spinodal curve in Figure 9. In diagram c, region M$_1$ + M$_2$ arises instead of region L$_1$ + L$_2$ and denotes the condition for the coexistence of two mesophases of different compositions. The presence of a M$_1$ + M$_2$ region has not yet been demonstrated experimentally. In all three diagrams, the line AC denotes a eutectic temperature at which three phases, A, B, and C, coexist. Our chief concern here is the region denoted M + L *above* the eutectic temperature. The upper binodal of this M + L region should lie somewhat above the spinodal line for microphase separation given in Figure 9. Let us study what will happen when we start with a mixture having a composition denoted by an arrow in the disordered, homogeneous state, and cool it. In the case of diagram a, it will hit the binodal of L$_1$ + L$_2$ region and separate into two disordered phases having very different compositions. The mixture will then turn cloudy. In the case of diagrams b and c it will, on cooling, first encounter the upper binodal of M + L region, at which a mesophase, having a composition corresponding to the lower binodal at the temperature, starts to appear. Thermodynamically it is a macrophase separation, and as the temperature is gradually lowered, the volume of mesophase increases and the compositions of the disordered phase and the mesophase both shift along the upper and lower binodals, respectively. Visually observable turbidity might not develop, however, because the composition difference between the disordered phase and the emerging mesophase is relatively small and, moreover, the particle size of the latter might not grow large for kinetic reasons. The presence of such coexisting phases of small sizes nevertheless might produce sufficient scattering of X-rays observable at very small angles. The validity of the above explanation can only be confirmed fully by quantitative comparison of our data with any theories capable of predicting binodals that might be developed in the future. The speculative discussion offered above, however, seems to be able, for the moment, to explain most of the qualitative features observed in our study.

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**Registry No.** (Styrene)(butadiene) (block copolymer), 106107-54-4; polystyrene, 9003-53-6.

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# Blends of Polycarbonate and Poly(methyl methacrylate) and the Determination of the Polymer–Polymer Interaction Parameter of the Two Polymers

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ABSTRACT: Blends of bisphenol A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) prepared by screw extrusion and solution casting have been investigated by differential scanning calorimetry and scanning electron microscopy. From the measured glass transition temperatures ($T_g$) and specific heat increments ($\Delta C_p$) at the $T_g$, the PMMA appears to dissolve more in the PC-rich phase than does the PC in the PMMA-rich phase. The blend appears to be near equilibrium under extrusion as well as solution-casting conditions so that the Flory–Huggins interaction parameter between PC and PMMA was calculated and found to be 0.039 ± 0.004 for extruded blends at 250 °C and 0.043 ± 0.004 for solution-cast blends at 25 °C. Scanning electron microscopy supports the conclusion that the compatibility increases more in the PMMA-rich compositions than in the PC-rich compositions of the PC/PMMA blends.

## I. Introduction

The blending of bisphenol A polycarbonate (PC) with various polymers has been of interest in recent years.[1,2] Many investigators have studied the blends of PC with polystyrene,[3–6] polyethylene,[4,7] polypropylene,[5,8] poly(methyl methacrylate),[9] poly(styrene-*co*-acrylonitrile),[10] poly(acrylonitrile–butadiene–styrene),[11] and some polyesters.[12–14] PC and poly(methyl methacrylate) (PMMA) are known to be partially miscible,[9] and two glass transition regions are observed. In the study of blends of PC and PMMA, Gardlund[9] has found two $T_g$s by differential

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scanning calorimetry (DSC). Thermal analysis of polymer blends has shown that a miscible polymer blend will exhibit a single glass transition between the $T_g$s of the components,[1,2] while for partially miscible systems the $T_g$s approach each other but do not become identical.[3,15] Recently, some investigators[15-19] have also used the specific heat increment ($\Delta C_p$) at the $T_g$ to investigate the polymer–polymer compatibility by DSC.

The method of determining the polymer–polymer interaction parameter between component polymers in a miscible blend has been studied widely.[20-28] Several techniques can be used to determine the thermodynamic polymer–polymer interaction parameter ($\chi$) such as melting point depression[20-22], vapor sorption,[22,23] inverse-phase gas chromatography,[24-26] and some light-scattering methods.[27,28] Only a few methods have been developed which can be applied in incompatibile polymer blend systems, however, and most of these are ternary solution methods.[29-32]

In our present study we are examining the miscibility of blends of PC and PMMA by determining experimentally the glass transition temperature ($T_g$) and the specific heat increment ($\Delta C_p$) at the $T_g$ of the blends by thermal analysis, and the morphology of blends of PC and PMMA is being examined by scanning electron microscopy (SEM). Also, a method is presented to determine the polymer–polymer interaction parameter ($\chi_{12}$) in partially miscible systems by using the experimentally determined glass transition temperature. Since the interaction parameter is an equilibrium property, experimental tests were carried out to verify that both the screw-extruded blends and the solution-cast blends are close to their equilibrium conditions.

## II. Theory

**Polymer–Polymer Interaction Parameter ($\chi$).** For miscible polymer blends, several techniques[20-28] have been used to determine the Flory–Huggins polymer–polymer interaction parameter ($\chi$).

Scott[33] and Tompa[34] were the first to apply the Flory–Huggins theory[35] of polymer solutions to mixtures of polymers, with and without added solvent, in order to determine the polymer–polymer interaction parameter. For polydisperse polymers, it has been found[36] that number-average molecular weights can be used in place of monodisperse molecular weights in the modified Flory-Huggins equation with very little effect on the consequent value of $\chi$.

