Phase Behavior and Transreaction Studies of Model Polyester/Bisphenol-A Polycarbonate Blends. 2. Molecular Weight, Composition, and End-Group Effects

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ABSTRACT: The equilibrium phase behavior of poly(2-ethyl-2-methylpropylene terephthalate) (PEMPT)/Bisphenol-A polycarbonate (PC) blends is monitored as a function of polyester and polycarbonate molecular weight, composition ratio, and end-group type. Six polyesters, number-average molecular weights (M_ns) varying from 4100 to 37 500, and two PCs, M_ns of 11 000 and 21 000, are studied at PEMPT/PC composition ratios of 15/85, 30/70, 50/50, 70/30, and 85/15 (w/w). PEMPT/PC blends are found to be two phase at all but the lowest molecular weight pairs examined. Composition effects are most apparent in blends containing components with low molecular weight. Hydroxyl- and benzoate-terminated PEMPT/PC 50/50 blends exhibit similar phase behavior and qualitatively follow Flory–Huggins theory with enhancement in miscibility as molecular weight is decreased. Blends containing polyesters with heptafluorobutyrate end groups show substantially different phase behavior. Virtually no enhancement in partial miscibility of the components is observed as the molecular weight of the polyester is lowered. These results are explained in terms of a multicomponent interaction parameter that accounts for both midchain/midchain interactions and midchain/end-group interactions. The interaction parameter of the blend, as calculated from critical point data, is 0.044.

Introduction

Before the phase behavior shifts of a transreacting polyester/Bisphenol-A polycarbonate (PC) blend can be quantified, the equilibrium phase behavior prior to transreaction must be identified. This information is critical in establishing a baseline on which to judge the reacting blends. As noted in the preceding paper, poly(ethylene terephthalate) (PET)/PC and poly(butylene terephthalate) (PBT)/PC blends are a logical choice for study due to their commercial importance. However, as discussed, several factors limit their usefulness for quantitative phase behavior and transreaction studies.[1] Problems arise when annealing the blends above the component glass transition (T_g) and/or melting temperatures (T_ms) to ensure that equilibrium phase behavior is observed. At these temperatures, polyester/PC blends can transreact, altering their phase behavior. Other factors also hinder the analysis including the inability to clearly identify blend phase behavior, the inability to quantitatively measure low levels of transreaction, and the potential for side reactions. To circumvent these problems, a novel amorphous polyester, poly(2-ethyl-2-methylpropylene terephthalate)(PEMPT), has been synthesized as a model for PET and PBT.[1]

Several characteristics of PEMPT minimize the potential for transreaction during phase behavior studies. The fact that PEMPT is amorphous allows the studies to be carried out at lower temperatures, slowing the rate of interchange reaction. The catalyst used in the synthesis of the polyesters was selected to minimize transreaction. PEMPT was synthesized with titanium isopropoxide which can be inhibited from catalyzing transreaction in polyester/PC blends by the addition of phosphite compounds.[2,3] Finally, the improved solubility of PEMPT allows spectroscopic monitoring for the absence/presence of transreaction, ensuring that the observed phase behavior does represent that of the unreacted binary blend.

Several other characteristics of PEMPT make it uniquely suitable for these studies. Replacement of the β-hydrogens by ethylmethyl substitution creates an amorphous polyester with improved thermal stability. The lack of crystallinity also allows phase behavior studies to be carried out at lower annealing temperatures, 200 °C. Improved thermal stability and reduced annealing temperatures will minimize the level of side reactions. The fact that both polymers used in this study are amorphous with well-separated T_gs enables clear identification of the phase behavior by thermal analysis. Of particular importance is the elimination of crystallization exotherms and endotherms from obscuring T_g shifts which are used to monitor blend phase behavior. The lack of crystallinity also simplifies the thermodynamic analysis of the blend. The enhanced solubility of PEMPT compared to PET and PBT facilitates blend preparation, characterization, and analysis.

In addition to phase behavior identification of unreacted blends, use of the phase behavior data to determine thermodynamic parameters is also desired. Of particular interest are the blend interaction parameter (χ_{12}) and number-average degree of polymerization at the critical point (X_{nc}). This thermodynamic information will aid in later theoretical interpretations of the transreacting blend. Several authors have studied mixtures of low molecular weight polymers/oligomers to examine phase behavior near the critical point.[4–7] With knowledge of the critical molecular weights, estimates of the interaction parameter can be made by applying appropriate thermodynamics equations. A similar approach will be used here by applying classical Flory–Huggins theory to critical point data.

Overall, phase behavior studies as a function of degree of polymerization (X_n) and the subsequent construction of miscibility diagrams (X_n vs phase composition) are used to identify the critical point region. To do so, the

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degree of compatibility between blend components must be quantified. The shifting of T_gs as measured by thermal analysis is one commonly used method to monitor phase behavior. This information can be transformed into quantitative estimates of the phase compositions by use of the Couchman equation.[8,9] One inherent drawback to this analysis is that, in the region of the critical point, the molecular weight of the polyesters may be low and not conform to the random walk statistics of Flory–Huggings theory. Additionally, the assumption of monodisperse polymers is also violated.

A phase behavior study examining the effectiveness of dioctadecyl phosphite (DNOP) as a transreaction inhibitor is first carried out. Phase behavior studies are then conducted as a function of composition ratio. This enables the identification of composition effects and also verifies that the miscibility diagrams deduced from T_g shifts are an adequate representation of the blend's phase behavior. The effect of end-group type on miscibility is also monitored. End-capping is one alternative technique to eliminate hydrolysis transreaction. However, it has been reported that end groups can alter the blend thermodynamics,[5,10] the final result being modification of the blend phase behavior.

Theoretical Background

Polymer Solutions. The thermodynamics of mixing polymer/solvent and polymer/polymer solutions has been developed by Flory, Huggins, Scott, and others.[11–18] The resulting lattice model, eq 1, represents a general expression for the free energy of mixing per lattice site of a monodisperse binary polymer blend composed of $N_1X_1 + N_2X_2$ sites, where the subscripts indicate components 1 and 2.

