



# Blends of high temperature copolycarbonates with bisphenol-A-polycarbonate and a copolyester

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## Abstract

The phase behavior of blends of copolycarbonates containing 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexanone (TMC-PC) and bisphenol-A repeat units with its constituent homopolymers was determined using melt mixing, solution casting, and precipitation casting methods. Miscibility was observed for all combinations except for some involving the TMC-PC homopolymer. Phase behavior was assessed using differential scanning calorimetry and visual assessment of optical clarity. The blending procedure was found to affect the phase behavior in some blends due to interchange reactions and casting methods. Based on the observations of the cast blends, the intramolecular interaction energy of the copolycarbonate was determined to be between 0.029 and 0.036 cal/cc. The phase behavior of these copolycarbonates and a copolyester based on 1,4-cyclohexanedimethanol with terephthalic and isophthalic acids was determined after melt mixing. The copolyester is miscible with all of the copolycarbonates, even in the absence of interchange reactions.

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**Keywords:** Polymer blends; Polycarbonate; Blend preparation

## 1. Introduction

The polycarbonate homopolymer derived from bisphenol-A (BPA-PC) is a transparent, amorphous material with excellent toughness and a relatively high glass transition temperature ( $T_g$ ). In addition to its uses in neat form, blends of BPA-PC with other polymers have been of considerable practical and fundamental interest. Copolycarbonates of bisphenol-A combined with other bisphenol monomers have also attracted attention as a means of tuning specific physical properties. For example, a series of random copolycarbonates based on bisphenol-A (acetone) and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexanone (TMC-PC) has become available to meet the demand for amorphous materials with higher heat resistance, i.e. higher  $T_g$  than BPA-PC [1].

The availability of these materials and the long-term interest of this laboratory in blends based on polycarbonates, including the effects of structure on miscibility (or interactions) with other polymers, stimulated this study [2]. This paper considers the miscibility of these copolycarbonates

with BPA-PC, with each other, and with a copolyester based on 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids that is known to be miscible with BPA-PC [3–7].

## 2. Theory

The Gibbs' free energy density for mixing two polymers is described by the Flory–Huggins equation [8,9]

$$\Delta g_{\text{mix}} = B\phi_A\phi_B + RT \left[ \frac{\rho_A\phi_A \ln \phi_A}{M_A} + \frac{\rho_B\phi_B \ln \phi_B}{M_B} \right] \quad (1)$$

where  $\phi_i$ ,  $\rho_i$ , and  $M_i$  refer to the volume fraction, density, and molecular weight of polymer  $i$  respectively. The second term on the right hand side of Eq. (1) accounts for the incompressible lattice entropy of mixing. The quantity,  $B$ , is the non-combinatorial free energy. If we assume that  $B$  is not a function of composition, differentiation of Eq. (1) yields the following spinodal condition [8,9]

$$\frac{d^2\Delta g}{d\phi_A^2} = -2B + RT \left[ \frac{\rho_A}{(\bar{M}_W)_A\phi_A} + \frac{\rho_B}{(\bar{M}_W)_B\phi_B} \right] = 0 \quad (2)$$

where  $(\bar{M}_W)_i$  represents the weight average molecular

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weight of component *i*. This equation gives a rough approximation to the equilibrium boundary separating miscible and immiscible blends. As molecular weight or copolymer composition is varied, the observed location of this boundary may be used to estimate *B*. For blends involving statistical copolymers, *B* can be expanded in terms of interactions between individual repeat units in the following form [10–12]:

$$B = \sum_{i>j}^{\text{Inter}} B_{ij} \phi_i \phi_j - \sum_{i>j}^{\text{Intra}} B_{ij} \phi_i \phi_j \quad (3)$$

Where the notation of the summations prevents double counting of interactions. When mixing a copolymer containing repeat units 1 and 2 with a homopolymer containing repeat unit 3, Eq. (3) becomes

$$B = B_{13} \phi_1' + B_{23} \phi_2' - B_{12} \phi_1' \phi_2' \quad (4)$$

where  $\phi_i'$  refers to the volume fraction of monomer units in the copolymer. If the copolymer and homopolymer both contain repeat unit 1, Eq. (4) reduces to

$$B = B_{12} \phi_2'^2 \quad (5)$$

### 3. Experimental

The polymers used in this study, shown in Table 1, were used as received except for the TMC-PC homopolymer, which was precipitated in methanol three times from a dichloromethane solution to remove residual monomer. The compositions of the copolymers were determined previously [13]. The molecular weight information shown in Table 1 was obtained by gel permeation chromatography using a Polymer Laboratories 5  $\mu\text{m}$  column, a Waters 515 HPLC pump, and a Viscotek model 250 refractive index

detector. Crosslinked polystyrene was used as the fixed phase and tetrahydrofuran was the carrier phase. The column was calibrated with polystyrene standards. The copolyester molecular weight information was determined by viscometry [5].