The Flory–Huggins equation was developed for systems at equilibrium. In order to ascertain how close the PC/PMMA blend system is to equilibrium in extrusion as well as in solution casting, we have tested the two criteria of equilibria, specifically that the properties are constant with time and that the final conditions can be achieved from opposite directions.

If the above equilibrium condition is met for the PC/PMMA blend system, then an expression can be developed to determine the Flory–Huggins polymer–polymer interaction parameter ($\chi_{12}$) of the mixture without solvent in partially miscible blends, similar to the earlier work of Scott.[33] Let us consider a mixture of two polymers in the absence of solvent and assume that equilibrium is reached. From the Flory–Huggins theory,[35] the Gibbs' free energy of mixing, $\Delta G_m$, for a system consisting of two polymers can be written as[34]

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12}\phi_1\phi_2(m_1n_1 + m_2n_2) \quad (1)$$

where $n_i$ is the number of moles of the $i$th component in the mixture and $\phi_i = m_in_i/(m_in_i + m_jn_j)$, which is the volume fraction of the $i$th component ($i, j = 1, 2$ and $i \neq j$). $\chi_{12}$ is the Flory–Huggins interaction parameter. Subscripts 1 and 2 denote polymers 1 and 2. $m_i$ is essentially the degree of polymerization, relating the molar volumes $V_1$ and $V_2$ of the polymers to a fictitious molar volume $V_0$ of one submolecule of polymer. Thus, $m_1$ and $m_2$ will give

$$\frac{m_1}{m_2} = \frac{\bar{M}_{n,1}/\rho_1}{\bar{M}_{n,2}/\rho_2} \quad (2)$$

where $\bar{M}_n$ is the number-average molecular weight and $\rho$ is the density of polymer. The choice of a lattice site volume can be rather arbitrary, but once a site volume has been chosen for one of the components, it must be the same for the other component. Here, a repeat unit of polymer 1 is chosen as a lattice site volume.

The chemical potential of mixing of component $i$, as discussed by Tompa,[34] is obtained as the partial derivative of eq 1 with respect to $n_i$:

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right)\phi_2 + m_1\chi_{12}\phi_2^2 \quad (3)$$

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 + \left(1 - \frac{m_2}{m_1}\right)\phi_1 + m_2\chi_{12}\phi_1^2 \quad (4)$$

Equations 3 and 4 are not mathematically independent but are equivalent to 1a and 1b of Scott,[33] respectively. From the lattice fluid theory of solutions,[37] Sanchez[38] has derived an expression for the chemical potential of one component in a binary mixture which leads to expressions similar to eq 3 and 4.

At equilibrium the chemical potential of each component must be the same in both phases. Denoting the two conjugate phases by single and double primes, we have $\Delta\mu_1' = \Delta\mu_1''$ and $\Delta\mu_2' = \Delta\mu_2''$.

Thus, eq 3 will give

$$\chi_{12} = \frac{\ln \dfrac{\phi_1''}{\phi_1'} + \left(1 - \dfrac{m_1}{m_2}\right)(\phi_2'' - \phi_2')}{m_1(\phi_2'^2 - \phi_2''^2)} \quad (5)$$

Similarly eq 4 yields

$$\chi_{12} = \frac{\ln \dfrac{\phi_2''}{\phi_2'} + \left(1 - \dfrac{m_2}{m_1}\right)(\phi_1'' - \phi_1')}{m_2(\phi_1'^2 - \phi_1''^2)} \quad (6)$$

Although eq 5 and 6 should give the same value of $\chi_{12}$, the experimental error involved in the different experimental measurements in each equation leads to slightly different values. To minimize this error in $\chi_{12}$, the values from eq 5 and 6 can be averaged.

By use of eq 5 and 6, the polymer–polymer interaction parameters ($\chi_{12}$) are determined for this system from measured volume fractions of PC and PMMA dissolved in the PMMA-rich phase and the PC-rich phase, respectively, and are reported in section IV. In our early study[3] of blends of bisphenol A polycarbonate (PC) and polystyrene (PS), two $T_g$s had also been found and eq 5 and 6 were used to determine the Flory–Huggins interaction parameter ($\chi_{12}$) of PC/PS blends. Also for PS and polybutadiene (PBD) blends, the $\chi_{12}$ values from the solid state which are obtained from eq 5 and 6 compared[3] favorably with the values of $\chi_{12}$ from solution studies.[36]

## III. Experimental Section

**Polymers.** The polymers used in this study were obtained from commercial sources (Table I). The universal calibration me-

**Table I**
**Characteristics of Polymer Samples Used in PC/PMMA Blends**

| sample | $\bar{M}_w$[a] | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ | $T_g$, K[b] | $\Delta C_p$, $J \cdot g^{-1} \cdot K^{-1}$[b] |
|---|---|---|---|---|---|
| PC 101[c] | 29 000 | 12 300 | 2.36 | 421.5 | 0.222 |
| PMMA[d] | 83 700 | 37 000 | 2.26 | 380.4 | 0.200 |

[a] Measured in our laboratory by GPC (tetrahydrofuran, 25 °C). [b] Measured in our laboratory by DSC. [c] Supplied by General Electric Co. (Lexan polycarbonate). [d] Supplied by Scientific Polymer Products, Inc.

