blends were also tested for lower critical solution temperature behaviour using a procedure previously described<sup>15</sup>. The density of the miscible amorphous blends were measured in a density gradient column based on aqueous solutions of calcium nitrate as described earlier<sup>16</sup>.

## RESULTS FOR BLENDS WITH POLYSTYRENE

Toluene was found to be inadequate to cast films of MPC blends with PS, due to solvent induced crystallization of MPC during the solvent evaporation in the film drying process. In order to find a solvent that would not induce crystallization of MPC, tetrahydrofuran (THF) and methylene chloride (MeCl<sub>2</sub>) were tried. A cloudy MPC film was obtained when THF was used as the solvent and the d.s.c. thermogram revealed a melting peak around 280°C with an enthalpy of fusion of 4.7 cal/g. The film cast from MeCl<sub>2</sub> was transparent and no crystallinity was observed by d.s.c.

Since MeCl<sub>2</sub> did not induce any MPC crystallinity, it was selected as the solvent and transparent MPC/PS blends were obtained. On heating, these blends turned cloudy due to phase separation. The cloud point curve is shown in Figure 1 together with other systems to be discussed later. LCST behaviour for MPC/PS blends was first noted by Shaw<sup>2</sup> and was later established in detail by Casper and Morbitzer<sup>4</sup>. The cloud point curve observed

in this study is in good agreement with that obtained by the latter authors<sup>4</sup>.

When these blends were examined by d.s.c., a single glass transition was observed as shown in Figure 2 together with other systems to be discussed later. To obtain reliable results the samples were never heated beyond the cloud points shown in Figure 1.

In contrast, MPC/PS blends, rich in MPC cast from toluene were cloudy at room temperature and remained so during heating to the decomposition temperature. Pure MPC cast from toluene showed a melting peak at 280°C by d.s.c. with an enthalpy of fusion equal to 3.4 cal/g. Melting peaks were also observed for MPC/PS blends rich in MPC, at slightly lower temperatures than for pure MPC. Although this crystallinity was eliminated by heating above the MPC melting point and immediately quenching, we were not able to reproduce the previous results obtained with blends cast from MeCl<sub>2</sub> the reason being that in order to destroy MPC crystallinity the blends were heated beyond their phase separation temperature and two  $T_g$ s were obtained in the second heating. LCST behaviour also explains why the blends that initially showed some crystallinity never became clear at temperatures higher than the MPC melting point.

As for MPC, solvent induced crystallization has been observed with polycarbonate, PC<sup>17</sup>. The usual arguments advanced to explain the variation in degree of crystallinity induced by different solvents involve evaporation rate and effectiveness of the solvent to plasticize the polymer. If the solvent is rapidly removed, as in the case of MeCl<sub>2</sub>, the  $T_g$  is not sufficiently depressed to allow crystallization. However, if the solvent is removed slowly, as with THF or toluene and if it interacts strongly with the polymer, it can act as a plasticizer and give the polymer chains enough mobility to allow crystallization.

Density measurements were performed with the MeCl<sub>2</sub> blends to find the excess volume of mixing. Hildebrand and Scott showed<sup>18</sup> that for a large number of liquid mixtures, a negative enthalpy of mixing results in a negative excess volume of mixing. Similar reasoning should apply to polymer blends, and, indeed, many miscible blends do show a negative excess volume of mixing<sup>19-25</sup> which may be attributed to better packing in blends as a result of strengthened interactions and/or geometric effects. The original observations refer to mixtures in thermodynamic equilibrium while the miscible blends investigated in this study are all in the non-equilibrium, glassy state.

In order to make comparisons between different glassy blends it is generally assumed that all the blends are equidistant from equilibrium<sup>6</sup>. To minimize such problems and to make consistent comparisons, all blends were subjected to the same thermal history described in the Experimental section.

The specific volume for blends of MPC with PS is shown as a function of composition in Figure 3. The excess volume is small and does not exceed the accuracy of the density measurements ( $\pm 8 \times 10^{-4}$ ). For practical purposes, we consider it to be zero. Our results are slightly different from those obtained by Yee *et al.*<sup>6</sup> which may reflect the different temperatures of the measurements and the different thermal histories involved.

