Macromolecules 1987, *20*, 2828–2832

but contains carbon–carbon double and triple bonds which are capable of further reaction to yield PTFE, surface derivatized with halogen, hydroxyl, amino, or carboxylic acid functionalities.

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Registry No. $KClO_3$, 3811-04-9; BH_3, 13283-31-3; $F_3CCO_2COCF_3$, 407-25-0; $ClCOC_3F_7$, 375-16-6; HO_2CCO_2H, 108-31-6; C_6F_5CHO, 653-37-2; $N_2H_3C_3COC_3H_3N_2$, 530-62-1.

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Miscibility of Blends of Tetramethylbisphenol A Polycarbonate and Styrene/Methyl Methacrylate Copolymers

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ABSTRACT: The phase behavior of blends of tetramethylbisphenol A polycarbonate, MPC, with styrene/methyl methacrylate copolymers, SMMAs, was examined by differential scanning calorimetry and for lower critical solution temperature behavior. MPC was found to be completely miscible with SMMAs having MMA contents less than 35%. Small amounts of MMA in the copolymer greatly increase the temperature at which phase separation occurs on heating relative to that observed for polystyrene blends with MPC. The phase behavior of MPC with SMMA copolymers appears to be strongly affected by intramolecular repulsion between the styrene and MMA units in addition to the intermolecular interactions of these units with MPC.

Introduction

The miscibility behavior of polymer blends has been an active area of investigation for more than a decade.[1-3] For high molecular weight components, the free-energy conditions for miscibility are primarily dominated by energetic considerations. The needed exothermic heat of mixing can arise from intermolecular specific interactions or from intrachain repulsion effects as recognized recently for systems based on copolymers.[4-6] These "pull" and "push"

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Table I
Polymer Used in This Study

abbreviation	polymer	copolymer[a] composition, wt % styrene	density, g/cm^3	intrinsic viscosity	T_g, °C	source
MPC	tetramethylbisphenol A polycarbonate		1.0824	0.096[b]	192	Bayer AG
SMMA95	styrene/methyl methacrylate copolymer	95.5	1.0626	0.321[c]	98	synthesized
SMMA80	same	79.5	1.0746	0.359[c]	98	Richardson Polymer [NOAN 81]
SMMA68	same	67.5	1.0795	0.358[c]	96	synthesized
SMMA66	same	66.5	1.0938	0.447[c]	96	synthesized
SMMA65	same	65.0	1.0958	0.631[c]	97	synthesized
SMMA61	same	61.5	1.1031	0.736[c]	98	synthesized
SMMA53	same	53.5	1.1147	0.612[c]	99	synthesized
SMMA40	same	41.5	1.1317	0.696[c]	102	Richardson Polymer [RPC 100]

[a] Determined by elemental analysis. [b] In methylene chloride at $T = 21.5$ °C. [c] In methyl ethyl ketone at $T = 21.5$ °C.

forces for miscibility may act simultaneously in the same system, and they provide useful concepts for manipulating polymer structure to control blend phase behavior. Small variations in the molecular structure of one component may cause large changes in the phase behavior of blends.[7,8] This is particularly true for systems having a net interaction on either side of, but very near, the borderline for miscibility.

The following examples motivated this work. Polystyrene, PS, is not miscible with bisphenol A polycarbonate, PC. However, methyl substitutions onto the 2,6 and 2′,6′ ring positions of the latter give a polymer, tetramethylbisphenol A polycarbonate or MPC, which is well-known to be miscible with styrenic polymers.[9-13] Evidently, the electronic effects that result from these substitutions produce exothermic interactions with PS analogous to those for PS and poly(phenylene oxide) whose structure is similar to that of MPC.[14] Blends of MPC and PS phase separate on heating because of lower critical solution temperature, LCST, behavior. A recent study[15] has shown that finite amounts of certain comonomers whose homopolymers are not miscible with MPC, such as acrylonitrile or maleic anhydride, can be incorporated into the styrenic polymer while maintaining miscibility with MPC. However, beyond a certain limiting comonomer content, MPC is no longer miscible with these copolymers as might be expected. Interestingly, the temperature at which the blends phase separate on heating, i.e., the cloud point, increased dramatically with comonomer content and then decreased again as the limiting content for miscibility was approached.