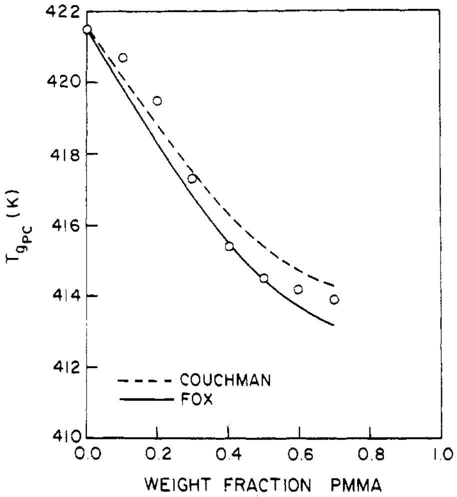

**Figure 1.** Effect of blend composition of the $T_g$(PC) for PC/PMMA blends from screw extrusion. The curves represent the mathematical models for Fox[47] and Couchman.[48]

thod[39,40] based on hydrodynamic volume was used for the PC and PMMA. Mark–Houwink constants of $K = 3.89 \times 10^{-4}$ dL/g and $\alpha = 0.766$ for the PC were used.[41] For the PMMA, the Mark–Houwink constants used were $K = 1.28 \times 10^{-4}$ dL/g and $\alpha = 0.690$ in THF at 25 °C.[42]

The glass transition temperature ($T_g$) and specific heat increment ($\Delta C_p$) at $T_g$ were measured by differential scanning calorimetry (DSC), using procedures reported earlier.[15] Methylene chloride, used as solvent for the preparation of cast films, was spectroquality grade, supplied by Matheson, Coleman and Bell.

**Blend Preparations.** For solution casting, a total of 1.5 g of PC/PMMA mixtures in weight fractions of PMMA of 1.00–0.00 was dissolved in 50 mL of methylene chloride at room temperature [3.0% (w/v) solution] for at least 1 day. Blends were cast on glass plates, and all film samples were dried under vacuum for 15 days at room temperature. Cast film thickness was 15 ± 3 μm. For melt blending, all polymers were dried in a vacuum oven at 80 °C for 2 days before use. Temperatures of the extruder[3,5] were set at 250 °C in each zone (die, die head, and barrel zones) for the pure PC material. The temperature was gradually decreased for the weight fraction of PC of 0.40, 0.30, 0.20, and 0.10 to 230 °C.

**Scanning Electron Microscopy (SEM).** The morphology of the cross section of extrudate and solution-cast films after cryogenic fracturing[4] was examined by SEM in a JOEL Model JSM-840 microscope at 15-kV accelerating voltage after sputter coating (500 Å).

**Differential Scanning Calorimetry Measurements.** The thermal properties of all samples were measured calorimetrically by using a Perkin-Elmer differential scanning calorimeter.[3]

## IV. Results and Discussion

**$T_g$ of PC/PMMA Blends.** PC and PMMA are known to be partially miscible,[9] and two glass transition regions are observed which we designate as $T_g$(PC), associated with PC-rich regions, and $T_g$ (PMMA), associated with PMMA-rich regions. The $T_g$s of PC for the PC/PMMA screw-extruded blends and solution-cast blends are shown to decrease almost linearly with an increase in the PMMA weight fraction in Figures 1 and 2, respectively. The $T_g$s of PMMA for the PC/PMMA screw-extruded blends and solution-cast blends are shown to increase linearly with PC weight fraction in Figures 3 and 4, respectively.

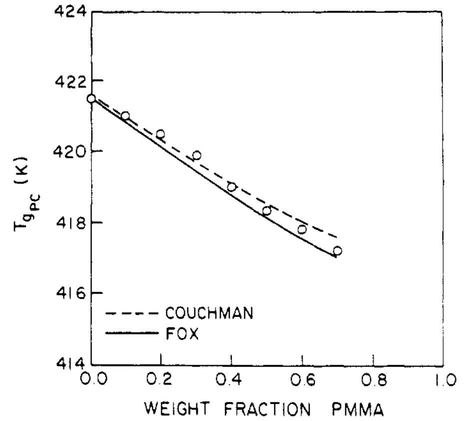

**Figure 2.** Effect of blend composition on the $T_g$(PC) for PC/PMMA blends by solution casting from 3.0% (w/v) methylene chloride solution. The curves represent the mathematical models for Fox[47] and Couchman.[48]

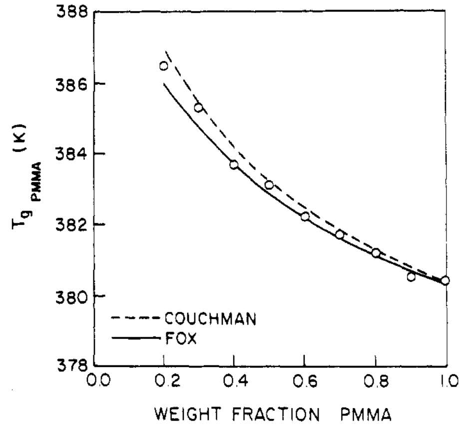

**Figure 3.** Effect of blend composition on the $T_g$(PMMA) for PC/PMMA blends from screw extrusion. The curves represent the mathematical models of Fox[47] and Couchman.[48]

