

# Solvent Effects on the Miscibility of Poly(methyl methacrylate)/Poly(bisphenol A carbonate) Blends

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**ABSTRACT:** Blends of atactic or syndiotactic poly(methyl methacrylate) (designated as aPMMA or sPMMA) and poly(bisphenol A carbonate) (PC) were prepared from solution casting. Tetrahydrofuran (THF) and chloroform were used as solvent. Experimental results indicated that the as-cast blends from THF were quite different from the chloroform-cast ones. After film preparation, THF-cast blends did not show any visible phase separation. However, chloroform-cast blends formed a phase-separated structure. The as-cast PC from either solvent was not completely amorphous, and had a melting point at 239–242°C, indicating a certain degree of crystallinity. In contrast, the quenched samples of aPMMA/PC blends prepared from the two solvents behaved virtually the same. They both showed aPMMA dissolves better in PC, but PC solubility in aPMMA is very little. Using sPMMA instead of aPMMA to blend with PC, different results were obtained. The quenched sPMMA/PC blends cast from THF showed only one  $T_g$ . However, immiscibility (i.e., two  $T_g$ s) was found in the same blend system when cast from chloroform. THF was believed to cause the observation of single  $T_g$  due to the following kinetic reason. sPMMA and PC were still trapped together even after THF removal in a homogeneous, but nonequilibrium state below the glass transition. Therefore, the quenched sPMMA/PC blends were not truly thermodynamically miscible. From the results of aPMMA or sPMMA with PC, increasing syndiotacticity seemed to improve the miscibility between PMMA and PC. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2842–2850, 2001

**Key words:** solvent effect; miscibility; poly(methyl methacrylate); poly(bisphenol A carbonate)

## INTRODUCTION

Poly(methyl methacrylate) (PMMA), having the highest transparency among commercial plastics, provides various industrial applications such as optical fiber, disks, films, and grating. However, PMMA possesses some disadvantages for practi-

cal uses such as brittleness. To improve its toughness, many efforts for modification of PMMA have been made through copolymerization and blending. Among a number of miscibility studies on PMMA blends,<sup>1–7</sup> the mixture of PMMA and poly(bisphenol A carbonate) (PC) is one of the most deeply studied. This may be attributed to the excellent properties of PC, including outstanding ductility and high glass transition temperature ( $T_g$ ).

A number of articles<sup>8–12</sup> have described methods for preparing homogeneous blends of PMMA and PC. Tetrahydrofuran (THF) was used as sol-

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vent in most cases for making single-phase PMMA/PC blends. Chiou et al.<sup>8</sup> showed that melt processed blends of PMMA and PC have two distinct phases. A variety of solvent preparation methods<sup>8,13</sup> also lead to phase separated mixtures. Nishimoto et al.<sup>14</sup> presented evidence that the solvent preparation methods used cause the two polymers (PMMA and PC) to become kinetically trapped in a homogeneous, but nonequilibrium, mixture below the glass transition. The phase separation that occurs on heating above the glass transition is not a result of a lower critical solution temperature (LCST) just above  $T_g$ , but stems from an extremely slow rate of phase separation from the trapped nonequilibrium state.

This work was motivated by the aforementioned results. Because PC in previous studies was often amorphous, a semicrystalline PC was used instead in our study. Two kinds of PMMA, such as atactic and syndiotactic, were used to blend with PC from THF and chloroform solvents. THF was chosen because in this solvent single-phase PMMA/PC blends can be made. Chloroform was used to produce immiscible PMMA/PC blends similar to methylene chloride used by Kim et al.<sup>13</sup> Calorimetry was used as the principal tool for investigation. Results of the role of solvent, PC crystallinity, and thermal treatments on the glass transition temperature of prepared PMMA/PC blends were presented and discussed.

## EXPERIMENTAL

### Materials

Atactic and syndiotactic PMMAs (designated as aPMMA and sPMMA in this study) were purchased from Polysciences, Inc., Warrington, PA. According to supplier information, the molecular weights ( $M_w$ s) of aPMMA and sPMMA are the same about 100,000. Molecular weight distributions of aPMMA and sPMMA were not measured, but the effect is believed to be minimal when compared with the effect of tacticity. Poly(bisphenol A carbonate) used for this study was obtained from Scientific Polymer Products, Inc., Ontario, NY. The  $M_w$  value for PC is approximately 60,000.

