# Phase Behavior of Blends of Polycarbonate with Partially Miscible Polymers

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## Synopsis

Phase behavior of blends of bisphenol A polycarbonate (PC) with polystyrene (PS), poly(styrene-co-acrylonitrile) (SAN), poly(acrylonitrile-butadiene-styrene) (ABS), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT) has been investigated. Blends were prepared by screw extrusion and solution casting with weight fractions of PC in the blends varying from 0.90 to 0.10. From the phase diagram of the blends, it appears that PS, SAN, ABS, PMMA, PET, and PBT dissolve more in the PC-rich phase than does PC in the PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich phases. Also, from the measured glass transition temperature ($T_g$) of the screw-extruded blends and the solution-cast blends, it appears that compatibility increases more in the PS-, SAN-, ABS-, PMMA, PET-, and PBT-rich compositions than in the PC-rich compositions. Composition-dependent values of the polymer–polymer interaction parameters ($g_{12}$) of various blends were calculated and found to be from 0.034 to 0.053 for equal weights of each of the polymers with PC.

## INTRODUCTION

Blends of compatible polymers typically have certain advantages in physical properties.[1-5] However, incompatible blends also have utility. Impact polystyrene is an example of a useful incompatible system, although impact resistance is improved when the incompatible rubber is partially grafted to the rigid polystyrene matrix. In partially miscible blends phase separation occurs, but at the same time a certain number of molecules of A penetrate phase B and vice versa. The interface between the two phases becomes diffuse and good mechanical properties may result. Such blends are often called compatible, although they cannot be considered miscible since they are heterogeneous.[6]

In recent years, many investigators have studied the partially miscible blends of bisphenol A polycarbonate (PC) with polystyrene (PS),[7-13] poly-(styrene-co-acrylonitrile) (SAN),[14] poly(acrylonitrile-butadiene-styrene) (ABS),[15,16] poly(butylene terephthalate) (PBT),[17-20] poly(ethylene terephthalate) (PET),[21-24] polyethylene (PE),[9,25] and polypropylene (PP).[8,26] For blends of PC with poly(methyl methacrylate) (PMMA), Chiou et al.[27] have observed a single glass transition temperature ($T_g$) for the solution blend using tetrahydrofuran (THF) and heptane as a solvent and nonsolvent, respectively. However, they have also observed two $T_g$s both for the melt blend and for the solution blend using methylene chloride as a solvent. Other investigators[28-32] have observed that PC–PMMA blends are partially miscible and reported two

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$T_g$s.[29-30] This discrepancy was due to the so-called solvent effect[33-36] and lower critical-solution temperature (LCST) behavior of the solution blends and melt blends, respectively.[27]

Thermal analysis has shown that for a fully miscible polymer blend a single glass transition will be exhibited between the $T_g$s of the components while for a partially miscible blend the two $T_g$s approach each other but do not become identical.[1,2,7] In our earlier studies of blends of bisphenol-A polycarbonate (PC) with polystyrene (PS)[7] and poly(methyl methacrylate) (PMMA),[30] we have investigated the thermal behavior and the morphology of the blends.[37] We have also calculated a polymer–polymer interaction parameter ($\chi_{12}$) of the blends based on Flory–Huggins theory.[38]

In the present study we are examining the phase behavior of screw-extruded and solution-cast blends of PC with PS, SAN, ABS, PMMA, PET, and PBT by thermal analysis. By using the experimentally determined glass transition temperatures for the various blends, we also determine a composition-dependent value of the polymer–polymer interaction parameters.

## EXPERIMENTAL

### Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the polymers are shown in Table I. Molecular weights for the polymers were measured by gel permeation chromatography (GPC) at 25°C in tetrahydrofuran (THF).[39,40] The PC and the PBT were supplied by General Electric Co., the PS was supplied by Polysciences, Inc., and the SAN containing 23% acrylonitrile was supplied by Monsanto Co. The PMMA was supplied by Scientific Polymer Products, Inc., and the PET was supplied by Aldrich Chemical Co., Inc. The ABS was a medium impact

TABLE I
Characteristics of Polymer Samples Used

| Sample | $\bar{M}_w{}^a$ | $\bar{M}_n{}^a$ | $\bar{M}_w/\bar{M}_n$ | $T_g$ (K)[b] | $T_m$ (K)[b] | $\Delta C_p$ (J/gK)[b] |
|---|---|---|---|---|---|---|
| PC 101[c] | 29,000 | 12,300 | 2.36 | 421.5 | — | 0.220 |
| PC 141[d] | 26,700 | 11,800 | 2.26 | 421.0 | — | 0.220 |
| PS[e] | 237,700 | 98,600 | 2.41 | 373.5 | — | 0.282 |
| PMMA[f] | 83,700 | 37,000 | 2.26 | 380.4 | — | 0.200 |
| SAN[g] | 176,200 | 59,000 | 2.99 | 375.6 | — | 0.345 |
| PBT[h] | | 42,800 | $\simeq 2.00$ | 314.6 | 494.2 | 0.280 |
| PET[i] | | 29,700 | $\simeq 2.00$ | 352.2 | 525.2 | 0.362 |

[a] Measured in our laboratory by GPC.
[b] Measured in our laboratory by DSC.
[c,d,h] Supplied by General Electric Co.
[d] Used only for PBT blends.
[e] Supplied by Polysciences, Inc.
[f] Supplied by Scientific Polymer Products, Inc.
[g] Supplied by Monsanto Co.
[i] Supplied by Aldrich Chemical Co., Inc.

grade of injection moulding resin designated Lustran ABS 440 supplied by Monsanto Co.

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.[41] Methylene chloride, used as solvent for the preparation of cast films, was spectroquality grade, purchased from Matheson, Coleman, and Bell. The 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), used as solvent for the molecular weight of the PET,[42] and used for the preparation of cast films of the PC–PET blends and the PC–PBT blends, was purchased from Aldrich Chemical Co., Inc.

## Blend Preparations

For solution casting, the mixtures of PC–PS, PC–SAN, PC–ABS, and PC–PMMA were dissolved in methylene chloride at 3.0% (w/v) solution. For PC–PET and PC–PBT, the mixtures were dissolved in HFIP at 1.5% (w/v) solution. Blends were cast on glass plates and all films were dried under vacuum for 15 days at room temperature. Cast film thickness was $15 \pm 3$ $\mu$m. To prepare melt blends, all polymers were dried in a vacuum oven at 80°C for 2 days before use. Blends were prepared using a one-half inch (12.7 mm) diameter laboratory scale screw extruder.[7,8] Temperatures of the extruder were set at 230–250°C in each zone (die, die head, and barrel zones) depending on blend composition. For the PC–PET and PC–PBT blends, temperatures of the extruder were set at 275 and 250°C, respectively. In order to minimize hydrolysis, the extruder hopper was connected to a desiccating dryer that pumped warm, dry air through the mixtures.

