

# The Phase Behavior of Ternary Blends Containing Polycarbonate, Phenoxy, and Polycaprolactone

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## Synopsis

Ternary blends comprising bisphenol-A polycarbonate (PC), the polyhydroxyether of bisphenol-A (Phenoxy), and poly( $\epsilon$ -caprolactone) (PCL) were found to be generally miscible at PCL levels greater than 60% by weight and to show multiple amorphous phases at lower PCL levels. The melting point depression of PCL in the miscible region of the ternary and in the miscible binary blends with PC and Phenoxy was examined to obtain the enthalpic interaction parameters,  $B_{ij}$ , for each of the three binary interactions. The parameters associated with the miscible binary blends were negative, as expected, and indicated that PCL interacts more exothermically with Phenoxy than with PC. The parameter associated with the Phenoxy/PC interaction was strongly positive as expected from the complete immiscibility shown by these materials. The interaction parameters were used to calculate the locus of compositions for which the heat of mixing is zero. The locus was found to agree well with the observed boundary between miscible and multiphase behavior in the ternary. This suggests that the phase behavior of ternary blends is largely determined by the same enthalpic considerations known to govern the phase behavior of binary blends.

## INTRODUCTION

The phase behavior of binary polymer blends has been a topic of great academic and industrial interest over the last 15 years.<sup>1-6</sup> This interest arises primarily from the profound influence of phase behavior on the rheological and mechanical properties of the blend and from the practical need to develop blend materials with appropriate properties. The most successful approach to understanding the formation of single amorphous phase, miscible, binary blends has been to recognize the predominant influence of the heat of mixing contribution to the thermodynamics which govern the phase formation process.<sup>1-6</sup> This approach has shown that miscible or partially miscible binary blends form when the heat of mixing between the blend components is exothermic, negative, and this approach, when applied to mixtures of low molecular weight analogs, has led to the understanding and discovery of a variety of new miscible binary polymer blends.<sup>7-12</sup>

Only two miscible ternary polymer blends were reported prior to 1985.<sup>13,14</sup> Consequently, there have been very little data with which to develop and apply thermodynamic relationships for understanding the phase behavior of multicomponent blends. Seven new, miscible, ternary polymer blends were reported in 1986.<sup>15-18</sup> Most of these were discovered by using the known miscibility of polymer binaries to find polymeric solvents for solubilizing an

immiscible binary: That is, polymers A and B may not be miscible; however, each is miscible with polymer C, and addition of sufficient C to A and B leads to a miscible ternary composition. A thermodynamic analysis was attempted for one of these ternaries,<sup>15</sup> PC/SAN/PCL, in which the melting point depression of the PCL in the miscible region of the ternary and in the miscible binary solutions with PC and SAN, respectively, was used to evaluate the binary interaction parameters associated with the heat of mixing. These parameters were then used to predict the locus of ternary compositions which separate miscible from multiphase behavior. Unfortunately, the thermodynamic correlations were somewhat inconclusive because the precision associated with the measurement of the small interaction parameters from melting point depression in this system was poor and because the observed boundary between multiphase and single phase behavior was quite different in shape from that predicted by the heat of mixing model.

This paper presents a similar attempt to use the binary interaction parameters, obtained from PCL melting point depression, to predict the boundary between miscible and multiphase behavior. In contrast to the previous study, the precision of the interaction parameters is better, a much better prediction of the boundary is obtained, and the approximation that  $\Delta H_{\text{mix}} = 0$  defines the miscibility boundary in a ternary system seems better justified.

## MATERIALS AND PROCEDURES

The polymers used in this study were bisphenol-A polycarbonate (PC), supplied by the Dow Chemical Company under the designation XP-73009.00; the polyhydroxyether of bisphenol-A, Phenoxy, supplied by the Union Carbide Corporation under the trade name Phenoxy PKHH; and poly( $\epsilon$ -caprolactone) (PCL) also supplied by the Union Carbide Corporation under the trade name PCL-700. The thermal properties and molecular weights of these polymers are summarized in Table I.