The glass transition temperatures shown in Table 2 were obtained with a Perkin–Elmer DSC7, where scans and calibrations were performed at 20 °C/min. Glass transition temperatures are defined here by the onset method.

Polymer blends were made by both melt and solution methods. Melt blending was performed in a Brabender outfitted with a 50 cm<sup>3</sup> batch mixing head at a temperature 85 °C above the highest component glass transition temperature. Blends were also cast from approximately 10 wt% polymer in dichloromethane solutions onto glass slides at room temperature or precipitated into a non-solvent. Phase homogeneity of each blend was judged by both glass transition behavior and visual observation of scattered light.

The polycarbonate and polyester materials were dried for a minimum of 24 h at 80 °C in a vacuum oven prior to melt processing. A Killion single screw extruder ( $L/D = 30$   $D = 2.54$  cm) operating at 60 rpm was used to disperse a catalyst deactivating agent, arsenic (III) oxide, into the copolyester [5]. Notched Izod bars 3.18 mm thick by 12.7 mm wide and ASTM D638 type I dogbone bars were formed in an Arburg Allrounder injection molder. The nozzle temperature was held 110 °C above the glass transition of the material, the injection pressure was 75 bar, and the holding pressure was 70 bar. Tensile testing was performed with a computerized Instron at a crosshead speed of 5.1 cm/min. Notched Izod impact tests were performed with a TMI tester using a 6.8 J hammer and 3.5 m/s impact velocity. The Izod impact specimens had the standard notch radius of 0.25 mm.

Table 1  
Polymers used in this study

Polymer	Source	Commercial description	Composition (wt%)	$M_w$ (Da)	$M_n$ (Da)
PCTMC11	Bayer AG	Apec 9330	11.1%TMC <sup>a</sup>	54,600	23,700
PCTMC30	Bayer AG	Apec 9340	30.2%TMC <sup>a</sup>	61,400	26,800
PCTMC40	Bayer AG	Apec 9358	38.9%TMC <sup>a</sup>	64,100	26,400
PCTMC64	Bayer AG	Apec 9371	64.2%TMC <sup>a</sup>	65,800	30,300
TMC-PC	Bayer AG	N/A	Homopolymer	137,100	66,100
BPA-PC(63)	Mitsubishi Corp.	E-2000	Homopolymer	62,800	29,500
BPA-PC(46)	Dow Chemical Co.		Homopolymer	45,700	17,500
BPA-PC(31)	Dow Chemical Co.		Homopolymer	31,400	12,800
BPA-PC(19)	Dow Chemical Co.		Homopolymer	18,900	6,900
TMPC-PC	Bayer AG	N/A	Homopolymer	37,900 <sup>b</sup>	13,700 <sup>b</sup>
Copolyester	Eastman Chemical Co.	Eastar <sup>c</sup> A-150	80%Terephthalic <sup>c</sup> 20% Isophthalic	–	22,000

Note that the number in the notation of the PCTMC materials reflects the TMC content while the number in the notation for BPA-PC materials refers to their molecular weight.

<sup>a</sup> [13].

<sup>b</sup> This commercial copolymer is formed from 1,4-cyclohexanedimethanol and the indicated mixtures of phthalic acids. The polymer was characterized previously [28].

<sup>c</sup> This copolyester is formed from 1,4-cyclohexanedimethanol and the indicated mixtures of phthalic acids; this material was formerly designated as Kodar 150 and was characterized in our laboratories [5].

Table 2  
Polymer properties

Polymer	$T_g$ (°C)	Refractive index (25°C)	Elongation at break (%)	Tensile modulus (GPa)	Notched Izod impact energy (J/m)	Yield stress (MPa)
PCTMC11	156	1.581 <sup>a</sup>	133	2.15	855	57.4
PCTMC30	167	1.578 <sup>a</sup>	121	2.25	94.3	64.8
PCTMC40	180	1.572 <sup>a</sup>	117	2.32	81.9	65.0
PCTMC64	203	1.565 <sup>a</sup>	47.8	2.43	70.9	68.4
TMC-PC	237	1.554 <sup>b</sup>	–	–	–	–
BPA-PC	149	1.586 <sup>a</sup>	139	2.36	954	57.3
TMPC	190	1.602 <sup>a</sup>	–	–	–	–
Copolyester <sup>c</sup>	87	–	–	–	–	–

<sup>a</sup> Product literature.