## Differential Scanning Calorimetry Measurements

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, Model DSC-4, with a Perkin-Elmer thermal analysis data station, Model TADS-101.[7] Blend samples were initially heated from 298 to 453 K at a heating rate of 20 K min$^{-1}$ and cooled immediately at 135 K min$^{-1}$ for the PC–PS, PC–SAN, PC–ABS, and PC–PMMA blends. For the PC–PET blends, samples were heated from 298 to 548 K at a heating rate of 20 K min$^{-1}$ and cooled at 10 K min$^{-1}$. For the PC–PBT blends, samples were heated from 288 to 523 K at a heating rate of 20 K min$^{-1}$ and then quenched in liquid nitrogen. Several cycles of heating and cooling in liquid nitrogen were performed on the extrudates to make the $T_g$ of PBT clearer and to minimize the crystallization of PBT in the blends. Finally the samples were heated with a heating rate of 20 K min$^{-1}$ and cooled immediately with a cooling rate of 320 K min$^{-1}$. The sample size was between 10 and 20 mg using standard aluminum sample pans. A blend of PC and ABS is a three-component system consisting of a PC phase and polybutadiene (PBD) particles in a continuous matrix of SAN polymer so that three glass transition regions are observed. Because the weight fraction of PBD in the overall compositions is very low, however, the magnitude of the PBD transition is very small so that the $T_g$ of PBD is not readily detected by DSC. Therefore, only the $T_g$s of PC and SAN are reported for the PC–ABS blends.

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## Measurement of Extrudate Swell

In order to measure the extrudate swell, extruded round filament was air-quenched and collected in lengths of about 10 cm. After standing at room temperature for more than 1 day, the extrudate diameter was measured with a micrometer at points around the circumference about 1 cm from the leading end of the sample. Extrudate swell was calculated as the ratio of the diameters of the extrudate and capillary die.[7,8]

## RESULTS AND DISCUSSION

### Glass Transition Temperatures of the Blends

In Figures 1–4, we can see the two $T_g$s for the various compositions of the blends of PC with PS, SAN, ABS, PMMA, PET, and PBT. In Figures 1 and 2, the $T_g$ of PC for screw-extruded and solution-cast blends, respectively, is seen to decrease almost linearly with a decrease in the PC weight fraction. From these figures, the decrease of $T_g$(PC) is found to be greatest in the PC–PBT blends. In Figure 1, for a composition of 0.30 weight fraction of PC, the $T_g$(PC) of the screw-extruded blends is seen to decrease by about 8, 7, 11, 7.5, 15, and 25 K with PS, SAN, ABS, PMMA, PET, and PBT, respectively. In
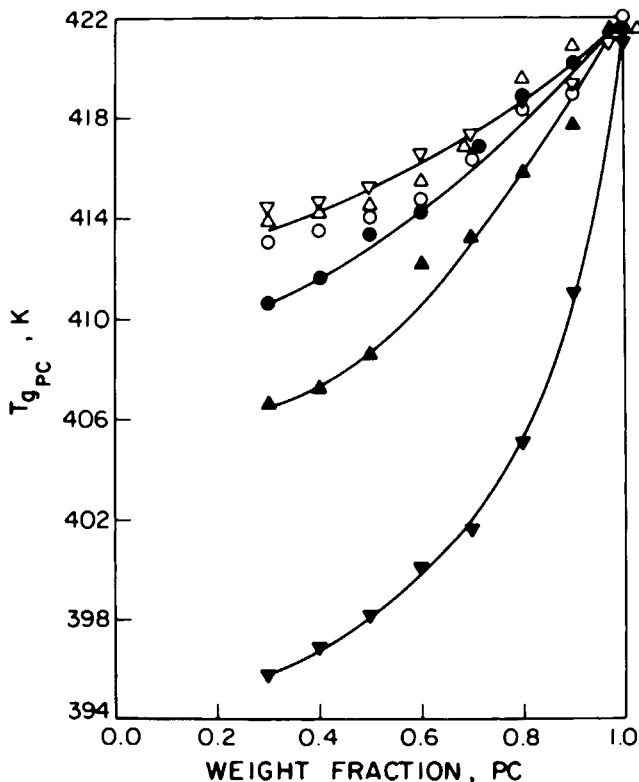


Fig. 1.   Effect of blend composition on the $T_g$(PC) for the blends from screw extrusion: (○) PC–PS; (△) PC–PMMA; (▽) PC–SAN; (●) PC–ABS; (▲) PC–PET; (▼) PC–PBT.
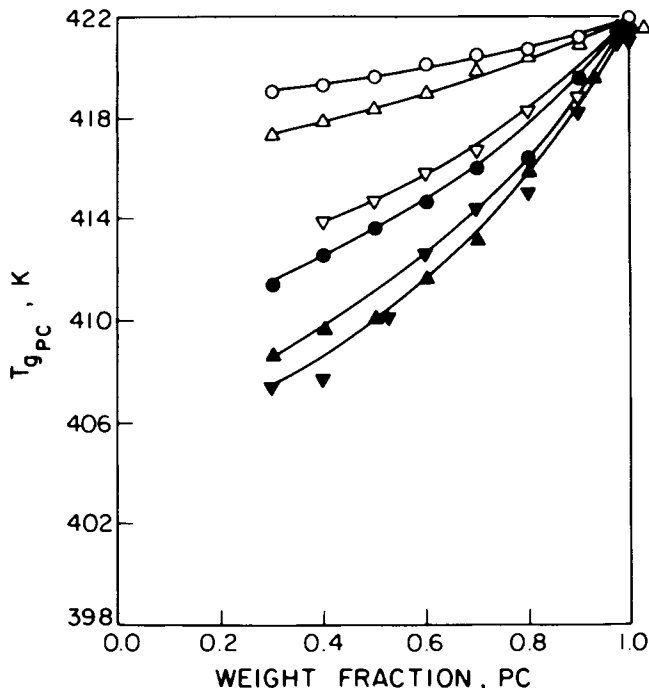
Fig. 2.    Effect of blend composition on the $T_g$(PC) for the blends by solution casting: (○) PC–PS; (△) PC–PMMA; (▽) PC–SAN; (●) PC–ABS; (▲) PC–PET; (▼) PC–PBT.

Figure 2, for a similar composition of 0.30 weight fraction of PC, the $T_g$(PC) of the solution-cast blends is seen to decrease by about 2.5, 7.5, 10, 4, 13, and 13.5 K with PS, SAN, ABS, PMMA, PET, and PBT, respectively. From Figures 1 and 2, the decrease of $T_g$(PC) is seen to be somewhat less in the solution-cast blends than in the extruded blends.

In Figures 3 and 4 are presented the $T_g$s of PS, SAN, ABS, PMMA, PET, and PBT for screw-extruded and solution-cast blends, respectively. From these figures the $T_g$ of PS, SAN, ABS, and PMMA is seen to increase almost linearly with an increase in the PC weight fraction. For the PC–PET and PC–PBT blends, however, we can see that the $T_g$(PET) and the $T_g$(PBT) increase in the regions of 0.10, 0.20, and 0.30 weight fraction PC and then decrease with a further increase in the PC weight fraction.