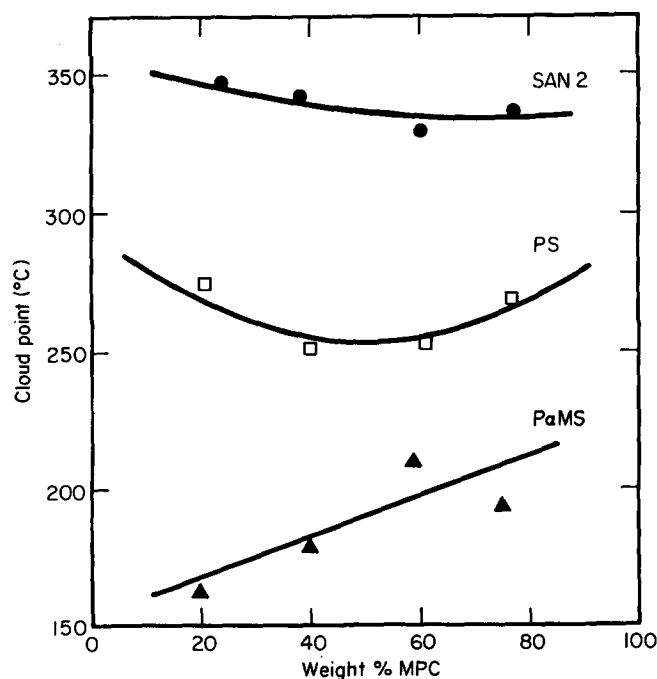


Figure 1 Cloud point curves for blends of MPC with SAN 2, PS and PaMS

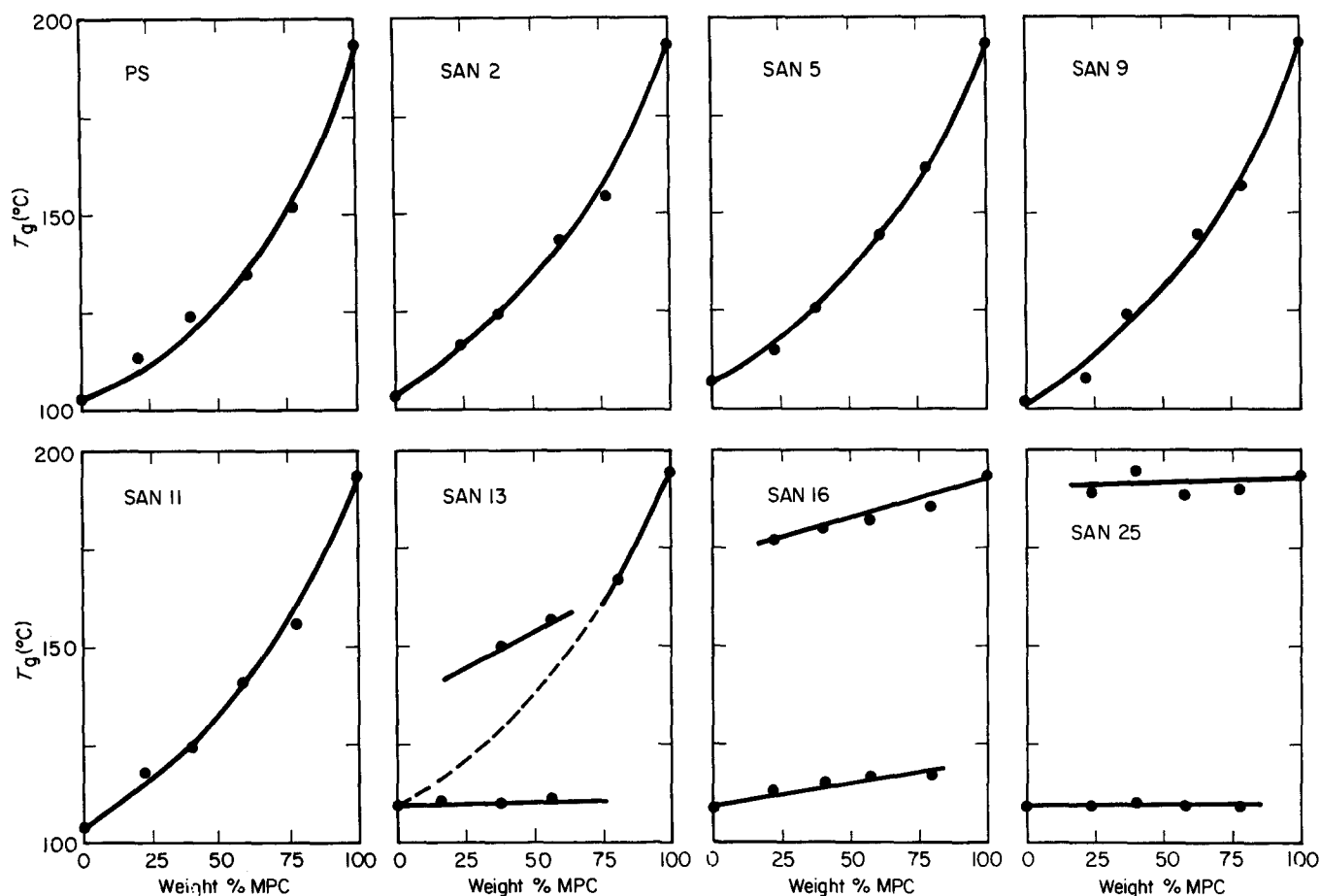


Figure 2 Glass transition behaviour for MPC blends with PS and with various SAN copolymers

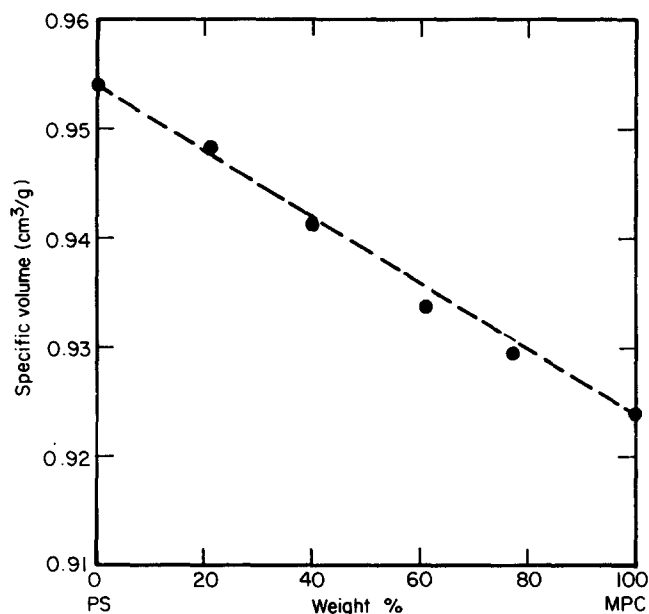


Figure 3 Specific volume for MPC/PS blends at 30°C

### RESULTS FOR BLENDS WITH STYRENE/ACRYLONITRILE COPOLYMERS

As mentioned earlier, MPC has been reported to be immiscible with a styrene/acrylonitrile copolymer containing approximately 25% acrylonitrile<sup>5</sup>. Figure 2 shows the glass transition versus composition relations for blends of MPC, with SAN copolymers ranging in AN levels from 25% down to pure PS. For acrylonitrile

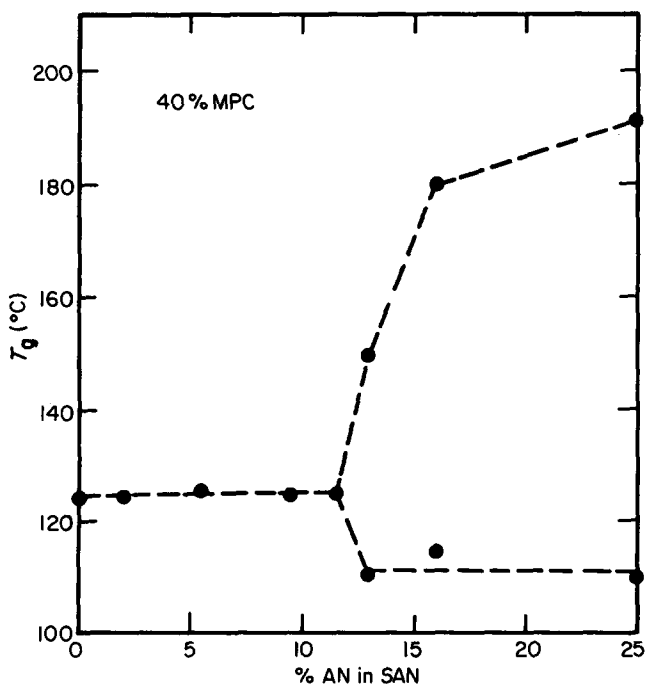
contents equal to or less than 11.5% by weight, a single glass transition is observed which changes regularly with blend composition. Based on this and the fact that the films were transparent at room temperature, we conclude that blends based on SANs below this level of AN are miscible with MPC. On the other hand, blends of MPC and a copolymer containing 25% AN by weight were cloudy at room temperature and exhibited two glass transitions occurring at essentially the same temperature as for the pure components in agreement with the previously published report<sup>5</sup>.