All polymer ingredients were carefully dried before use. The PC and Phenoxy components were typically dried in an air oven at 100°C for 24 h, and the PCL was dried at 50°C for 2 days prior to blend preparation. Depending on the composition, binary and ternary polymer blends were prepared either by melt blending with a Brabender Plasticorder or by casting from solutions of the polymers with an appropriate solvent. For the melt

TABLE I  
Summary of Polymer Properties

Polymer	Abbreviation	Mol wt	$T_g$ (°C)	$T_m$ (°C)
Polycarbonate (molding grade)	PC	—	145	230
Polyhydroxy ether of bisphenol-A	Phenoxy	$M_n = 23,000$ $M_w = 80,000^4$	96	—
Poly( $\epsilon$ -caprolactone)	PCL	$M_n = 15,500$ $M_w = 40,500^4$	-69	57

mixing process, approximately 50 cc of the dried polymers were added to the preheated Brabender mixing head at 180–230°C and allowed to flux for 10 min at 60 rpm. Solution-cast films were prepared by dissolving 2 g of the dried polymers in 20 mL of a mutual solvent (methylene chloride or tetrahydrofuran). The solutions were poured into aluminum pans, covered with perforated foil, and allowed to dry at ambient temperature in a fume hood for a minimum of 24 h. Residual solvent was removed *in vacuo* at 90–100°C for an additional 48 h.

Glass transition temperatures were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter, equipped with a mechanical refrigeration assembly. The DSC-2 was fitted with liquid nitrogen cooling when low temperature analysis of PCL-rich blends was desired. Glass transition temperatures were measured at a 20°C/min heating rate after quenching at 320°C/min from the melted state. In all cases, the glass transition temperature was taken as the onset of the endothermic transition.

PCL melting temperatures were obtained by first heating the samples in the DSC-2 at 10°C/min from room temperature to 87°C, annealing at this temperature for 5 min to insure complete melting of the PCL, and then quenching at 320°C/min to 27°C. The samples were maintained at this temperature for 30 min in order to obtain consistent levels of PCL crystallinity.<sup>19</sup> PCL melting temperatures were then measured at 10°C/min on the second heating pass.

Blend clarity as a function of temperature was studied by placing a sample of the blend between two glass slides and heating it with a hot plate at 2–3°C/min.<sup>20</sup> Changes in opacity related to melting transitions were easily seen by this technique.

## BINARY BLENDS

Although the main intent of this work is to examine the phase behavior of ternary PC/Phenoxy/PCL blends, a thorough understanding of the three binary blends associated with this ternary system is necessary before conclusions concerning the ternary blends can be drawn. The discussion, below, summarizes behavior of the PC/Phenoxy, PC/PCL, and Phenoxy/PCL binary blends important to understanding that of the ternary.

**PC / Phenoxy Blends.** These blends are immiscible and form two distinct phases when cast from solution or when melt-blended. DSC analysis shows the presence of two distinct glass transition temperatures  $T_g$ 's, corresponding to those of the pure components. As indicated by Figure 1, the  $T_g$  of each material is virtually independent of blend composition. This suggests nearly complete immiscibility of PC and Phenoxy. In addition, PC/Phenoxy samples, which were slightly opaque at room temperature, retained their opacity upon heating above 250°C with a hot plate. This observation confirms that opacity in the binary is simply due to the presence of multiple amorphous phases.

**Binary Blends with PCL.** PCL has previously been reported to form miscible binary blends with both PC<sup>21</sup> and Phenoxy.<sup>22,23</sup> These blends show the monotonic  $T_g$  vs. composition behavior expected for miscible blends (Figs. 2 and 3).