The purpose of this paper is to examine the effect of methyl methacrylate as a comonomer with styrene on the phase behavior of blends with MPC. The MMA content of SMMA copolymers was systematically varied to find the upper limit for miscibility with MPC. Note that PMMA is not miscible with MPC. The effect of MMA content on the cloud point of the blends was examined carefully to determine whether there is a dramatic increase like that reported previously.[15] This effect has been attributed to repulsion between comonomer units, and this principal, if generally valid, could be a very useful way to increase the range of temperatures available for melt processing systems with relatively low cloud points to produce homogeneous blends.

Materials and Procedures

Information about all of the polymers used in this work is listed in Table I. The MPC was supplied by Bayer AG through the courtesy of Drs. V. Serini and L. Bottenbruch. The SMMAs, except for two obtained commercially, were synthesized by typical suspension polymerization at 80 °C using benzoyl peroxide as initiator. The numerical value included as part of the acronym for those copolymers indicates the nominal percent of styrene by weight. All polymer blends were prepared by casting from methylene chloride solutions to avoid solvent-induced crystallization of MPC during film drying which occurs for some other solvents,[15] e.g., toluene. The desired polymer solutions were poured into disposable aluminum pans and allowed to stand at room temperature until most of the solvent evaporated. The resulting films were further dried under vacuum at 150 °C for 1 week and then slowly cooled to room temperature.

Thermal analysis was performed at a heating rate of 20 °C/min on samples weighing 10–15 mg by using a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a thermal analysis data station. The glass transition temperature, T_g, was defined as the onset of the shift in heat capacity during the second heating from 47 to 227 °C. The cloud points caused by the LCST were measured visually. The film specimens were sandwiched between two glass slides and heated on a metal plate at a rate of 5 °C/min. The temperature at which the clear film began to turn cloudy was taken as the cloud point. The reproducibility of cloud points from several runs was ±2 °C.

The densities of miscible blends and pure polymers were measured at 30 °C by a density gradient column based on aqueous solutions of calcium nitrate. Several columns with different density levels but having a gradient range of about 0.1 g/cm^3 were used for this measurement. At least three measurements per sample were carried out, and the average value is reported.

Results and Discussion

Glass Transition Behavior. Glass transition behavior for blends of MPC with each of the copolymers listed in Table I was determined at composition intervals of roughly 10% by weight MPC. Figure 1 shows representative results for SMMA copolymers having MMA contents from 35% up to 60% by weight. For blends with all copolymers having MMA contents of less than 35% by weight, a single glass transition that varied regularly with overall blend composition was observed (not shown). Blends of MPC and the SMMA copolymer containing 38.5% MMA by weight were partly cloudy at room temperature depending on the blend composition. The upper glass transition for these blends is significantly lower than that of pure MPC, but the lower transition is essentially the same as that for pure SMMA61, as may be seen in Figure 1. From these results, we conclude that the SMMA61 copolymer is just beyond the critical limit to form completely miscible blends with MPC. Blends of MPC with SMMA copolymers containing more than 38.5% MMA by weight, show upper glass transitions which are slightly lower than that of pure MPC, while the lower transition was always substantially the same as that for the pure SMMA. These blends were cloudy at room temperature and did not become clear on heating. The glass transition behavior for blends containing 50% MPC are summarized in Figure 2 by plotting the observed glass transitions versus MMA content of the copolymer. A single, composition-dependent glass transition is observed for copolymers containing 35.0% MMA or less, while two glass transitions are observed for co-