Blends of MPC with SAN 13 or SAN 16 fall on the border between complete miscibility and immiscibility. The glass transition versus composition curve for MPC/SAN 13 shows a single  $T_g$  at high MPC concentrations, but as the SAN 13 content increases the  $T_g$  curve splits into two suggesting the presence of two phases. One of the glass transitions is lower than that of pure MPC but the other one is essentially the same as that for pure SAN 13, suggesting that one of the phases is essentially pure SAN 13, while the other one contains both polymers but is richer in MPC. The blend containing about 80% MPC was clear but when heated became cloudy at 300°C. The blends with a lower content of MPC were cloudy and remained so on heating to the decomposition temperature. Based on this, we conclude that MPC/SAN 13 blends are homogeneous when the MPC content is higher than 80% but form two separate phases when the concentration of MPC is less than about 80%. Blends of MPC with an SAN copolymer containing 16% by weight acrylonitrile were cloudy and showed two glass transitions slightly displaced from those of the pure

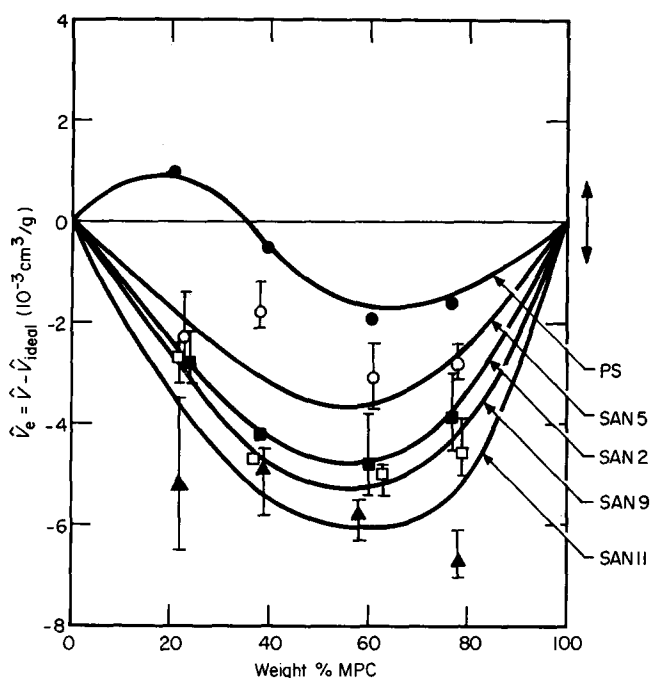
polymers. This system is then classified as partially miscible. The above results demonstrate that MPC will tolerate a limited amount of AN in copolymers with styrene before phase separation occurs as shown graphically in *Figure 4* where glass transition behaviour versus % AN level is plotted for blends containing about 40% MPC.

To ensure that the behaviour indicated in *Figure 4* continues at even higher AN levels a blend containing 50% MPC with an SAN copolymer composed of 69.7% acrylonitrile by weight was prepared. The polymers were dissolved in a mixture of two solvents: dimethylformamide, DMF and MeCl<sub>2</sub>, and a clear solution was obtained. Methanol was added to the solution and a white precipitate was formed. The solids were separated from solution by filtration and the blend obtained was placed in a vacuum oven for one day at room temperature and for three days at 110°C. This blend was found, by d.s.c., to have two glass transitions at the same temperatures as those the pure polymers and it remained cloudy during heating up to the decomposition temperature. Thus, this blend is clearly immiscible.

It would be of interest to know more about how the interaction between MPC and SAN changes as the % AN in the copolymer increases. Since none of these polymers are crystalline, melting point depression analysis cannot be used to obtain this information<sup>26</sup>. One way of assessing this qualitatively is through comparison of cloud point curves. Generally, the more exothermic the interaction between components, the higher the temperature at which phase separation occurs<sup>27</sup>. Interestingly, blends based on the copolymer containing 2% by weight acrylonitrile phase separated on heating at higher temperatures than blends based on pure PS (*Figure 1*). Blends of MPC with SAN 5, SAN 9 and SAN 11 showed no evidence of phase separation on heating up to the decomposition temperature. These results suggest that the miscible SAN copolymers interact more exothermically with MPC than does PS, and that the



**Figure 4** Glass transitions for blends containing 40% MPC and 60% SAN copolymer versus AN content of copolymer



**Figure 5** Excess volume for blends of MPC with PS and with various SANs at 30°C. Arrows on the right indicate the accuracy of the experimental data

maximum strength of interaction occurs at an AN content between 5 and 10% by weight.

To supplement these results, density measurements were made to determine the excess volume of mixing<sup>28</sup> and the results are shown in *Figure 5*. Careful analysis of *Figure 5* shows that, with the exception of SAN 2 and SAN 5, the excess volume becomes more negative as the % AN increases. The differences between SAN 2 and SAN 5 may not be significant considering the accuracy of the density measurements ( $\pm 8 \times 10^{-4} \text{ g cm}^{-3}$ ) and the scatter of the data (as shown by the bars in *Figure 5*). *Figure 6* combines the cloud point and excess volume results as a function of % AN in the copolymer for blends containing about 80% MPC. We choose this particular composition for this plot in order to make use of the cloud point observed for the MPC/SAN 13 blend of this composition. The fact that no cloud points were observed for MPC/SAN 5, MPC/SAN 9 or MPC/SAN 11 makes comparisons impossible within this range. However, based on all of the evidence we can draw the relationship between cloud point and AN content of the copolymer as shown in the lower part of *Figure 6*.

Evidently, incorporation of a small amount of AN increases the strength of the interactions with MPC. However, further increase in the amount of acrylonitrile eventually causes MPC to become completely immiscible with SAN copolymers.

In order to see if similar behaviour exists for other styrene copolymers, MPC was blended with styrene/maleic anhydride and styrene/allyl alcohol copolymers. The results for these systems are summarized next.

#### RESULTS FOR BLENDS WITH STYRENE/MALEIC ANHYDRIDE COPOLYMERS

Glass transitions as a function of composition for blends of MPC with styrene/maleic anhydride copolymers,