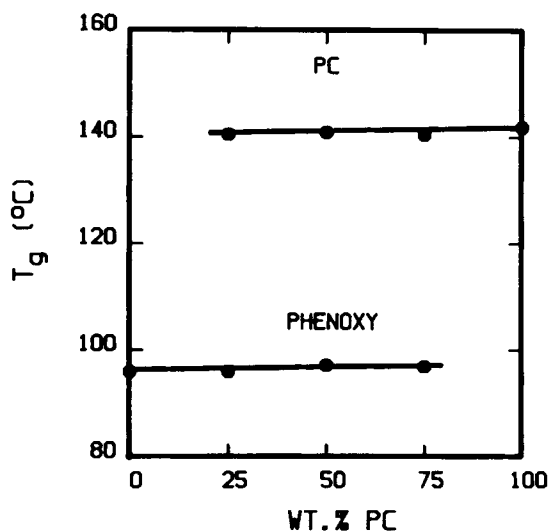


Fig. 1. Glass transition behavior of PC/phenoxy blends.

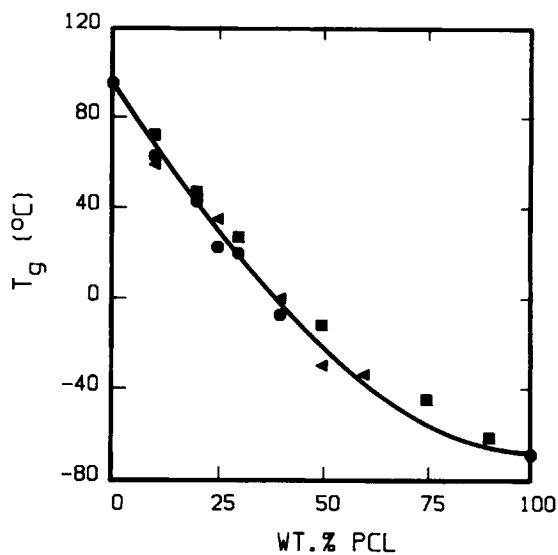


Fig. 2. Composition dependence of the glass transition in miscible phenoxy/PCL blends: (●) this work; (▲) Harris et al.<sup>9</sup>; (■) Brode and Koleske.<sup>22</sup>

The PC/PCL blends prepared in this work and by Cruz et al.<sup>21</sup> were opaque due to solvent-induced and PCL-induced crystallization of the PC, PCL crystallization, or both of these factors. Heating the blends above the melting point of PC (about 230°C) caused the PC crystals to melt and the blends to become transparent. Further heating caused opacity to return as the result of crossing the lower critical solution temperature, LCST, between 260 and 265°C.<sup>21</sup> On the other hand, Phenoxy/PCL blends containing less than 40 wt % PCL were transparent, but increasing amounts of PCL rendered the blends

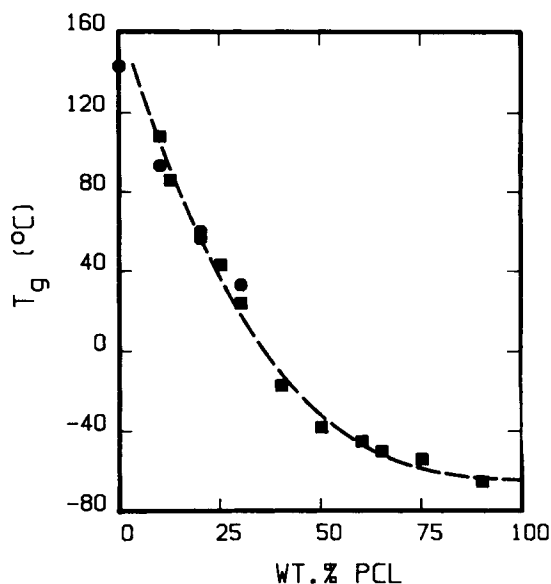


Fig. 3. Composition dependence of the glass transition in miscible PC/PCL blends: (●) this work; (■) Cruz. et al.<sup>21</sup>

opaque due to PCL crystallization. Optical studies indicate that there is no LCST for this system below the decomposition temperatures of the polymers.<sup>23</sup>