$$\Delta G_m = kT\left[\frac{\phi_1 \ln \phi_1}{X_1} + \frac{\phi_2 \ln \phi_2}{X_2} + \psi\right] \quad (1)$$

$$\psi = \chi_{12}\phi_1\phi_2 \quad (2)$$

where N_i is the number of polymer molecules of component i, X_i is the relative chain length of component i (based on reference molar volume $\tilde{v}_i$), ϕ_i is the volume fraction of component i, ψ is the interaction term, χ_{12} is the interaction parameter, k is the Boltzmann constant, and T is the absolute temperature. One important aspect of eq 1 lies in its ability to predict the effect varying composition and chain length have on the free energy of mixing. From the free energy of mixing equation, the binodal and spinodal curves can be calculated by applying the appropriate stability conditions.[19,20] The effect of varying molecular weight on the blend phase behavior is of particular interest. A schematic representation of a binodal surface as a function of temperature, composition, and the number-average degree of polymerization of component one, X_{n1}, is shown in Figure 1. Note, for the present discussion, component two's degree of polymerization is assumed constant. The surface shown represents the boundary between the single-phase region (outside the surface) and two-phase region (enclosed by the surface). At constant molecular weight, represented by bisecting axis X_{n1} with plane P1 (plane P1 is perpendicular to axis X_{n1}), a typical temperature vs composition phase diagram depicting upper critical solution temperature (UCST) behavior is shown, curve acb. Molecular weight effects at constant temperature are represented by a perpendicular slice through the temperature axis, plane P2. Curve dce represents the "phase diagram" developed by treating the degree of polymerization as the independent variable. Phase diagrams of this nature are constructed during the course of this study. In addition, point c represents the critical point and designates the appropriate critical temperature, composition, and degree of polymerization at constant pressure. The term "phase diagram" is normally associated with a temperature vs composition plot (curve acb). To avoid confusion with this nomenclature, the molecular weight vs composition diagrams will be designated as "miscibility diagrams". One additional point should be made. In this study, all blends are annealed at constant temperature for long time periods and then rapidly quenched below the T_g of the component polymers. The identified phase behavior is assumed to represent that of the blend at the constant annealing temperature. Thus, a temperature-dependent interaction parameter is not used in the analysis and is not specified above.

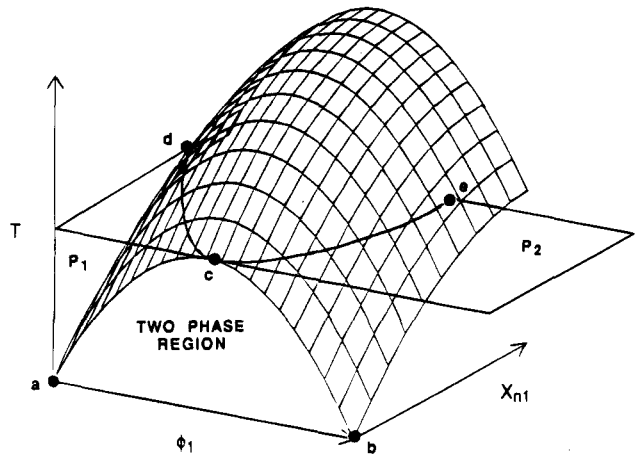

Figure 1. Three-dimensional phase behavior diagram; temperature, T, volume fraction, ϕ_1, and number-average degree of polymerization of component 1, X_{n1}.

Interest will also focus on the equations for the critical composition, ϕ_{1c}, and the interaction parameter at the spinodal and critical point.

$$\phi_{1c} = \frac{1}{1 + (X_1/X_2)^{1/2}} \quad (3)$$

$$\chi_{12s} = \frac{1}{2}\left[\frac{1}{X_1\phi_{1s}} + \frac{1}{X_2\phi_{2s}}\right] \quad (4)$$

$$\chi_{12c} = \frac{1}{2}\left[\frac{1}{(X_1)^{1/2}} + \frac{1}{(X_2)^{1/2}}\right]^2 \quad (5)$$

Mixtures composed of two polydisperse macromolecules have also been discussed.[21,22] The corresponding thermodynamic equations for these quasi-binary systems are shown below.

$$\Delta G_m = kT\left[\sum_i \frac{\phi_{1i} \ln \phi_{1i}}{X_{1i}} + \sum_j \frac{\phi_{2j} \ln \phi_{2j}}{X_{2j}} + \chi_{12}\phi_1\phi_2\right] \quad (6)$$

$$\phi_{1c} = \frac{1}{1 + \dfrac{X_{w1}X_{z2}^{1/2}}{X_{w2}X_{z1}^{1/2}}} \quad (7)$$

$$\chi_{12s} = \frac{1}{2}\left[\frac{1}{X_{w1}\phi_{1s}} + \frac{1}{X_{w2}\phi_{2s}}\right] \quad (8)$$

For component 1, X_{1i} is the chain length of species i, ϕ_{1i}

Table 1. Molecular Weight and Distribution Data of PEMPT and PC

polymer	M_n[a]	X_n[a]	X_w/X_n[b]	X_z/X_w[b]
PEMPT 1	4 100	16.5	1.44	1.40
PEMPT 2	6 100	24.6	1.53	1.44
PEMPT 3	9 500	38.3	1.76	1.52
PEMPT 4	11 500	46.4	1.81	1.52
PEMPT 5	18 200	73.4	1.87	1.52
PEMPT 6	37 500	151	1.94	1.53
PC1	11 300	45	1.52	1.39
PC2	21 200	85	1.44	1.36

[a] From fluoride end-group analysis. [b] From GPC analysis.

is the volume fraction of species i, X_{w1} is the weight-average chain length, and X_{z1} is the z-average chain length.

End-Group Effects. Previously, modifications to the blend interaction parameter, χ_{blend}, to account for end-group effects have been described in terms of a multicomponent interaction parameter that defines both midchain/midchain interactions and midchain/end-group interactions.[10] The binary interaction model initially developed for copolymer blends was used in this prior work.[23-25] A similar analysis will be used here to qualitatively determine the effect of end-group type and concentration on blend phase behavior via changes in the calculated interaction parameter. Designating midchain groups of polymer 1 as A, polymer 2 as B, and end-groups as A′ and B′, respectively, the interaction parameter of a binary blend with end-group effects is defined by the following:

$$\chi_{blend} = \phi_a\phi_b\chi_{AB} + (1-\phi_a)\phi_b\chi_{A'B} + \phi_a(1-\phi_b)\chi_{AB'} + (1-\phi_a)(1-\phi_b)\chi_{A'B'} - \phi_a(1-\phi_a)\chi_{AA'} - \phi_b(1-\phi_b)\chi_{BB'} \quad (9)$$

where ϕ_a is the volume fraction of midchain groups in polymer A based on the molar volume of A and ϕ_b is the volume fraction of midchain groups in polymer B based on the molar volume of B. At high degrees of polymerization, end-group effects are negligible, $\phi_a = \phi_b \sim 1$ and $(1-\phi_a) = (1-\phi_b) \sim 0$, and χ_{blend} of eq 9 reduces to that described by classical Flory–Huggins theory. In the present analysis, it will be assumed that the molecular weight of polymer B is high, such that its end-group effects can be ignored. All terms involving $\chi_{iB'}$ interactions are zero and $\phi_b \sim 1$. Equation 9 can be rewritten

$$\chi_{blend} = \phi_a\chi_{AB} + (1-\phi_a)\chi_{A'B} - \phi_a(1-\phi_a)\chi_{AA'} \quad (10)$$