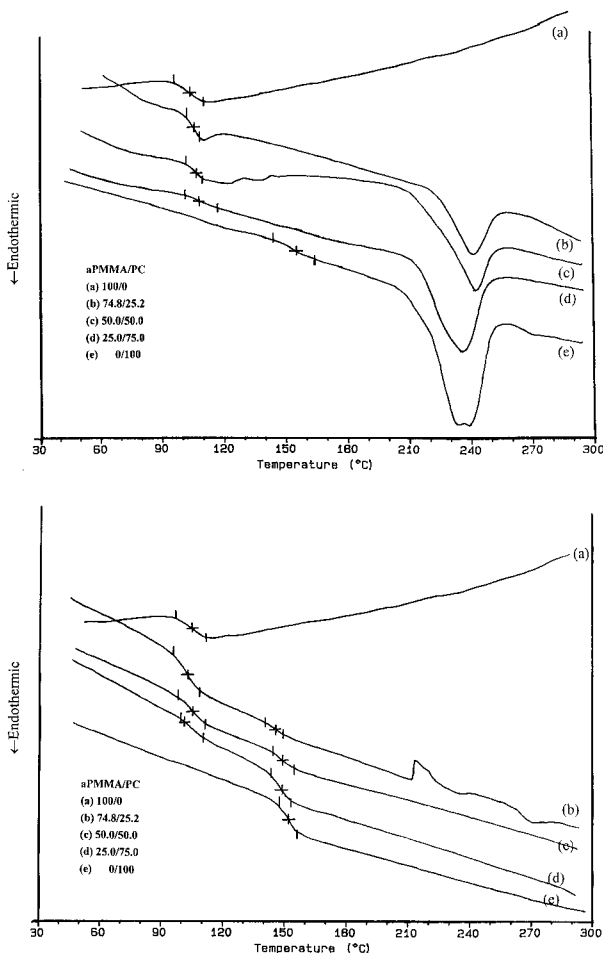
### Film Preparation

Thin films of PC and its blends with PMMA in three different weight ratios (ca. 3/1, 1/1, 1/3)

were made by solution casting. Tetrahydrofuran (THF) and chloroform were used as solvent for all the blend compositions. For PMMA, toluene solvent was used instead. THF, chloroform, and toluene are A.C.S. reagent purchased from Fisher Scientific, Fair Lawn, NJ. For using chloroform as the solvent at room temperature, the blends dissolved well. However, two blends of PMMA/PC in THF needed heating to ca. 50–60°C to have a complete dissolution. All the solutions were cast onto glass plates and covered with Petri dishes for slow evaporation overnight. Then the films were placed inside a vacuum oven for the removal of solvent. The final drying steps for all the films took place at temperatures slightly higher than the  $T_g$  of the blends for about 18 h. Then the films were slowly cooled to room temperature by air to make as-cast samples. The as-cast samples were used for DSC study.

### Differential Scanning Calorimetry (DSC)

Glass transition temperatures ( $T_g$ s) of the polymer blends were determined by a Dupont 2000 thermal analyzer. Experiments were often performed in two consecutive scans from 30 to 300°C in the ambient environment of nitrogen gas at a flowing rate of 100–110 mL/min. At the end of the first thermal scan, the samples stayed at 300°C for 1 min. The samples were then quenched to 0°C immediately, using an ice-water bath, and were scanned the second time. A heating rate of 20°C/min was used in each scan. For two special cases, an additional third scan was needed to remove any artifact or the effect of PC crystallinity. The inflection point of the specific jump of a thermal scan was taken as the glass transition temperature. The glass transition temperatures determined from the first and second thermal scans were often designated as  $T_{gsc}$  and  $T_{gq}$ , respectively. Therefore,  $T_{gsc}$  is the  $T_g$  of the slowly cooled (as-cast) films, and  $T_{gq}$  that of the quenched films. The glass transition temperature regions ( $\Delta T_{gq}$ ) were calculated as differences between the onset and end points of  $T_{gq}$ .  $T_m$  was determined from the minimum of the enthalpy peak, and  $\Delta H_{blend}$  was estimated as integration over the peak area. Because the  $T_m$  was estimated from a nonisothermal heating scan, it is not truly in an equilibrium state.  $T_m$  values only reflect the cast state of blends.



**Figure 1** (a) First DSC thermogram of THF-cast aPMMA/PC blends. (b) Second DSC thermogram of THF-cast aPMMA/PC blends.

## RESULTS

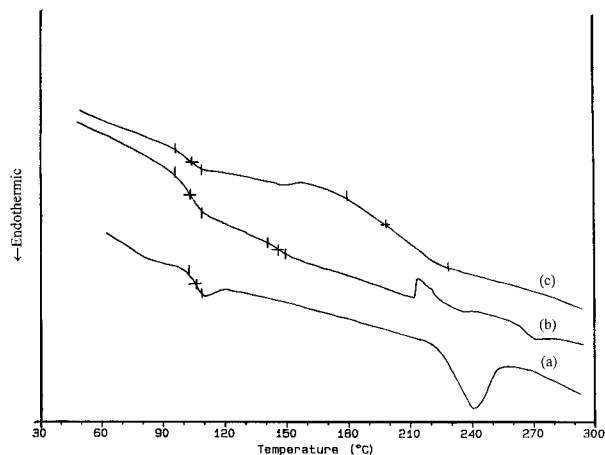
After film preparation, those blends cast from chloroform showed an obvious two-phase structure. Although no picture was shown here, based on the experimental observations the white color region indicates the presence of PC, and the transparent one is composed mainly of PMMA. However, for the THF-cast blends no visible phase separation was observed.