The driving force for PC/PCL miscibility is an exothermic heat of mixing which results from interaction between the aromatic carbonate of PC and the carbonyl group of PCL.<sup>21</sup> The heat of mixing parameter  $B$  associated with the equation,

$$\Delta H_{\text{mix}} = V \sum_i \sum_{j \neq i} B_{ij} \Phi_i \Phi_j \quad (1)$$

where  $\Delta H_{\text{mix}}$  is the heat of mixing,  $V$  is the system volume, and  $\Phi_i$  is the volume fraction of component  $i$  in the blend, has been previously found to be  $-0.39$  cal/cc from studies of the melting point depression of PCL in PC.<sup>15</sup> In contrast, while it has been shown that there is also a relatively small exothermic interaction between the aromatic group of Phenoxy with the carbonyl group of PCL,<sup>9</sup> the miscibility of the PCL/Phenoxy system is mostly the result of specific interactions between the hydroxyl groups of Phenoxy (proton donor) with PCL carbonyl groups (proton acceptor).<sup>9,24</sup> The interaction parameter  $B$  calculated from PCL melting point depression in Phenoxy has been found to be  $-2.41$  cal/cc.<sup>23</sup> Comparison of this value with that for the PC/PCL system suggests that PCL will tend to partition more strongly in Phenoxy than in PC in the ternary blend.

### TERNARY BLENDS

PC/Phenoxy/PCL ternary blends covering the full range of compositions were prepared by the solution casting method described above. Blends containing less than 60 wt % PCL had two distinct and separate phases: an

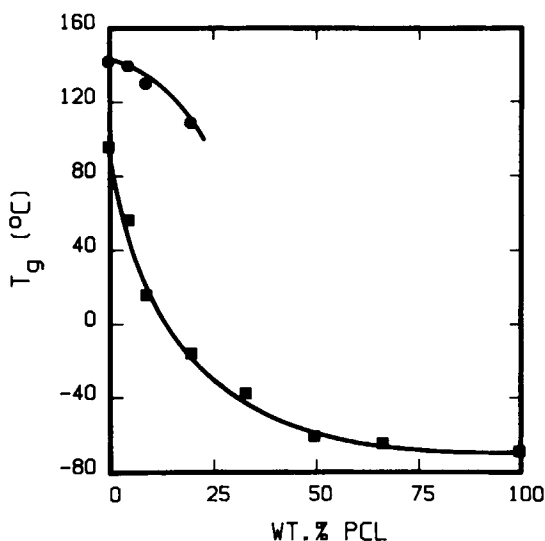


Fig. 4. Effect of PCL addition on the glass transition behavior of ternary blends containing a PC/phenoxy ratio of 3: (●) PC-rich phase; (■) Phenoxy-rich phase.

opaque PC-rich phase (opacity due to PC crystallization) and a relatively transparent Phenoxy-rich phase. The remaining solution cast blends appeared to be single phase, yet were opaque as a result of either PC or PCL crystallization. PC/Phenoxy/PCL ternary blends containing less than 60 wt % PCL were also prepared by melt mixing in order to eliminate the gross phase separation problems associated with the solution casting process. These blends were cloudy at the mixing temperature and remained cloudy upon cooling to room temperature.

Glass transition temperatures of the ternary PC/Phenoxy/PCL blends are shown in Figs. 4–6 for several PC/Phenoxy ratios. Blends containing less than 30 wt % PCL had two distinct  $T_g$ 's which appear to correspond to a PC-rich phase containing mostly PC and PCL and a Phenoxy-rich phase containing mostly Phenoxy and PCL. The  $T_g$ 's of these two phases are depressed from those of the pure components by the plasticizing action of PCL, and the  $T_g$  of the Phenoxy-rich phase is depressed considerably more than that of the PC-rich phase at any particular overall PCL content in the blend. This difference suggests that Phenoxy has a greater affinity for PCL than does PC, a result which is qualitatively consistent with the more negative  $B$  parameter for the Phenoxy/PCL interaction.

