Phase Behavior and Transreaction Studies of Model Polyester/Bisphenol-A Polycarbonate Blends. 1. Synthesis, End-Capping, and Characterization of Poly(2-ethyl-2-methylpropylene terephthalate)

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ABSTRACT: The synthesis, end-capping, and characterization of a novel, amorphous polyester, poly(2-ethyl-2-methylpropylene terephthalate) (PEMPT), is described. PEMPT is synthesized by standard two-stage polycondensation techniques. End-group modification employs nucleophilic substitution reactions with heptafluorobutyryl chloride and benzoyl chloride. In addition to the assignment of midchain ^{1}H and ^{13}C NMR resonances, end-group resonances of hydroxyl-terminated PEMPTs are identified by proton NMR and confirmed by NMR analysis of the end-capped polyesters. The glass transition temperature (T_g) increases with M_n, following the functional form predicted by Fox and Flory. T_gs range from 55.2 to 65.4 °C with $T_{g,\infty} = 67$ °C. TGA indicates PEMPT to have improved thermal stability compared to linear aliphatic–aromatic polyesters. PEMPT is soluble in numerous solvents with a solubility parameter of 9.4 (cal/cm^3)$^{1/2}$. Observed property differences between the hydroxyl-terminated PEMPTs (as synthesized) and the end-capped polyesters are attributed to the hydrogen-bonding capability of the former.

Introduction

As well documented, binary polymer blends, which can undergo exchange reactions in the melt, have received considerable academic and industrial attention in recent years.[1] Of particular interest have been the industrially significant blends based on polyester/polyester or polyester/polycarbonate compositions.[2–38] Blends of this nature are capable of exchange reaction between the ester–ester or ester–carbonate functional groups. Alcohol or acid end groups may also react with the ester and/or carbonate functional groups in an alcoholysis or acidolysis exchange reaction.[39] The result of these "exchange reactions", "transreactions", or "interchange reactions", as they are often called, is the formation of block/random copolymers from the original binary pair. These block/random copolymers have a homogenizing effect on the blend which enhances the miscibility between components leading to a single-phase blend.[2–9] With the extent of interchange reaction being a key variable in regards to phase behavior, it is surprising that little or no quantitative information exists relating transreaction to changes in phase behavior. The role of the separate reactions, intermolecular alcoholysis, intermolecular acidolysis, and direct midchain transreaction in relation to shifts in phase behavior is also unknown.

The majority of studies have qualitatively monitored transreaction through phase changes as measured by DSC, DMTA, or microscopy. Indeed, monitoring a blend's phase behavior with annealing time has become the one commonly employed method to indirectly identify if a particular blend is capable of transreaction. These indirect measures cannot provide quantitative information in regards to blend reaction. Other studies have employed direct measurements, such as IR, DRIFT, ^{1}H and ^{13}C solution NMR, and solid-state ^{13}C NMR, to identify transreaction.[10–16,40–43] None of these studies, however, have correlated phase changes to extent of reaction. Our goal is to obtain quantitative information relating the extent of transreaction to blend phase behavior and to identify the direct role of midchain reaction relative to end-group reactions.

Several factors unique to these reacting blends complicate their study. Before one can examine the effect of transreaction, the equilibrium phase behavior prior to transreaction must be known. To obtain such information, the blend must be elevated to temperatures above the melt temperatures (T_ms) or glass transition temperatures (T_gs) of the component polymers. At these temperatures, transreaction can occur, altering the phase behavior. Thus, information on the unreacted blend can only be obtained if the rate of exchange reaction is slow relative to the kinetics of phase separation. Conflicting reports as to the degree of miscibility of poly(butylene terephthalate) (PBT)/Bisphenol-A polycarbonate (PC) and poly(ethylene terephthalate) (PET)/PC blends may in part be attributed to shifts in the phase behavior caused by undetected reaction.[17–29] Due to their academic as well as industrial importance, PET/PC and PBT/PC blends are the first choice for study. However, in addition to the phase behavior discrepancies, other difficulties with these blends are apparent.