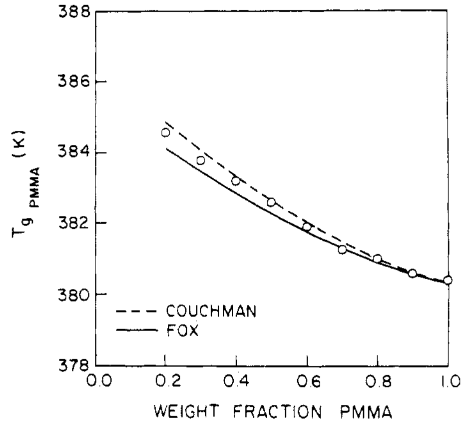

**Figure 4.** Effect of blend composition on the $T_g$(PMMA) for PC/PMMA blends by solution casting from 3.0% (w/v) methylene chloride solution. The curves represent the mathematical models of Fox[47] and Couchman.[48]

One explanation of the difference between the two blending methods is that in solution-cast blends, the polymer chains do not have sufficient time or mobility to intermix as the solvent evaporates, which could lead to more facile phase separation in the final dry film.[43,44]

The apparent weight fractions of PC were determined in the PC-rich phase and the PMMA-rich phase by the

**Table II**
**Apparent Weight Fraction ($w$) and Apparent Volume Fraction ($\phi$) of PC and PMMA Components in the PC-Rich Phase and the PMMA-Rich Phase**

| | | | PC-rich[b] | | PMMA-rich[b] | | PC-rich | | PMMA-rich | |
|---|---|---|---|---|---|---|---|---|---|---|
| blend[a] | $T_{g_1}$, K | $T_{g_2}$, K | $w_1'$ | $w_2'$ | $w_1''$ | $w_2''$ | $\phi_1'$ | $\phi_2'$ | $\phi_1''$ | $\phi_2''$ |
| | | | | | Extruder Blending | | | | | |
| 1.00 | 421.5 | | 1.0000 | 0.0000 | | | 1.0000 | 0.0000 | | |
| 0.80 | 419.5 | 386.5 | 0.9513 | 0.0487 | 0.1484 | 0.8516 | 0.9501 | 0.0499 | 0.1452 | 0.8548 |
| 0.70 | 417.3 | 385.3 | 0.8978 | 0.1022 | 0.1192 | 0.8808 | 0.8955 | 0.1045 | 0.1166 | 0.8834 |
| 0.60 | 415.4 | 383.7 | 0.8516 | 0.1484 | 0.0803 | 0.9197 | 0.8484 | 0.1516 | 0.0785 | 0.9215 |
| 0.50 | 414.5 | 383.1 | 0.8297 | 0.1703 | 0.0657 | 0.9343 | 0.8261 | 0.1739 | 0.0642 | 0.9358 |
| 0.40 | 414.2 | 382.4 | 0.8224 | 0.1776 | 0.0487 | 0.9513 | 0.8187 | 0.1813 | 0.0475 | 0.9525 |
| 0.00 | | 380.4 | | | 0.0000 | 1.0000 | | | 0.0000 | 1.0000 |
| | | | | | Solution Casting | | | | | |
| 1.00 | 421.5 | | 1.0000 | 0.0000 | | | 1.0000 | 0.0000 | | |
| 0.80 | 420.5 | 384.6 | 0.9757 | 0.0243 | 0.1022 | 0.8978 | 0.9750 | 0.0250 | 0.1000 | 0.9000 |
| 0.70 | 419.9 | 383.8 | 0.9611 | 0.0389 | 0.0827 | 0.9173 | 0.9601 | 0.0399 | 0.0808 | 0.9192 |
| 0.60 | 419.0 | 383.2 | 0.9392 | 0.0608 | 0.0681 | 0.9319 | 0.9377 | 0.0623 | 0.0665 | 0.9335 |
| 0.50 | 418.3 | 382.6 | 0.9221 | 0.0779 | 0.0535 | 0.9465 | 0.9203 | 0.0797 | 0.0522 | 0.9478 |
| 0.40 | 417.8 | 381.9 | 0.9100 | 0.0900 | 0.0365 | 0.9635 | 0.9079 | 0.0921 | 0.0356 | 0.9644 |
| 0.00 | | 380.4 | | | 0.0000 | 1.0000 | | | 0.0000 | 1.0000 |

[a] Blend composition given as overall weight fraction PC in the PC/PMMA blend. [b] Single prime and double prime denote PC-rich phase and PMMA-rich phase, respectively, and subscripts 1 and 2 denote PC and PMMA components. All *w's* calculated from eq 8.

following empirical equation,[45] which is often used to describe the dependence of $T_g$ on composition in random copolymers and plasticized systems:

$$T_g = w_1 T_{g_1} + w_2 T_{g_2} \qquad (7)$$

where $T_g$ is the observed $T_g$ of the copolymer, $w_1$ is the weight fraction of homopolymer 1 having $T_{g_1}$, and $w_2$ is the weight fraction of homopolymer 2 having $T_{g_2}$. Equation 7 may be rearranged[46] to

$$w_1' = \frac{T_{g_1,b} - T_{g_2}}{T_{g_1} - T_{g_2}} \qquad (8)$$

where $w_1'$ is the apparent weight fraction of polymer 1 in the polymer 1 rich phase, $T_{g_1,b}$ is the observed $T_g$ of polymer 1 in the blends, and $T_{g_1}$ and $T_{g_2}$ are the $T_g$s of homopolymers 1 and 2, respectively.