### Glass Transition Temperatures

The first and second thermal scans of the THF-cast aPMMA/PC blends are presented in Figure 1(a) and 1(b), respectively. From Figure 1(a), the as-cast PC was not completely amorphous, and showed a seemingly double melting peak. The double melting point may be due to different sizes

of PC crystals. Similar melting points but single peaks were also found in the blends containing PC. After quenching, all the three aPMMA/PC blends [as in Figure 1(b)] showed two  $T_g$ 's, indicating two separate phases. For the aPMMA/PC(74.8/25.2) blend shown in Figure 1(b), phenomenon of recrystallization and remelting of PC seemed to be observed. Because the main thrust of this study is miscibility, we did not repeat the experiment to check reproducibility of this phenomenon. It is possible the phenomenon is due to an artifact of DSC scan. An additional scan was performed for this blend, and all the three scans of aPMMA/PC(74.8/25.2) blend are shown in Figure 2 for comparison. The third thermal scans of this same blend had two  $T_g$ 's. The low  $T_g$  is close to aPMMA's  $T_g$ , but the high  $T_g$  (ca. 200°C) is much higher than that of PC, probably due to the transesterification that occurred between aPMMA and PC. All the  $T_g$ ,  $T_m$ , and  $\Delta H_{\text{blend}}$  values were calculated based on the data in Figures 1(a), 1(b), and 2, and tabulated in Table I.

The first and second thermal scans of the THF-cast sPMMA/PC blends are shown in Figure 3(a) and 3(b), respectively. The melting peak found in Figure 3(a) in the blends containing PC was similar to that observed in Figure 1(a), whereas the increase of  $T_m$  with increasing PMMA concentration was observed more clearly than that in Figure 1(a). After quenching, all the three sPMMA/PC blends showed one  $T_g$ , indicating possible miscibility. Interestingly, the sPMMA/PC(75.0/25.0) blend seemed to still maintain a certain degree of PC crystallinity after quenching.



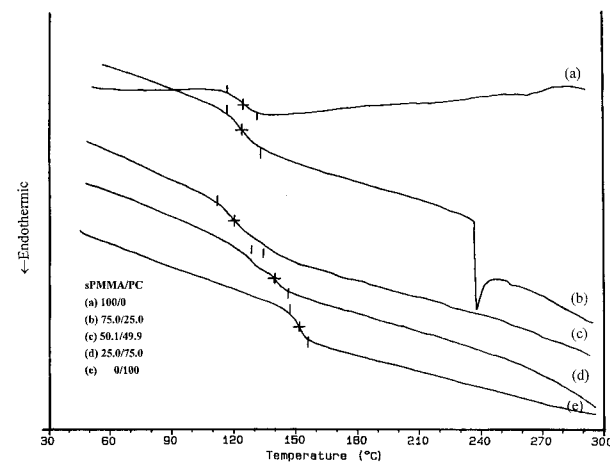
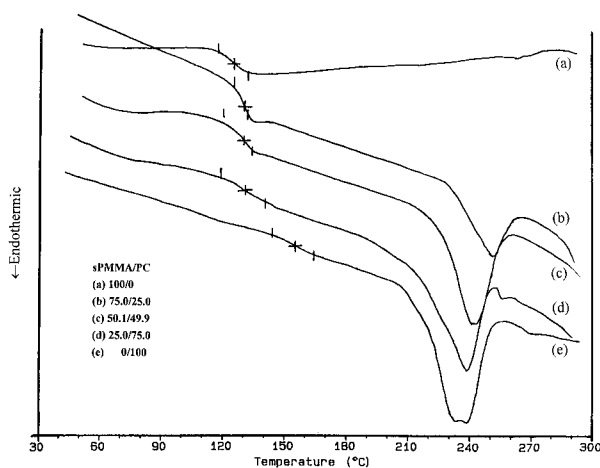
**Figure 2** DSC thermogram of THF-cast aPMMA/PC(74.8/25.2) blends: (a) First scan, (b) second scan, (c) third scan.

**Table I Thermal Characteristics of THF-Cast aPMMA/PC Blends**

aPMMA/PC	First Scan			Second Scan	
	$T_{gsc}$ (°C)	$T_m$ (°C)	$\Delta H_{blend}$ (J/g)	$T_{gq}$ (°C)	$\Delta T_{gq}$ (°C)
(1) 100/0	103.4	—	—	102.7	12
(2) 74.8/25.2	105.7, n.d. <sup>a</sup>	241.2	7.40	102.4, 145.2	13, 8
(3) 50.0/50.0	107.0, n.d.	242.4	13.96	104.5, 143.5	13, 13
(4) 25.0/75.0	107.7, n.d.	235.3	21.16	100.3, 148.2	11, 10
(5) 0/100	154.6	239.3	32.36	151.0	9

<sup>a</sup> n.d.: not detected.