<sup>b</sup> Calculated [29].

<sup>c</sup> Melting temperature = 265 °C, crystallization temperature = 150 °C.

## 4. Results and discussion

### 4.1. Mechanical properties of TMC-PC

Since many applications of BPA-PC and associated blends depend on their modulus and ductility, we sought to investigate changes in these properties encountered upon the addition of TMC-PC units to form copolymers with BPA-PC. The mechanical properties of BPA-PC and the various copolycarbonates determined here are shown in Table 2. The elongation at break and the notched Izod impact energy, which are measures of ductility, are reduced by the addition of the TMC-PC monomer unit as shown in Fig. 1(a) and (b), respectively. It should be noted that a step decrease in the impact strength at a TMC-PC content between that of 11.1 and 30.2% is observed here, while information from the manufacturer indicates a more gradual decrease. The modulus and yield stress increase slightly with an increase in TMC-PC content.

### 4.2. Blends with bisphenol-A-polycarbonate

Each of the four copolycarbonates shown in Table 1 were melt blended with the highest molecular weight bisphenol-A-polycarbonate in Table 1, BPA-PC(63). All of the resulting mixtures were transparent and exhibited a single glass transition by DSC. The glass transition data for these blends are shown in Fig. 2 along with the corresponding predictions of the Fox equation. These data are also plotted in Fig. 3 as a function of the weight fraction of TMC-PC repeat units contained in the blend. The observed glass transition appears completely specified by the TMC-PC content in the blend. Blends of these components prepared by solution casting or precipitation in methanol also showed a single glass transition. These results suggest that physically miscible blends are formed and that either the copolymers interact favorably with BPA-PC or the entropy of mixing is able to offset any unfavorable interaction.

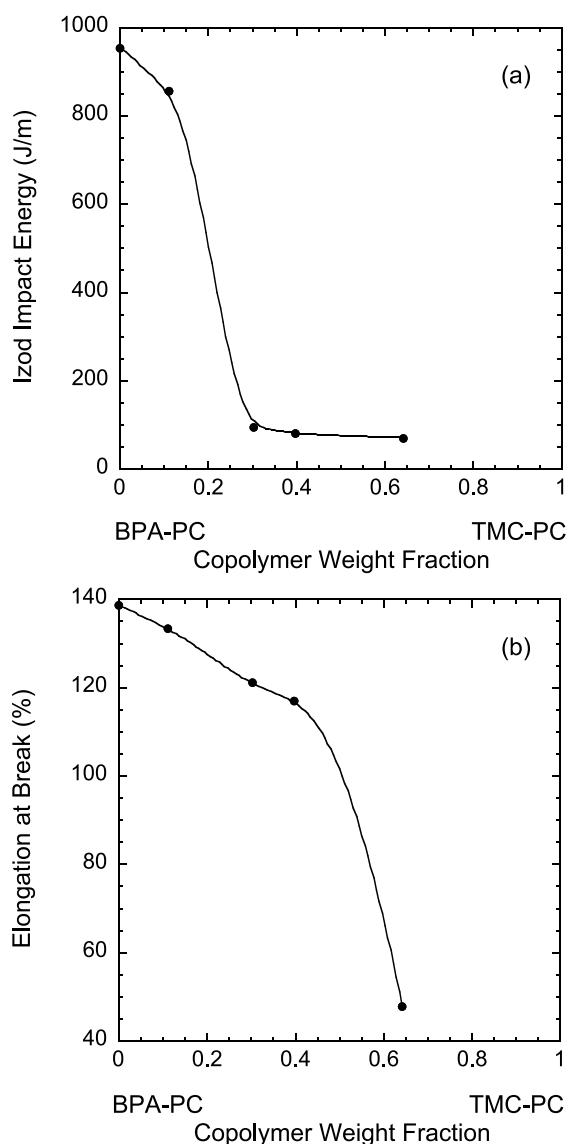


Fig. 1. Mechanical properties of BPA/TMC copolycarbonates as a function of their composition. (a) Notched Izod impact energy and (b) % elongation at break.

