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Polycarbonate/Copolyester Blends Having Optical-Grade Clarity and Their Upper Critical Solution Temperature Type Phase Behavior

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The miscibility of bisphenol A polycarbonate (PC) and poly(ethylene terephthalate-co-1,4-dimethyl cyclohexane terephthalate) copolyesters (PECT) containing various amount of 1,4-dimethyl cyclohexane were explored to produce a blend having optical-grade clarity. It is known that PC does not form miscible blends with poly(ethylene-terephthalate) (PET), while it forms a miscible blend with poly(1,4-dimethyl cyclohexane terephthalate) (PCT). PC blends with PECT copolyesters prepared by solvent casting were not miscible regardless of the copolyester composition. However, PC and PECT copolyesters containing 1,4-dimethyl cyclohexane from 32 to 80 mol % formed homogeneous mixtures upon heating. Since immiscibility of solvent casting samples can be driven by solvent effects even though PC/PECT binary blends are miscible, upper critical solution temperature (UCST) type phase behavior was confirmed by exploring phase reversibility. The phase homogenizing temperature of PC/PECT blends exhibiting UCST-type phase behavior was increased by decreasing the 1,4-cyclohexane dimethanol (CHDM) content in copolyester. The metastable blends obtained by quenching from above the phase-homogenization temperature exhibited a single glass transition temperature and had optical-grade clarity.

Introduction

Bisphenol A polycarbonate (PC) is increasingly used as a homopolymer since it combines optical-grade clarity with toughness, rigidity, and a high heat deflection temperature. However, drawbacks of PC such as poor resistance to solvent stress cracking and poor processability caused by its high melt viscosity often deterred its applications. Since one may achieve useful combinations of the advantages of each polymer into single product by blending, numerous studies related to the PC blends have been performed. Among these, PC blends with polyesters, both aliphatic and those containing aromaticity, have been investigated extensively to overcome the drawbacks of PC.^{1–17} The focus of attention is directed to find homogeneous mixture and to explore the beneficial properties that may be gained by blending. From early investigations related to the PC blends with aliphatic polyester, it was concluded that miscibility occurred when the methylene content of polyester is approximately between two and seven methylene segments per ester group.^{3–5,9} It has been also confirmed the miscibility of PC with polyesters containing alicyclic structures such as PCDS (poly(1,4-cyclohexane dimethylene succinate)) and PCDACD (polyester derived from 1,4-cyclohexanedimethanol and 1,4-cyclohexanedicarboxylic acid).^{15,18–19} Among these miscible blends, PC blends with polyester containing alicyclic structure are using commercially as optical grade (GE, trade name: Xylex). Miscible PC blends with semi-aromatic polyesters such as poly(1,4-dimethyl cyclohexane terephthalate) (PCT, trade

name: Kodel) and polyester based on 1,4-cyclohexane dimethanol/terephthalic acid/isophthalic acid (PCDT, trade name: Kodar) have been also reported in the literature.^{1,15,20} Even though these blends are miscible at the processing temperature, they cannot be used as optical grades because of the crystalline content in PCT or PCDT.

Poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) (PECT) is a copolyester with optical clarity, good low temperature toughness, chemical resistance, and excellent processability. However, the low glass transition temperature of PECT deterred its application. Blending of PC with PECT offers an attractive opportunity for the development of novel materials exhibiting useful combination of the properties. Compared to PC, the PECT in blend provides enhanced chemical resistance and permits lower processing temperatures than PC. Optically clear grades are often developed from the blends that are miscible at the processing temperature. It is known that PC does not form miscible blends with poly(ethylene-terephthalate) (PET),^{2,16} while it forms a miscible blend with PCT.^{1,15,20} It has been also shown previously that addition of comonomer units to one of the homopolymers may be an effective way of developing a miscible blend.^{21–27} These previous results indicate that blending of PC with PECT containing desired amounts of the 1,4-dimethyl cyclohexane unit in copolyesters may be an effective strategy for the development of miscible blends having optical-grade clarity. It has been reported that PC blends with a PECT, which was synthesized from 1,4-cyclohexane dimethanol (CHDM), ethylene glycol (EG), and terephthalic acid in a molar ratio of approximately 1/2/3, were not miscible.¹⁷