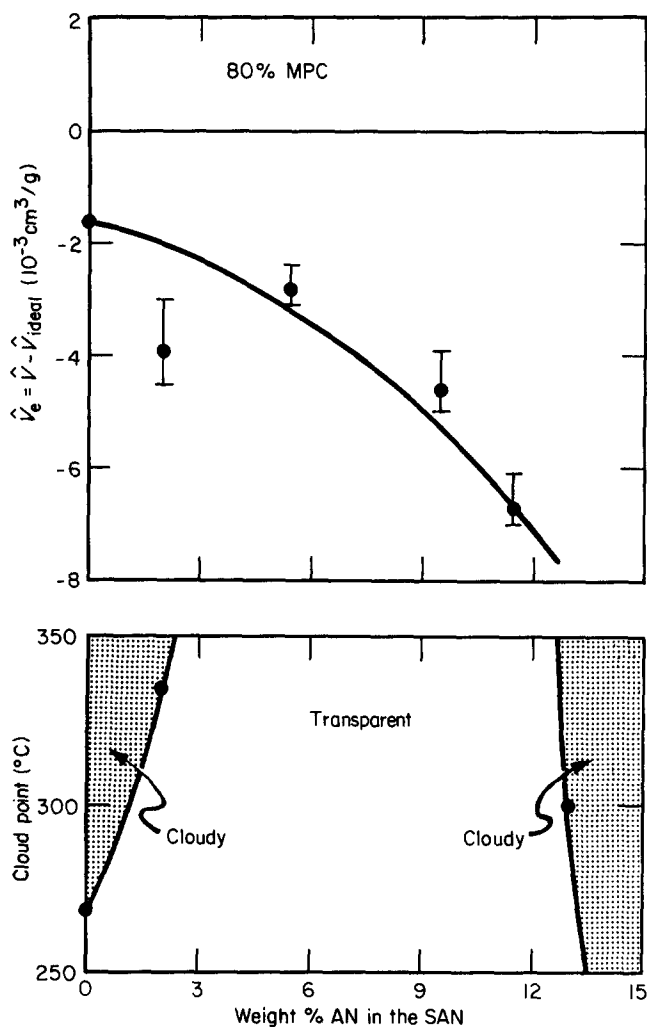


Figure 6 Excess volume and cloud points for blends containing 80% MPC with various SANs

SMA, are shown in Figure 7. Blends with the SMA containing 8% by weight maleic anhydride show a single glass transition located at temperatures intermediate between those of the pure copolymer and homopolymer. These blends were transparent at room temperature. Based on this, we conclude that MPC is miscible with this copolymer. However, blends with the SMA containing approximately 14% by weight MA were cloudy at room temperature and show two glass transitions at temperatures close to those for the homopolymer and copolymer. Thus, MPC is immiscible with SMA 14.

The miscible blend MPC/SMA 8 was examined for lower critical solution temperature behaviour but no cloud point could be detected for any composition prior to the decomposition temperature. Density measurements for MPC/SMA 8 revealed a large negative excess volume of mixing as shown in Figure 8, together with the excess volume of mixing for MPC/PS. In conclusion, as observed for MPC/SAN blends, miscibility of SMA copolymers with MPC ceases beyond a certain MA level, however, a small amount of maleic anhydride seems to enhance the strength of interactions with MPC as suggested by the elevation of the cloud point curve and by the larger excess volume of mixing relative to pure polystyrene. It should be noted here that, since copolymers of styrene and maleic anhydride are reported to have higher heat and solvent resistance than commercial grades of PS<sup>10</sup>, miscible blends of MPC with SMA 8 may have potential commercial importance.

#### RESULTS FOR BLENDS WITH STYRENE/ALLYL ALCOHOL COPOLYMERS

The as-cast blends of MPC with the four styrene/allyl alcohol copolymers were cloudy or opaque and quite brittle. The d.s.c. thermograms, obtained in the first heat, revealed in every case the presence of two glass

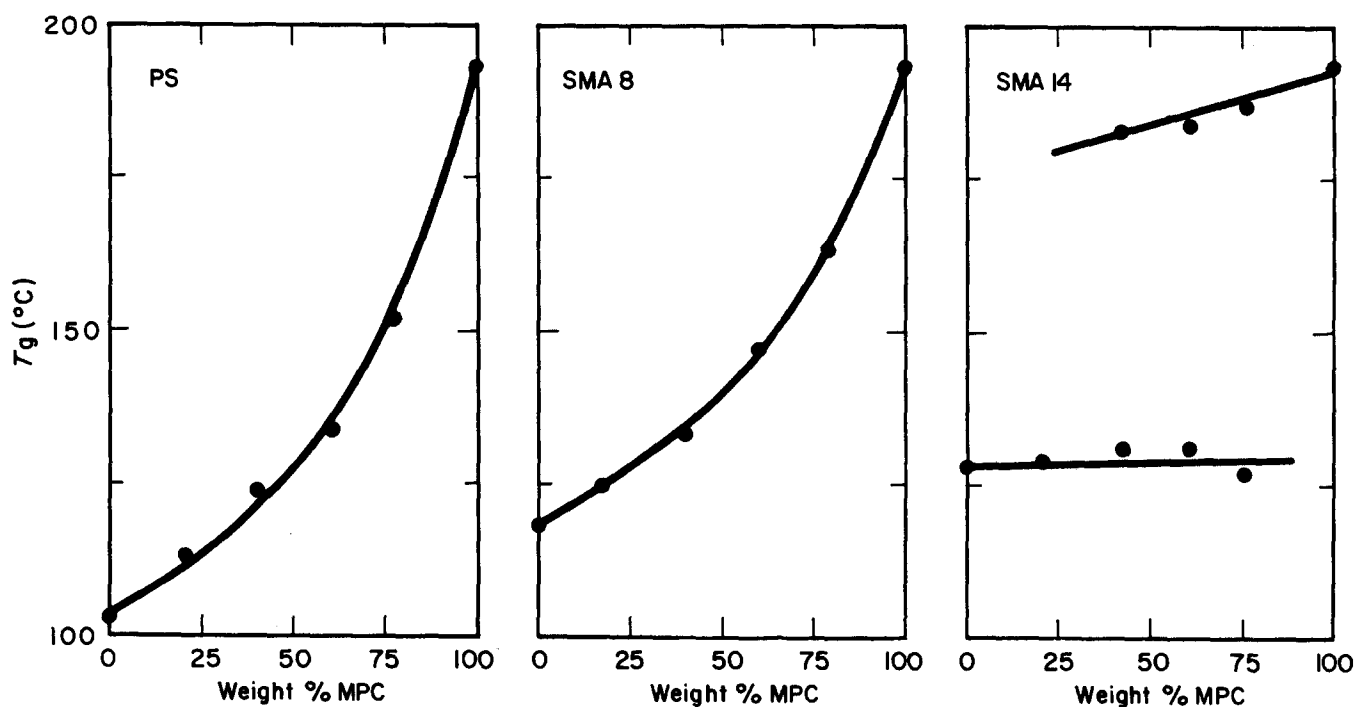


Figure 7 Glass transitions for MPC blends with PS and with styrene/maleic anhydride copolymers