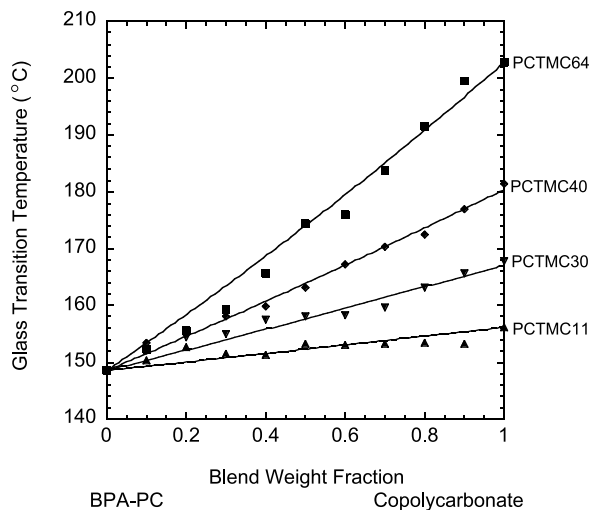


Fig. 2. Glass transition temperatures vs. composition for blends of Bisphenol-A polycarbonate (63) and the various copolycarbonates shown in Table 1 prepared blending in the melt. The curve shows the prediction by the Fox equation.

For a mixture of two copolymers based on the same two monomers, but with different compositions, Eq. (3) reduces to

$$B = B_{12}(\phi'_1 - \phi''_1)^2 \quad (6)$$

where  $\phi'_1$  and  $\phi''_1$  represent the volume fractions of component 1 in the compositionally different copolymers. Changes in copolymer composition have a large effect on the calculated interaction energy since it is modulated by the square of the composition difference. The most extreme value of the interaction energy of mixing exists for blends of two homopolymers, as can be seen in Eq. (6), since the difference between volume fractions are at a maximum. If  $B_{12}$  in Eq. (6) were negative, then miscibility of the two homopolymers would be assured. However, if the  $B_{12}$  is a

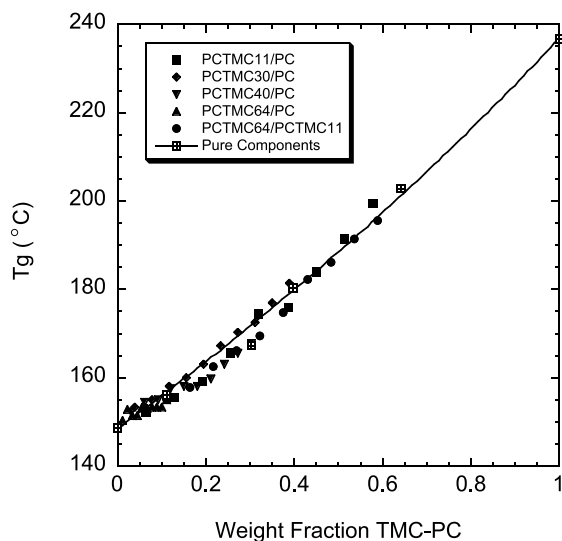


Fig. 3. Glass transition data shown in Fig. 2, re-plotted as a function of TMC-PC content. The curve shows the prediction by the Fox equation.

positive quantity and the entropy of mixing drives miscibility, then miscibility of the two homopolymers is not assured since the value of Eq. (6) is a maximum. The available supply of TMC-PC precluded melt mixing it with BPA-PC, so evaluation of these blends was limited to solution casting methods. It was found that the resulting phase behavior of the TMC-PC/BPA-PC homopolymer blends is strongly affected by the conditions of mixing and the thermal history of the blends.