From Figures 1–4 we can see that the decrease of $T_g$(PC) in PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich compositions is greater than the increase of the $T_g$s of the second polymers in the PC-rich compositions. From this result, it is suggested that compatibility increases more in the regions of PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich compositions than in the regions of PC-rich compositions of the PC–PS, PC–SAN, PC–ABS, PC–PMMA, PC–PET, and PC–PBT blends. We have seen the same results in the scanning electron microscopy study, which has been reported earlier.[7,30] The difference in compatibility between the conjugate phases can be explained by the differences in the flexibility of polymer backbones of the amorphous phase. Therefore, the more flexible polymers SAN, ABS, PET, and PBT diffuse more easily into
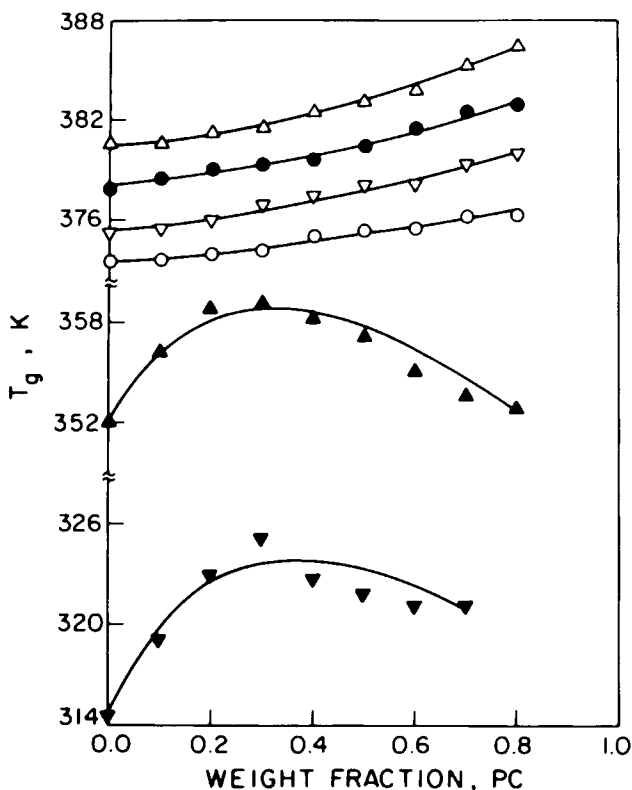
Fig. 3. Effect of blend composition on the other $T_g$s for the blends from screw extrusion: (○) $T_g$(PS); (△) $T_g$(PMMA); (▽) $T_g$(SAN); (●) $T_g$(ABS); (▲) $T_g$(PET); (▼) $T_g$(PBT).

the PC phase than does the less flexible PC into the SAN, ABS, PET, and PBT phases.

Some investigators have observed that transesterification has occurred between PC and polyester and that copolyesters are formed.[20,43,44] Other investigators, however, have observed that no significant interchange reaction between PC and PET has been found.[21,22] In our study of blends of PC and PBT,[45] we have not detected any significant interchange reaction because the $T_g$s of blends after remelting were not found to have been changed significantly.

From the glass transition temperatures of the blends, we can estimate the apparent weight fractions of PC in the PC-rich phase and the PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich phases by the Fox equation,[46] which is used to predict $T_g$s for miscible polymer blends. The Fox equation is

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \tag{1}$$

where $\omega_1$ and $\omega_2$ represent the weight fraction 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. Equation (1) may be rearranged to
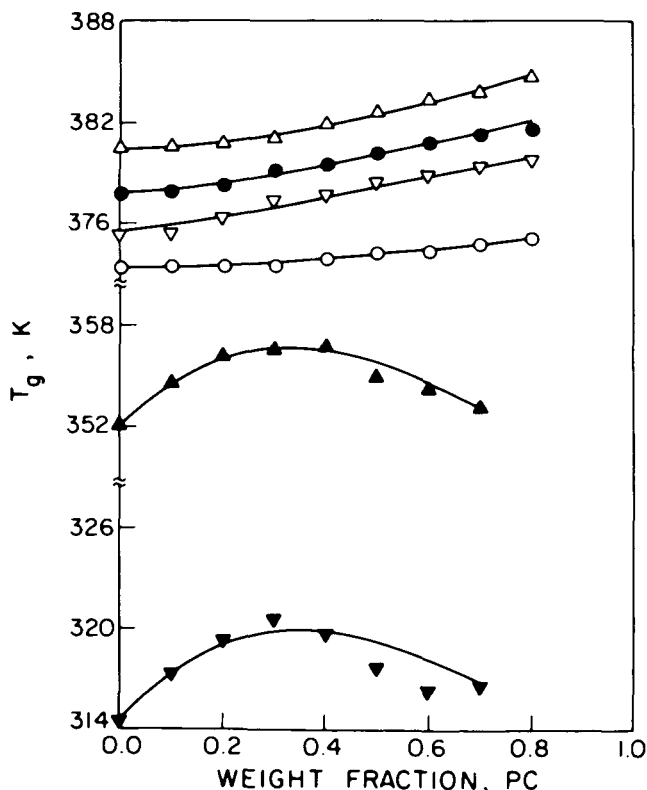
Fig. 4.  Effect of blend composition on the other $T_g$s for the blends by solution casting: (○) $T_g$(PS); (△) $T_g$(PMMA); (▽) $T_g$(SAN); (●) $T_g$(ABS); (▲) $T_g$(PET); (▼) $T_g$(PBT).

$$\omega_1' = \frac{T_{g1}(T_{g1,b} - T_{g2})}{T_{g1,b}(T_{g1} - T_{g2})} \tag{2}$$

where $\omega_1'$ is the apparent weight fraction of polymer 1 in the polymer 1-rich phase, and $T_{g1,b}$ is the observed $T_g$ of polymer 1 in the blends. Similarly eq. (1) may be rearranged to

$$\omega_1'' = \frac{T_{g1}(T_{g2,b} - T_{g2})}{T_{g2,b}(T_{g1} - T_{g2})} \tag{3}$$

where $\omega_1''$ is the apparent weight fraction of polymer 1 in the polymer 2-rich phase, and $T_{g2,b}$ is the observed $T_g$ of polymer 2 in the blends.