Because we did not rerun the experiment, the observation may be to an artifact of DSC scan. Like the aPMMA/PC(74.8/25.2) blend, additional scan was made and all the three scans of the sPMMA/PC(75.0/25.0) blend are presented in Fig-

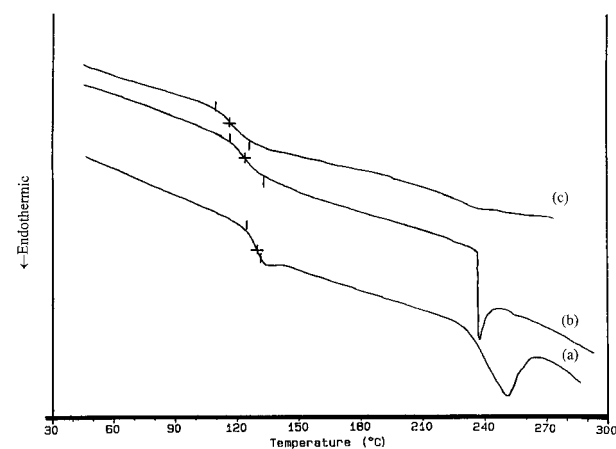


**Figure 3** (a) First DSC thermogram of THF-cast sPMMA/PC blends. (b) Second DSC thermogram of THF-cast sPMMA/PC blends.

ure 4 for comparison. All the  $T_g$ ,  $T_m$ , and  $\Delta H_{blend}$  values were calculated based on the data in Figures 3(a), 3(b), and 4, and tabulated in Table II.

The first and second thermal scans of the chloroform-cast aPMMA/PC blends are presented in Figure 5(a) and 5(b), respectively. From Figure 5(a), it is obvious that PC and its blends all showed a melting peak indicating crystallinity. Because the  $\Delta H_{blend}$  of chloroform-cast PC is smaller than that of THF-cast one, the chloroform-cast PC had a lower crystallinity than the THF one. All the three blends presented in Figure 5(b) had two  $T_g$ s after quenching showing immiscibility between aPMMA and PC. Due to phase-separated nature of the chloroform-cast blends,  $\Delta H_{blend}$  values were not calculated because the small-sized DSC samples did not accurately represent the original weight ratios of blending. However, the  $T_g$  and  $T_m$  values were still estimated from Figure 5(a) and 5(b), and are listed in Table III.

Figure 6(a) and (b) shows the first and second thermal scans of the chloroform-cast sPMMA/PC



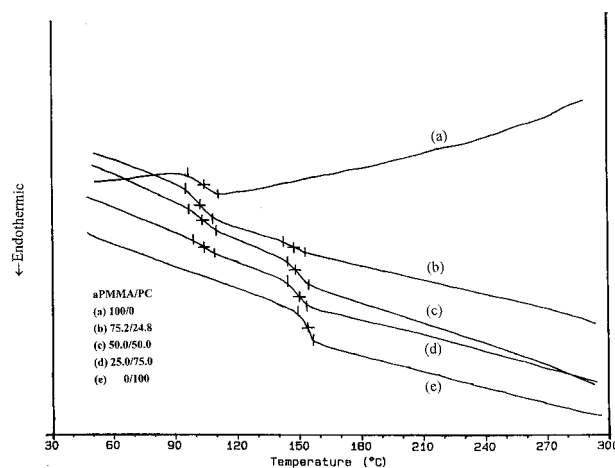
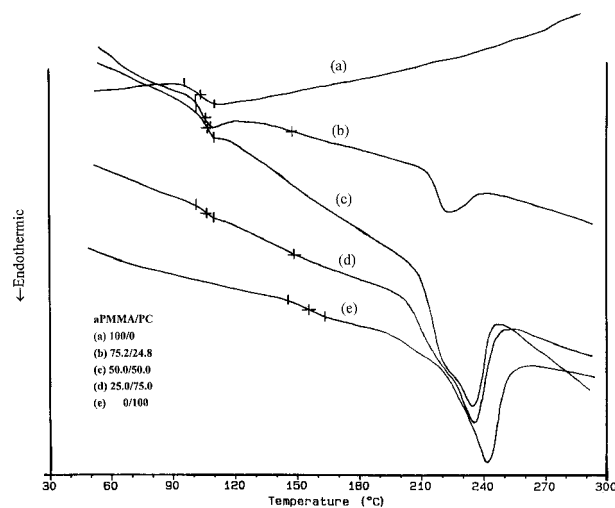
**Figure 4** DSC thermogram of THF-cast sPMMA/PC(75.0/25.0) blends: (a) first scan, (b) second scan, (c) third scan.

**Table II Thermal Characteristics of THF-Cast sPMMA/PC Blends**

sPMMA/PC	First Scan			Second Scan		
	$T_{gsc}$ (°C)	$T_m$ (°C)	$\Delta H_{blend}$ (J/g)	$T_{gq}$ (°C)	$\Delta T_{gq}$ (°C)	$T_m$ (°C)
(1) 100/0	121.4	—	—	122.4	13	
(2) 75.0/25.0	129.2	250.5	6.66	123.3 <sup>a</sup> 115.5	22 13	237.5
(3) 50.1/49.9	129.9	241.4	14.88	119.8	22	
(4) 25.0/75.0	130.6	239.4	19.13	139.1	18	
(5) 0/100	154.6	239.3	32.36	151.0	9	

<sup>a</sup> Data of the third scan.

blends, respectively. The blends containing PC all had a melting point indicating PC crystallinity. After quenching, all the three blends showed two



**Figure 5** (a) First DSC thermogram of chloroform-cast aPMMA/PC blends. (b) Second DSC thermogram of chloroform-cast aPMMA/PC blends.