In this study, the phase behavior of PC blends with PECT copolyesters containing various amounts of the 1,4-dimethyl

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Table 1. Polymers Used in This Study

abbreviation ^a	\bar{M}_w^b	\bar{M}_n^b	T_g (°C)	source
PC	39 000	23 000	148	LG chemicals, grade 300–10
PECT 5	38 000	26 000	93	SK chemicals
PECT 32	40 000	27 000	79	SK chemicals
PECT 60	37 000	25 000	85	SK chemicals, grade JN–100
PECT 80	42 500	28 000	89	SK chemicals

^a The numerical value included as part of the code for these copolyesters indicates the nominal percent by mole of CHDM of the total diol composition in the copolyester. ^b Molecular weight information was provided by the suppliers.

cyclohexane unit was explored to develop a blend that overcomes the drawbacks of PC and has optical-grade clarity.

Materials and Procedure

The polymers used in this study were listed in Table 1. PC was of commercial grade (300-10) supplied by LG Chemicals. PECT copolyesters were obtained from SK Chemicals. A PECT copolyester designated PECT 60 was of commercial grade (trade name: JN-100), while other PECT copolyesters were experimental grades specially synthesized by SK Chemicals for this study. According to the supplier, copolyesters consist of diol (EG and CHDM) and terephthalic acid in a molar ratio of 1/1. The numerical value included as part of the code for these copolyesters indicates the nominal percent by mole of CHDM of the total diol composition in the copolyester. PC and PECT were dried in a vacuum oven for a day prior to processing at 120 and 80 °C, respectively.

The blends of PC and PECT 80 (or PECT 5) were prepared in film form by casting solutions containing 5 wt % total polymer in *o*-chlorophenol onto a petri dish. After drying at 120 °C for a day to remove most of the solvent, the blends were finally dried in a vacuum oven at 120 °C for a week. The blends of PC and other PECT copolyesters were prepared via solution casting from methylene chloride. The casting solutions were dried at room temperature until most of the solvent had evaporated, and then, the resulting films were further dried in a vacuum oven at 120 °C for a week. Blends were also prepared by melt mixing. Melt mixing was performed in a twin screw extruder (Bau Tech, model BA-11, *L/D* ratio = 40) at 270 °C. Melt mixed blends were immediately quenched into a water bath after extrusion.

Transition temperatures of blends, i.e., the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m), were measured at a heating rate of 20 °C/min by using differential scanning calorimetry (DSC) (TA Instrument, model: DSC-2010). The first scan was run to 280 °C to erase the previous thermal history during sample preparation, and then, the sample was quenched to room temperature to start the second scan. T_g was defined as the onset of change in the heat capacity. The phase homogenization temperature caused by the upper critical solution temperature (UCST) type phase behavior was measured by an annealing technique to access the closest true equilibrium temperature.^{24–28} Changes in the morphology of blends with temperature were observed by an image analyzer [Bummi Universe, model: I-Top] equipped with a hot stage [Linkam THMS 600]. The total light transmittance and haze of PC, copolyesters, and blends were then investigated. The total light transmittance and haze were measured in accordance with the American Standards Testing Method (ASTM) specification No. D1003. Each experiment was performed at least five times, and data are reported as the means of these values.