Applying eqs. (2) and (3) to the DSC results of $T_g$s in the blends, we have calculated the apparent weight fraction of PC in the PC-rich phase ($\omega_1'$) and the apparent weight fraction of PC in the PS-, SAN-, ABS-, and PMMA-rich phase ($\omega_1''$) for the 0.50 weight fraction of PC (Table II). Using the apparent weight fractions that we have calculated from the glass transition temperatures of the blends, we can then estimate the Flory–Huggins polymer–polymer interaction parameter provided that the system is at equilibrium or nearly so.[7,47]

TABLE II
Apparent Weight Fraction ($\omega$) and Apparent Volume Fraction ($\phi$) of the PC-Rich Phase and
the PS-, SAN-, ABS-, and PMMA-Rich Phase and the Polymer–Polymer Interaction
Parameter ($g_{12}$) of the 0.5 weight fraction PC Blends

| Blend | $T_{g1,b}{}^{a}$ | $T_{g2,b}{}^{a}$ | $\omega_1'{}^{b}$ | $\omega_1''{}^{b}$ | $\phi_1$ | $\phi_1$ | $g_{12}{}^{c}$ | $\chi_{12}{}^{d}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Extruder blending | | | | |
| PC–PS | 414.0 | 375.3 | 0.8591 | 0.0421 | 0.8420 | 0.0370 | 0.036 | 0.041 |
| PC–SAN | 415.3 | 378.0 | 0.8778 | 0.0583 | 0.8658 | 0.0527 | 0.037 | 0.039 |
| PC–ABS | 413.3 | 380.4 | 0.8285 | 0.0659 | 0.8127 | 0.0596 | 0.034 | 0.038 |
| PC–PMMA | 414.5 | 383.1 | 0.8437 | 0.0723 | 0.8403 | 0.0706 | 0.037 | 0.040 |
| | | | | Solution casting | | | | |
| PC–PS | 419.7 | 374.0 | 0.9666 | 0.0117 | 0.9620 | 0.0103 | 0.053 | 0.051 |
| PC–SAN | 414.6 | 378.4 | 0.8638 | 0.0680 | 0.8507 | 0.0614 | 0.035 | 0.038 |
| PC–ABS | 413.6 | 380.2 | 0.8349 | 0.0609 | 0.8194 | 0.0550 | 0.035 | 0.039 |
| PC–PMMA | 418.3 | 382.6 | 0.9292 | 0.0623 | 0.9275 | 0.0519 | 0.043 | 0.044 |

[a] Subscript 1 denotes PC component. $T_g$s are in K.
[b] Single prime denotes PC-rich phase; $\omega_2' = 1 - \omega_1'$ and $\omega_2'' = 1 - \omega_1''$. $\omega_1'$ and $\omega_1''$ are calculated
from eqs. (2) and (3), respectively.
[c] All $g_{12}$s are calculated from eqs. (14) and (15).
[d] All $\chi_{12}$s are calculated from eq. (16) in Ref. 7.

## Phase Behavior of Blends

In Figures 1–4, we have seen that the decrease of $T_g(\text{PC})$ with decreasing
weight fraction of PC is larger than the increase of $T_g$s of PS, SAN, ABS,
PMMA, PET, and PBT with increasing weight fraction of PC. This behavior
can be explained quantitatively in Figures 5–10 in which are presented phase
diagrams of screw-extruded and solution-cast PC–PS, PC–SAN, PC–ABS, PC–
PMMA, PC–PET, and PC–PBT blends, respectively. From Figure 5 we can
see the amount of PS dissolved in the PC-rich phase ($\omega_2'$) is greater than the
amount of PC dissolved in the PS-rich phase ($\omega_1''$). Therefore, the overall weight
fraction of PC-rich phase ($W'$) after blending is slightly greater than the overall
weight fraction of PS-rich phase ($W''$) after blending. We see this behavior in
both the screw-extruded and the solution-casting case. The magnitude of the
amounts of PS and PC dissolved in the PC-rich and the PS-rich phase, re-
spectively, is smaller in the solution-cast blends than in the extruded blends.
The overall weight fraction of PC-rich phase ($W'$) and PS-rich phase ($W''$) is
calculated by the following material balance equations:

$$W_{1T} = \omega_1' W' + \omega_1'' W'' \tag{4}$$

$$W_{2T} = \omega_2' W' + \omega_2'' W'' \tag{5}$$

where $W_{1T}$ and $W_{2T}$ are the overall weight fraction of components 1 and 2
before the blends, respectively, and $\omega_1'$ and $\omega_1''$ are obtained from eqs. (2) and
(3), respectively.

From Figures 6–10, we can see that similar phase behavior is observed for
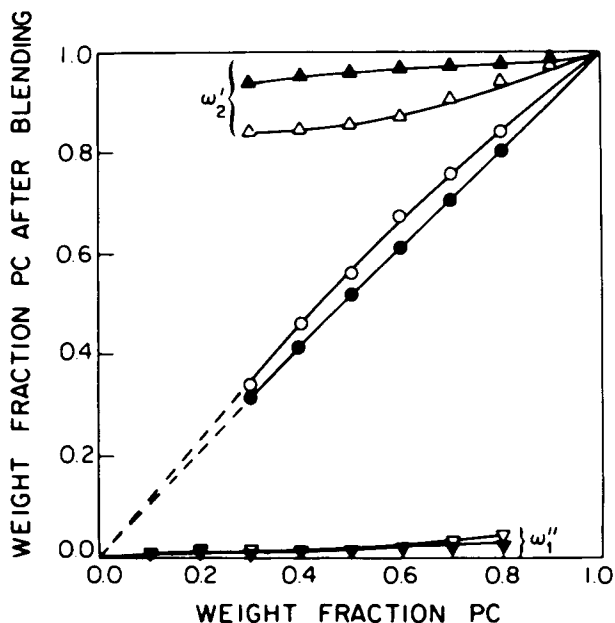the PC–SAN, PC–ABS, PC–PMMA, PC–PET, and PC–PBT blends, respec-

Fig. 5.   Phase diagram of PC–PS blends from screw extrusion ($\bigcirc$, $\triangle$, $\triangledown$) and solution casting ($\bullet$, $\blacktriangle$, $\blacktriangledown$): weight fraction of PC in the PC-rich phase ($\triangle$); weight fraction of PC in the PS-rich phase ($\triangledown$); overall weight fraction of PC-rich phase after blending ($\bigcirc$). For overall compositions of 0.9–0.4 PC, the extruder temperature was 250°C; for 0.3–0.1, 230°C.
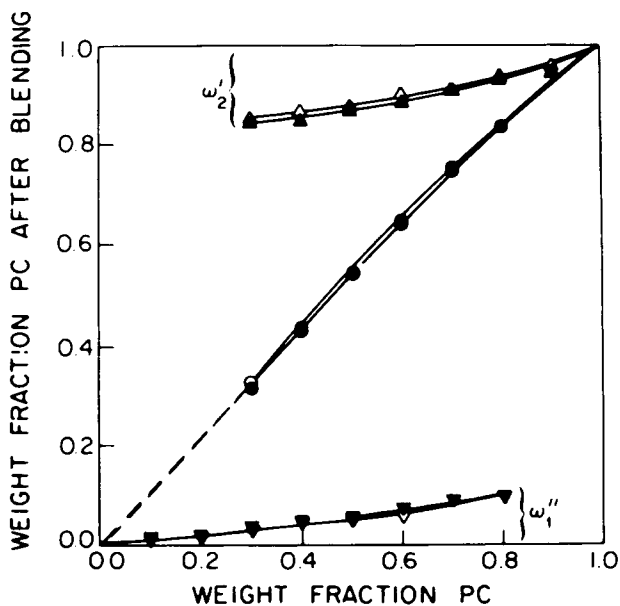