$T_g$ s, and therefore, were immiscible. The  $T_g$  and  $T_m$  values were computed from Figure 6(a) and 6(b), and are listed in Table IV. For the same reason as in the aPMMA/PC blends,  $\Delta H_{blend}$  values were not calculated. Additionally, based on the observation of the melting peaks as shown in Figure 5(a) and 6(a), double melting point behavior seemed to occur at mid or high PC concentrations in chloroform-cast blends. The reason may be caused by different sizes of PC crystals formed during film casting.

## DISCUSSION

### Glass Transition Temperatures

The  $T_{gsc}$  values of the aPMMA/PC blends cast from THF and chloroform as shown respectively in Tables I and III are similar, both indicating immiscible behaviors, although in a lot of cases, only one low  $T_g$  close to that of aPMMA was observed. The high  $T_g$  one often not detected may be suppressed by the effect of PC crystallinity. However, the THF and chloroform cast

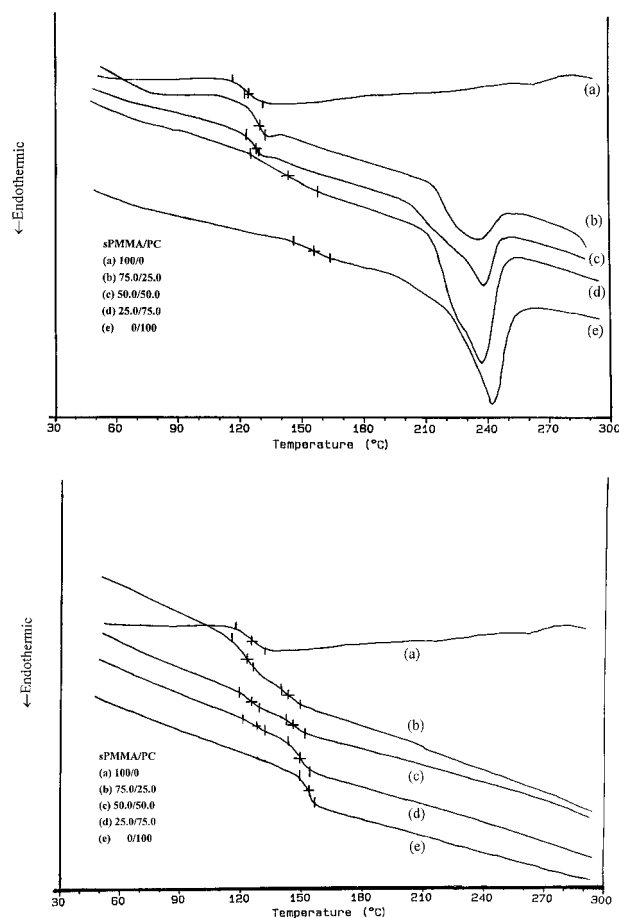
**Table III Thermal Characteristics of Chloroform-Cast aPMMA/PC Blends**

aPMMA/PC	First scan		Second scan	
	$T_{gsc}$ (°C)	$T_m$ (°C)	$T_{gq}$ (°C)	$\Delta T_{gq}$ (°C)
(1) 100/0	103.4	—	102.7	13
(2) 75.2/24.8	105.7, 150.0	223.6	101.9, 147.2	15, 11
(3) 50.0/50.0	107.3, n.d. <sup>a</sup>	235.4	103.0, 147.7	13, 11
(4) 25.0/75.0	106.8, 149.5	236.6	103.6, 149.7	10, 9
(5) 0/100	156.0	242.2	153.3	7

$\Delta H_m$  of PC = 25.34 (J/g).

<sup>a</sup> n.d.: not detected.





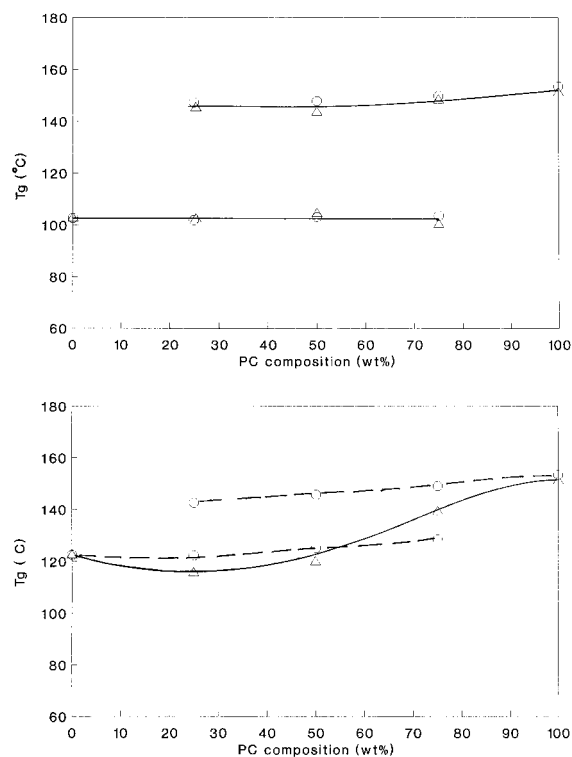
**Figure 6** (a) First DSC thermogram of chloroform-cast sPMMA/PC blends. (b) Second DSC thermogram of chloroform-cast sPMMA/PC blends.