In this manner we have calculated the apparent weight fractions of PC and PMMA in the PC-rich phase and in the PMMA-rich phase which are shown in Table II. From the calculated apparent weight fractions of the PC-rich phase ($w_1'$ and $w_2'$) and the PMMA-rich phase ($w_1''$ and $w_2''$), the $T_g$s of PC (Figures 1 and 2) and PMMA (Figures 3 and 4) have been predicted by using the Fox equation[47] and the Couchman equation,[48,49] which are used to predict $T_g$s for miscible polymer blends.

The Fox equation is

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \qquad (9)$$

Equation 9 may be rearranged to

$$w_1' = \frac{T_{g_1}(T_{g_1,b} - T_{g_2})}{T_{g_1,b}(T_{g_1} - T_{g_2})} \qquad (10)$$

where $w_1'$ is the apparent weight fraction of polymer 1 in the polymer 1 rich phase, and $T_{g_1,b}$ is the observed $T_g$ of polymer 1 in the blends. The Couchman relation is given by

$$\ln T_g = \frac{w_1 \Delta C_{p_1} \ln T_{g_1} + w_2 \Delta C_{p_2} \ln T_{g_2}}{w_1 \Delta C_{p_1} + w_2 \Delta C_{p_2}} \qquad (11)$$

where $\Delta C_p = C_p^{\,l}(T_g) - C_p^{\,s}(T_g)$ = difference in molar heat capacity at $T_g$, where $C_p^{\,l}(T_g)$ is the molar heat capacity of the liquid at $T_g$ and $C_p^{\,s}(T_g)$ is the molar heat capacity of the solid at $T_g$. Equation 11 may be rearranged to

$$w_1' = \frac{\Delta C_{p_2}(\ln T_{g_1,b} - \ln T_{g_2})}{\Delta C_{p_1}(\ln T_{g_1} - \ln T_{g_1,b}) + \Delta C_{p_2}(\ln T_{g_1,b} - \ln T_{g_2})} \qquad (12)$$

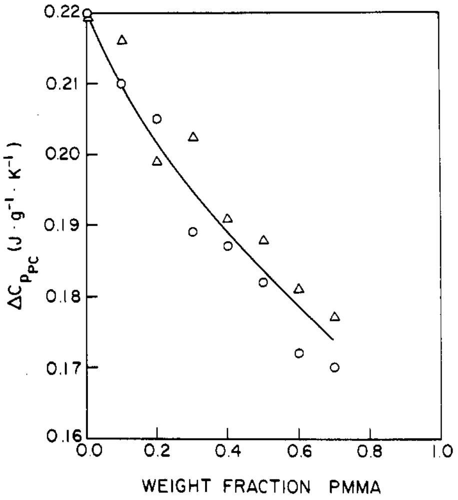

**Figure 5.** Specific heat increment ($\Delta C_p$) at the $T_g$ of polycarbonate for PC/PMMA blends from screw extrusion (○) and solution casting (△).

The apparent volume fractions of PC and PMMA in the PC-rich phase and in the PMMA-rich phase are shown in Table III. We can then estimate the Flory–Huggins polymer–polymer interaction parameter ($\chi_{12}$), provided that the system is at equilibrium or nearly so.

In the extruded blends of Figures 1 and 3, we can see that the decrease of $T_g$(PC) with weight fraction of PMMA is more significant than the increase of $T_g$(PMMA) with weight fraction of PC. Similarly, in Table II the weight fraction of PMMA dissolved in the PC-rich phase ($w_2'$) is higher than the weight fraction of PC component dissolved in the PMMA-rich phase ($w_1''$). These results suggest that the PMMA dissolves more in the PC-rich phase than does the PC in the PMMA-rich phase.

**$\Delta C_p$ of PC/PMMA Blends.** The values of $\Delta C_p$ of PC and PMMA in PC/PMMA blends prepared by screw extrusion and solution casting are presented in Figures 5 and 6. In Figure 5, the $\Delta C_p$ of PC is seen to decrease linearly

**Table III**
**Comparison of Polymer–Polymer Interaction Parameter ($\chi_{12}$) from Different Values of Apparent Volume Fraction ($\phi$) of PC and PMMA by the Wood, Fox, and Couchman Relations**