Experimental Section

Materials. The synthesis, end-capping, and characterization of the polyesters used in this study is described in the preceding paper.[1] Six polyesters of varying molecular weight were synthesized, PEMPT 1A-OH through PEMPT 6A-OH ("OH" indicates hydroxyl end groups). Samples of these six polyesters were then end-capped with benzoyl chloride (PEMPT 1-BNZ through PEMPT 6-BNZ) and heptafluorobutyryl chloride (PEMPT 1-HFB through PEMPT 6-HFB). A third set of samples were used as a control for the end-capping reactions (PEMPT 1B-OH through PEMPT 6B-OH). Table 1 identifies the number-average molecular weights (M_ns) determined from fluoride analysis of PEMPT HFB polyesters and number-average degree of polymerization based on the molar volume per repeat of PEMPT, 208.4 cm³/mol. The polydispersities X_w/X_n and X_z/X_w based on GPC results of the PEMPT BNZ series of polyesters are also displayed. A seventh polyester (designated PEMPT 7-OH) having a M_n of 17 700 was used in an initial study where an inhibitor to prevent transreaction, dioctadecyl phosphite (DNOP), was also added to the blend. The two Bisphenol-A polycarbonates used in this study were provided by the General Electric Co. They contain no additives. They are reported to have weight-average molecular weights (M_ws) of 17 200 and 30 600 and are designated PC1 and PC2, respectively. The PC's M_ns were calculated from the polydispersity index X_w/X_n and the above M_ws (Table 1). From the M_ns, the X_ns were calculated based on the molar volume per repeat of PEMPT. The T_gs for PC1 and PC2 are 145 and 149 °C, respectively. The DSC equipment and scanning conditions are similar to those reported below for PEMPT 7-OH/PC2 blends.

Blend Preparation: DNOP Stabilization Study. Based on the polymerization, the polyesters contained ca. 2.71×10^{-6} mol of Ti catalyst/g of polymer. This value is used as the basis for calculating the DNOP/Ti ratios to be examined. Equal amounts by weight of PEMPT 7-OH and PC2 were placed in a vial and dissolved in a 7.12×10^{-7} M DNOP/chloroform solution. Blends with theoretical DNOP/Ti ratios of 1.5/1, 2.5/1, and 5/1 were prepared by varying the amount of DNOP/chloroform solution added. Pure chloroform was added to each vial to produce a final polymer/chloroform ratio of 10% (w/v). After thorough mixing, the samples were dried in vacuum at 75–80 °C for ~26 h.

Blend Preparation: Phase Behavior Studies. Blends for phase behavior studies were prepared similarly to that described above. A 5/1 DNOP/Ti ratio was used for all samples. Longer drying times under full vacuum, 8–14 days, were the only significant variation to the blending procedure. Initial phase behavior studies examined PEMPT A-OH/PC blends at composition ratios of 15/85, 30/70, 50/50, 70/30, and 85/15 (w/w). For the PEMPT B-OH/PC, PEMPT HFB/PC, and PEMPT BNZ/PC blends, only the 50/50 ratios were prepared. Samples were stored in a vacuum desiccator under calcium sulfate prior to thermal analysis.

Analysis. Thermal analysis for the DNOP stabilization study (PEMPT 7-OH/PC2 blends) was conducted in a Perkin-Elmer DSC-4 with a System 4 thermal analysis microprocessor controller and a thermal analysis data station. A dry ice/ethanol slurry was used for subambient cooling. Indium was the calibration standard, and baseline subtraction was used during the runs. Sample size was 6–8 mg and reported T_gs are midpoint values determined from a single heating run. The annealing and scanning temperature ramps used for this study are shown below.

annealing	scanning
load at 20 °C	load at 20 °C
heat at 100 °C/min to 280 °C	1st scan, 20 °C/min to 200 °C
hold 0.2 min	cool at 50 °C/min to 20 °C
cool at 100 °C/min to 240 °C	
annealing time at 240 °C: variable	
cool at 50 °C/min to 20 °C	

The short annealing period at 280 °C was used to melt any PC crystals that had formed during the blend casting procedure.

Thermal analysis for the phase behavior studies was conducted in a Perkin-Elmer DSC-7 with nitrogen as the purge gas. Indium and recrystallized dimethyl isophthalate were used for calibration standards. All scans were conducted at 20 °C/min with baseline subtraction. Sample size was ~6 mg. During these studies, a Perkin-Elmer Intercooler II was used for subambient cooling. The annealing and scanning programs are outlined below.

annealing	scanning
load at 20 °C	load at 20 °C
heat at 100 °C/min to 280 °C	1st scan, 20 °C/min to 200 °C
hold 0.2 min	cool at 50 °C/min to 20 °C
cool at 100 °C/min to 200 °C	hold 2 min
annealing time: 60 min at 200 °C	2nd scan, 20 °C/min to 200 °C
cool at 50 °C/min to 20 °C	cool at 50 °C/min to 20 °C

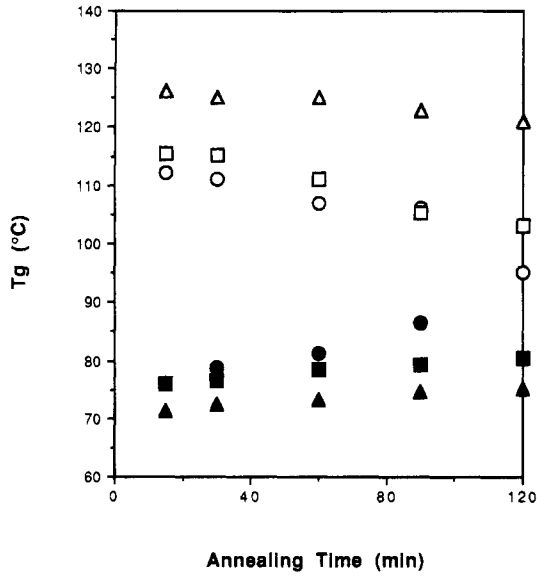

Figure 2. T_g vs annealing time at 240 °C for PEMPT OH7/PC2 50/50 wt% blends at varying DNOP/Ti ratios. PC-rich phase: 1.5/1 (○), 2.5/1 (□), 5/1 (△); PEMPT-rich phase: 1.5/1 (●), 2.5/1 (■), 5/1 (▲).

The first blends examined were PEMPT A-OH/PC2 at varying composition ratios. Only a single heating scan was run for these blends. It was found that in some cases, particularly samples containing low molecular weight PEMPTs, T_g identification was complicated by a particularly large endothermic overshoot. In these instances, second heating scans were run. To ensure uniform heat treatments, all remaining blends were scanned twice, with the second heating scan used for T_g identification. Agreement between T_gs identified from first and second heating scans was good.

Following DSC runs, the sample pans were opened and the blends removed for NMR analysis. Proton NMR was conducted on a Varian 300-XL spectrometer (300 MHz). The pulse angle was 67.7° with an acquisition time of 3.725 s and a delay time between pulses of 7.0 s. Samples solutions were ~1% (w/v) with deuterated chloroform as solvent and TMS used as an internal reference. Sixty-four scans per sample were recorded.