sPMMA/PC blends in Tables II and IV had only one  $T_{gsc}$ . It is interesting to note that the chloroform-cast sPMMA/PC blends showed one  $T_g$  but had a phase-separated structure. One possible explanation is that the mixture separates into

**Table IV Thermal Characteristics of Chloroform-Cast sPMMA/PC Blends**

sPMMA/PC	First Scan		Second Scan	
	$T_{gsc}$ (°C)	$T_m$ (°C)	$T_{gq}$ (°C)	$\Delta T_{gq}$ (°C)
(1) 100/0	121.4	—	122.4	13
(2) 75.0/25.0	129.7	232.9	122.1, 142.5	11, 9
(3) 50.0/50.0	128.3	237.8	125.0, 145.6	10, 9
(4) 25.0/75.0	143.2	237.3	128.3, 148.9	11, 11
(5) 0/100	156.0	242.2	153.3	7

$$\Delta H_m \text{ of PC} = 25.34 \text{ (J/g)}.$$



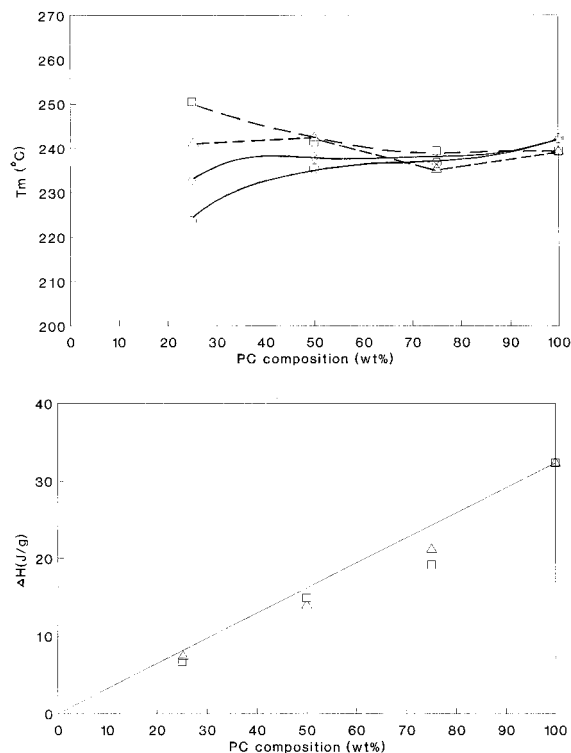
**Figure 7** (a) Glass transition temperatures of aPMMA/PC blends:  $\Delta$ : THF-cast,  $\circ$ : chloroform-cast. (b) Glass transition temperatures of sPMMA/PC blends:  $\Delta$ : THF-cast,  $\circ$ : chloroform-cast.

sPMMA-rich and PC-rich phases with close  $T_g$ s likely not resolved by DSC. This explanation was later substantiated by the observation of two  $T_{gq}$  values in Table IV after quenching. Note the  $T_{gsc}$  value is just intermediate between the two  $T_{gq}$  values, although in most cases, the differences between the  $T_{gsc}$  and  $T_{gq}$  values are not great. Because the  $T_{gq}$  values are considered to be free of annealing or other thermal/solvent effects, they are therefore used in the following discussion. The only exception is the THF-cast sPMMA/PC(75.0/25.0) blend. For this case the  $T_g$  value determined from the third scan is used. For the THF-cast aPMMA/PC(74.8/25.2) blend, the  $T_g$  value from second scan was still used because data of the third scan were not applicable. The glass transition temperatures ( $T_{gq}$ ) of both THF and chloroform-cast aPMMA/PC blends are presented in Figure 7(a). The same blends cast from two different solvents had virtually the same  $T_{gq}$  independent of solvent, as previously noted. They both showed two  $T_g$ s, and therefore, were not miscible. There seemed to be two phases detected in the aPMMA/PC blends. One phase is almost

100% aPMMA; the other one is PC-rich phase. The PC-rich phases cast from the two solvents all showed a general trend of a slight increase of aPMMA solubility with the increase of aPMMA concentration. However, the results of sPMMA/PC blends are very different from those of aPMMA/PC blends, and are presented as follows. The  $T_{gq}$  values of THF-cast and chloroform-cast sPMMA/PC blends are given in Figure 7(b). The blends cast from THF had one  $T_g$ , and were miscible based on the single  $T_g$  criterion. However, the  $T_g$  behavior of those chloroform-cast was very different from THF ones. Two  $T_g$ s were found in the blends, and therefore immiscible. For each blend, there appeared to be two phases. One is PC-rich phase, and the other phase is composed mainly of sPMMA. The THF-cast blends had one  $T_g$  (as already mentioned) but the  $T_g$  values of those blends containing 25.0 and 49.9 wt % PC are close to that of sPMMA. Possible comments for the observation are as the following: according to the report of Nishimoto et al.<sup>14</sup> and chloroform-cast results of this study, it is likely that sPMMA and PC are immiscible. Solvent casting procedures can trap two polymers into a homogeneous mixture, but they are not in the equilibrium state. In the present case, both sPMMA and PC tend to have high viscosities because of their stiff polymer chains. Even at slow rates of solvent removal, this pair can be formed into a homogeneous mixture in THF. Therefore, sPMMA and PC are not truly miscible when cast from THF. All the  $\Delta T_{gq}$  values of the blends are listed in Tables I to IV for the sake of comparison. As shown in Table II, broadening of the glass transition region ( $\Delta T_{gq}$ ) was detected in the THF-cast sPMMA/PC blends. This might be taken as a sign for detection of some degree of heterogeneity in the blend systems.