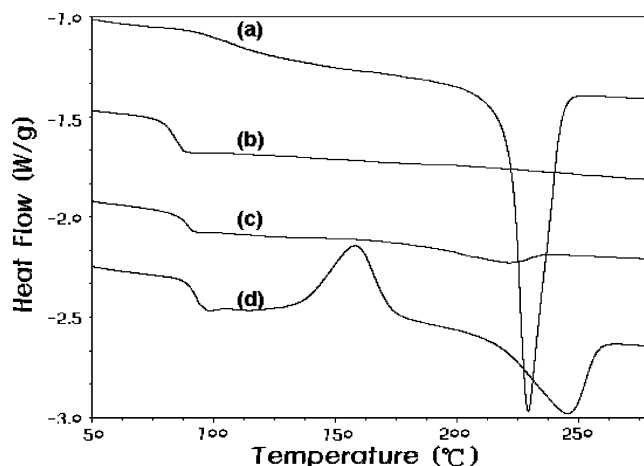


Figure 1. DSC thermograms of various PECT copolyesters: (a) PECT 5; (b) PECT 32; (c) PECT 60; (d) PECT 80.

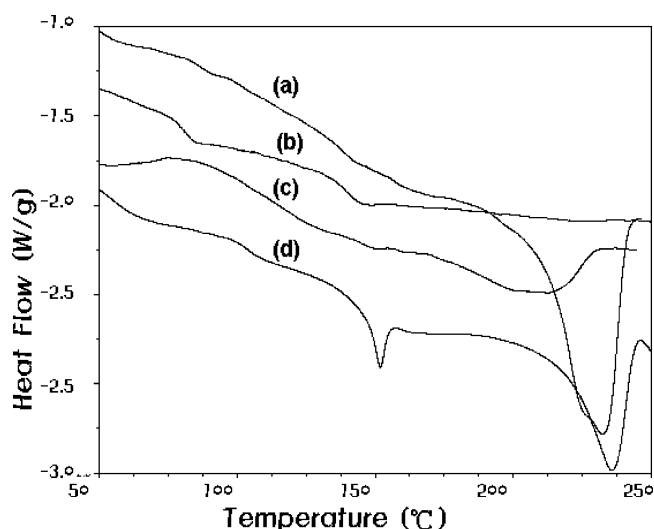


Figure 2. DSC thermograms of PC/PECT = 50/50 blends (first scan) prepared by solvent casting. Note that the first scan was run from room temperature to 280 °C: (a) PC/PECT 5 = 50/50; (b) PC/PECT 32 = 50/50; (c) PC/PECT 60 = 50/50; (d) PC/PECT 80 = 50/50.

Results and Discussion

Thermal Behavior of PECT Copolyesters and Blends.

PECT copolyesters as received samples were transparent except for PECT 5. Figure 1 shows DSC thermograms of various PECT copolyesters. For PECT 5, a melting endotherm (229 °C) was observed upon heating. PECT 32 and PECT 60 showed a T_g at 79 and at 85 °C, respectively. For PECT 80, a crystallization exotherm (158 °C) was observed upon heating above the T_g (89 °C).

Figure 2 shows DSC thermograms of PC/PECT = 50/50 blends prepared by solvent casting. The blends cast from solvent were translucent and visually heterogeneous, and each DSC thermogram showed two T_g s indicating that phase separation occurred. Figure 3 exhibits thermograms of PC/PECT = 50/50 blends observed at the second scan after the first scan was run to 280 °C. PC blends with PECT copolyesters containing CHDM from 32 to 80 mol % exhibited a single T_g at a temperature intermediate between the glass transition of PC and PECT. However, the thermogram of PC blend with PECT 5 still showed two T_g s. All blends prepared at other compositions showed a similar thermal behavior. These results indicated that PC formed homogeneous mixtures with PECT copolyesters containing CHDM from 32 to 80 mol % upon heating.