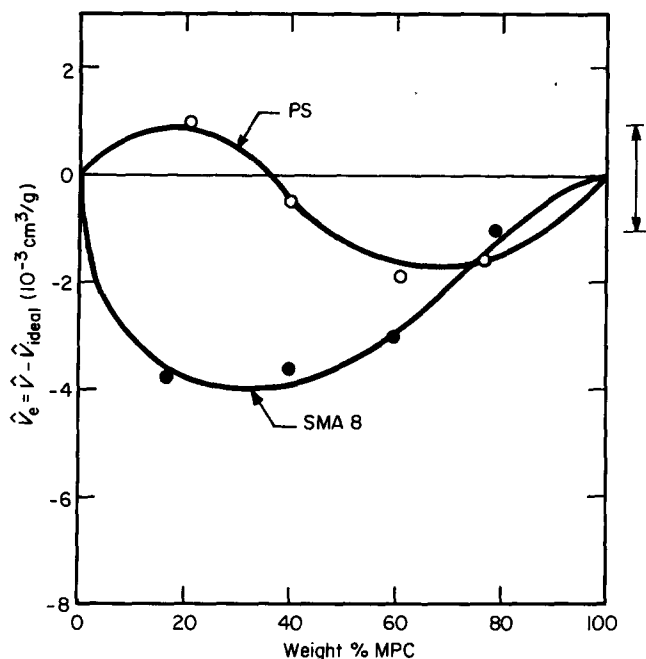


Figure 8 Excess volume for blends of MPC with PS and with SMA 8 at 30°C. Arrows on the right have the same meaning as in Figure 5

transitions, one at the same temperature as the  $T_g$ s for the SAA and the other one depressed with respect to the  $T_g$  of MPC. The blends cast from THF (MPC/SAA 1) showed a melting peak, due to solvent induced crystallization of MPC. Both melting point and enthalpy of fusion *versus* composition are shown in Figure 9. Both curves show a maximum displaced to high MPC concentrations. This kind of dependence of  $T_m$  or  $\Delta H_f$  on blend composition was previously observed for polycarbonate in blends with polyesters<sup>29</sup>. No such peaks were detected in blends cast from  $\text{MeCl}_2$ . After being conditioned at 317°C and quenched, a single glass transition was obtained for blends of MPC with SAA 1, SAA 2 and SAA 5, as shown in the middle part of Figure 10. In contrast, the thermograms for blends of MPC with SAA 7 showed no significant change after undergoing the same thermal treatment (see plot on extreme right in Figure 10).

Based on the above, we conclude that MPC is miscible with SAA 1, SAA 2 and SAA 5 and is only partially miscible with SAA 7. We believe that the initial cloudiness of the blends was in part due to MPC crystallinity (in the case of MPC/SAA 1) and to phase separation during solvent evaporation in the film drying process owing to the difference in affinity of the solvent for the two polymers. By heating the blends to 317°C, single homogeneous phases were obtained in all cases with the exception of MPC/SAA 7 mixtures.

Visual observations of the blend films on heating confirmed the previous statements, i.e. MPC/SAA 1 blends became clear after the melting of MPC and MPC/SAA 2 or MPC/SAA 5 blends became clear at temperatures above the higher  $T_g$  detected in the first heat. For these blends a slight increase in cloudiness was observed above this temperature, possibly due to thermal induced crystallization of MPC. This crystallization could not be observed in the d.s.c. which is not surprising considering the large range of temperatures over which this takes place and the small order of magnitude of the enthalpy of crystallization. Due to decomposition and

development of bubbles the samples could not be observed at higher temperatures.

In conclusion, we can say that MPC miscibility with the SAAs decreases as the AA content increases, as apparent from Figure 11. Since no cloud points were detected before decomposition took place, at relatively lower temperatures than for blends containing SAN or SMA copolymers, it was not possible to rank the strength of interactions within this set of systems.

## RESULTS FOR BLENDS WITH METHYL STYRENE POLYMERS

Poly( $\alpha$ -methyl styrene) and poly( $p$ -methyl styrene) differ from polystyrene by the presence of a methyl group in the repeat unit. Blends of MPC with the oligomeric P $\alpha$ MS show a single composition dependent glass transition as seen in Figure 12; whereas blends with the high molecular weight PpMS show two glass transitions at the same temperatures as the glass transitions of the pure polymers (Figure 12). A high molecular weight copolymer of  $\alpha$ -methyl styrene and 30% by weight of acrylonitrile produced blends with MPC which also showed to  $T_g$ s. The miscible blend, MPC/P $\alpha$ MS, was examined for lower critical solution temperature behaviour with the results shown in Figure 1. The cloud point curve for this system

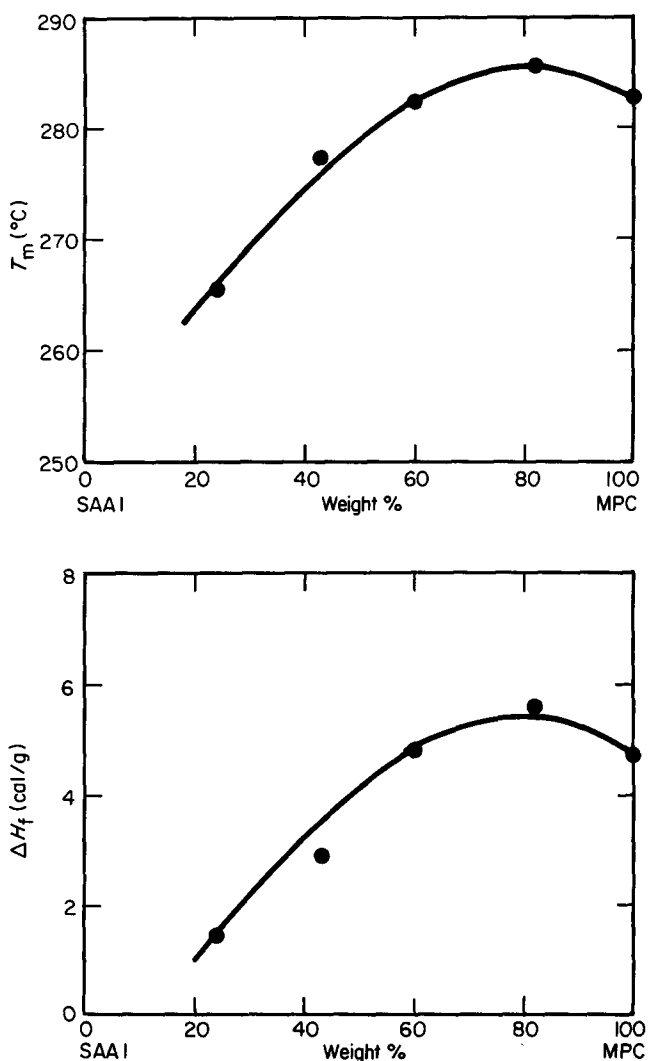


Figure 9 Melting point and enthalpy of fusion for MPC in blends with SAA 1, cast from THF