### Melting Points and Heat Enthalpies of PC in the Blends

The  $T_m$  values of all the as-cast PMMA/PC blends were plotted vs. PC composition and shown in Figure 8(a). For those sPMMA/PC blends cast from THF,  $T_m$  increases with increasing PMMA concentration. Whereas  $T_m$  of the THF-cast aPMMA/PC blends decreases with PMMA concentration first, then reaches an almost constant value and is still higher than PC's  $T_m$  at high PMMA concentrations. sPMMA with a higher  $T_g$  than aPMMA causes a higher  $T_m$  of the blends



**Figure 8** (a) Melting point of PC in PMMA/PC blends:  $-\triangle-\ominus$ : aPMMA/PC (THF-cast, chloroform-cast);  $-\square-\diamond$  sPMMA/PC (THF-cast, chloroform-cast). (b) Melting enthalpy of PC in THF-cast PMMA/PC blends:  $\triangle$ : aPMMA/PC,  $\circ$ : sPMMA/PC.

than PC likely due to the effect of its stiffer polymer chains. aPMMA and sPMMA seemed to be dispersed well in PC when cast from THF, and had a retardation effect on PC crystallization. However, the chloroform-cast blends behave differently. Decreasing  $T_m$  was observed with the increase of PMMA composition in both aPMMA/PC and sPMMA/PC blends. As shown in Figure 8(a), the melting point of PC in the studied blends are markedly different at a low PC concentration (ca. 25%). THF solvent and high syndiotacticity of PMMA seem to cause high  $T_m$  of the blends.

Figure 8(b) presents a plot of  $\Delta H_{\text{blend}}$  vs. PC composition. Chloroform-cast blends were not included for the aforementioned reason.  $\Delta H_{\text{blend}}$  values of THF-cast aPMMA/PC and sPMMA/PC blends are close to but always smaller than the weight average value [shown as the solid line in Figure 8(b)]. This phenomenon reemphasizes the retardation effect of PMMA on PC when THF is used as the solvent.

**Table V Phase Compositions of PMMA/PC Blends**

(a) THF-cast blends		
aPMMA/PC	aPMMA-rich phase	PC-rich phase
( $W_{1T}(\%)/W_{2T}(\%)$ )	$w'_1(\%) (W'(\%))$	$w''_1(\%) (W''(\%))$
74.8/25.2	100 (72.0)	10 (28.0)
50.0/50.0	97 (44.0)	13 (56.0)
25.0/75.0	100 (22.7)	3 (77.3)
(b) Chloroform-cast blends		
(1) aPMMA/PC		
( $W_{1T}(\%)/W_{2T}(\%)$ )	aPMMA-rich phase	PC-rich phase
	$w'_1(\%) (W'(\%))$	$w''_1(\%) (W''(\%))$
75.2/24.8	100 (72.1)	11 (27.9)
50.0/50.0	100 (44.4)	10 (55.6)
25.0/75.0	98 (20.7)	6 (79.3)
(2) sPMMA/PC		
( $W_{1T}(\%)/W_{2T}(\%)$ )	sPMMA-rich phase	PC-rich phase
	$w'_1(\%) (W'(\%))$	$w''_1(\%) (W''(\%))$
75.0/25.0	100 (62.7)	33 (37.3)
50.0/50.0	91 (39.7)	23 (60.3)
25.0/75.0	80 (17.9)	13 (82.1)

### Phase Compositions of Quenched PMMA/PC Blends

Because two  $T_{gq}$ s were detected in most of the studied blends, PMMA-rich and PC-rich phases were assumed rightfully. Estimations of the compositions of these two phases were attempted and illustrated as the following. If the  $T_g$  of the PMMA-rich phase is equal to or slightly lower than that of PMMA, the composition is considered to be 100% PMMA. If  $T_g$  is located between PMMA and PC, its composition was estimated from the Fox equation<sup>15</sup> shown below as in eq. (1)

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (1)$$

where  $w_1$  and  $w_2$  represent the weight fractions of the components, and  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the  $T_g$ s of the blend and components 1 and 2, respectively. Although the Fox equation was derived for and is often used in miscible blends, attempts made here for immiscible blends were a qualitative estimation. Equation (1) can be rearranged to

$$w'_1 = T_{g1}(T_{g1,b} - T_{g2})/(T_{g1,b}(T_{g1} - T_{g2})) \quad (2)$$

where  $w'_1$  is the apparent weight fraction of PMMA in the PMMA-rich phase,  $T_{g1,b}$  is the observed  $T_g$  of PMMA-rich phase. Similarly, eq. (1) can also be rearranged to

$$w''_1 = T_{g1}(T_{g2,b} - T_{g2})/(T_{g2,b}(T_{g1} - T_{g2})) \quad (3)$$

where  $w''_1$  is the apparent weight fraction of PMMA in the PC-rich phase,  $T_{g2,b}$  is the observed  $T_g$  of the PC-rich phase.