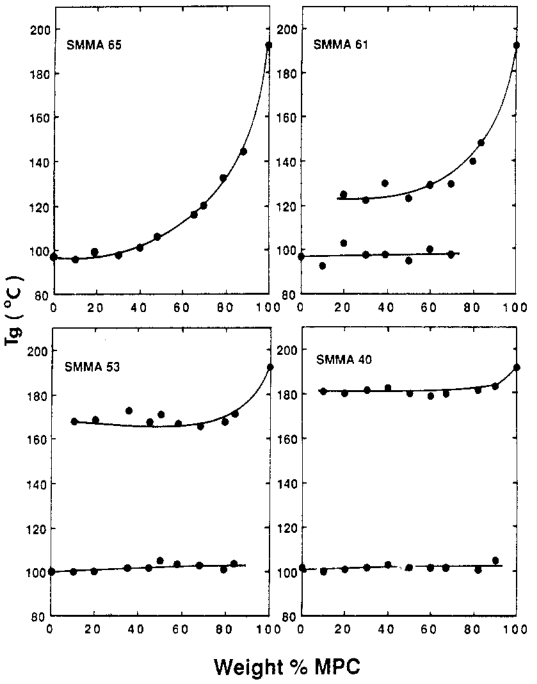


Figure 1. Glass transition behavior for MPC blends with various SMMA copolymers containing 35% by weight or more MMA. Blends with copolymers containing less MMA than this all showed single, composition-dependent glass transitions.

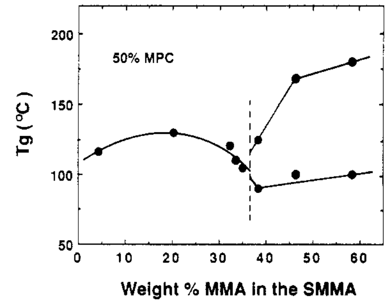


Figure 2. Glass transitions for blends containing 50% MPC versus MMA content of copolymer.

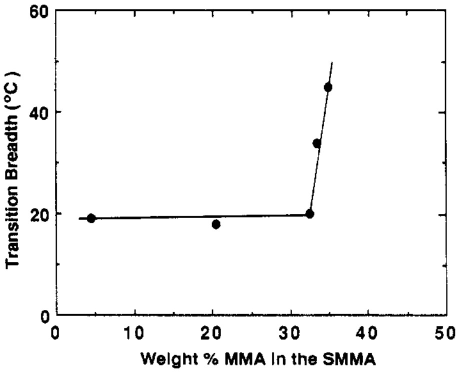


Figure 3. Breadth of glass transition from DSC for MPC blends versus weight percentage MMA in the copolymer.

polymers containing 38.5% MMA or more.

The breadth of the glass transition region is a measure of the sharpness of the critical copolymer composition for forming miscible blends with MPC and gives some qualitative indication of the interaction between the blend components near this point.[16] Figure 3 shows the transition breadth for MPC–SMMA copolymer blends containing about 50% MPC as a function of the MMA content of the SMMA copolymer. The transition breadth used here is the temperature interval between the onset and completion of the heat capacity change at the glass transition.[16] The transition breadth remains constant until about 32% MMA, where there is an abrupt increase just prior to the limiting content of MMA for miscibility with MPC. Similar behavior has been noted for blends involving other homopolymer–copolymer systems.[17] This broadening is believed to reflect compositional fluctuations in the blend,[18-20] which grow as the interaction between the blend components weaken with increased comonomer content. These fluctuations eventually become unstable and lead to immiscible mixtures at high contents of MMA.

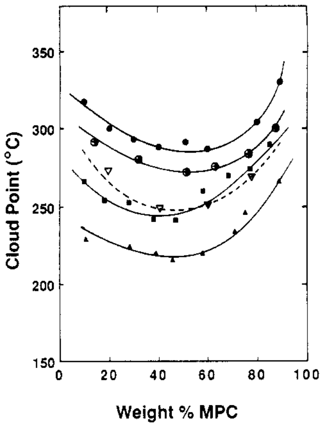


Figure 4. Cloud point curves for blends of MPC with various SMMa copolymers: (●) SMMA68, (◑) SMMA95, (■) SMMA66, and (▲) SMMA65. Data for MPC–PS from ref 15 (▽, dashed line).

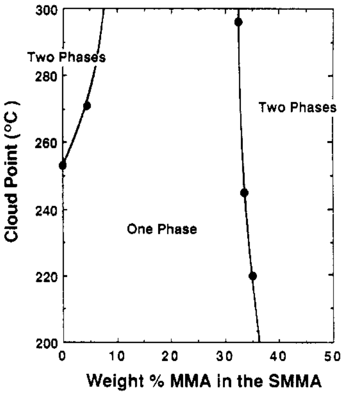


Figure 5. Cloud points for blends containing 50% MPC versus MMA content of copolymer.