DNOP Stabilization Study. Plots of T_g vs annealing time for blends containing varying DNOP/Ti ratios are shown in Figure 2. Shifts in the T_gs of both the PEMPT-rich (low T_g) and PC-rich (high T_g) phases are observed as annealing time increases for blends containing a 1.5/1 and 2.5/1 ratio. This indicates some degree of phase behavior modification due to transreaction. The T_gs of both phases of the 5/1 DNOP/Ti ratio blend are relatively stable as annealing time increases. T_g shifts of only 3−4 °C are observed after annealing 120 min at 240 °C, implying little or no interchange reaction. Figure 3 is the 300 MHz proton NMR of a 5/1 ratio PEMPT 7-OH/PC2 blend after annealing 60 min at 200 °C (identical to the thermal program used for the phase behavior studies). The terephthalate region of the spectrum is displayed. Interchange reaction in PBT/PC blends has previously been identified by the appearance of new resonances shifted 0.1−0.3 ppm downfield from the main terephthalate resonance.[26] No evidence of any new resonances is observed in this region, confirming the absence of interchange reaction. On the basis of these results, all other DNOP-stabilized blends were prepared using a 5/1 theoretical DNOP/Ti mole ratio.

Equilibrium Criterion for Phase Behavior Studies. The criterion for establishing that the blends had reached equilibrium prior to DSC scanning should be noted. The criterion is based on the phase behavior of a transreacting blend (no DNOP stabilization). A PEMPT 7-OH/PC2 blend was observed to have a single, broad T_g after annealing 64 min at 200 °C. This result indicates that diffusion of the polymer chains occurs at a sufficient rate to produce a nearly single-phase blend from an initially two-phase system after annealing ~1 h at 200 °C. The result reflects both a diffusion effect and a kinetic effect associated with the rate of interchange reaction. Additionally, the majority of blends studied contained polyesters with M_ns lower than PEMPT 7-OH. Lowering the molecular weight will enhance chain mobility and decrease the time required to reach equilibrium. Thus, an annealing time of 60 min at 200 °C should produce blends at or very near equilibrium.

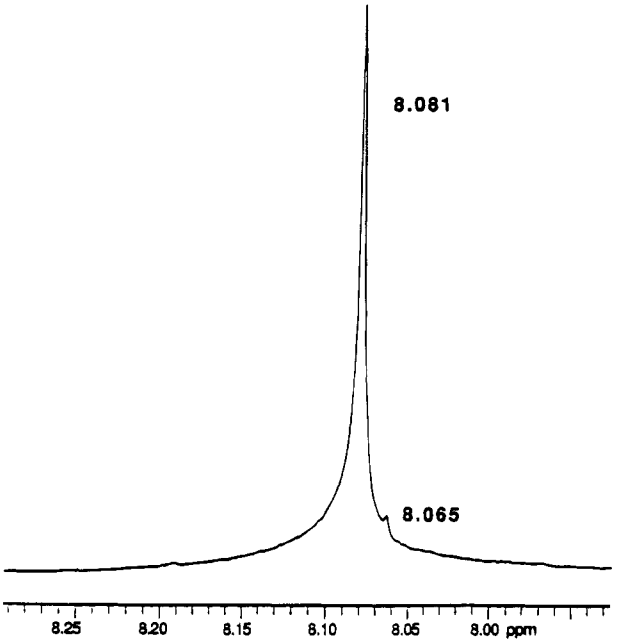

Figure 3. 300 MHz ^{1}H NMR of PEMPT OH7/PC2 50/50 wt % blends at 5/1 DNOP/Ti ratio after annealing 60 min at 200 °C. The terephthalate region of PEMPT is displayed.

Table 2. Actual vs Calculated Volume Fraction Data of Miscible Binary Blends

blend	$\phi_{1,actual}$	$\phi_{1,calc}$	$\lvert\Delta\phi_1\rvert$
PEMPT 1A-OH15/PC1 15/85	0.15	0.15	0.00
PEMPT 2A-OH15/PC1 15/85	0.15	0.18	0.03
PEMPT 1A-OH15/PC2 15/85	0.15	0.17	0.02
PEMPT 1A-OH15/PC1 30/70	0.30	0.32	0.02
PEMPT 2A-OH15/PC1 30/70	0.30	0.32	0.02
PEMPT 1A-OH15/PC2 30/70	0.30	0.35	0.05
PEMPT 1A-OH15/PC1 50/50	0.50	0.53	0.03
PEMPT 1A-OH15/PC1 70/30	0.70	0.72	0.02
PEMPT 1A-OH15/PC2 70/30	0.70	0.74	0.04
PEMPT 1A-OH15/PC1 85/15	0.85	0.82	0.03
PEMPT 2A-OH15/PC1 85/15	0.85	0.86	0.01
PEMPT 1A-OH15/PC2 85/15	0.85	0.84	0.01

Results

Molecular Weight and Composition Ratio Effects: PEMPT A-OH/PC Blends. The DSC heating scans for PEMPT A-OH/PC1 50/50 blends at varied polyester molecular weight are shown in Figure 4. As the molecular weight of the polyester is lowered, the T_gs merge. Indeed, one of these blends, PEMPT 1A-OH/PC1, is miscible (miscibility being defined as the observation of a single T_g). Similar studies are conducted on PEMPT A-OH/PC blends as a function of molecular weight and composition. Eleven additional blends are found to be miscible (Table 2).

In order to construct miscibility diagrams (X_{n1} vs ϕ_1) for these blends, the volume fractions of PEMPT in the PEMPT-rich phase, ϕ_1' (lower T_g phase), and PC-rich phase, ϕ_1'' (upper T_g phase), are required. Throughout this paper PEMPT is designated as component 1. The Couchman equation with $\Delta C_{p2}/\Delta C_{p1} = 0.7$ is used to calculate these volume fractions.[27] The Couchman