Fig. 6.   Phase diagram of PC–SAN blends from screw extrusion ($\bigcirc$, $\triangle$, $\triangledown$) and solution casting ($\bullet$, $\blacktriangle$, $\blacktriangledown$): weight fraction of PC in the PC-rich phase ($\triangle$); weight fraction of PC in the SAN-rich phase ($\triangledown$); overall weight fraction of PC-rich phase after blending ($\bigcirc$). For overall compositions of 0.9–0.4 PC, the extruder temperature was 250°C; for 0.3–0.1, 230°C.
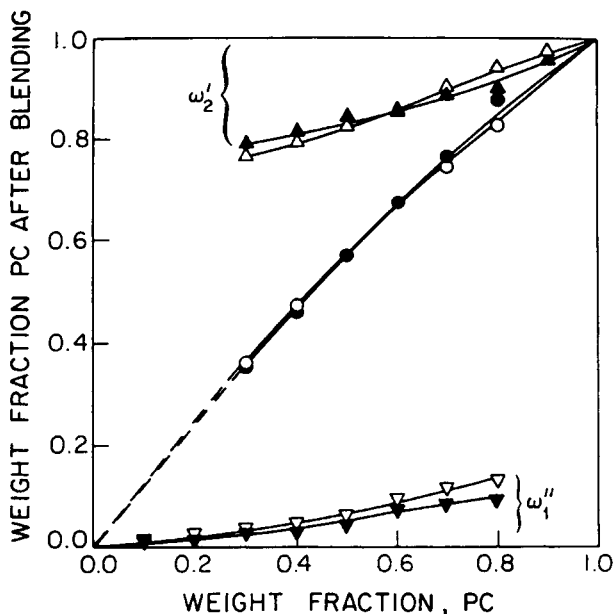
Fig. 7.   Phase diagram of PC–ABS blends from screw extrusion (○, △, ▽) and solution casting (●, ▲, ▼): weight fraction of PC in the PC-rich phase (△); weight fraction of PC in the ABS-rich phase (▽); overall weight fraction of PC-rich phase after blending (○). For overall compositions of 0.9–0.4 PC, the extruder temperature was 250°C; for 0.3–0.1, 230°C.

tively, as we have seen in Figure 5 for PC–PS blends. From these results, it appears that PS, SAN, ABS, PMMA, PET, and PBT dissolve more in the PC-rich phase than does the PC in the PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich phases. In Figure 9, however, the amount of PET in the PC-rich phase $(\omega_2')$ and the amount of PC in the PET-rich phase $(\omega_1'')$ are greater in the PET-rich compositions than in the PC-rich compositions. We can also see this behavior in Figure 10 of the PC–PBT blends.

## Heat Capacity Increments ($\Delta C_p$) at $T_g$s of the Blends

The values of $\Delta C_p$ for PC, PS, SAN, ABS, PMMA, PET, and PBT by screw-extruded blends are presented in Figures 11 and 12. In Figure 11, the $\Delta C_p$ at the $T_g$ of the PC-rich phase is seen to decrease approximately linearly with a decrease in the overall PC weight fraction. In Figure 12, the $\Delta C_p$ at the $T_g$s of the phases rich in PS, SAN, ABS, PMMA, PET, and PBT is seen to decrease with the weight fraction of PC in the blends. The decrease of $\Delta C_p$ of each of the two components is largest in the PC–PBT blends. From Figures 11 and 12, it appears that the reduction in the $\Delta C_p$ of each component results from the dissolution of that component in the conjugate phase.

## Extrudate Swell of Blends

In Figure 13 is presented the extrudate swell ratio over the composition range. The extrudate swell ratio of the PC–SAN, PC–ABS, PC–PET, and PC–PBT blends is compared with PC–(KODAR A-150) blends, which we have also measured in our laboratory.[37] For the PC–PBT blends, we can see that
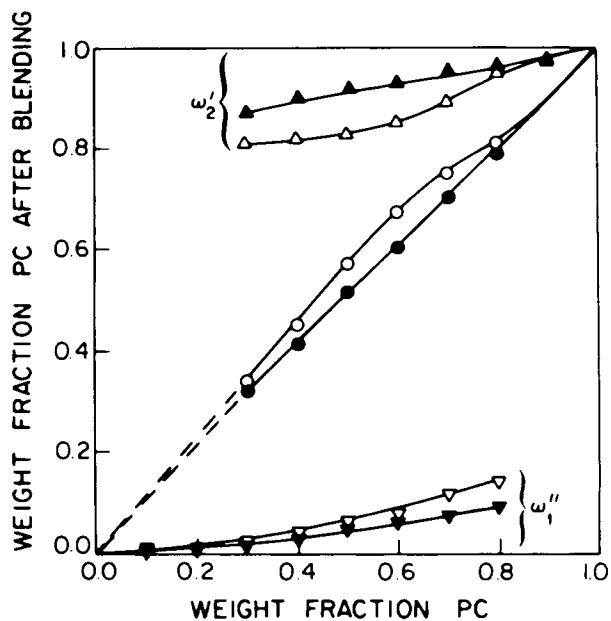
Fig. 8. Phase diagram of PC–PMMA blends from screw extrusion ($\bigcirc$, $\triangle$, $\triangledown$) and solution casting ($\bullet$, $\blacktriangle$, $\blacktriangledown$): weight fraction of PC in the PC-rich phase ($\triangle$); weight fraction of PC in the PMMA-rich phase ($\triangledown$); overall weight fraction of PC-rich phase after blending ($\bigcirc$). For overall compositions of 0.9–0.4 PC, the extruder temperature was 250°C; for 0.3–0.1, 230°C.
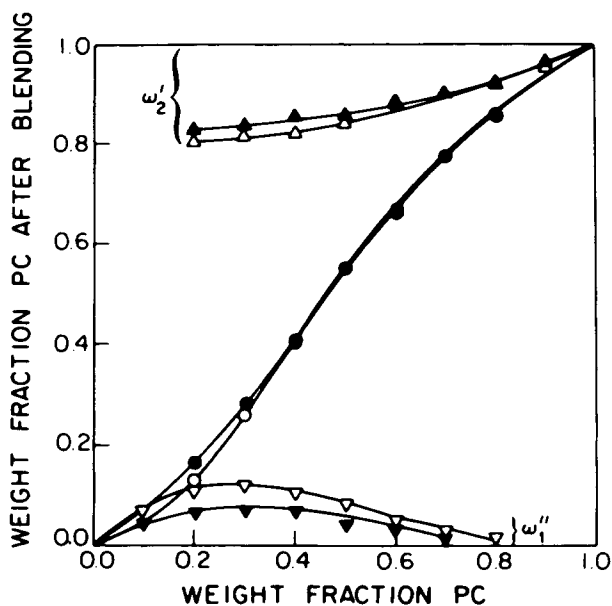


Fig. 9. Phase diagram of PC–PET blends from screw extrusion ($\bigcirc$, $\triangle$, $\triangledown$) and solution casting ($\bullet$, $\blacktriangle$, $\blacktriangledown$): weight fraction of PC in the PC-rich phase ($\triangle$); weight fraction of PC in the PET-rich phase ($\triangledown$); overall weight fraction of PC-rich phase after blending ($\bigcirc$). Extruder temperature was 275°C for all blends.