It must be remembered that non-equilibrium effects may be encountered in preparing blends by solution casting methods. For example, a pair of polymers that are thermodynamically immiscible may become trapped in a homogenous state due to rapid solvent removal by hot casting or by precipitation with a non-solvent [14]. Alternatively, solution cast blends of polymer pairs that are thermodynamically miscible may become phase separated during solution casting due to the so-called ' $\Delta\chi$ ' effect [15–17]. The  $\Delta\chi$  effect occurs because of a closed two phase region in the ternary phase diagram that results when the two polymers interact very differently with the solvent. When further solvent is removed, the polymers may not have enough mobility to re-form a single phase even though it is the condition of lowest free energy. This situation may be avoided by using a solvent that has similar interactions with both polymers. Blends of the TMC-PC homopolymers with the higher molecular weight BPA-PC homopolymers were phase separated when cast from dichloromethane, tetrahydrofuran, dioxane, bromobenzene or chloroform, and when precipitated from solution in an excess of methanol or *n*-heptane. It is unlikely that all of these observations stem from the  $\Delta\chi$  effect. It seems reasonable to conclude that the interaction energy between the repeat unit pairs of the homopolymers is sufficiently repulsive to cause thermodynamic immiscibility of these homopolymers. Blends of TMC-PC with the lower molecular weights of BPA-PC in Table 1 made by solution casting and precipitation into methanol produced single phase blends. Apparently, there is a repulsive interaction between the homopolymers that can be offset by the slightly larger entropy of mixing created by reducing the BPA-PC molecular weight.

To quantify the interaction between repeat units, it would be useful to anneal the blends above their glass transition temperatures to obtain physical equilibrium. However, if a phase separated TMC-PC/BPA-PC homopolymer blend is held at a temperature above its glass transition, interchange reactions, which have been noted in many polyester and polycarbonate systems, may occur. A useful way to confirm this is to redissolve and recast the blends. If no reaction occurred, then the original phase separated structure should reform again. Observation of a single phase in this experiment would indicate a permanent change in phase behavior due to interchange reactions.

A small number of interchange reactions can lead to homogenization through creating block copolymers at phase boundaries. With extended time, the interchange reactions

essentially create random copolymers. The number of interchanges depends on the time at the elevated temperature [18]. Blends of TMC-PC with BPA-PC(63) have two glass transitions as cast, one transition after being held at 260 °C for 10 min, and then two phases form again after the same sample is recast from heptane or methanol. The TMC-PC/BPA-PC(31) blends continued to have one glass transition after experiencing the same thermal treatment and then being recast into heptane or methanol. The number of interchanges should be similar for the two blends, with the difference in the recast solution behavior being due to the BPA-PC molecular weight difference.

All of the possible blend combinations were made by solution casting from dichloromethane, precipitation of these mixtures in heptane, and precipitation in methanol as shown in Table 3. By rearranging Eq. (5) to read  $\phi_2' = \sqrt{B/B_{12}}$ , a plot of the volume fraction of the monomer unique to the copolymer ( $\phi_2$ ) vs.  $\sqrt{B}$  calculated from Eq. (2) yields a line whose slope is  $\sqrt{1/B_{\text{TMC-PC/BPA-PC}}}$  [19]. Thus, the phase behavior listed in Table 3 can be plotted in this manner, and the phase state boundary can be analyzed in the context of Eqs. (2) and (5) to extract an estimate for the binary interaction energy  $B_{\text{TMC-PC/BPA-PC}}$ . Fig. 4 shows the observed phase behavior of the BPA-PC/copolycarbonate and TMC-PC/copolycarbonate blends listed in Table 3 when they are precipitation cast into methanol or solution cast from dichloromethane at room temperature, plotted in the manner described above. In order to use phase state observations about the copolycarbonates blended with both homopolymers in Fig. 4, plotting the volume fraction of the

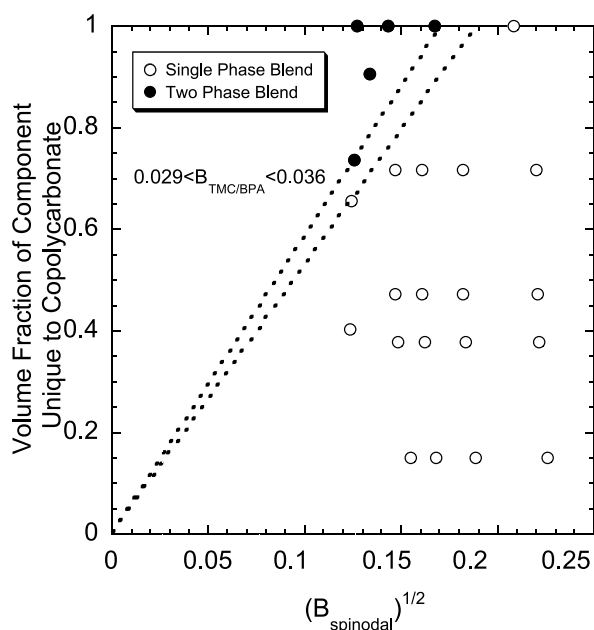


Fig. 4. Phase behavior of blends solution cast and precipitated into methanol plotted such that the slope of the line separating single and two phase behavior is related to the TMC-PC/BPA-PC binary interaction energy as outlined in the text. The dashed lines shown correspond to binary interactions between TMC-PC and BPA-PC between 0.029 and 0.036 cal/cm<sup>3</sup>.