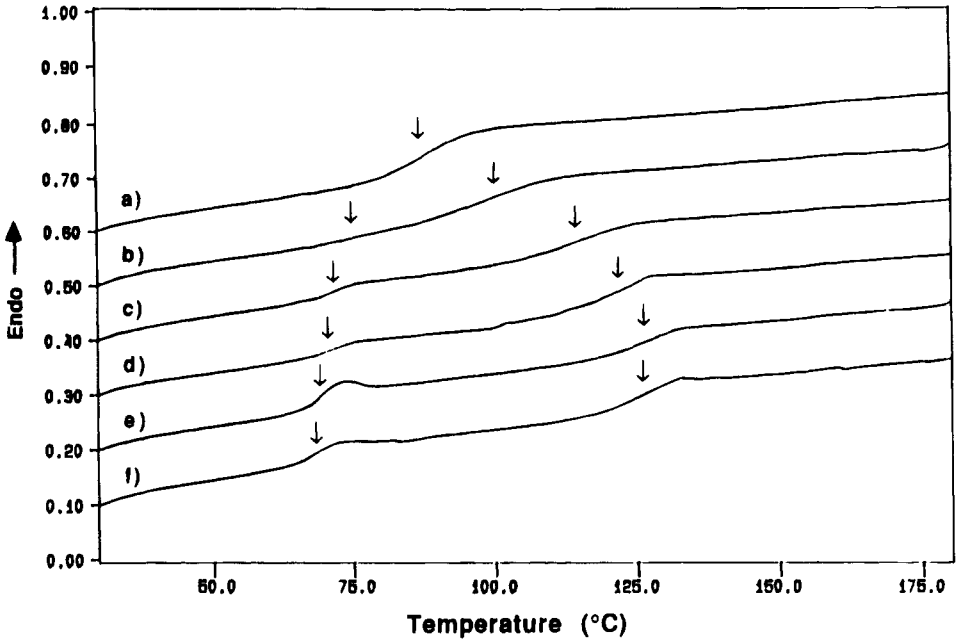

Figure 4. DSC heating scans of PEMPT A-OH/PC1 blends at PEMPT M_ns of (a) 4100, (b) 6100, (c) 9500, (d) 11 500, (e) 18 200, and (f) 37 500. Arrows indicate T_g shifts.

equation is normally used to calculate the weight fractions of the components in the blend. However, with the density of PEMPT (1.19 g/cm^3) being nearly identical to the density of PC (1.20 g/cm^3), weight fractions and volume fractions are equivalent. The value for $\Delta C_{p2}/\Delta C_{p1}$, 0.7, is determined by fitting the calculated volume fractions to the known volume fractions of the previously identified 12 miscible blends. For the miscible blends, the volume fraction of PEMPT in the single phase is equivalent to that of the initial blend composition, ϕ_1. The data of Table 2 show that the calculated volume fraction, $\phi_{1,calc}$, agrees with ϕ_1 across the entire composition range. The absolute value of the difference between ϕ_1 and $\phi_{1,calc}$ is shown in the last column of Table 2. The average deviation is 0.02, which serves as a measure of the uncertainty in a given volume fraction calculation.

Applying the Couchman equation to the appropriate pure component and blend T_g data, the volume fractions, ϕ_1' and ϕ_1'', are calculated. The miscibility diagrams for the PEMPT A-OH/PC1 and PEMPT A-OH/PC2 50/50 blends are displayed in Figure 5. Examining the PEMPT-rich phase (right branch), an increase in the amount of miscible PC is observed as the polyester molecular weight is lowered. Similarly, the PC-rich phase (left branch) shows a continuous increase of miscible PEMPT as the molecular weight of the polyester is lowered. This greater degree of partial miscibility is the result of a change in the entropic contribution to the free energy of mixing (eqs 1 and 6). As the polyester molecular weight is lowered, the entropic portion of ΔG_m decreases (greater negative value) and leads to enhanced mixing. In general, blends containing PC1 have a greater level of partial miscibility compared to those composed with PC2. This is also related to a decrease in the entropic contribution to the free energy of mixing associated with the lower molecular weight of PC1 relative to PC2.

The miscibility diagrams at composition ratios of 15/85, 30/70, 50/50, and 70/30 for PEMPT A-OH/PC1 and PEMPT A-OH/PC2 blends are shown in Figures 6 and 7, respectively. At all composition ratios, molecular weight effects are similar to those displayed by the 50/50 blends. As the molecular weights of the polyester and polycarbonate are lowered, enhancement in miscibility is observed. Once again these trends are in qualitative agreement with entropic effects encompassed by Flory–Huggins theory. Additionally, the identified miscible blends, indicated by asterisks, are in general agreement with the single-phase region predicted by T_g shifts (designated by the region outside the solid curve in Figures 6 and 7).

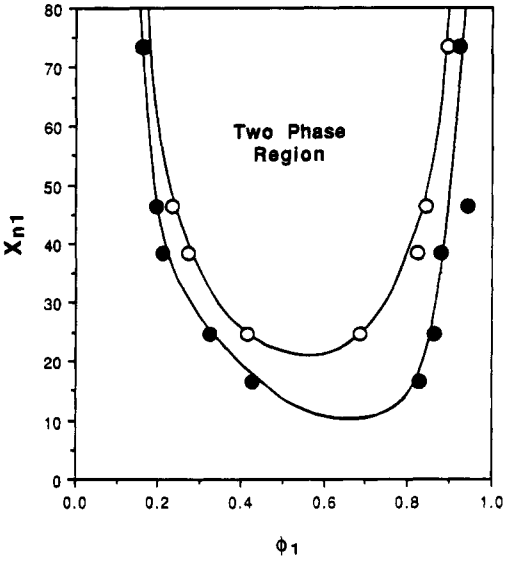

Figure 5. Miscibility diagrams at 200 °C of PEMPT A-OH/PC1 (○) and PEMPT A-OH/PC2 (●) 50/50 wt % blends. X_{n1} is the number-average degree of polymerization of PEMPT, and ϕ_1 is the volume fraction of PEMPT.

Focusing on composition effects at a given molecular weight, the amount of PC in the PEMPT-rich phase (right branch) is relatively independent of composition ratio. The amount of PEMPT in the PC-rich phase appears to contrast this, having some dependence on blend composition. In general, as the composition of PEMPT in the blend increases from 15 to 70%, the level of partial miscibility increases ~0.10–0.20 volume fraction units. For blends containing high molecular weight PEMPT, the levels of partial miscibility agree with the

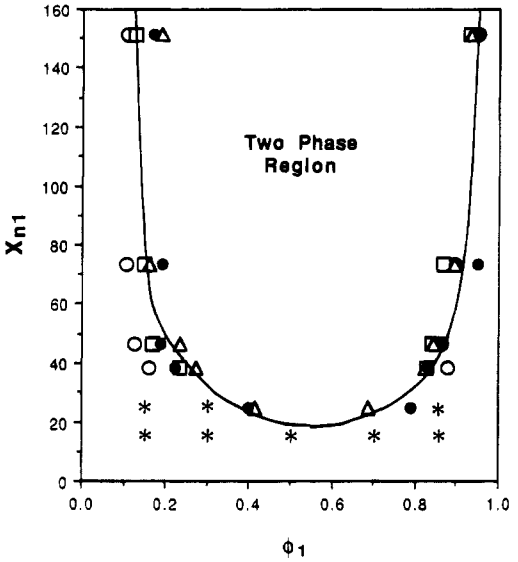

Figure 6. Miscibility diagrams at 200 °C of PEMPT A-OH/PC1 blends at composition ratios of 15/85 (○), 30/70 (□), 50/50 (△), and 70/30 (●). X_{n1} is the number-average degree of polymerization of PEMPT, and ϕ_1 is the volume fraction of PEMPT. Asterisks indicate miscible blends.