Fig. 10.    Phase diagram of PC–PBT blends from screw extrusion (○, △, ▽) and solution casting (●, ▲, ▼): weight fraction of PC in the PC-rich phase (△); weight fraction of PC in the PBT-rich phase (▽); overall weight fraction of PC-rich phase after blending (○). Extruder temperature was 250°C for all blends.
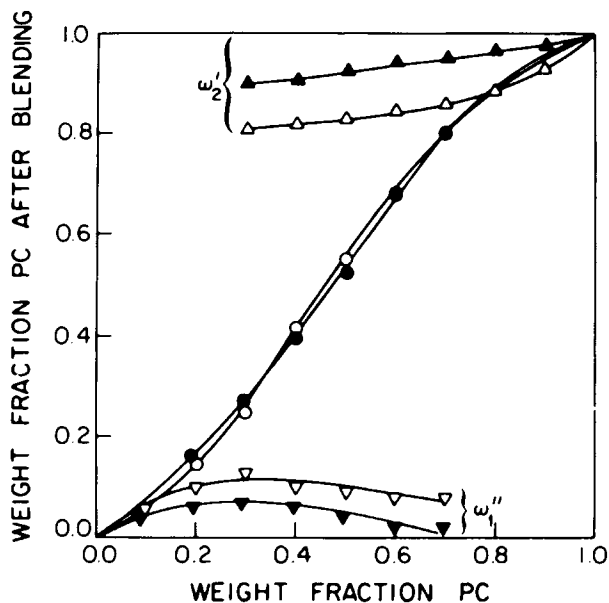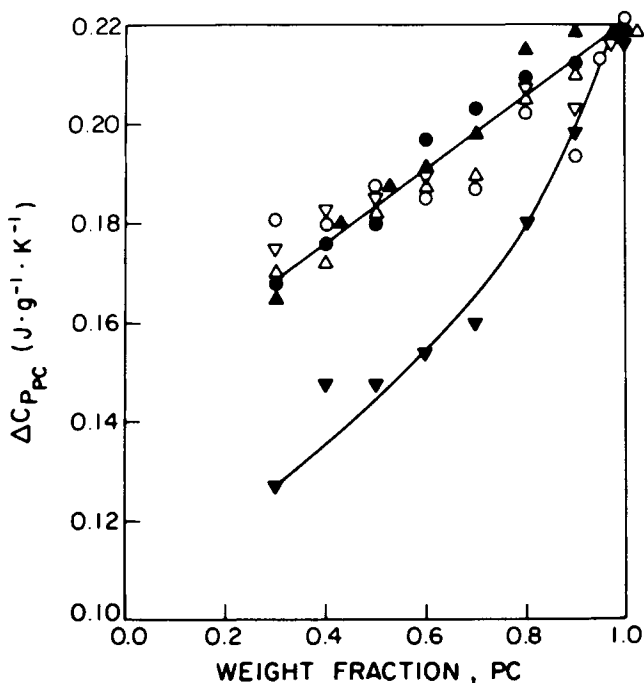


Fig. 11.    Specific heat increment ($\Delta C_p$) at the $T_g$ of PC for the blends from screw extrusion: (○) PC–PS; (△) PC–PMMA; (▽) PC–SAN; (●) PC–ABS; (▲) PC–PET; (▼) PC–PBT.
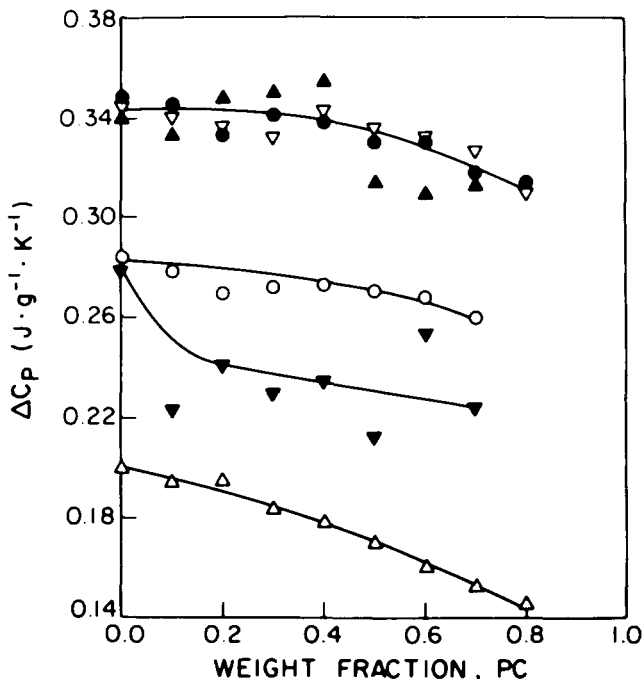
Fig. 12.   Specific heat increment ($\Delta C_p$) at the other $T_g$ of the blends from screw extrusion: (O) $\Delta C_p$(PS); ($\triangle$) $\Delta C_p$(PMMA); ($\nabla$) $\Delta C_p$(SAN); ($\bullet$) $\Delta C_p$(ABS); ($\blacktriangle$) $\Delta C_p$(PET); ($\blacktriangledown$) $\Delta C_p$(PBT).

the extrudate swell ratio in blends of 0.90, 0.20, and 0.10 weight fraction PC appears to be lower and close to that of the unblended polymers. Also for the PC–PET blends, the extrudate swell ratio in blends of 0.30, 0.20, and 0.10 weight fraction PC appears to be close to that of the unblended polymers. From Figure 13, the maximum level of extrudate swell is reached at 0.50 weight fraction of PC in all the blends. It should be kept in mind that the extrudate swell ratio shown in Figure 13 is not an absolute value. The ratio depends on extrusion conditions such as screw speed, extrusion temperature, shear rate, etc. The existence of maximum viscous and elastic properties of two-phase systems at certain composition ratios has been explained by Han.[48]

In all the blends shown here, the viscosities are lower and the elasticities are higher than would be expected if a linear blending rule were to be valid. It is expected that under flow conditions the dispersed phase would dissipate less of the energy than the continuous phase that wets the tube wall. Hence, the dispersed phase would store more recoverable elastic energy than would the continuous phase. Therefore, the total recoverable elastic energy at the die exit would be greater in the two-phase system than in a single-phase system.