monomer unique to the copolymer, ( $\phi_2$ ), requires the ordinate to correspond to the volume fraction of TMC-PC in the copolymer with blends containing the homopolymer BPA-PC, and correspond to the BPA-PC content with

Table 3  
Summary of blend phase behavior

Blend	Solution cast DSC/optical	Precipitation <i>n</i> – heptane	Precipitation methanol
TMC-PC/BPA-PC(63)	2 $T_g$ /Cloudy	2 $T_g$	2 $T_g$
TMC-PC/BPA-PC(46)	2 $T_g$ /Cloudy	2 $T_g$	2 $T_g$
TMC-PC/BPA-PC(31)	2 $T_g$ /Cloudy	2 $T_g$	2 $T_g$
TMC-PC/BPA-PC(19)	1 $T_g$ /Hazy	2 $T_g$	1 $T_g$
TMC-PC/PCTMC64	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
TMC-PC/PCTMC40	1 $T_g$ /Clear	2 $T_g$	1 $T_g$
TMC-PC/PCTMC30	2 $T_g$ /Hazy	2 $T_g$	1 $T_g$
TMC-PC/PCTMC11	2 $T_g$ /Cloudy	2 $T_g$	2 $T_g$
PCTMC64/BPA-PC(63)	1 $T_g$ /Clear	2 $T_g$	1 $T_g$
PCTMC64/BPA-PC(46)	1 $T_g$ /Clear	2 $T_g$	1 $T_g$
PCTMC64/BPA-PC(31)	1 $T_g$ /Clear	2 $T_g$	1 $T_g$
PCTMC64/BPA-PC(19)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC40/BPA-PC(63)	1 $T_g$ /Clear	2 $T_g$	1 $T_g$
PCTMC40/BPA-PC(46)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC40/BPA-PC(31)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC40/BPA-PC(19)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC30/BPA-PC(63)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC30/BPA-PC(46)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC30/BPA-PC(31)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC30/BPA-PC(19)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC11/BPA-PC(63)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC11/BPA-PC(46)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC11/BPA-PC(31)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$
PCTMC11/BPA-PC(19)	1 $T_g$ /Clear	1 $T_g$	1 $T_g$

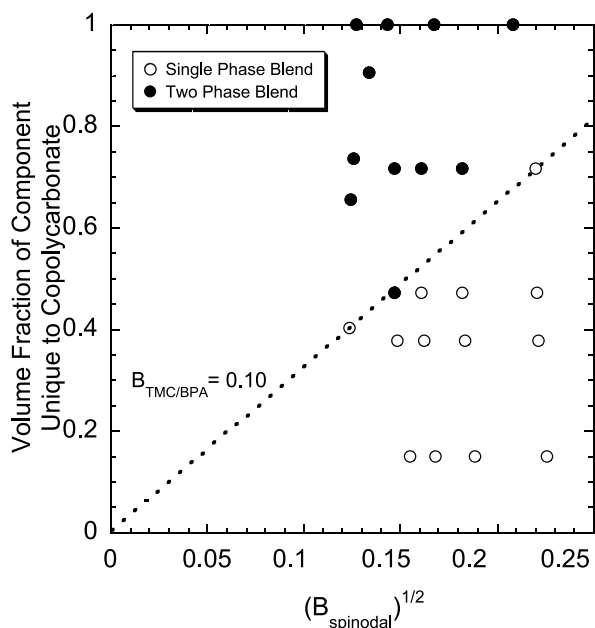


Fig. 5. Phase behavior of blends precipitated into heptane plotted such that the slope of the line separating single and two phase behavior is related to the TMC-PC/BPA-PC binary interaction energy as outlined in the text. The dashed line represents a TMC-PC and BPA-PC interaction of 0.1 cal/cm<sup>3</sup>.

blends containing the homopolymer TMC-PC. The phase state data shown in Fig. 4 bounds the range of possible  $B_{\text{TMC-PC/BPA-PC}}$  interaction energy densities between 0.029 and 0.036 cal/cm<sup>3</sup> as shown by the dashed lines. The phase behavior of blends solution cast into heptane at room temperature, plotted in the same way as Fig. 4, is shown in Fig. 5. A single line drawn through the origin will intersect observations of both single and two phases, therefore a best fit of the data suggests an interaction energy density of 0.10 cal/cm<sup>3</sup>.