Applying eqs. (2) and (3) to the  $T_{gq}$  values of PMMA/PC blends, the apparent weight fractions of PMMA in the PMMA-rich phase ( $w'_1$ ) and in the PC-rich phase ( $w''_1$ ) were calculated. The results are tabulated in Table V. For THF-cast and chloroform-cast aPMMA/PC blends, aPMMA composition of the aPMMA-rich phase is almost independent of concentration at around 97–100%. However, aPMMA concentration in the PC-rich phase of the same blends range from 3–13% in chloroform-cast blends and 6–11% in THF-cast blends. Taking into consideration errors involved in estimation, the two different solvent cast systems have almost the same compositions and both show qualitatively a higher solubility of aPMMA in the PC-rich phase with increasing aPMMA composition. The results are not surprising, because these two blends show virtually the same  $T_g$ s [as shown in Figure 7(a)].

For chloroform-cast sPMMA/PC blends, the behavior of sPMMA-rich phase is similar to that of aPMMA-rich phase in aPMMA/PC blends with a sPMMA composition 80–100%. The number 80% indicates PC dissolves better in sPMMA than in aPMMA. On the other hand, data of the PC-rich one show a higher solubility of sPMMA (ca. 13–33%) in PC than that of aPMMA in PC (ca. 6–11%) in the same PMMA concentration range. For the blend with 75% PC and 25% sPMMA, the sPMMA-rich phase has a sPMMA concentration



of 80% and sPMMA concentration of the PC-rich phase is 13%. Therefore, at this composition, PC and sPMMA show some degree of mutual solubility. However, for the same composition blend but using aPMMA instead, the blend separates into an almost pure (ca. 98%) aPMMA phase and a PC-rich phase with a low aPMMA (ca. 6%) concentration.

The overall weight fraction of PMMA-rich phase ( $W'$ ) and PC-rich phase ( $W''$ ) is calculated by the following material balance equations:

$$W_{1T} = w'_1 W' + w''_1 W'' \quad (4)$$

$$W_{2T} = w'_2 W' + w''_2 W'' \quad (5)$$

where  $W_{1T}$  and  $W_{2T}$  are the overall weight fraction of PMMA and PC for blending, respectively, and  $w'_1$  and  $w'_2$  are obtained from eqs. (2) and (3), respectively. The  $W'$  and  $W''$  values were calculated and are also listed in Table V. For the THF-cast and chloroform-cast aPMMA/PC blends, their  $W'$  and  $W''$  values are virtually the same within the error of estimation. For using chloroform as the solvent, sPMMA/PC blends have quite different phase compositions from aPMMA/PC blends. sPMMA/PC blends have obviously higher  $W''$  values than aPMMA/PC blends. Take the PMMA/PC (ca. 75/25) blend for example. The  $W''$  value for the sPMMA blend is 37.3% much higher than 27.9% found in aPMMA blends. Therefore, more sPMMA enters into PC-rich phase than aPMMA. This number offers an additional proof of higher sPMMA solubility in PC than aPMMA.

## CONCLUSIONS

The solvent effect is demonstrated clearly in the PMMA/PC blends prepared from THF and chloroform. The blends cast from THF do not show visible phase separation. However, those chloroform-cast indicate obvious a phase-separated structure. When sPMMA is blended with PC from chloroform, even the as-cast blends show only one glass transition temperature but have a visible phase-separated structure. This can be explained by that the mixture separates into sPMMA-rich and PC-rich phases with close  $T_g$ s therefore not resolved by DSC. The quenched samples of aPMMA/PC blends cast from either solvent behave virtually the same and have almost the same glass transition temper-

atures. However, different results were obtained in the quenched samples of sPMMA/PC blends. Chloroform-cast blends show two  $T_g$ s, but for THF-cast ones a single  $T_g$  was detected. THF is believed to cause sPMMA and PC to be trapped together even after solvent removal. According to the experimental results, it is possible to prepare a well-dispersed mixture of PC and sPMMA when THF is used as solvent. Based on the DSC data, sPMMA dissolves better in PC than aPMMA, and PC has a higher solubility in sPMMA than in aPMMA. The as-cast blends containing PC all show a melting point in the proximity of the  $T_m$  of PC, indicating the presence of PC crystallinity. Different melting point behaviors were observed in THF-cast and chloroform-cast blends. For THF-cast blends,  $T_m$  of most blends is equal to or higher than PC's  $T_m$ , showing a retardation effect of PMMA on PC crystallization. However, melting point depressions were detected in the chloroform-cast PMMA/PC blends.

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