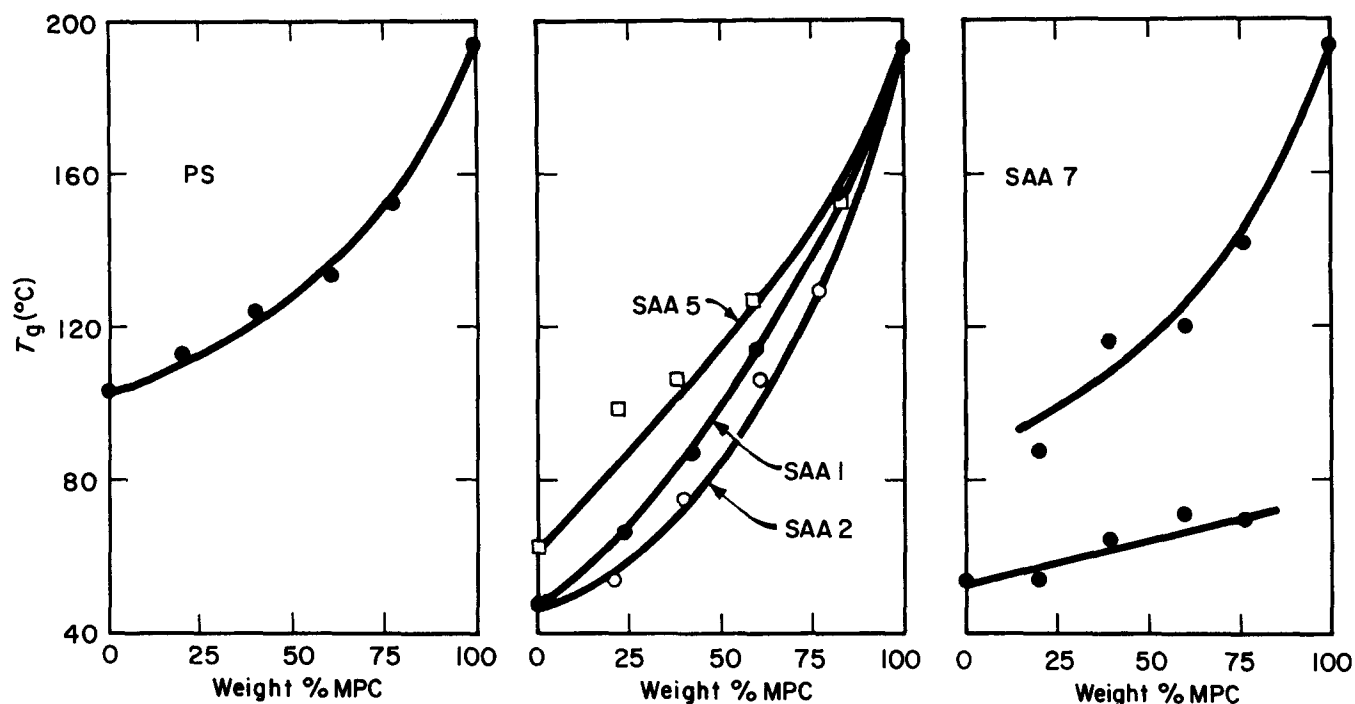


Figure 10 Glass transitions for MPC blends with PS and with styrene/allyl alcohol copolymers

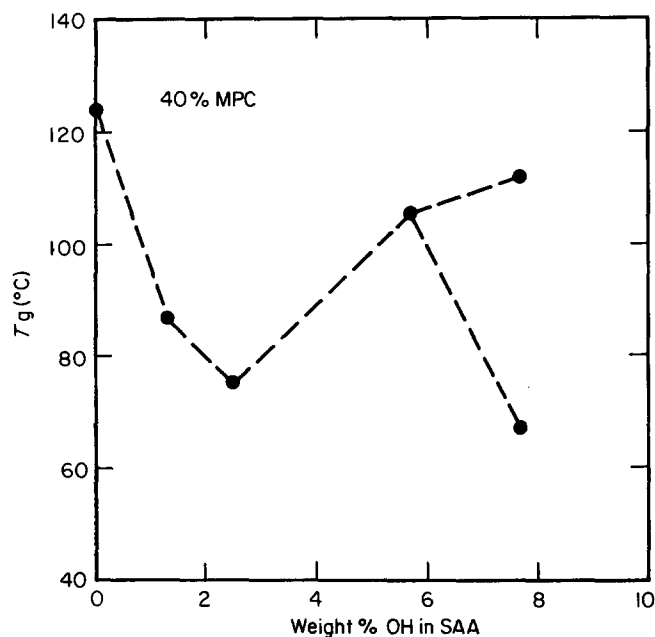


Figure 11 Glass transitions for blends containing 40% MPC with various SAAs as a function of the hydroxyl content of the copolymer

lies at lower temperatures than the curves for either MPC/SAN 2 or MPC/PS blends. Since P $\alpha$ MS is an oligomeric material, the phase behaviour of its blends with MPC will be greatly influenced by the favourable combinatorial entropy of mixing. As the molecular weight increases the temperature at which phase separation occurs should decrease owing to reduction of the combinatorial entropy of mixing. In the limit for very high molecular weights this temperature may be lower than the glass transition of the system and for practical purposes such mixtures might be regarded as immiscible<sup>30</sup>.

The volumetric data for this system are compared in Figure 13 with that for PS/MPC blends. The excess volume of the former is very small at high MPC concentrations but is negative for P $\alpha$ MS rich blends. At this point, no explanation for this observation can be offered.

In conclusion, addition of small amounts of comonomers to styrene seems to enhance the favourable interaction with MPC. However, the inclusion of a methyl group in the alpha or para position in the styrene repeat unit apparently decreases the strength of the interactions with MPC.

Considering the relatively weaker interactions of MPC with P $\alpha$ MS than with PS and the relatively large amount of AN in the  $\alpha$ -methyl styrene/acrylonitrile copolymer (30%) it is not surprising that MPC is immiscible with this copolymer (Figure 12).

