Polycarbonate–Styrene / Methyl Methacrylate Copolymer Blends

It has been shown recently¹⁻³ that bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA), can form completely miscible blends at equilibrium. However, these mixtures phase separate at temperatures not much above the glass transition. This results in heterogeneous blends when this pair is melt-mixed at reasonable processing temperatures⁴ and precludes many opportunities to take advantage of the observed miscibility of these transparent, amorphous polymers. In fact, much care has to be exercised in solution preparation of blends of PC and PMMA to prevent their phase separation.¹

It has also been shown recently⁵⁻⁸ that the temperature at which a blend phase separates, namely, the cloud point, on heating because of lower critical solution temperature (LCST) behavior can be significantly elevated by incorporating relatively small amounts of a suitable comonomer into one of the component polymers. This effect may result from a strong interchain attraction mechanism such as hydrogen bonding introduced by addition of the comonomer⁸ or by a strong intrachain repulsion of the added comonomer with the original monomer units as proposed recently.⁵⁻⁷ The latter promises to be of more practical use than the former. The purpose here is to illustrate how the cloud point of PC-acrylic blends can be elevated by copolymerization of MMA with the inexpensive monomer styrene.

The polymers used in this study are described in Table I. The styrene/methyl methacrylate (SMMA) copolymers were synthesized in our laboratory by a typical suspension method at 80° C using benzoyl peroxide as initiator. Blends of each of these copolymers were made with PC by dissolving both in tetrahydrofuran (THF) to obtain 5% total polymer by weight. One part of this solution was added to five parts heptane with vigorous agitation at room temperature to form a precipitated blend. The THF and heptane were removed as before.¹

All blends of PC with the SMMA copolymers of Table I prepared in this way exhibited a single, composition-dependent glass transition temperature by differential scanning calorimetry (DSC),

Abbreviation	Polymer	Weight % Styrene	<i>T</i> g (°C)	Intrinsic Viscosity* (dL/g)
PC	Bisphenol-A polycarbonate ^b	—	149	
SMMA3	Styrene/methyl methacrylate copolymer	3	105	0.486
SMMA4	Styrene/methyl methacrylate copolymer	4	112	0.587
SMMA7	Styrene/methyl methacrylate copolymer	7	110	0.553
SMMA14	Styrene/methyl methacrylate copolymer	14	112	0.604

TABLE I Polymers Used in This Study

^aMeasured in CH₂Cl₂ at 25°C.

^bFrom General Electric Co., Lexan[®] 131-111.

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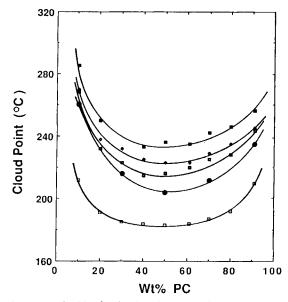


Fig. 1. Cloud point curves for blends of polycarbonate with PMMA, lower curve (\Box) and with SMMA copolymers containing 3% (\bullet), 14% (\Box) , 4% (\diamondsuit) , and 7% (\blacksquare) by weight styrene.

indicating that completely mixed blends had been obtained. The first DSC scan for blends showed some PC crystallinity that was not present on a second scan. The level of PC crystallinity in blends with SMMA copolymers was generally less than when PMMA was used.¹

Cloud points caused by LCST behavior were measured visually as before.¹

At least three determinations, which differed by 10% at most, were averaged and are reported here. Figure 1 shows the complete cloud point curves for the various systems plotted versus PC content of the blend. The trends with copolymer composition become more clear by plotting the cloud point of a 50% PC blend versus the amount of styrene in the copolymer as shown in Figure 2. Here, we see that the cloud point is first elevated by addition of styrene, reaches a maximum, and then decreases. At styrene contents beyond about 15 to 16% by weight, we do not expect SMMA copolymers to form miscible blends with PC using any preparation method.

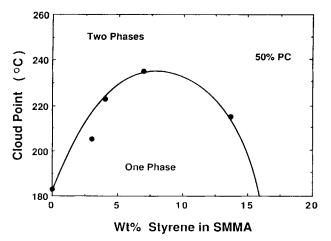


Fig. 2. Effect of styrene content of SMMA copolymer on cloud point of blends with 50% by weight polycarbonate.

The pattern of behavior shown in Figure 2 has been observed for other homopolymer-copolymer blend systems, and the intramolecular repulsion notion mentioned earlier seems to provide a rational explanation. $^{5-8}$

The key point here is that the minimum cloud point (see Fig. 1) has been raised to nearly 240°C using only 7% styrene in the acrylic. This is almost but not quite enough improvement to have a PC/acrylic system from which single-phase blends of any proportion can be made by melt-processing methods. Future work will seek to identify comonomers that are more efficient for this particular system than styrene and to establish rational methods for comonomer selection applicable to any system.

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