LCST Behavior

The temperature at which phase separation occurs on heating provides a qualitative indication of the interaction between blend components.[21] The cloud point curves which reflect the LCST behavior of blends of the various copolymers with MPC are shown in Figure 4. The dashed line is the curve for pure PS with MPC reported earlier.[15] The effect of comonomer content can be seen more easily by plotting the cloud point for a fixed MPC content of the blend, e.g., 50%, versus the MMA content of the copolymer, as shown in Figure 5. Small amounts of MMA raise the cloud point. Blends of MPC with SMMA80 did not exhibit phase separation at all on heating to the highest temperature possible without severe decomposition of the polymers (>350 °C). However, blends with SMMA68, SMMA66, and SMMA65 do show cloud points which decrease precipitously with MMA content. These observations suggest that the LCST first increases with MMA content, goes through a maximum that cannot be experimentally observed owing to degradation of the components, and then decreases rapidly just prior to the limiting

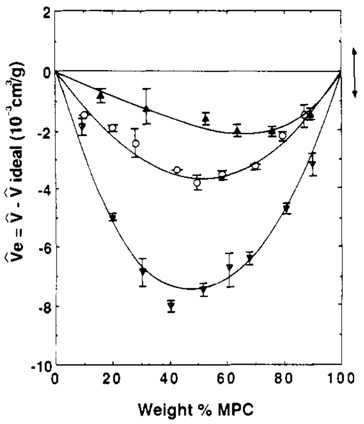


Figure 6. Excess volumes for blends of MPC with various SMMAs at 30 °C: (▲) SMMA95, (○) SMMA80, and (▼) SMMA68. The arrow on the right indicates the accuracy of the experimental data.

content of MMA for miscibility with MPC. In fact, we may conclude that the immiscibility at higher MMA contents is the result of an LCST which is too low to permit practical formation of homogeneous blends. This pattern of behavior is entirely analogous to that observed for MPC blends when acrylonitrile and maleic anhydride were used as comonomers with styrene.[15]

These results suggest that incorporation of small amounts of MMA increases the net strength of the interactions with MPC and that the maximum strength of these interactions occurs in the range 20–30% MMA by weight.

Volumetric Behavior

Deviation from volume additivity provides yet another qualitative indication of the interactions between the blend components.[22-25] Figure 6 shows the excess volumes for blends of MPC with selected copolymers of styrene and methyl methacrylate. The excess volume is defined as the difference between the observed specific volume, $\hat{V}$, for the blend relative to the ideal volume, $\hat{V}_{\mathrm{ideal}}$, expected for volume additivity, i.e.,

$$\hat{V}_{\mathrm{e}} = \hat{V} - \hat{V}_{\mathrm{ideal}} = \hat{V} - w_1\hat{V}_1 - w_2\hat{V}_2 \qquad (1)$$

where $\hat{V}_i$ is the specific volume of component i and w_i is the weight fraction of i in the blend. These results show that the excess volume becomes increasingly more negative as the MMA content of the copolymer increases, which is generally similar to that observed for blends of MPC with styrene/acrylonitrile copolymers.[15] Two separate determinations made earlier in our laboratory (15, 26) differ somewhat in the values of $\hat{V}_{\mathrm{e}}$ for MPC–PS blends which reflect differences in thermal history of the samples. One set[26] shows a more negative $\hat{V}_{\mathrm{e}}$ for MPC–PS blends than seen here for MPC–SMMA95, while another set[15] gives values comparable to or slightly less than the MPC–SMMA95 data in Figure 6. For comparable sample histories, there appears to be a consistent trend for greater departure from volume additivity as the MMA content of the copolymer is increased.

Theoretical Interpretation

The phase behavior of blends is determined by the net energetic interactions between the components and by equation of state effects.[27,28] It has not been possible to quantify these interactions by the simple melting point depression approach since neither component of these blends crystallizes readily. However, if we assume that the LCST behavior reflects the interactions between components and that equation of state effects do not vary greatly, the present observations can be rationalized, as suggested previously,[15] by using the binary interaction model introduced earlier[4-6] for copolymer systems. For blends of a homopolymer, **3**, with a copolymer of monomers **1** and **2**, this model gives the following result for the overall blend interaction parameter B