As the PCL content is increased, the  $T_g$  of the Phenoxy-rich phase continues to monotonically decline, while that of the PC-rich phase first declines then becomes nonobservable as the PCL content in the blend becomes greater than about 40% by weight. The point at which this glass transition temperature is no longer seen corresponds to the onset of PCL crystallization exotherms and melting endotherms in the DSC traces. It seems reasonable to conclude that these PCL exotherms and endotherms overlap the temperature region corresponding to the  $T_g$  of the PC-rich phase. The PCL crystallization peaks which occur on heating in the DSC-2 can be eliminated by allowing the PCL to

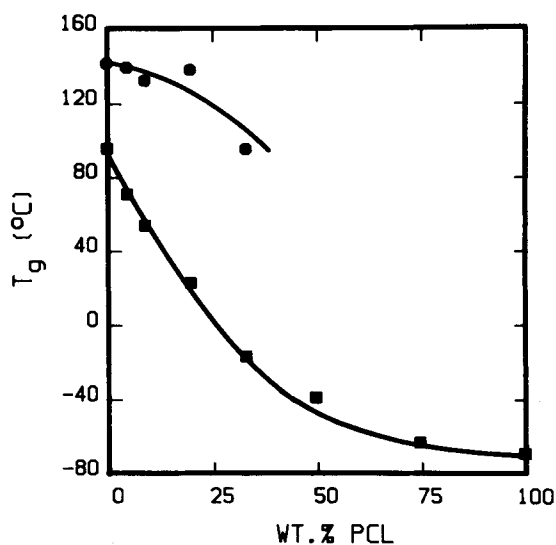


Fig. 5. Effect of PCL addition on the glass transition behavior of ternary blends containing a PC/phenoxy ratio of 1: (●) PC-rich phase; (■) Phenoxy-rich phase.

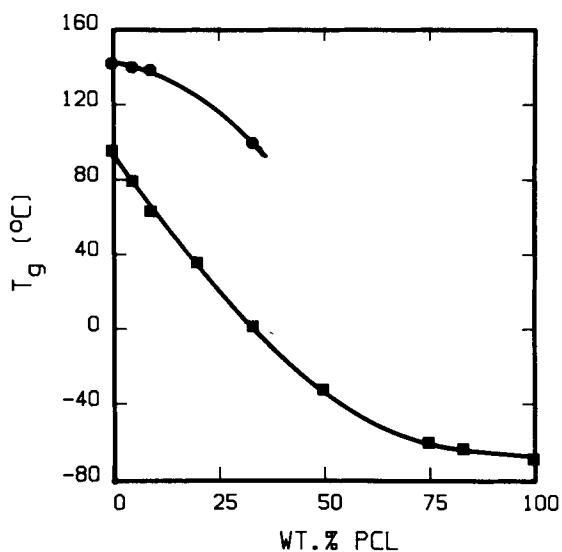


Fig. 6. Effect of PCL addition on the glass transition behavior of ternary blends containing a PC/phenoxy ratio of 1/3: (●) PC-rich phase; (■) Phenoxy-rich phase.

crystallize before a DSC run is made. The resulting DSC traces show an increase in the  $T_g$  of the Phenoxy-rich phase due to the loss of PCL from this phase; yet in no case is the glass transition temperature of the PC-rich phase visible in the DSC traces when the PCL content in the blend is greater than 40% by weight. The shifts toward higher  $T_g$  of the Phenoxy-rich phase when PCL crystallization is developed suggest that PCL is crystallizing primarily from this phase. This result is consistent with studies of crystallization of crystallizable components from binary blends which suggest that crystalliza-