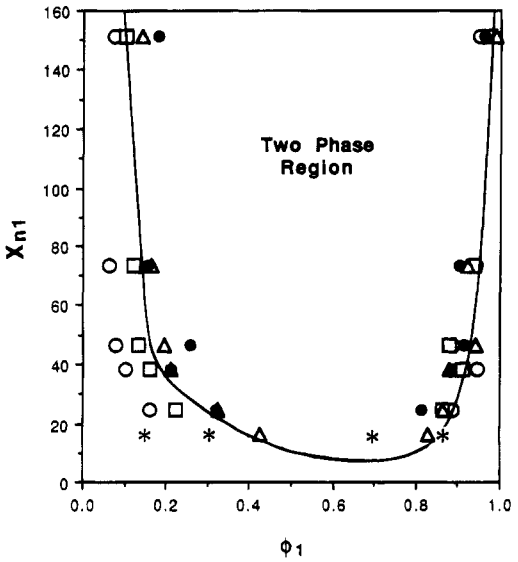

Figure 7. Miscibility diagrams at 200 °C of PEMPT A-OH/PC2 blends at composition ratios of 15/85 (○), 30/70 (□), 50/50 (△), and 70/30 (●). X_{n1} is the number-average degree of polymerization of PEMPT, and ϕ_1 is the volume fraction of PEMPT. Asterisks indicate miscible blends.

values reported by Kim and Burns in their studies of PBT/PC and PET/PC blends.[8,9] Similar to the present study, Kim and Burns report an increase in partial miscibility of the polyester in the PC-rich phase as polyester composition increases. They also report an increase in partial miscibility of PC in the polyester-rich phase as the polyester composition increases, contrary to the current observations.

Although a compositional dependence exists, the miscibility diagrams of Figures 6 and 7 show that the molecular weight effects follow the same general trends at all PEMPT/PC compositions. Thus, to facilitate further studies, the miscibility diagram at a single blend composition is assumed to be an adequate representation of the phase behavior across the entire composition range. Due to the nearly identical volume fractions of the components, the identification of the T_gs is most

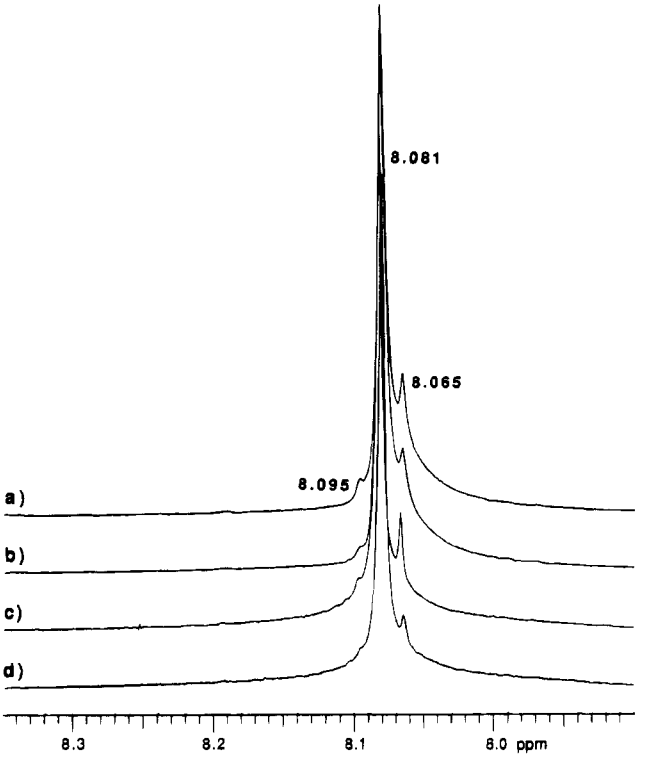

Figure 8. 300 MHz ^{1}H NMR of (a) PEMPT 1A-OH/PC1, (b) PEMPT 2A-OH/PC1, (c) PEMPT 1A-OH/PC2, and (d) PEMPT 3A-OH/PC2 50/50 wt % blends after DSC annealing/scanning. The terephthalate region of PEMPT is displayed.

accurately obtained at a 50/50 composition ratio. Hence, further studies are carried out on PEMPT/PC 50/50 blends.

Evidence of Alcoholysis Transreaction. Figure 8 shows the ^{1}H NMR of several PEMPT A-OH/PC 50/50 blends after DSC annealing/scanning. A resonance is observed at 8.095 ppm, which will be shown in the following paper to correspond to alcoholysis transreaction. Thus, in spite of all the precautions taken to eliminate/minimize interchange reaction, a small percentage of the hydroxyl end groups of PEMPT react via an alcoholysis transreaction with the carbonate group of PC. There is no evidence to indicate that any direct midchain transreaction occurs. Small amounts of alcoholysis reaction are also observed in PEMPT/PC blends at other composition ratios. Overall, the NMR results indicate that ~16% of the hydroxyl groups had undergone alcoholysis in these series of blends. From extrapolations, it is determined that this level of exchange reaction resulted in ~0.02−0.04 unit shift in volume fraction for each branch of the diagram (creating a smaller two-phase region).[28]

PEMPT B-OH/PC blends prepared in a similar fashion to the PEMPT A-OH/PC series underwent complete alcoholysis after the identical thermal treatment. DNOP appears to be an excellent inhibitor of midchain transreactions but data on its ability to inhibit alcoholysis reactions are inconsistent. This may in part be due to preparation/drying effects as the two series of samples were prepared at different times during the course of this study. In order to identify phase behavior in complete absence of alcoholysis, the phase behavior of the end-capped PEMPT/PC blends is examined.

End-Group Effects: PEMPT BNZ/PC and PEMPT HFB/PC Blends. Miscibility diagrams for the PEMPT BNZ/PC1 and PEMPT BNZ/PC2 50/50 blends are shown in Figure 9. The PEMPT 1-BNZ/PC1 and PEMPT

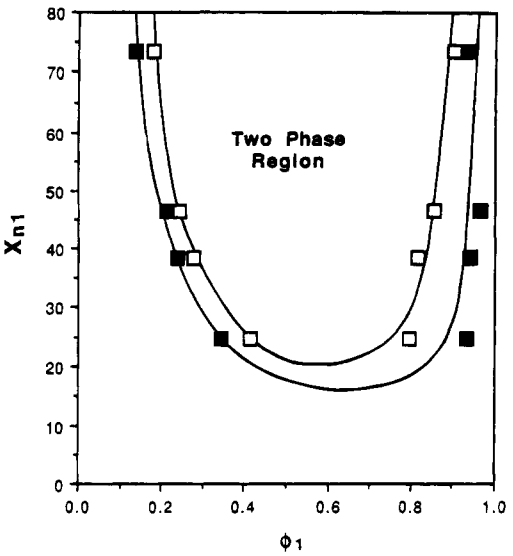

Figure 9. Miscibility diagrams at 200 °C of PEMPT BNZ/PC1 (□) and PEMPT BNZ/PC2 (■) 50/50 wt % blends. X_{n1} is the number-average degree of polymerization of PEMPT, and ϕ_1 is the volume fraction of PEMPT.