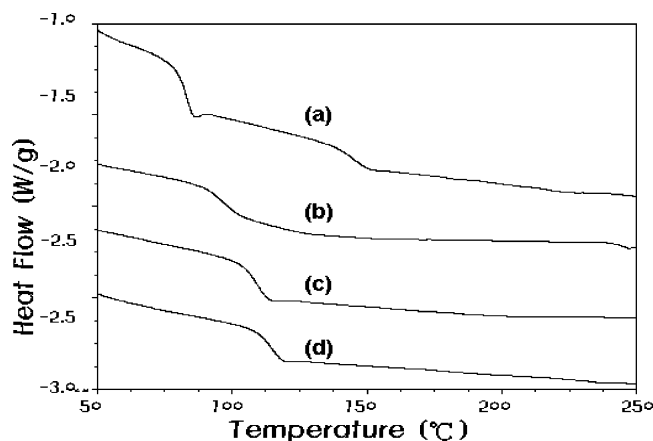


Figure 3. DSC thermograms of PC/PECT = 50/50 blends observed at the second scan after the first scan was run to 280 °C: (a) PC/PECT 5 = 50/50; (b) PC/PECT 32 = 50/50; (c) PC/PECT 60 = 50/50; (d) PC/PECT 80 = 50/50.

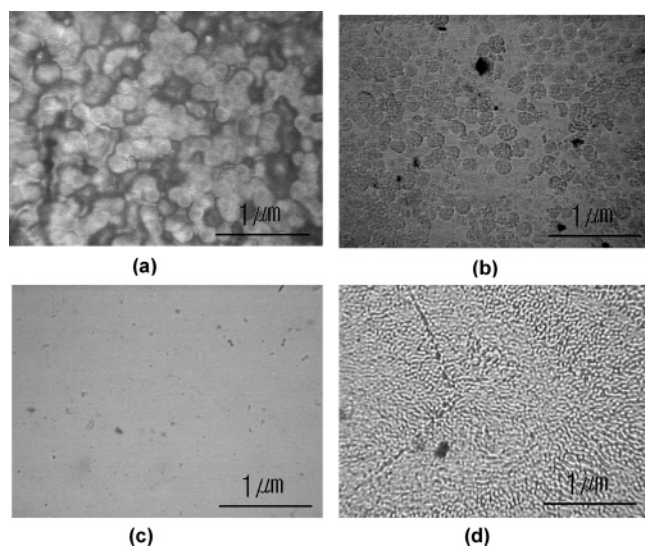


Figure 4. Morphology changes of PC/PECT 32 = 60/40 blend with temperature.

The blend was heated from room temperature to 280 °C at a scanning rate of 10 °C/min and then cooled to 260 °C at the same scanning rate: (a) blend morphology prepared by solvent casting; (b) blend morphology observed at 250 °C on heating; (c) blend morphology observed at 280 °C on heating; (d) blend morphology observed after cooling from 280 to 260 °C (Note that the image was captured after annealing at 260 °C for 5 min.).

When the phase separated polymer mixture reaches the upper critical solution temperature (UCST) type phase boundary upon heating, it undergoes phase homogenization. On the other hand, the fact that each binary pair is miscible does not guarantee that all ternary compositions will be. Immiscibility can be driven by an asymmetry of binary interactions, the so-called $\Delta\chi$ effects, just like ternary solvent/polymer/polymer mixtures.^{29–32} This means that the immiscibility of a polymer–polymer mixture may be induced by using solvent in the preparation of samples, even though the polymer–polymer mixture is miscible. To confirm that the observed phase behavior of PC/PECT blends stemmed from UCST-type phase behavior, phase reversibility of the blends was explored. Figure 4 exhibits the morphology changes of the PC/PECT 32 = 60/40 blend observed at various temperatures with an image analyzer. As shown in Figure 4a, PC/PECT 32 = 60/40 blends prepared by solvent casting exhibited phase separated structures. When the blend was heated up to 280 °C at a scanning rate of 10 °C/min, a homogeneous mixture was formed (See Figure 4c). When the homogenized