The blend of PC and KODAR A-150, a copolyester formed from 1,4-cyclo-hexanedimethanol and a mixture of terephthalic and isophthalic acids, is known to be miscible.[49,50] In Figure 13, we can see that no maximum peak is achieved in the PC–(KODAR A-150) blends, and the extrudate swell is almost the same as that of unblended polymers. These results support the conclusion that compatibility increases more in the regions of the SAN-, ABS-, PET-, and PBT-rich compositions than in the regions of the PC-rich composition of the PC–SAN, PC–ABS, PC–PET, and PC–PBT blends.
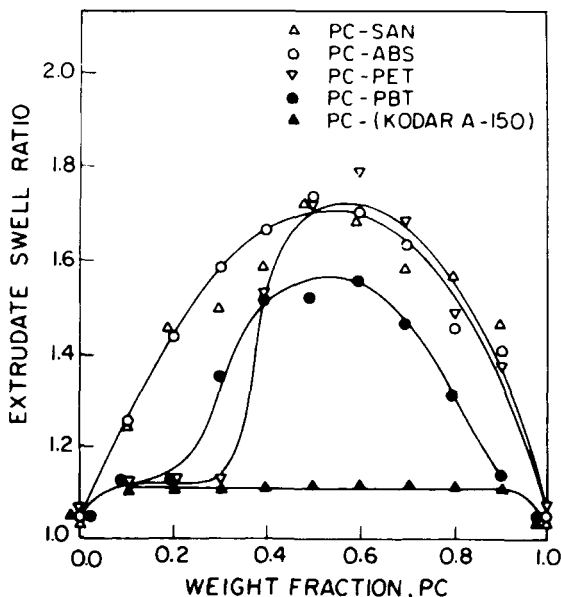
Fig. 13. Extrudate swell ratios for different weight compositions: PC–SAN blends (△); PC–ABS blends (○); PC–PET blends (▽); PC–PBT blends (●); PC–(KODAR A-150) blends (▲).

## Polymer–Polymer Interaction Parameter

Let us consider a mixture of two polymers in the absence of solvent and assume that equilibrium is reached. From the Flory–Huggins theory,[38] the Gibbs' free energy of mixing, $\Delta G_m$, for a system consisting of two polymers at equilibrium can be written as follows[51]:

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \phi_2 + \chi_{12} \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \tag{6}$$

where $R$ is the universal gas constant, $T$ is the system temperature in degrees Kelvin, $n_i$ is the number of moles of the $i$th component in the mixture, and $\phi_i$ is $m_i n_i / (m_i n_i + m_j n_j)$, 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.[7,51]

The chemical potential of mixing of component $i$, as discussed by Tompa,[52] is obtained as the partial derivative of eq. (6) with respect to $n_i$:

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + \left(1 + \frac{m_1}{m_2}\right) \phi_2 + m_1 \chi_{12} \phi_2^2 \tag{7}$$

$$\frac{\Delta \mu_2}{RT} = \ln \phi_2 + \left(1 + \frac{m_2}{m_1}\right) \phi_1 + m_2 \chi_{12} \phi_1^2 \tag{8}$$

Equations (7) and (8) are not mathematically independent but are equivalent to eqs. (1a) and (1b) of Scott,[51] respectively. We may obtain the critical con-

dition by the familiar requirements that the first and second derivatives of either eq. (7) and (8) be zero.[51] Solving such equations with respect to $\phi_i$, we find

$$(\chi_{12})_c = \tfrac{1}{2}(m_1^{-1/2} + m_2^{-1/2})^2 \tag{9}$$

Several assumptions are made in the theory discussed here. The most important assumptions are that the $\chi_{12}$ is taken to be constant and that both components of the blends are considered to be monodisperse. To examine $\chi_{12}$ as a function of composition, we can treat the chemical potential equation, eq. (6), with a function of $\chi_{12}$ such that $\chi_{12}$ is a linear function to $\phi_2$. Then we can rewrite eq. (6) as follows:

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + g_{12}(\phi_2)\phi_1\phi_2(m_1 n_1 + m_2 n_2) \tag{10}$$

where $g_{12}(\phi_2) = g_0 + g_1\phi_2$ is employed.[53,54] Equation (10), then, becomes

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 (g_0 + g_1\phi_2)\phi_1\phi_2(m_1 n_1 + m_2 n_2) \tag{11}$$

Partial differentiation of eq. (11) with respect to $n_i$ gives

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right)\phi_2 + m_1 g_0 \phi_2^2 + m_1 g_1 (1 - 2\phi_1)\phi_2^2 \tag{12}$$

$$\frac{\Delta \mu_2}{RT} = \ln \phi_2 + \left(1 - \frac{m_2}{m_1}\right)\phi_1 + m_2 g_0 \phi_1^2 + 2m_2 g_1 \phi_1^2 \phi_2 \tag{13}$$

At equilibrium the chemical potential of each component is the same in both phases. Denoting the two conjugate phases by single and double primes, we have $\Delta \mu_1' = \Delta \mu_1''$ and $\Delta \mu_2' = \Delta \mu_2''$. Then, eq. (12) will give

$$\ln\left(\frac{\phi_1'}{\phi_1''}\right) + \left(1 - \frac{m_1}{m_2}\right)(\phi_2' - \phi_2'') + m_1 g_0 (\phi_2'^2 - \phi_2''^2) + m_1 g_1$$

$$\times [(1 - 2\phi_2')\phi_2'^2 - (1 - 2\phi_1'')\phi_2''^2] = 0 \tag{14}$$

Similarly eq. (13) yields

$$\ln\left(\frac{\phi_2'}{\phi_2''}\right) + \left(1 - \frac{m_2}{m_1}\right)(\phi_1' - \phi_1'') + m_2 g_0 (\phi_1'^2 - \phi_1''^2)$$

$$+ 2m_2 g_1 (\phi_1'^2\phi_2' - \phi_1''^2\phi_2'') = 0 \tag{15}$$

Using eqs. (14) and (15), we can get $g_0$ and $g_1$ so that the composition-dependent polymer–polymer interaction parameter, $g_{12} = g_0 + g_1\phi_2$, is determined. Here $\phi_2$ is defined as the overall volume fraction of polymer 2 in the blends. From eqs. (14) and (15), we have calculated the $g_{12}$ of the PC–PS, PC–SAN, and PC–ABS blends for 0.50 weight fraction PC (Table II). A value for $m_1$ of 48.4 was used for PC, and for $m_2$, values of 443.4, 285.6, and 285.6 were used for PS, SAN, and ABS, respectively (Table I). A repeat unit of PC was chosen as a lattice site volume. We have assumed that the molecular weight of SAN in the PC–ABS blends is the same as that used in the PC–SAN blends.