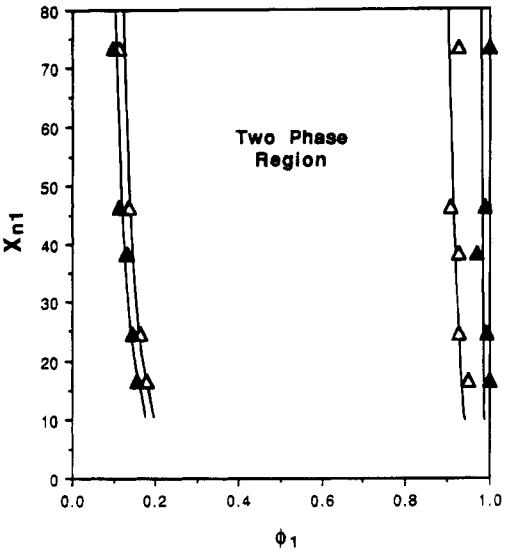

Figure 10. Miscibility diagrams at 200 °C of PEMPT HFB/PC1 (△) and PEMPT HFB/PC2 (▲) 50/50 wt % blends. X_{n1} is the number-average degree of polymerization of PEMPT, and ϕ_1 is the volume fraction of PEMPT.

1-BNZ/PC2 blends are both single phase. The single T_g of PEMPT 1-BNZ/PC2 blend is broader than that observed for the PEMPT 1-BNZ/PC1 blend, indicating this system is near the edge of the immiscible/miscible window. The improvement in partial miscibility between the two phases as both the PEMPT and PC molecular weights are lowered is again observed, conforming to entropic considerations. To ensure that improved mixing is not a result of transreaction, ^{1}H NMR is run on the PEMPT 1-BNZ/PC2 blend. No evidence of reaction is found.

The miscibility diagrams of the PEMPT A-OH/PC1 and PEMPT BNZ/PC1 blends, Figures 5 and 9, show little difference in the level of partial miscibility. The PEMPT/PC2 blends do show a more pronounced difference, with the PEMPT A-OH blends exhibiting greater phase separation than the PEMPT BNZ blends. This effect is prominent only at the lowest polyester molecular weights where the concentration of end groups is high. Comparing PEMPT/PC2 blends containing the lowest molecular weight polyester (X_{n1} = 16.5), the PEMPT 1A-OH/PC2 is two phase while the PEMPT 1-BNZ/PC2 is single phase. These data indicate that the end-group type can cause variations in phase behavior. However, the effect is only significant at the lowest molecular weights where the end-group concentrations are high, ~8−12%. Overall, the fact that PEMPT A-OH/PC and PEMPT-BNZ/PC blends exhibit similar phase behavior verifies that the small level of alcoholysis reaction did not significantly alter the phase behavior of the PEMPT A-OH/PC blends. Additionally, at all but the lowest molecular weights, hydrogen bonding does not appear to be a dominating driving force for increasing or decreasing the level of partial miscibility.

Figure 10 shows the miscibility diagrams of PEMPT HFB/PC1 and PEMPT HFB/PC2 blends. The degree of partial miscibility shows little or no increase as the molecular weight of the polyester is lowered. The PC-rich phase (left branch) shows nearly a constant amount of included PEMPT, ~15%, for all PEMPT and PC molecular weights studied. The PEMPT-rich phase has 5−10% included PC1 (PEMPT/PC1 blends) and 0−3% included PC2 (PEMPT/PC2 blends) over the range of polyester molecular weights examined. In general, the blends containing PEMPT HFB show no improvement in partial miscibility as the polyester molecular weight is lowered. This is in stark contrast to both the PEMPT BNZ and PEMPT OH blends, which show considerable enhancement as both the polyester and PC molecular weights are decreased. These results also disagree with entropic considerations. The obvious conclusion is that the HFB end groups are altering the phase behavior of the blends.

Discussion

By applying eq 10, the interaction parameter as a function of varying end-group concentration can be calculated if the individual χ_{ij}s can be determined.[29] Although the end-capped polyester is not a random copolymer, it will be assumed that the end groups cannot phase separate themselves and, when a miscible blend is formed, they are randomly distributed throughout the blend. The χ_{ij}s are obtained using a solubility parameter approach. Using the group contribution parameters of Van Krevelen, the molar volume of component i, $\tilde{v}_i$, the molar attraction constant of component i, F_i, and subsequently the solubility parameter of component i, δ_i, are calculated.[30] The interaction parameters are then calculated from eq 11.

$$\chi_{ij} = \frac{\tilde{v}_i(\delta_i - \delta_j)^2}{RT} \tag{11}$$

where R is the gas constant and T is the absolute temperature (473.3 K in all cases).

Designating a midchain group of PEMPT as "A" and a midchain group of PC as "B", the calculated values for the interaction parameters, $\chi_{A\,B}$, $\chi_{A\,BNZ}$, $\chi_{B\,BNZ}$, $\chi_{A\,HFB}$, and $\chi_{B\,HFB}$, are 0.054, 0.0084, 0.020, 0.84, and 1.3, respectively. χ_{blend} is then calculated (eq 10). Plots of χ_{blend} vs X_{n1} for the PEMPT BNZ/PC and PEMPT HFB/PC blends are shown in Figure 11. The interaction parameter of the PEMPT BNZ/PC blends is nearly constant as a function of degree of polymerization. Blends containing PEMPT with heptafluorobutyrate end groups show the interaction parameter to nearly double as X_{n1} decreases from 151 to 16.5, Figure 11.

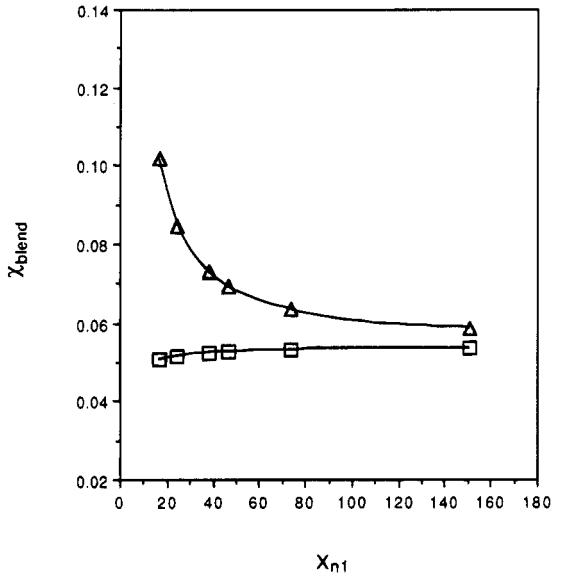

Figure 11. Variations in χ_{blend} as a function of the number-average degree of polymerization of PEMPT, X_{n1}, for PEMPT BNZ/PC blends (□) and PEMPT HFB/PC blends (△). Values calculated from eq 10.