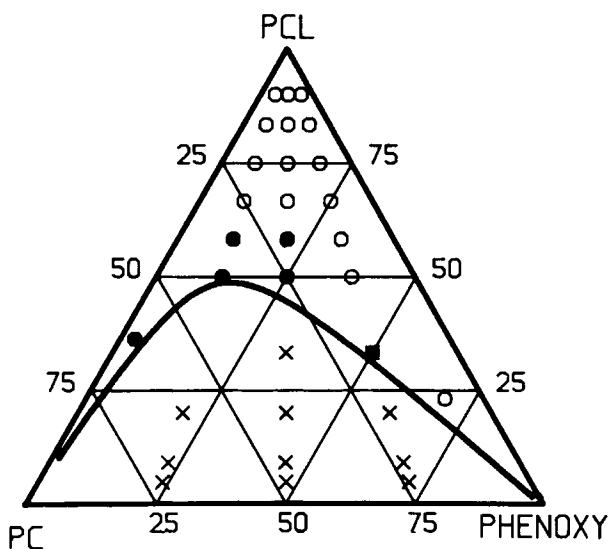


Fig. 7. Ternary diagram of the PC/Phenoxy/PCL System: (○) compositions with single  $T_g$  and clear melts; (×) compositions with two  $T_g$ 's and cloudy melts; (●) compositions with one  $T_g$  and cloudy melts; (—) calculated boundary between single and multiple phase behavior.

tion is most likely to occur when the component becomes the majority component and when the blend  $T_g$  is below its melting temperature.<sup>25</sup> Both conditions are met by the Phenoxy-rich phase when the PCL content in the blend approaches 40% by weight (see Figs. 4–6).

Because of difficulty of interpreting the single glass transition temperature behavior at high PCL loadings, cited above, the optical clarity of these blends was also examined. All blends remained opaque at temperatures between the melting point of PCL (about 60°C) and 230°C at which point they begin to clarify due to the melting of PC. Blends containing more than 60% by weight PCL became completely transparent above this temperature, indicating the presence of a single amorphous phase, and retained their transparency even at temperatures above the published LCST for the PC/PCL binary.<sup>20</sup> Blend transparency was observed to temperatures as high as 280°C, at which point polymer decomposition became severe. On the other hand, blends containing less than 50% PCL by weight also showed the PC melting transition at about 230°C but remained cloudy at higher temperatures.

The combination of the optical and DSC studies enabled the phase envelope for this ternary system to be approximated as shown by Figure 7, where the region above the envelope is the single phase region. Since this figure was determined with measurements made at a variety of temperatures, it does not strictly represent the usual isothermal phase behavior of a system. The phase diagram does indicate that less PCL is required to solubilize Phenoxy-rich blends with PC than to solubilize Phenoxy-lean blends. This behavior is probably the result of the Phenoxy/PCL interactions being more exothermic than the PC/PCL interactions.

**PCL Melting Point Depression.** Shah et al.<sup>15</sup> have recently shown that the melting temperature of the crystallizable component in a miscible ternary



blend can be related to the melting point of the pure component by the following equation:

$$T_m = T_m^0 + B(v_{2u}/\Delta h_{2u})T_m^0(1 - \Phi_2)^2 \quad (2)$$

where

$$B = B_{12}\psi_1^2 + B_{23}\psi_3^2 + \Delta B\psi_1\psi_3 \quad (3)$$

$$\Delta B = B_{12} + B_{23} - B_{13} \quad (4)$$

$$\psi_i = \Phi_i/(1 - \Phi_2) \quad (5)$$

and where  $T_m$  is the melting point of crystalline component 2 in the blend,  $T_m^0$  is the equilibrium melting temperature of the pure crystalline component,  $\Delta h_{2u}/v_{2u}$  is the heat of fusion per unit volume of pure crystal,  $\Phi_i$  is the volume fraction of component  $i$  in the blend, and  $B_{ij}$  is the interaction parameter describing enthalpic interactions between blend components  $i$  and  $j$ , described in eq. (1). As discussed in Ref. 15, eqs. (2)–(5) are equivalent to analyses by Scott<sup>26</sup> and Flory<sup>27</sup> when the combinatorial entropy of mixing is very small. For a miscible binary blend containing crystalline component 2 and amorphous component 1,  $\Phi_3 = 0$ ,  $\psi_3 = 0$ ,  $\Phi_1 = (1 - \Phi_2)$ ,  $\psi_1 = 1$ , and eq. (2) reduces to the well-known relationship for the melting point depression in a high molecular weight binary blend.<sup>27–29</sup>