The discrepancy between the two casting methods was probed by recasting a blend showing inconsistent phase behavior from the higher boiling point (156 °C) solvent bromobenzene at room temperature. It is unlikely that the observations from this method are biased towards phase homogeneity due to fast solvent removal. The resulting blend of TMC-PC/PCTMC40 produced the same phase behavior as the lower boiling point (40 °C) solvent dichloromethane. The blends prepared by solvent casting and precipitation into methanol show the same phase behavior; thus, we believe they represent the equilibrium phase behavior. We observed that the precipitation of the polycarbonates in the non-solvent occurred more rapidly in methanol than in heptane. The extra time during precipitation may have allowed for a metastable phase dissolution instead of the assumed spinodal one, which would account for the larger number of two phase blends observed while using heptane. The magnitude of the predicted interaction energies suggested by all blend preparation methods would preclude inducing miscible phase behavior due to the

intramolecular repulsion as seen in blends containing styrene/acrylonitrile copolymers, where the intramolecular interaction is on the order of 7 cal/cm<sup>3</sup> [20]. The source of the discrepancy between precipitation in heptane and other methods is unknown; however, the difference in the estimated interaction energies between the two methods is not very significant in the context of designing polymer blends.

#### 4.3. Blends with copolyesters

The commercial polyester made from cyclohexanedi-methanol and a mixture of about 80% terephthalic acid and 20% isophthalic acid are known to form miscible blends with BPA-PC [4–6,21,22]. An important benefit of blending these materials from a commercial point of view is that the copolyester retards the yellowing during radiation sterilization, which is a severe limitation for BPA-PC in some medical applications [23]. Blends of polyesters with TMC-PC copolycarbonates have been described as clear and miscible in the patent literature [24–27]. Thus, it is of interest here to examine in more depth the possible miscibility of the copolycarbonates in Table 1 with this commercial copolyester.

Blends of the copolyester with the various copolycarbonates were mixed in the melt with a Brabender batch mixing device. The total time spent in the mixer was less than 5 min for all blends and the temperature used was 85 °C above the  $T_g$  of the polycarbonate in the blend. The resulting blends were cooled rapidly after blending to reduce the thermal history and also to observe optical clarity without the interference of crystallinity. All of the copolyester/copoly-carbonate blends were transparent, and their first heat DSC scans displayed a single glass transition indicating that all of the blends exist as a single phase. To remove any possible

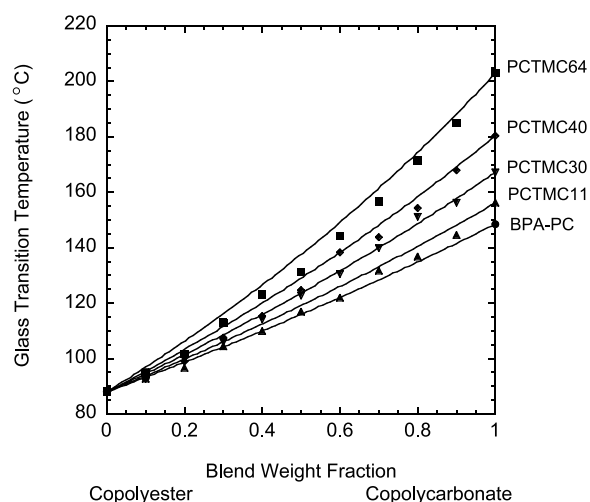


Fig. 6. Glass transition temperatures of blends of the copolyester with the various copolycarbonates prepared by melt mixing. The curves show the prediction by the Fox equation.

effects of crystallinity, the blends were held above their melting temperature for 1 min and then quenched at 200 °C/min to below their glass transition. The DSC scans after this thermal treatment also displayed a single glass transition temperature. The glass transition temperatures obtained after the thermal treatment in the DSC are shown in Fig. 6. These glass transition temperatures are similar to the locations predicted for miscible blends using the Fox equation.