| | | | Wood[b] | | | Fox | | | Couchman | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| blend[a] | $T_{g_1}$, K | $T_{g_2}$, K | $\phi_1'$ | $\phi_2''$ | $\chi_{12}$[c] | $\phi_1'$ | $\phi_2''$ | $\chi_{12}$[c] | $\phi_1'$ | $\phi_2''$ | $\chi_{12}$[c] |
| | | | | | Extruder Blending | | | | | | |
| 1.00 | 421.5 | | 1.0000 | 0.0000 | | 1.0000 | 0.0000 | | 1.0000 | 0.0000 | |
| 0.80 | 419.5 | 386.5 | 0.9501 | 0.8548 | 0.036 | 0.9548 | 0.8415 | 0.036 | 0.9476 | 0.8612 | 0.036 |
| 0.70 | 417.3 | 385.3 | 0.8955 | 0.8834 | 0.036 | 0.9046 | 0.8724 | 0.036 | 0.8904 | 0.8887 | 0.037 |
| 0.60 | 415.4 | 383.7 | 0.8484 | 0.9215 | 0.039 | 0.8611 | 0.9138 | 0.038 | 0.8413 | 0.9253 | 0.040 |
| 0.50 | 414.5 | 383.1 | 0.8261 | 0.9258 | 0.041 | 0.8403 | 0.9294 | 0.040 | 0.8183 | 0.9390 | 0.042 |
| 0.40 | 414.2 | 382.4 | 0.8187 | 0.9525 | 0.044 | 0.8334 | 0.9477 | 0.043 | 0.8106 | 0.9594 | 0.044 |
| 0.00 | | 380.4 | 0.0000 | 1.0000 | | 0.0000 | 1.0000 | | 0.0000 | 1.0000 | |
| | | | | | Solution Casting | | | | | | |
| 1.00 | 421.5 | | 1.0000 | 0.0000 | | 1.0000 | 0.0000 | | 1.0000 | 0.0000 | |
| 0.80 | 420.5 | 384.6 | 0.9750 | 0.9000 | 0.041 | 0.9774 | 0.9012 | 0.041 | 0.9738 | 0.9047 | 0.041 |
| 0.70 | 419.9 | 383.8 | 0.9601 | 0.9192 | 0.041 | 0.9639 | 0.9199 | 0.042 | 0.9580 | 0.9230 | 0.042 |
| 0.60 | 419.0 | 383.2 | 0.9377 | 0.9335 | 0.042 | 0.9320 | 0.9340 | 0.042 | 0.9345 | 0.9366 | 0.042 |
| 0.50 | 418.3 | 382.6 | 0.9203 | 0.9478 | 0.044 | 0.9275 | 0.9481 | 0.044 | 0.9163 | 0.9503 | 0.044 |
| 0.40 | 417.8 | 381.9 | 0.9079 | 0.9633 | 0.047 | 0.9162 | 0.9645 | 0.047 | 0.9033 | 0.9661 | 0.047 |
| 0.00 | | 380.4 | 0.0000 | 1.0000 | | 0.0000 | 1.0000 | | 0.0000 | 1.0000 | |

[a] Blend composition given as overall weight fraction PC in the PC/PMMA blend. [b] Single prime and double prime denote PC-rich phase and PMMA-rich phase, respectively, and $\phi_2' = 1 - \phi_1'$ and $\phi_1'' = 1 - \phi_2''$. Subscripts 1 and 2 denote PC and PMMA components, respectively. [c] All $\chi_{12}$'s are calculated from eq 5 and 6.

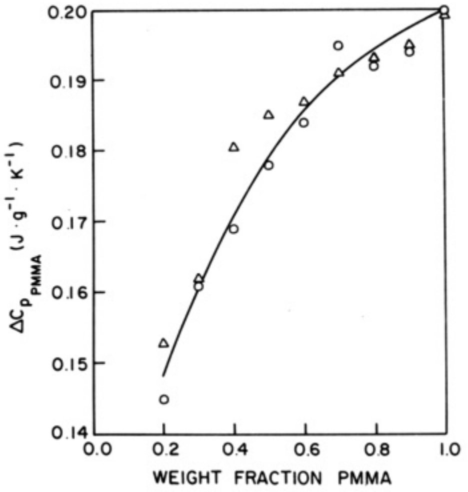

**Figure 6.** Specific heat increment ($\Delta C_p$) at the $T_g$ of poly(methyl methacrylate) for PC/PMMA blends from screw extrusion (○) and solution casting (△).

with composition of PMMA in PC/PMMA blends for screw-extruded and solution-cast blends. In Figure 6, the $\Delta C_p$ of PMMA is seen to decrease linearly with composition of PC in PC/PMMA blends.

In our earlier paper,[15] we attributed the reduction in the $\Delta C_p$ at $T_g$ of each component to the dissolution of that component in the conjugate phase. The results in Figures 5 and 6, then, would indicate that some of the PC is dissolving in the PMMA-rich phase and some of the PMMA is dissolving in the PC-rich phase.

**Scanning Electron Microscopy of PC/PMMA Blends.** The micrographs of 0.90, 0.80, 0.70, 0.30, 0.20, and 0.10 weight fractions of PC in PC/PMMA solution-cast blends are presented in Figure 7. We can see that phase separation between the PC-rich phase and the PMMA-rich phase is more pronounced in the cases of 0.90, 0.80, and 0.70 weight fractions of PC (PC-rich compositions) than in the 0.30, 0.20, and 0.10 weight fractions of PC (PMMA-rich compositions). The above observation is consistent with the situation that the PMMA dissolves more in the PC-rich phase than does the PC in the PMMA-rich phase.

The micrographs of 0.80, 0.70, 0.20, and 0.10 weight fractions of PC in PC/PMMA extruded blends are presented in Figure 8. Phase separation between the two phases is more pronounced in the 0.80 and 0.70 weight fractions of PC (PC-rich compositions) than in the 0.20 and 0.10 weight fractions of PC (PMMA-rich compositions). From the microscopy study, it appears that the compatibility increases more in the regions of PMMA-rich compositions than in the regions of PC-rich compositions.