Equation (2) suggests that the observed interaction parameter for the ternary blend,  $B$ , can be evaluated from melting point depression data in the same manner as is done for binary blends. Performing this analysis at several PC/Phenoxy ratios in the region of high PCL content where the blends are miscible should then allow the unknown PC/Phenoxy interaction parameter  $B_{13}$  to be determined through eqs. (3)–(5).

The melting points of PCL in the ternary PC/Phenoxy/PCL blends are plotted vs. the square of the volume fraction of amorphous diluent in Figure 8. As suggested by eq. (2), rather good straight lines result. The observed values of  $B$  evaluated from the slopes of the lines in Figure 8 and  $\Delta h_{2u}/v_{2u} = 35$  cal/cc<sup>30</sup> are plotted vs. the PC fraction of amorphous diluent,  $\psi_1$ , in Figure 9. These data follow the expected parabolic trend suggested by eq. (3) quite well considering the inaccuracies associated with melting point measurement and the determination of the slopes of the lines in Figure 8. The average  $B_{13}$  value obtained from these slopes with eqs. (3)–(5) is  $+4.6 \pm 0.4$  cal/cc, which indicates the presence of substantial endothermic PC/Phenoxy interactions and substantiates the observation of complete PC/Phenoxy immiscibility (Fig. 1).

**Estimation of Phase Behavior.** To the extent that the primary requirement for binary blend miscibility is a negative heat of mixing between blend components,<sup>1–5</sup> it seems reasonable that the same criterion should hold in multicomponent polymer blends. It follows that one should be able to estimate the locus of blend compositions which define the boundary between miscible and immiscible behavior by setting eq. (1) to zero. As described by Shah et al.,<sup>15</sup> the locus of these compositions is given by the following

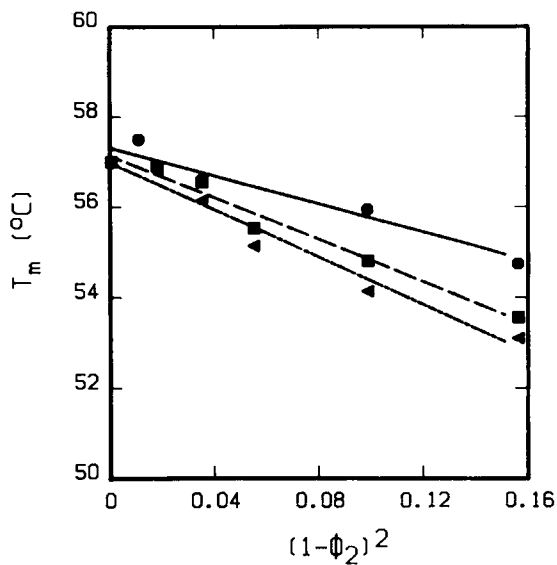


Fig. 8. PCL melting temperatures in ternary compositions: (●) a PC/Phenoxy ratio of 3; (■) a PC/Phenoxy ratio of 1; (▲) a PC/Phenoxy ratio of 1/3.

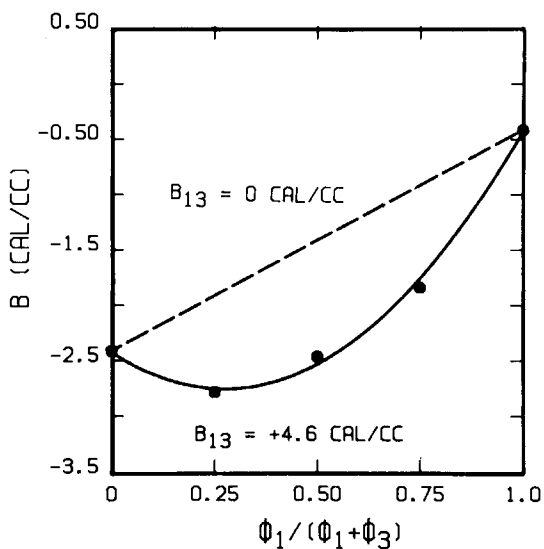


Fig. 9. Interaction parameter  $B$  vs. the fraction of PC in the amorphous diluent comprising PC and Phenoxy.