Table 3. Critical Point and Interaction Parameter Data of PEMPT BNZ/PC Blends

parameter	exptl value	calcd value: monodisperse	calcd value: polydisperse
X_{n1c}(PEMPT/PC1)	21		
X_{n2c}(PEMPT/PC1)	45		
ϕ_{1c}(PEMPT/PC1)	0.56	0.59	0.60
X_{n1c}(PEMPT/PC2)	17		
X_{n2c}(PEMPT/PC2)	85		
ϕ_{1c}(PEMPT/PC2)	0.66	0.67	0.69
χ_{12s}(PEMPT/PC1)		0.067	0.045
χ_{12c}(PEMPT/PC1)		0.068	
χ_{12s}(PEMPT/PC2)		0.062	0.043
χ_{12c}(PEMPT/PC2)		0.062	

The differences in the phase behavior of the PEMPT BNZ/PC blends vs the PEMPT HFB/PC blends can be qualitatively explained by these changes in the interaction parameter. As the molecular weight of the polyester is lowered in the PEMPT BNZ/PC blends, the entropic effects enhancing partial miscibility are not affected by the minor changes in the interaction parameter. In this case, increased partial miscibility is observed as X_{n1} is lowered. For blends containing PEMPT HFB, as the molecular weight of the polyester is lowered, the entropic contribution that improves partial miscibility is countered by the increase in the enthalpic contribution associated with the increase in χ_{blend}. In the present case, these effects must nearly cancel, leading to no change in the level of partial miscibility with decreasing X_{n1}.

Examining Figure 9, a miscibility diagram represents a curve on the boundary surface similar to curve dce of Figure 1. Thus, each miscibility diagram also contains a single critical point of interest. The assumption will be made that the minimum of each miscibility diagram corresponds to the critical point. Within the constraints of Flory–Huggins theory, this fact is true if both blend components are monodisperse. The extent to which the above assumption is valid will be judged by the comparison between the experimentally determined critical compositions and the values derived from eqs 3 and 7. Table 3 contains the critical chain lengths, X_{n1c}, and critical compositions, ϕ_{1c}, determined from the minimums of the miscibility diagrams of Figure 9.

Table 4. Ratio of Polydispersity Indices of PEMPT BNZ/PC Blends

blend	$\left(\frac{X_{w1}/X_{n1}}{X_{w2}/X_{n2}}\right)^{1/2}$	$\left(\frac{X_{z2}/X_{w2}}{X_{z1}/X_{w1}}\right)^{1/2}$	$\left(\frac{X_{w1}/X_{n1}}{X_{w2}/X_{n2}}\right)^{1/2} \times \left(\frac{X_{z2}/X_{w2}}{X_{z1}/X_{w1}}\right)^{1/2}$
PEMPT1-BNZ/PC1	0.98	0.99	0.97
PEMPT2-BNZ/PC1	1.00	0.98	0.98
PEMPT1-BNZ/PC2	1.00	0.98	0.98
PEMPT2-BNZ/PC2	1.03	0.97	1.00

The experimentally determined values of ϕ_{1c} agree with the calculated values from both eqs 3 and 7 (Table 3). This indicates that the critical points do lie close to the minimum of the miscibility diagrams. The fact that values of ϕ_{1c} calculated from eqs 3 and 7 agree is somewhat fortuitous, being associated with the observed polydispersities of the polyesters and polycarbonates. Rewriting eq 7 in terms of the polydispersity indices (measurable quantities), one obtains

$$\phi_{1c} = \frac{1}{1 + \left(\frac{X_{n1}}{X_{n2}}\right)^{1/2}\left(\frac{X_{w1}/X_{n1}}{X_{w2}/X_{n2}}\right)^{1/2}\left(\frac{X_{z2}/X_{w2}}{X_{z1}/X_{w1}}\right)^{1/2}} \quad (12)$$

Using the values of X_w/X_n and X_z/X_w of Table 1 for PEMPT 1-BNZ/PC and PEMPT 2-BNZ/PC blends, the values of the ratio of polydispersity indices are calculated (Table 4). With the product of these ratios ~ 1.00, the denominator of eq 12 reduces to $[1 + (X_{n1}/X_{n2})^{1/2}]$ and eq 12 becomes equivalent to eq 3. The critical point region corresponds to these ratios; hence, in this molecular weight range the blends behave as quasi-monodisperse binary pairs. In this case, the critical points are theoretically expected to be at the minimum in the phase diagram, as was assumed above. Results of this nature have been predicted by Koningsveld et al.[22]

The miscibility diagrams of Figure 9 can also be used to calculate the interaction parameter of the blend. The critical point represents the one point on the boundary surface of Figure 1 where the spinodal and binodal surfaces coincide. The critical point also represents a point on the boundary surface where the interaction parameter can be easily calculated from theory. With respect to Flory–Huggins theory, the interaction parameter of the blend calculated from either eq 4 or 5 should be identical if the critical point, molecular weight, and volume fraction data are applied. The calculated values of χ_{12s} and χ_{12c} determined from both equations agree with this statement (Table 3), with the interaction parameters all being ~0.065. Taking polydispersity into account (eq 8), χ_{12s} has an average value of 0.044.

The interaction parameters calculated from the two different theories (monodisperse vs polydisperse) do not agree. Unlike the equations describing ϕ_{1c}, the equations used to determine χ_{12} are not functions of the polydispersity index ratios which were previously shown to be ~1. Polydispersity effects are expected to lead to a difference in the calculated interaction parameters. Between the two sets of calculations, Flory–Huggins theory modified to account for polydispersity is a better representation of the current blends. The interaction parameter calculated from this model, 0.044, will be designated as the interaction parameter for the PEMPT/PC blends. It should be mentioned that the value for

χ_{12} calculated from the solubility parameter approach, 0.054, is in fair agreement with the values calculated from critical point data.

Conclusions

PEMPT OH/PC and PEMPT BNZ/PC blends are shown to be two phase for all but the lowest molecular weight pairs studied. Molecular weight effects in these two blend systems are in qualitative agreement with entropic terms in Flory–Huggins theory. Variations in the phase behavior with respect to blend composition ratio are observed, particularly in samples composed of low molecular weight PEMPTs. End-group type is shown to alter the blend phase behavior. End-group effects are seen to nullify the entropic driving force for mixing in PEMPT HFB/PC blends as the polyester molecular weight is lowered. From a qualitative standpoint, the binary interaction model successfully predicts that the PEMPT HFB blends should exhibit a greater level of phase separation compared to the PEMPT BNZ blends. This result is based on changes in the interaction parameter of the blend caused by the increasing number of end groups with decreasing polyester M_n. From critical point data determined from the PEMPT BNZ/PC miscibility diagrams, the interaction parameter is calculated to be 0.044. With the phase behavior studies of the PEMPT/PC blends (in the absence of transreaction) completed, the effect of interchange reaction on blend phase behavior can now be examined. This is the topic of the third paper of this series.

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