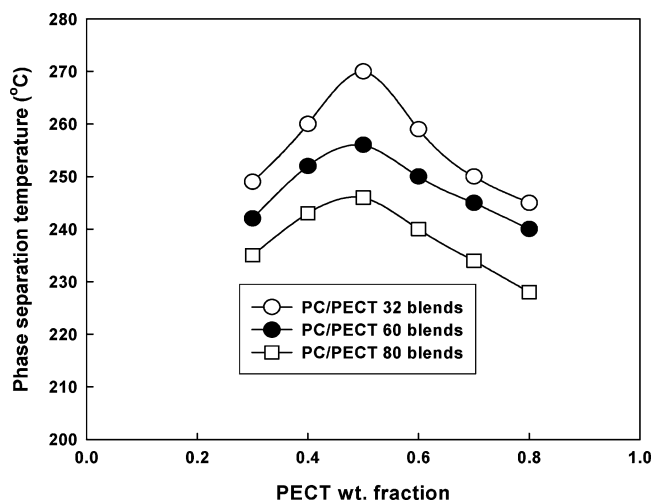


Figure 5. UCST-type phase boundaries of PC blends with PECT copolyesters containing various amounts of CHDM.

blend at 280 °C was cooled to 260 °C at a scanning rate of 10 °C/min, it underwent phase separation. Figure 4d exhibited the image captured after annealing at 260 °C for 5 min. The results observed here indicated that phase homogenization of PC/PECT blends upon heating stemmed from UCST-type phase behavior.

Interchange reactions involving an ester linkage and a carbonate linkage, i.e., transesterification, would affect the phase behavior of the blend.^{1–5,15–17} Interchange reactions between PC and PECT (or PECT) were studied in previous research.^{1,17} It was concluded that their effects on the miscibility of a blend are not of any major consequence. The phase reversibility observed here also confirmed that a transesterification reaction might be ruled out.

Phase Homogenization Temperature of PC/PECT Blends.

Phase homogenization temperatures of blends caused by UCST-type phase behavior were measured by an annealing technique. For example, the PC/PECT 60 = 50/50 blend was heated rapidly to a temperature about 200 °C and then heated at a rate of 5 °C/min. Changes in the image with temperature were observed as the specimens were heated at a rate of 5 °C/min. Changes in the image were observed at 265 °C. After determining the temperature at which phase homogenization occurred, blend specimens were annealed in the hot stage at a fixed temperature for 10 min. The blend annealed at 250 °C was still opaque and changes in the morphology of the blend were not observed, while that annealed at 260 °C became clear and changes in the morphology were observed during annealing, i.e., domains existing in the matrix disappeared completely. The phase boundary would appear to lie between 250 and 260 °C for this blend. By successively repeating the annealing process within the measured temperature range, the location of the phase boundary was determined.

Figure 5 shows the phase homogenization temperatures for PC/PECT blends. The phase homogenization temperature curves for PC/PECT blends are all very similar with each showing a maximum at about 50 wt % PC. The phase homogenization temperature of blends increases with the ethylene glycol content in PECT copolyesters. However, when PC was blended with PECT 5, phase homogenization did not occur upon heating until the thermal degradation temperature (330 °C).

The blends examined here are immiscible around room temperature. However, when blends exhibiting UCST-type phase behavior were taken above the homogenization temperature and quenched back to room temperature, the metastable blends that showed a single T_g at room temperature were

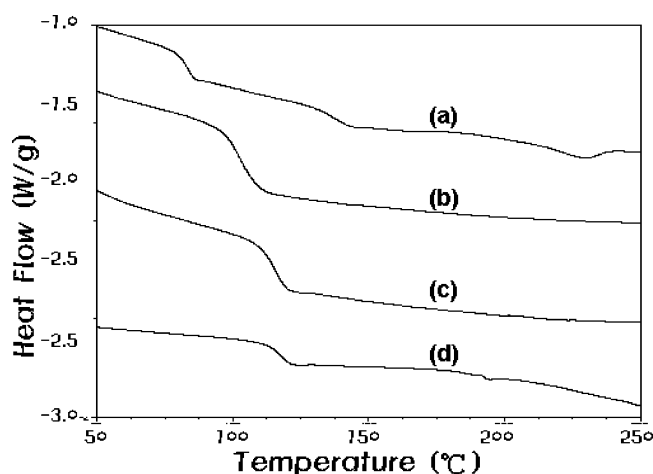


Figure 6. DSC thermograms of PC/PECT = 50/50 blends prepared by melt mixing at 270 °C: (a) PC/PECT 5 = 50/50; (b) PC/PECT 32 = 50/50; (c) PC/PECT 60 = 50/50; (d) PC/PECT 80 = 50/50.

