

Miscibility of Poly(chloromethyl Methacrylate) with Bisphenol-A Polycarbonate

Poly(methyl methacrylate) (PMMA) and bisphenol-A polycarbonate (PC) are important commercial polymers. PMMA/PC blends were once considered as immiscible blends.¹⁻³ However, recent studies have shown that the miscibility of PMMA/PC blends depends on the method of preparation.⁴⁻⁸ Chiou and co-workers⁴ reported that PMMA/PC blends prepared by solution casting and melt mixing were immiscible while blends prepared by precipitation from solution using *n*-heptane as nonsolvent were miscible over the whole composition range. Kyu and Salhanda⁵ reported that PMMA/PC blends cast from tetrahydrofuran (THF) at room temperature were immiscible but those cast from THF at temperatures above 47°C were miscible. In this communication, we report the miscibility of poly(chloromethyl methacrylate) (PCMMA) with PC. It will be shown that the miscibility behavior of PCMMA/PC blends is similar to that of PMMA/PC blends.

EXPERIMENTAL

Materials

Chloromethyl methacrylate (CMMA) was prepared following the procedure reported by Ueda and co-workers.⁹ CMMA was polymerized in 2-butanone at reflux temperature for 24 h using 0.25% by weight of azobisisobutyronitrile as initiator. The polymer was obtained by precipitation of the solution in excess methanol. The number average molecular weight (\bar{M}_n) of PCMMA was 58,000 from intrinsic viscosity measurements using the equation⁹ $[\eta] (dL/g, \text{ in THF at } 30^\circ\text{C}) = 1.0 \times 10^{-4} \bar{M}_n^{0.725}$. PC was obtained from BDH Chemicals; its weight average molecular weight (\bar{M}_w) was 22,000 from intrinsic viscosity measurements using the equation¹⁰ $[\eta] (dL/g, \text{ in THF at } 30^\circ\text{C}) = 3.8 \times 10^{-4} \bar{M}_w^{0.70}$.

Preparation of Blends

PCMMA/PC blends were prepared by the following four methods.

A. Appropriate amounts of PCMMA and PC were dissolved in THF to form a 5% (w/v) solution. The solvent was allowed to evaporate slowly at room temperature. The cast film was then dried *in vacuo* at 110°C for 72 h.

B. The THF solution was allowed to dry on a hot plate at about 60°C. The film was then dried *in vacuo* at 110°C for 72 h.

C. The THF solution was slowly poured into vigorously stirred excess methanol. The precipitated blend was then dried *in vacuo* at 110°C for 72 h.

D. The method followed the same procedure as C, except that the nonsolvent was *n*-heptane.

Calorimetric Measurements

The glass transition temperatures (T_g 's) of various samples were measured with a Perkin-Elmer DSC-4 Differential Scanning Calorimeter using a heating rate of 20°C/min. The T_g was taken as the onset of the change of slope in the heat capacity plot.

Measurements of Lower Critical Solution Temperature (LCST)

The blends were examined for the existence of LCSTs using the method described previously.¹¹

RESULTS AND DISCUSSION

Blends Prepared by Solution Casting

All the PCMMA/PC blends cast from THF at room temperature were opaque. The DSC curves of the blends, scanned between 40 and 160°C, are shown in Figure 1. The appearance of two T_g 's

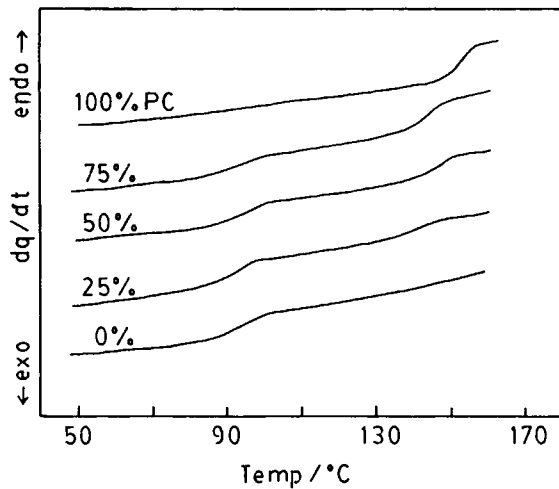


Fig. 1. DSC curves of PC/MMA blends cast from THF at room temperature.

in each blend shows that these blends are immiscible. Similar to PMMA/PC blends cast from THF at room temperature,⁴ PC/MMA blends also exhibited a melting peak of PC at about 235°C when DSC scans were carried to higher temperatures. Since PC does not crystallize when cast from THF at room temperature,⁴ PC/MMA has apparently induced crystallization of PC in the blends.