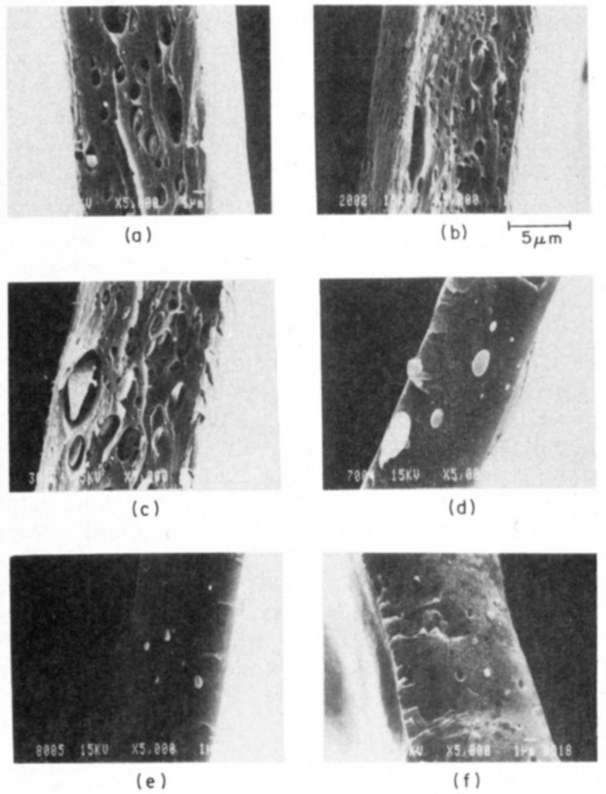

**Figure 7.** Scanning electron micrographs obtained from cryogenically fractured cross-sectional surfaces of solution-cast films of PC/PMMA blends: (a) 90/10, (b) 80/20, (c) 70/30, (d) 30/70, (e) 20/80, (f) 10/90.

**Polymer–Polymer Interaction Parameter of PC/PMMA Blends.** To test for equilibrium,[50] we took the extrudate, remelted it in the extruder, and extruded it a second time. In Table IV we can see that the $T_g$s of PC and PMMA of the remelted extrudate are very close to the

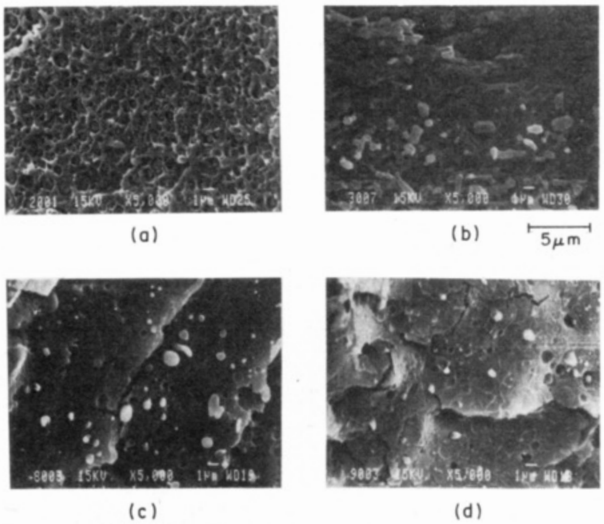

**Figure 8.** Scanning electron micrographs obtained from cryogenically fractured cross-sectional surfaces of PC/PMMA extruded blends: (a) 80/20, (b) 70/30, (c) 20/80, (d) 10/90.

**Table IV**
**Glass Transition Temperatures ($T_g$) of the First Extrudate, Remelted Extrudate in the Extruder, and Repeated Blending Experiment of PC/PMMA Blends**

| | first extrudate[b] | | remelted extrudate[c] | | repeated experiment[d] | |
|---|---|---|---|---|---|---|
| blend[a] | $T_{g1}$, K | $T_{g2}$, K | $T_{g1}$, K | $T_{g2}$, K | $T_{g1}$, K | $T_{g2}$, K |
| 1.00 | 421.5 | | 421.5 | | 421.5 | |
| 0.90 | 420.7 | | 420.5 | | 420.8 | |
| 0.80 | 419.5 | 386.5 | 419.3 | | 419.2 | |
| 0.70 | 417.3 | 385.3 | 417.2 | 385.1 | 418.1 | 385.4 |
| 0.60 | 415.4 | 383.7 | 415.1 | 384.0 | 415.2 | 383.8 |
| 0.50 | 414.5 | 383.1 | 413.9 | 382.5 | 414.2 | 382.5 |
| 0.00 | | 380.4 | | 380.4 | | 380.4 |

[a] Blend designation given as overall weight fraction PC in PC/PMMA blend. [b] Subscripts 1 and 2 denote PC and PMMA components, respectively. [c] Remelted extrudate after second extrusion. [d] Replicated experiment of blending from pure components.

$T_g$s of PC and PMMA of the first extrudate throughout the investigated composition range. In Table IV we also can see that the $T_g$s of PC and PMMA of the first extrudate are very close to the $T_g$s of PC and PMMA of the repeated extrusion for all the compositions. To test for reversibility, the extrudate compositions were obtained by blending pure components firstly with each other and secondly with previously blended components to the same final compositions (Table V). The $T_g$s of PC and PMMA are compared between the first extrudate and remelted extrudate which have been formulated by adding pure PC to the first extrudate. The values of the $T_g$s of PC and PMMA are seen to be in good agreement for both samples. From these results in Tables IV and V, it can be concluded that the PC/PMMA blend system in the extruder is very close to an equilibrium condition. For solution-cast blends we have redissolved the first cast film of the 0.6 weight fraction of PC in methylene chloride at room temperature [3.0% (w/v) solution]. The $T_g$s of PC and PMMA have been found to be 418.1 and 382.7 K, respectively, for the redissolved solution-cast film, similar to the original values (Table II). To test reversibility, the $T_g$s of PC and PMMA are compared between the first solution-cast film and the redissolved cast film which has been formulated to the same final composition by adding pure PC to the first cast film. The values of the $T_g$s of PC and PMMA are seen to be in good agreement for both samples (Table VI).