produced because of slow phase separation kinetics (Figure 3). This means that PC/PECT blends having optical-grade clarity could be produced by melt mixing even though they are not miscible in equilibrium at room temperature. Samios et al.¹⁷ examined the miscibility of PC and PECT containing about 33 mol % CHDM. The PECT used in their experiments is nearly the same as the PECT 32 used here. They performed melt mixing of PC/PECT blends in a homemade stainless steel bob-and-cup type mixer at 270 °C. Blend films were obtained by compression molding at 270 °C and 10 MPa, followed by pressure release and quenching to 0 °C. The reported results that PC/PECT blends are immiscible regardless of compositions are a contrast to our expectation. PC/PECT = 50/50 blends prepared by melt mixing at 270 °C in a twin extruder were immediately quenched into a water bath. Compression molding of the blend was performed under the conditions reported by Samios et al.¹⁷ Melt mixed PC blends with PECT copolyesters containing CHDM from 32 to 80 mol % were transparent and DSC thermograms of these blends exhibited a single T_g at a temperature intermediate between the glass transition of PC and PECT as shown in Figure 6. As expected, melt mixed PC/PECT 5 = 50/50 was translucent and its DSC thermogram showed two T_g s. From the results obtained here, it could be concluded that metastable blends quenched from above the homogenization temperature showed a single T_g and looked clear.

To examine the potential usefulness in optical applications, the total light transmittance and the haze of some of the PC/PECT = 50/50 blends were measured in accordance with ASTM specification No. D1003. As exhibited in Figure 7, the total light transmittance and the haze of blends were similar to those of PC and PECT copolymer. These results indicated that some of PC/PECT blends exhibiting UCST-type phase behavior might be used in optical applications.

Summary

The miscibility of PC and PECT copolyesters containing various amounts of 1,4-dimethyl cyclohexane was examined to develop blends having optical-grade clarity. PC/PECT blends prepared from solvent casting were not miscible regardless of copolyester composition and blend composition. However, PC blends containing CHDM from 32 to 80 mol % became miscible upon heating because of UCST-type phase behavior. UCST-type phase behavior of these blends was confirmed by examining phase reversibility. The homogenization temperature of blends

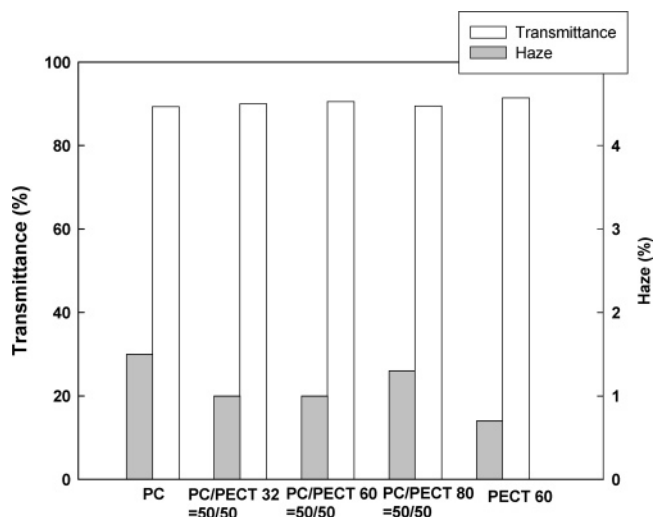


Figure 7. Total light transmittance and the haze of PC, PC/PECT blends, and PECT 60 measured in accordance with ASTM specification No. D1003.