Blends of BPA-PC and this copolyester are known to undergo interchange reactions which are catalyzed by the residual titanium catalyst contained in the copolyester [5]. However, the residual titanium catalyst can be deactivated with additives like phosphite or arsenic compounds so that essentially no interchange reactions occur between BPA-PC and various polyesters like the copolyester of interest here. In an attempt to determine if the phase behavior observed here was due to physical miscibility or interchange reactions, 0.1 wt% arsenic (III) oxide was mixed with the copolyester prior to blending in equal weight fractions with the copolycarbonates. These blends were also clear when quenched to prevent crystallization and possessed a single glass transition. Fig. 7 shows the heat of fusion (an indication of crystallinity) for blends containing equal parts by weight of copolycarbonates and the copolyester, with and without arsenic oxide, after being blended at 85 °C above the copolycarbonate glass transition and annealed for 20 min at 177 °C. The interchange reactions in the uninhibited blends reduce the crystallizable segment length, and thus, reduce the heat of fusion after annealing. Fig. 7 shows evidence of the interchange reactions in the uninhibited blends since the heat of fusion for the inhibited

blends are consistently higher than those of the uninhibited blends. The heats of fusion for the inhibited blends, except for the copolyester containing the highest amount of TMC-PC, are roughly equal to that of their pure copolyester content. This indicates that the interchange reactions are not significantly present in these one phase blends; thus, we conclude that these copolymers are physically miscible in the absence of interchange reactions.

## 5. Conclusions

All of the copolycarbonates based on bisphenol-A (BPA) and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexanone (TMC) were shown to be miscible with high molecular weight bisphenol-A-polycarbonate by solution casting and melt mixing methods. Two phase blends were observed between the homopolymer of TMC-PC and high molecular weight BPA-PC and also with copolycarbonates containing smaller amounts of TMC-PC. From these observations of phase behavior, it was estimated that the interaction energy between TMC-PC and BPA-PC units is between 0.029 and 0.036 cal/cm<sup>3</sup>. The magnitude of this interaction precludes significant effects of intramolecular repulsion for inducing miscibility with other polymers.

We observed that the phase behavior of the copolycarbonate blends was a function of thermal history and method of mixing. The two phase homopolymer blends of TMC-PC and BPA-PC can be permanently homogenized through interchange reactions at elevated temperatures. Some copolycarbonate blends that were solution cast into heptane produced two phase blends that had a single phase when prepared by precipitation into methanol or cast from a variety of solvents. It is unlikely that solution casting from a high boiling point solvent would produce a non-equilibrium homogenized blend, therefore the solution casting and precipitation into methanol is believed to produce equilibrium phase behavior.

Blends of all of the copolycarbonates with a copolyester, based on 1,4-cyclohexanedimethanol with terephthalic and isophthalic acids, had a single phase when melt mixed. Because of the known tendency of these blends to undergo interchange reactions, the titanium catalyst in the copolyester was inhibited with arsenic (III) oxide prior to formation of selected blends with the polycarbonate. These blends were found to have a single glass transition. Heat of fusion data suggest that relatively few interchange reactions occur in the inhibited blends. This would indicate that the copolymers are physically miscible in the absence of the interchange reactions.

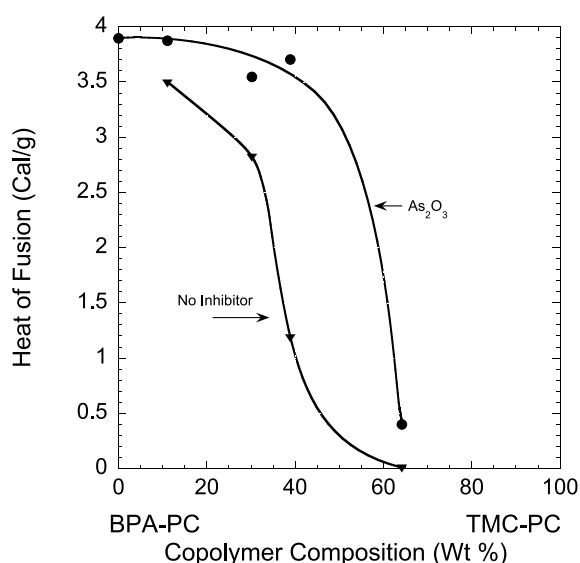


Fig. 7. Heat of fusion vs. copolymer composition for 50/50 wt% blends of copolycarbonates and the copolyester with and without 0.1 wt% As<sub>2</sub>O<sub>3</sub>. Blends were annealed at 177 °C for 20 min prior to the assessment. The curves are drawn to aid the eye.

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