relationships:

$$\Phi_2 = \frac{RB_{13}}{RB_{13} - (R + 1)(RB_{12} + B_{23})} \quad (6)$$

$$\Phi_3 = \frac{1 - \Phi_2}{1 + R} \quad (7)$$

$$\Phi_1 = R\Phi_3 \quad (8)$$

The volume fractions in the blend of PCL,  $\Phi_2$ , of Phenoxy,  $\Phi_3$ , and of PC,  $\Phi_1$ , are calculated from the binary interaction parameters, described above, by specifying a value of  $R$  and applying eqs. (6)–(8), respectively. Allowing  $R$  to vary from 0.01 to 100 covers nearly the full range of possible compositions.

Figure 7 compares the calculated miscibility boundary with the estimates of miscible behavior obtained experimentally. Generally, the calculated boundary agrees well with the experimental observations, and both indicate that greater levels of PCL are required to solubilize PC-rich compositions. These results seem to verify the approximation that  $\Delta H_{\text{mix}} = 0$  defines the miscibility boundary in ternary as well as binary polymer blends. The calculated boundary does appear to underestimate the amount of PCL required to solubilize the other ingredients. This may be the result of experimental uncertainties associated with ascertaining blend miscibility and/or PCL melting point depressions, or the underestimation may be associated with the nature of the heat of mixing model and assumptions employed.

That one can estimate the miscibility boundary of the ternary through use of binary interaction parameters obtained near the melting temperature of PCL suggests that there is, indeed, only a single binodal, independent of temperature. While this point has not been examined because of the experimental difficulties associated with establishing miscibility at arbitrary temperatures, it seems reasonable because experience with numerous binary compositions containing either polyesters or esters<sup>9–11</sup> has never shown a strong temperature dependency for the  $B$  parameters used to characterize the heats of mixing.

## SUMMARY AND CONCLUSIONS

At fairly high loadings, PCL is able to solubilize the immiscible PC/Phenoxy binary to form miscible ternary compositions. The amount of PCL required decreases with increasing Phenoxy/PC ratios in a manner consistent with the greater exothermicity of the PCL/Phenoxy binary interaction parameter as compared to that for PCL/PC interactions, observed by analysis of the melting point depression of PCL in both materials. These results seem to be consistent with the assertion that polymer blend miscibility requires an exothermic heat of mixing among the blend components.

Melting point depression analysis of PCL in the ternary blends yielded an estimate of +4.6 cal/cc for the PC/Phenoxy binary interaction parameter. Since so little has been done to evaluate the interaction parameters of immiscible mixtures, it is difficult to know if this estimate is reasonable or not; however, it is interesting to compare this value and the predicted phase envelope with the similar analysis on the PC/SAN/PCL ternary studied previously.<sup>15</sup> The SAN/PC interaction parameter was found to be quite small,  $+0.2 \pm 0.3$  cal/cc, and the SAN/PCL interaction parameter was  $-0.6$  cal/cc, a value somewhat smaller than the Phenoxy/PCL parameter found in the present study. It is interesting that far less PCL was required to achieve miscible PC/SAN/PCL blends than is required to achieve the same with the present system. The primary reason seems to be the much smaller endothermic interaction between PC and SAN relative to that between PC and Phenoxy. This comparison suggests that the polymeric cosolvent approach for forming miscible ternary blends from an immiscible binary will be most

successful when the endothermic interaction between immiscible ingredients is small.

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