increases with ethylene glycol content in the PECT copolyester. The phase homogenization of PC/PECT 5 blends was not observed until the thermal degradation temperature (~330 °C). To explore the possibility for the development of blends exhibiting optical-grade clarity, PC/PECT blends exhibiting UCST-type phase behavior were prepared by melt mixing at above the phase homogenization temperature and then their total light transmittance and haze were examined. These blends exhibited a single glass transition at a temperature intermediate between the glass transition of PC and PECT copolyester, and their total light transmittance values were similar with those of PC and copolyester.

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Literature Cited

- (1) Mohn, R. N.; Paul, D. R.; Barlow, J. W.; Cruz, C. A. Polyester-Polycarbonate Blends. III. Polyesters Based on 1,4-Cyclohexanedimethanol/Terephthalic acid/Isophthalic acid. *J. Appl. Polym. Sci.* **1979**, *23*, 575.
- (2) Nassar, T. R.; Paul, D. R.; Barlow, J. W. Polyester-polycarbonate blends. II. Poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **1979**, *23*, 85.
- (3) Cruz, C. A.; Paul, D. R.; Barlow, J. W. Polyester-Polycarbonate blends. IV. Poly(ϵ -caprolactone). *J. Appl. Polym. Sci.* **1979**, *23*, 589.
- (4) Cruz, C. A.; Paul, D. R.; Barlow, J. W. Polyester-polycarbonate blends. V. Linear aliphatic polyesters. *J. Appl. Polym. Sci.* **1979**, *23*, 2101.
- (5) Cruz, C. A.; Paul, D. R.; Barlow, J. W. The Basis for Miscibility in Polyester-Polycarbonate Blends. *Macromolecules* **1979**, *12*, 726.
- (6) Murff, R.; Barlow, J. W.; Paul, D. R. Thermal and mechanical behavior of polycarbonate-poly(ethylene terephthalate) blends. *J. Appl. Polym. Sci.* **1984**, *29*, 3231.
- (7) Smith, W. A.; Barlow, J. W.; Paul, D. R. Chemistry of miscible polycarbonate-copolyester blends. *J. Appl. Polym. Sci.* **1981**, *26*, 4233.
- (8) Jonsa, J. M.; Porter, R. S. Bisphenol A polycarbonate/poly(ϵ -caprolactone) blends: melting point depression and reactivity. *Macromolecules* **1986**, *19*, 1946.
- (9) Lai, C. H.; Barlow, J. W.; Paul, D. R. Group contribution methods for predicting polymer-polymer miscibility from heats of mixing of liquids. 2. Polyester-containing binary blends. *Macromolecules* **1989**, *22*, 374.
- (10) Ellis, T. S. Miscibility of Blends of Aliphatic Main-Chain Polyesters. *Macromolecules* **1995**, *28*, 1882.
- (11) Brostow, W.; Hess, M.; Lopez, B. L.; Sterzynski, T. Blends of a longitudinal polymer liquid crystal with polycarbonate: relation of the phase diagram to mechanical properties. *Polymer* **1996**, *37*, 1551.