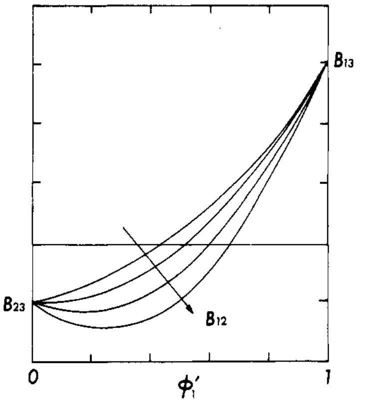
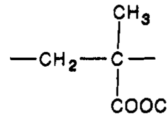


Figure 7. Predictions of the binary interaction model given by eq 2. The arrow represents the progressive positive variation in B_{12} while B_{23} and B_{13} are fixed.

$$B = B_{13}\phi'_1 + B_{23}\phi'_2 - B_{12}\phi'_1\phi'_2 \qquad (2)$$

where the B_{ij}'s are the binary interaction parameters for the various units or monomers and ϕ'_i's are the volume fractions of units i in the copolymer.

For the present case, we make the following assignments:



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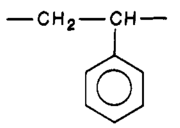

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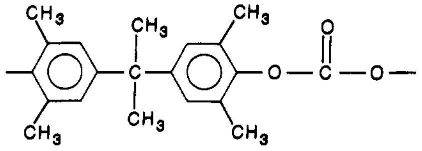

3

From the experimental results, we can state that $B_{23} < 0$,[9-13,15] $B_{12} > 0$,[29-31] and $B_{13} > 0$.[32] Figure 7 illustrates the predictions of the binary interaction model for this case where each line represents the relationship between the overall binary interaction parameter and the copolymer composition as the magnitude of B_{12} is varied while B_{23} and B_{13} are fixed. As the amount of MMA (ϕ'_1) in the copolymer increases, the value of B eventually increases and crosses the critical value for miscibility ($B = 0$ for infinite molecular weights) and then approaches B_{13}. However, when B_{12} is positive enough compared to the other two parameters, B_{13} and B_{23}, the value of B at low MMA contents can be more negative in value than B_{23}. The data in Figure 5 suggest that this situation exists if we assume as a first approximation that phase separation occurs at higher temperatures the more negative is B.[21] That is, the elevation of the cloud point upon adding MMA to the styrenic polymer is caused by the repulsion between the MMA and styrene units in the copolymer. It should be possible to test this argument by using appropriate experiments in the near future.

Summary

Since PMMA is not miscible with MPC, one expects that there ought to be a limited amount of MMA that can be incorporated into copolymers with styrene while maintaining miscibility with MPC. It was demonstrated here that this limit lies between 35.0% and 38.5% MMA by weight. Below this range, blends with MPC exhibit a single glass transition although the breadth of this transition increases sharply starting at about 32% MMA. For MMA contents beyond the critical limit, all blends showed two glass transitions. Interestingly, the volume contraction on mixing for these blends appears to increase continuously as MMA is added to the copolymer up to the region where immiscibility occurs.

Incorporation of MMA into the styrenic polymer initially increases the LCST rather dramatically; however, this temperature drops very rapidly just prior to the limiting MMA content for miscibility with MPC. This has also been observed for other comonomers and appears to be a rather general result. This suggests a useful means for increasing the window of temperature needed for successful melt processing systems whose cloud point curves are too low (i.e., near the T_g–composition relation) for producing a homogeneous blend.[33]

To reach these conclusions, we have assumed that copolymer composition is the most important variable affecting phase behavior of these blends. Of course, molecular weight of the copolymer can in principle be another factor; however, in the present case we do not believe it is. These copolymers all have molecular weights in excess of 10^5 as estimated from published intrinsic viscosity correlations[34,35] for homopolymers of styrene and methyl methacrylate and the data in Table I. The intent of the experimental design was for each copolymer to have the same molecular weight as nearly as possible. While this goal cannot be fully assured, it is important to note that it was appoached more closely than a cursory examination of the intrinsic viscosities in Table I might suggest. The general trend for higher values as the MMA content rises reflects in large measure the higher intrinsic viscosity in methyl ethyl ketone of PMMA than polystyrene at fixed molecular weight (above $\sim 10^4$).

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Registry No. MPC, 52684-16-9; SMMA (copolymer), 25034-86-0.

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