To evaluate the effect of casting temperature, a PC/MMA (1 : 3) blend was cast from THF at 60°C. The resulting film consisted of transparent and cloudy regions. Despite many attempts, we failed to obtain a totally transparent film. The DSC curve of the transparent region of the film showed a single T_g at 109°C, as shown in Figure 2. The transparency of the blend and a single T_g intermediate to those of PC/MMA and PC indicate that the transparent region is homogeneous. Moreover, the transparent region turned cloudy when it was heated above 165°C, showing LCST behavior. The transparency also indicates that PC does not crystallize when the blend is cast at 60°C. However, the DSC curve of the cloudy region of the same film showed two distinct T_g 's, indicating the two-phase nature of the cloudy region. The lower T_g is close to that of PC/MMA, but the higher T_g is about 20°C lower than that of PC. Kyu and Saldanha⁵⁻⁷ have found that PMMA/PC blends cast from THF at temperatures above 47°C were transparent, and they also pointed out that the rate of evaporation of solvent could affect the miscibility. It is likely that a

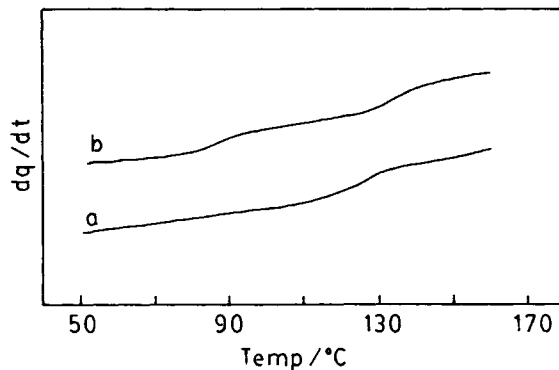


Fig. 2. DSC curves of PC/MMA blends cast from THF at 60°C: (a) transparent region, (b) cloudy region.

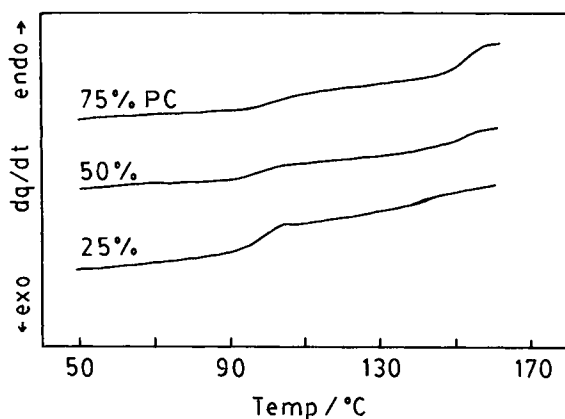


Fig. 3. DSC curves of PCMMA/PC blends precipitated from THF solution by methanol.

completely transparent PCMMA/PC blend could be obtained by properly controlling the rate of evaporation of THF.

Blends Prepared by Precipitation

The PCMMA/PC blends prepared by precipitation in methanol were in the form of white powder. When the blends were heated and pressed on the hot stage of the melting point apparatus, they turned into translucent films at about 140°C and became totally opaque at higher temperatures. The DSC curves of the blends, scanned between 40 and 160°C, are shown in Figure 3. The presence of two distinct T_g 's in each of the blends indicates that these blends are immiscible.

Blends prepared by precipitation in *n*-heptane were also in the form of white powder. They became transparent at about 140°C and turned cloudy around 168–180°C. The transformation from transparency to cloudiness indicates phase separation due to LCST behavior. The cloud points are 180, 168, and 172°C for blends containing 25, 50, and 75% by weight of PC, respectively. These values are about 10°C lower than those of PMMA/PC blends prepared by the same method.⁴ The DSC curves of the blends, scanned between 40 and 160°C, are shown in Figure 4. Each of the blends showed a rather broad glass transition. The broadening of T_g may arise from composition fluctuation in the blend.¹² Thus the use of *n*-heptane as nonsolvent resulted in the formation of miscible PCMMA/PC blends.

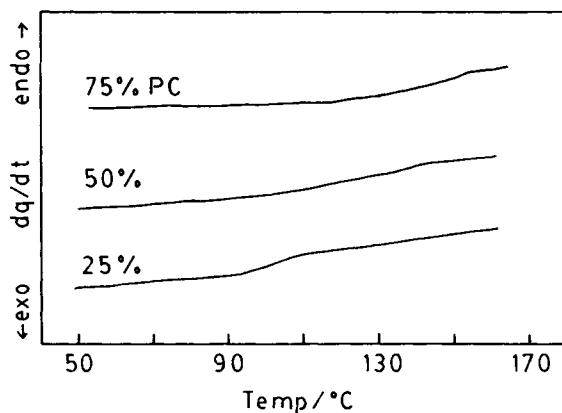


Fig. 4. DSC curves of PCMMA/PC blends precipitated from THF solution by *n*-heptane.

SUMMARY

It has been shown that the miscibility behavior of PC/MMA/PC blends is similar to that of PMMA/PC blends. PC/MMA/PC blends cast from THF at room temperature are immiscible, and miscible blends can be obtained if they are cast at 60°C under controlled experimental conditions. Blends prepared by precipitation can be miscible or immiscible depending on the choice of non-solvent. The solvent effect on the miscibility behavior has been discussed by Chiou and co-workers.⁴

PC is immiscible with polyvinyl chloride but is miscible with a vinylidene chloride/vinyl chloride copolymer containing 13.5% by weight of vinyl chloride when both blends are cast from THF at room temperature.¹² It appears that increasing the chlorine content of the chlorinated polymer improves its miscibility with PC. The present study shows that PC/MMA and PMMA have the same miscibility toward PC, indicating that the incorporation of chlorine atoms in the pendant methyl groups of PMMA does not have a profound effect on its miscibility with PC.

Financial support of this research by the National University of Singapore is gratefully acknowledged.

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Received February 10, 1989

Accepted April 17, 1989