- (12) Ignatov, V. N.; Carraro, C.; Tartari, V.; Pippa, R.; Scapin, M.; Pilati, F.; Berti, C.; Tosselli, M.; Fiorini, M. PET/PC blends and copolymers by one-step extrusion: 1. Chemical structure and physical properties of 50/50 blend. *Polymer* **1997**, *38*, 195.
- (13) Ignatov, V. N.; Carraro, C.; Tartari, V.; Pippa, R.; Scapin, M.; Pilati, F.; Berti, C.; Tosselli, M.; Fiorini, M. PET/PC blends and copolymers by one-step extrusion: 2. Influence of the initial polymer composition and type of catalyst. *Polymer* **1997**, *38*, 201.
- (14) Montaudo, G.; Poglisi, C.; Samperi, F. Mechanism of Exchange in PBT/PC and PET/PC Blends. Composition of the Copolymer Formed in the Melt Mixing Process. *Macromolecules* **1998**, *31*, 650.
- (15) Ellis, T. S. Phase behaviour of blends of polyesters and polycarbonates. *Polymer* **1998**, *39*, 4741.
- (16) Kong, Y.; Hay, J. N. Miscibility and crystallisation behaviour of poly(ethylene terephthalate)/polycarbonate blends. *Polymer* **2002**, *43*, 1805.
- (17) Samios, C. K.; Kalfoglou, N. K. Compatibility characterization of polycarbonate/copolyester blends. *Polymer* **2000**, *41*, 5759.
- (18) Shah, V. S.; Paul, D. R.; Barlow, J. W. Miscible ternary blends containing polycarbonate, SAN, and aliphatic polyesters. *J. Appl. Polym. Sci.* **1986**, *32*, 3863.
- (19) Paul, D. R.; Barlow, J. W. In *Polymer Science and Technology, Polymer Alloys II*; Klempner, D., Frisch, K. C., Eds.; Plenum Press: New York, 1977; Vol. 11, p 239.
- (20) Spall, S.; Goodwin, A. A.; Zipper, M. D.; Simon, G. P. Molecular dynamics in a miscible polyester blend. *J. Polym. Sci., Part B* **1996**, *34*, 2419.
- (21) Barlow, J. W.; Paul, D. R. A binary interaction model for miscibility of copolymers in blends. *Polymer* **1984**, *25*, 487.
- (22) ten Brinke, G.; Karasz, F. E.; Macknight, W. J. Phase behavior in copolymer blends: poly(2,6-dimethyl-1,4-phenylene oxide) and halogen-substituted styrene copolymers. *Macromolecules* **1983**, *16*, 1827.
- (23) Kim, J. H.; Hwang, M. S.; Kim, C. K. Novel Miscible Blends Composed of Poly(ether sulfone) and Poly(1-vinylpyrrolidone-co-styrene) Copolymers and Their Interaction Energies. *Macromolecules* **2004**, *37*, 2287.
- (24) Nishimoto, M.; Keskkula, H.; Paul, D. R. Role of slow phase separation in assessing the equilibrium phase behaviour of PC-PMMA blends. *Polymer* **1991**, *32*, 272.
- (25) Kim, C. K.; Paul, D. R. Interaction parameters for blends containing polycarbonates: 3. Polycarbonate copolymers/styrene-based copolymers. *Polymer* **1992**, *33*, 4941.
- (26) Kim, C. K.; Paul, D. R. Miscibility of poly(methyl methacrylate) blends with halogen-containing polycarbonates and copolymers. *Polymer* **1992**, *33*, 4929.
- (27) Kim, Y.; Yoo, J. E.; Kim, C. K. Miscibility of copolycarbonate blends with poly(styrene-co-acrylonitrile) copolymer and their interaction energies. *Polymer* **2003**, *44*, 5439.
- (28) Callaghan, T. A.; Paul, D. R. Estimation of interaction energies by the critical molecular weight method: 1. Blends with polycarbonates. *J. Polym. Sci., Part B* **1994**, *32*, 1813.
- (29) Brannock, G. R.; Paul, D. R. Phase behavior of ternary polymer blends composed of three miscible binaries. *Macromolecules* **1990**, *23*, 5240.
- (30) Landry, C. J. T.; Yang, H.; Machell, J. S. Miscibility and mechanical properties of a ternary polymer blend: polystyrene/polycarbonate/tetramethyl polycarbonate. *Polymer* **1991**, *32*, 44.
- (31) Sanchez, I. C. Volume fluctuation thermodynamics of polymer solutions. *Macromolecules* **1991**, *24*, 908.
- (32) Sanchez, I. C. *Encyclopedia of Physical Science and Technology*; Academic Press: New York, 1987; Vol. XI, p 1.

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