**Table V**
**Glass Transition Temperatures ($T_g$) of PC and PMMA Components after Adding Polycarbonate to the First PC/PMMA Extrudates**

| blend[a] | $T_{g1}$, K[b] | $T_{g2}$, K[b] | blend[a] | $T_{g1}$, K[c] | $T_{g2}$, K[c] |
|---|---|---|---|---|---|
| 0.70 | 417.3 | 385.3 | 0.40 → 0.70 | 418.2 | 385.6 |
| 0.60 | 415.4 | 383.7 | 0.30 → 0.60 | 416.8 | 383.8 |
| 0.50 | 414.5 | 383.1 | 0.20 → 0.50 | 415.5 | 383.3 |
| 0.40 | 414.2 | 382.2 | 0.10 → 0.40 | 414.3 | 382.4 |

[a] Blend designation given as overall weight fraction PC in PC/PMMA blend. [b] $T_g$s of the first extrudate. Subscripts 1 and 2 denote PC and PMMA components, respectively. [c] $T_g$s of extrudate after adding pure polycarbonate.

**Table VI**
**Glass Transition Temperatures ($T_g$) of PC and PMMA Components after Adding Polycarbonate to the First Solution-Cast Films of PC/PMMA Blends**

| blend[a] | $T_{g1}$, K[b] | $T_{g2}$, K[b] | blend[a] | $T_{g1}$, K[c] | $T_{g2}$, K[c] |
|---|---|---|---|---|---|
| 0.80 | 420.5 | 384.6 | 0.40 → 0.80 | 420.8 | |
| 0.70 | 419.9 | 383.8 | 0.30 → 0.70 | 419.7 | 383.3 |
| 0.60 | 419.0 | 383.2 | 0.20 → 0.60 | 418.8 | 382.9 |

[a] Blend designation given as overall weight fraction PC in PC/PMMA blend. [b] $T_g$s of the first solution-cast film. Subscripts 1 and 2 denote PC and PMMA components, respectively. [c] $T_g$s of film after adding pure polycarbonate.

For these cases, then, eq 5 and 6 can be used to determine the Flory–Huggins polymer–polymer interaction parameter ($\chi_{12}$) of the mixture without solvent in partially miscible blends. We have calculated the polymer–polymer interaction parameter ($\chi_{12}$) from measured volume fractions for PC/PMMA blend systems (Table III). The volume fraction was obtained from weight fraction divided by densities of each polymer.[51] Values of $m_1 = 48.4$ and $m_2 = 149.3$ were used for PC and PMMA, respectively (Table I), and a repeat unit of polycarbonate has been chosen as the lattice site volume. In Table III, the values of $\chi_{12}$ are compared for different ways of treatment of apparent weight fraction of PC and PMMA components by the Wood, Fox, and Couchman relations. From Table III the values of $\chi_{12}$ have been found to be $0.039 \pm 0.004$ for extruded blends at 250 °C and $0.043 \pm 0.004$ for solution-cast blends at 25 °C, and the values of $\chi_{12}$ are in good agreement among the three different ways of obtaining weight fractions, although this should not be expected in general. For the solution-cast blends case, the value of $\chi_{12}$ has been found to be higher than the value of $\chi_{12}$ of the extruder blends by about 0.0040. This is because the blending method and blending temperature are different for both samples.

## V. Conclusions

In the study of PC/PMMA blends, two $T_g$s have been found, $T_g$(PC), associated with PC-rich regions, and $T_g$(PMMA), associated with PMMA-rich regions, using DSC. In the study of the effect of blend composition on the $T_g$(PC) for PC/PMMA blends, the $T_g$(PC) decreased nearly linearly with an increase of the weight fraction of PMMA. In the $T_g$(PMMA) for PC/PMMA blends, the $T_g$(PMMA) increased linearly with an increase of PC weight fraction.

The specific heat increment ($\Delta C_p$) at $T_g$ for PC decreases linearly with composition of PMMA. The $\Delta C_p$ of PMMA also decreases linearly with composition of PC. This result suggests that some of the PC is dissolving in the PMMA-rich phase and some of the PMMA is dissolving in the PC-rich phase. The apparent weight fraction of the PMMA component dissolved in the PC-rich phase is higher than the apparent weight fraction of the PC component dissolved in the PMMA-rich phase. From the above results of $T_g$ and $\Delta C_p$ with various blend compositions, it can be concluded that PMMA dissolves more in the PC-rich phase than does the PC in the PMMA-rich phase.

In the study of morphology by scanning electron microscopy, phase separation between the PC-rich phase and PMMA-rich phase is more pronounced in the case of the solution-cast blends having PC-rich compositions than in blends having PMMA-rich compositions. This behavior has been found also in screw-extruded PC/PMMA blends. From the microscopy study and the behavior of $T_g$s of the blend with various compositions, it can be concluded that the compatibility increases more in the regions of PMMA-rich composition than in the regions of PC-rich composition.

The blend appears to be near equilibrium under extrusion and solution-casting conditions so that the polymer–polymer interaction parameter of PC/PMMA blends has been calculated and found to be 0.039 ± 0.004 for screw-extruded blends at 250 °C and 0.043 ± 0.004 for solution-cast blends at 25 °C.

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**Registry No.** PC (copolymer), 25037-45-0; PC (SRU), 24936-68-3; PMMA, 9011-14-7.

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