## DISCUSSION

The observed phase behaviour for MPC/SAN blends in many ways parallels that observed for PC/SAN blends<sup>9</sup>. Although PC is essentially immiscible with PS<sup>8</sup>, some partial miscibility is observed when small amounts of acrylonitrile are incorporated into the PS chain<sup>9</sup>. A maximum in partial miscibility was observed for SANs containing about 25% AN<sup>9</sup>. On the other hand, MPC is miscible with PS and with styrene/acrylonitrile copolymers when the AN content is less than 11%. A maximum in the strength of interactions seems to occur for AN contents between 5 and 11%. Keitz *et al.*<sup>9</sup> argued that the optimum AN content of about 25% partial miscibility of PC with SAN copolymers stems from intramolecular repulsive interactions between styrene and acrylonitrile units using a binary interaction model recently developed for blends of copolymers<sup>31-33</sup>. Similar reasoning ought to apply to the observed phase behaviour for MPC blends with SAN, SMA and SAA



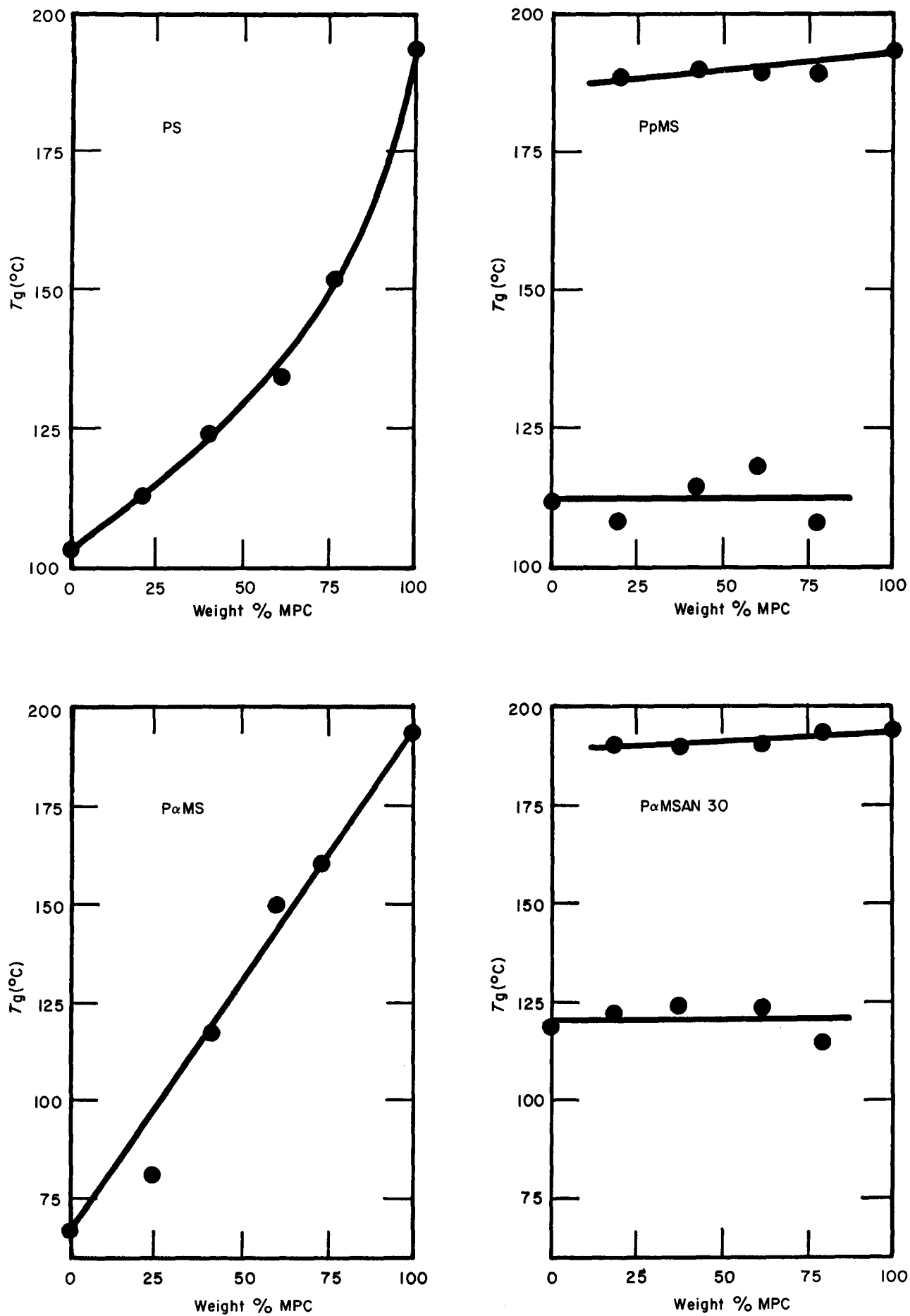


Figure 12 Glass transitions for MPC blends with PS, PpMS, P $\alpha$ MS and P $\alpha$ MSAN

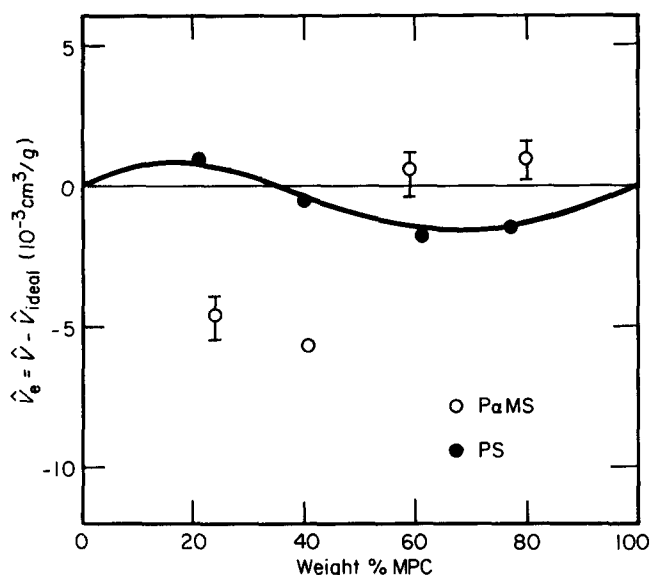
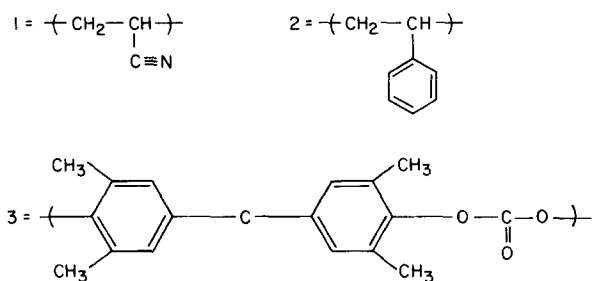


Figure 13 Excess volume for blends of MPC with PS and PαMS at 30°C

copolymers. This model gives for the overall blend interaction parameter:

$$B = B_{13}\phi_1 + B_{23}\phi_2 - B_{12}\phi_1\phi_2 \quad (1)$$

where the  $B_{ij}$  are the binary interaction parameters for the various units in the polymer being blended and  $\phi_1$  and  $\phi_2$  are the volume fractions of units 1 and 2 in the copolymer. To apply this model to our qualitative results we make the following assignments for the SAN case



Our experimental results indicate that  $B_{23} < 0$  and it seems reasonable to consider  $B_{13} > 0$  since evidence suggests that polyacrylonitrile would not be miscible with MPC (e.g. an SAN containing 69.7% AN is immiscible with MPC). That is, homopolymers 1 and 3 mix endothermically while homopolymers 2 and 3 mix exothermically. Figure 14 illustrates how the effective interaction parameter  $B$ , as given in equation (1), should vary with copolymer composition in this particular situation based on this model. The predicted responses have different curvatures depending on the sign of  $B_{12}$ . It is known that polystyrene is immiscible with polyacrylonitrile<sup>34</sup>, consequently one of the lower curves should apply in the present case.