In Table II, the values of $g_{12}$ and $\chi_{12}$ are compared for the PC–PS, PC–SAN, and PC–ABS extruded blends and the solution-cast blends with 0.50 weight fraction PC. The values of $g_{12}$ are very similar among the three different blends. However, for the PC–PS blends, the values of $g_{12}$ have been found to be higher in the solution-cast blends than in the melt blends. For the PC–SAN and PC–ABS blends, the values of $g_{12}$ are found to be similar between extruded and solution-cast blends. This behavior might be explained such that the copolymers of SAN and ABS behaved differently from the homopolymer of PS in the solution blends, which can be explained by the "solvent" effect.[34,35] It is rather difficult to get the $g_{12}$ value for the PC–ABS blends, but we have ignored the segmental interactions between the PC and the polybutadiene (PBD), and treated the system as if it were PC–SAN since the butadiene concentration in the ABS was 10–15%.

From eq. (9) we can also determine the critical value of $\chi_{12}$, $(\chi_{12})_c$, and it has been found to be 0.018 for the PC–PS blends and 0.020 for the PC–SAN blends. It can be concluded that if $\chi_{12} < (\chi_{12})_c$ is observed, then the polymers are compatible with each other and there will be no phase separation. If $\chi_{12} > (\chi_{12})_c$ is observed in the blends, phase separation will occur.[55] The values shown in Table II are greater than the values of $(\chi_{12})_c$, indicating the blends of PC and PS, SAN, and ABS are immiscible.

A model calculation of $g_{12}$ using eqs. (14) and (15) is shown in Figure 14. In Figure 14, the degree of polymerization of component 1 ($m_1$) and component 2 ($m_2$) is set equal, and the apparent volume fraction of component 1 in the component 1-rich phase ($\phi_1'$) is set equal to the apparent volume fraction of component 2 in the component 2-rich phase ($\phi_2''$). From Figure 14 we can see that the $g_{12}$ is decreasing with decrease of $\phi_1'$ at a certain degree of polymerization. A sample calculation is shown in Table III for the 0.50 weight fraction PC of the blends. In Table III we can see that the value of $g_{12}$ is lower in blend B than in blend A. This difference is because the amount of component 2 dissolved in the component 1-rich phase ($\phi_2'$) is greater in blend B than in blend A. The values of $g_{12}$ and $\chi_{12}$ are found to be the same if $m_1 = m_2$ and $\phi_1' = \phi_2''$ (Table III). Also from Table III, the value of $g_1$ is found to be zero so that the dependence on composition ($\phi_2$) would be negligible when $m_1 = m_2$ and $\phi_1' = \phi_2''$ are observed. From these results we can say that the values of the polymer–polymer interaction parameter depend on the degree of polymerization ($m_i$) as well as the apparent volume fraction ($\phi_i$) dissolved in each phase.

## CONCLUSIONS

In the study of the effect blend composition on the $T_{g1}$ and $T_{g2}$ of the blends of PC with PS, SAN, ABS, PMMA, PET, and PBT, a decrease of $T_{g1}$ and an
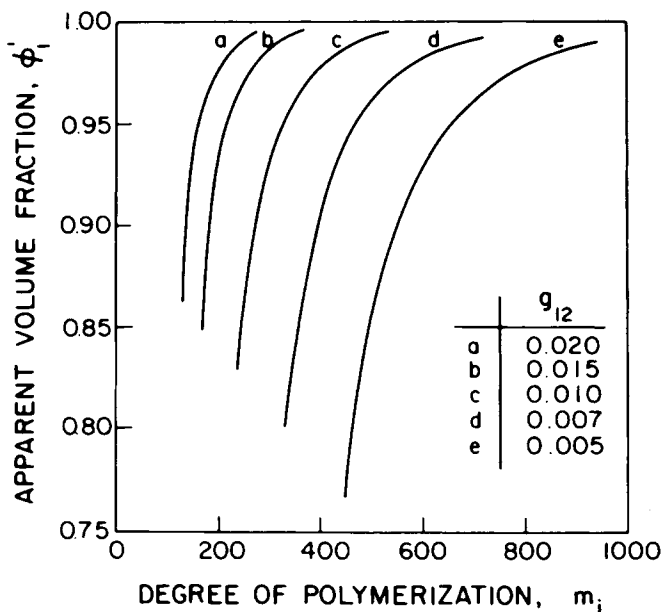
Fig. 14.  Model calculation of polymer–polymer interaction parameter ($g_{12}$) with degree of polymerization ($m_i$) and apparent volume fraction ($\phi_i$).

increase of $T_{g2}$ in the blends has been found for all the blend systems. This result leads to the conclusion that partial miscibility does exist between the two component polymers.

From the results of the $T_g$s, and $\Delta C_p$, and the phase diagrams of the blends, it can be concluded that PS, SAN, ABS, PMMA, PET, and PBT dissolve more in the PC-rich phase than does the PC in the PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich phases. Also, from the behavior of $T_g$s of the blends, it can be concluded that compatibility increases more in the PS-, SAN-, ABS-, PMMA-, PET-, and PBT-rich compositions than in the PC-rich compositions.

Using the apparent volume fractions dissolved in each phase, the polymer–polymer interaction parameter of PC–PS, PC–SAN, and PC–ABS blends with 0.50 weight fraction PC has been calculated based on Flory–Huggins theory

TABLE III
Model Calculation of the Polymer–Polymer Interaction Parameter, $g_{12} = g_0 + \phi_2 g_1$

| Blend | $\phi_2$[a] | $m_1 = m_2$[b] | $\phi_1' = \phi_2''$[c] | $\phi_2' = \phi_1''$[c] | $g_0$ | $g_1$ | $g_{12}$[d] | $\chi_{12}$[e] |
|-------|------|-----------|-------------|-------------|--------|-------|---------|----------|
| A | 0.5 | 200 | 0.97 | 0.03 | 0.0185 | 0.00 | 0.0185 | 0.0185 |
| B | 0.5 | 200 | 0.90 | 0.10 | 0.0137 | 0.00 | 0.0137 | 0.0137 |

[a] Overall volume fraction of component 2 before blending.

[b] Subscripts 1 and 2 denote component 1 and component 2, respectively.

[c] Single prime and double prime denote component 1-rich phase and component 2-rich phase, respectively.

[d] $g_{12}$s are calculated from eqs. (14) and (15).

[e] $\chi_{12}$s are calculated from eq. (16) in Ref. 7.

and found to be from 0.034 to 0.053 for extruded blends and solution-cast blends. By model calculation of the polymer–polymer interaction parameter, the value of $g_{12}$ has been found to be similar to the value of $\chi_{12}$, which is shown to be constant when the degrees of polymerization ($m_i$) of both components are close to each other or the same.

From the measurement of extrudate swell ratio, the maximum level of extrudate swell is reached at 0.5 weight fraction of PC in all the blends. The extrudate swell ratio of the blends of PC–PET for 0.1, 0.2, and 0.3 weight fraction PC, and the blends of PC–PBT for 0.1, 0.2, and 0.9 weight fraction PC was observed to be low and almost the same as the swell ratio of blends of PC–(KODAR A-150). From these results, it is concluded that these PC–PET and PC–PBT blends are mechanically compatible but not thermodynamically miscible.

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