As shown in Figure 14, as the amount of AN<sup>1</sup> in the SAN copolymer (1+2) increases, a condition of endothermic mixing is eventually reached and the point where this happens depends on the sign and magnitude of  $B_{12}$ . For large enough values of  $B_{12}$  relative to the values of the other two parameters,  $B$  may initially become more negative as AN is incorporated into the copolymer reaching a minimum value before turning upwards and

eventually becoming positive, i.e. the condition for immiscibility. Based on the cloud point data in Figure 6, this would seem to be the case here for blends of MPC with SAN copolymers. The fact that no cloud point could be detected prior to decomposition for blends of SMA 8 with MPC suggests that a similar situation exists in this case also. While no quantitative results are available for testing these speculations, the above arguments seem to be a reasonable way of rationalizing the current observations. Analog calorimetry for these copolymer systems<sup>35</sup> would be one way of verifying these speculations provided an appropriate analog for MPC can be identified.

### SUMMARY

Table 2 summarizes the phase behaviour of blends of tetramethyl bisphenol-A polycarbonate with polystyrene, poly( $\alpha$ -methyl styrene), poly( $p$ -methyl styrene) and with styrene based copolymers containing acrylonitrile, maleic anhydride and allyl alcohol plus one copolymer of  $\alpha$ -methyl styrene/acrylonitrile. An increase in acrylonitrile, maleic anhydride or allyl alcohol content in the copolymers ultimately has an unfavourable effect on miscibility with MPC. However, based on LCST behaviour it was found that small amounts of AN and MA have the opposite effect, i.e. while blends of MPC with PS undergo phase separation on heating at relatively low temperatures (250°C) an amount of AN as small as 2% increases this temperature by about 100°C. For AN

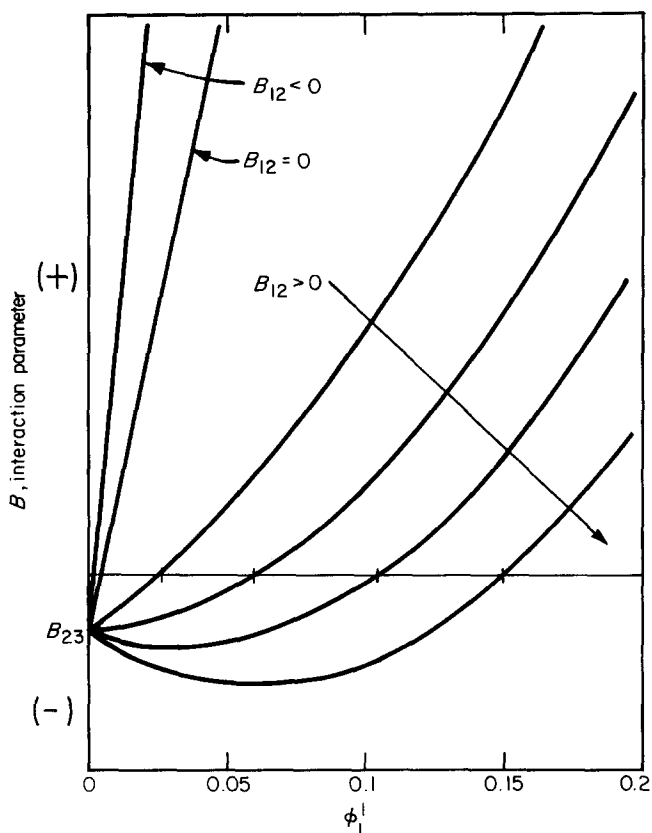


Figure 14 Predictions of interaction energy density for blends of copolymer (1+2) with homopolymer(3) given by equation (1), when  $B_{23} < 0$  and  $B_{13} > 0$ . The various curves show the effect of varying  $B_{12}$  (with  $B_{23}$  and  $B_{13}$  fixed) from a negative value, zero and progressively more positive values. All curves go to the same positive  $B_{13}$  value in the limit of  $\phi_1^1 = 1$

**Table 2** Phase behaviour for blends containing tetramethyl bisphenol-A polycarbonate

Blend	Phase behaviour
PS	miscible
P $\alpha$ MS <sup>a</sup>	miscible
PpMS	immiscible
SAN 2	miscible
SAN 5	miscible
SAN 9	miscible
SAN 11	miscible
SAN 13	partially miscible
SAN 16	partially miscible
SAN 25	immiscible
P $\alpha$ MSAN 30	immiscible
SMA 8	miscible
SMA 14	immiscible
SAA 1 <sup>a</sup>	miscible
SAA 2 <sup>a</sup>	miscible
SAA 5 <sup>a</sup>	miscible
SAA 7 <sup>a</sup>	partially miscible

<sup>a</sup>These materials have low molecular weight as shown in Table 1 and may be regarded as oligomeric

concentrations between 5 and 11% by weight no cloud point could be detected before decomposition of the polymers. This suggests there is an optimum content of AN in these copolymers at which the interactions are most favourable for miscibility with MPC. The fact that no cloud point could be detected for MPC/SMA 8 suggests that the same is true for styrene/maleic anhydride-copolymers. These observations seem to be explained by a binary interaction model recently developed for copolymer systems<sup>31-33</sup>.

For styrene/allyl alcohol copolymers, sufficiently large amounts of allyl alcohol causes phase separation to occur in blends with MPC. No cloud points were observed for these miscible systems, since decomposition occurs at lower temperatures than for other systems so it was not possible to rank the strength of interactions within this group of blends.

Small changes in repeat unit structure, e.g. poly( $\alpha$ -methyl styrene) or poly(*p*-methyl styrene) relative to polystyrene, apparently decreases the strength of the interactions with MPC relative to those for PS. MPC was found to be immiscible with PpMS and the low temperatures at which the cloud point curve was observed for blends of MPC with the oligomeric P $\alpha$ MS (well below the cloud point curve for MPC/PS blend) suggest that as the molecular weight of P $\alpha$ MS increases these two polymers may effectively become immiscible. A copolymer of  $\alpha$ -methyl/styrene/acrylonitrile was also found to be immiscible with MPC.

MPC was found to undergo solvent and thermal induced crystallization when THF or toluene were used for casting film. No crystallinity was observed when methylene chloride was used. Although thermal and solvent induced crystallization is a well-known phenomenon with PC<sup>17</sup>, to our knowledge, no previous reports have mentioned this for MPC.

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