The insolubility of PBT and PET in nearly all solvents commonly employed for spectroscopic examination inhibits NMR and IR analysis for quantitative measurement of transreaction. When extensive amounts of transreaction have occurred enhancing solubility, these spectroscopic techniques have successfully identified transreactions.[10–13] Decomposition reactions, particularly in PC/PET compositions, have been shown to complicate the analysis of the reacting blend.[12,13,30,31] Additionally, if one or both blend components can crystallize, clear identification of the level of partial miscibility, as measured by the shifting of T_gs, can be obscured by crystallization exotherms and endotherms.[7,9,29,31]

A model polyester/PC blend is desired for studies of transreaction. The model polyester should be structurally similar to PET and PBT, be amorphous or slow to

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Table 1. Second-Stage Synthesis Conditions and End-Group Analysis of PEMPT

polyester	time, min	temp, °C	vacuum, mmHg	mol of OH[a] / g of polymer (×10⁴)	mol of COOH / g of polymer (×10⁴)
PEMPT 1-OH	10	250	0.55	4.87	0.0093
PEMPT 2-OH	20	245	0.46	3.26	0.0141
PEMPT 3-OH	60	250	0.37	2.10	0.0112
PEMPT 4-OH	90	250	0.42	1.73	0.0174
PEMPT 5-OH	130	250	0.41	1.08	0.0115
PEMPT 6-OH	180	250	0.43	0.50	0.0314
PEMPT 7-OH	120	245	1.2	1.11	0.0245

[a] From fluoride end-group analysis.

crystallize, be soluble in common solvents, have a T_g well separated from that of PC, have a thermal stability at the temperatures required for transreaction, and be able to form a two-phase blend with PC. We have previously reported on several aliphatic–aromatic polyesters and their blends with PC that potentially meet the above criteria.[44] From that study, poly(2-ethyl-2-methylpropylene terephthalate) (PEMPT) was selected as the model polyester for phase behavior and transreaction studies. Besides our initial communications, PEMPT has not been reported, to our knowledge.[44,45]

The goal of this paper is to present the synthesis, end-capping, and characterization of this novel polyester. Previously, PEMPT was synthesized by standard two-stage polycondensation techniques, and the same approach is used here.[44] End-capping is carried out via nucleophilic substitution reaction with two different acid chlorines. End-capping verifies proton NMR resonances corresponding to PEMPT's end-group structure and is also a potential method to prevent alcoholysis interchange reaction. After characterization, these samples are used to examine the phase behavior of PEMPT/PC blends prior to transreaction followed by quantitative studies correlating phase behavior changes to the extent of transreaction. These topics are the focus of the second and third papers of this series.

Experimental Procedures

Materials. All chemicals were obtained from the Aldrich Chemical Co. Unless otherwise stated, solvents were of HPLC quality. Dimethyl terephthalate (DMT) (99+%) was purified by a recrystallization from a hot chloroform/*n*-heptane (2/3 v/v) solution. Short, needlelike, white crystals were recovered and dried under vacuum. 2-Ethyl-2-methyl-1,3-propanediol (EMPD) (98%) was purified by drying at 52 °C over magnesium sulfate followed by filtration and vacuum distillation at 94 °C (~1.5 mmHg). The condenser of the vacuum distillation column was connected to a circulating heated water bath (55 °C) to prevent EMPD crystallization. Titanium(IV) isopropoxide (97%) was used as received. Heptafluorobutyryl chloride (HFBCl) (98%) was distilled trap-to-trap and stored under N_2. Benzoyl chloride (BZCl) (99+%) and pyridine (99+%, anhydrous) were used as purchased. Chloroform for end-capping reactions was distilled under N_2 from P_2O_5 and stored under nitrogen.

Synthesis of Poly(2-ethyl-2-methylpropylene terephthalate). To a 500 mL reactor kettle were added DMT (204 g, 1.05 mol) and EMPD (219 g, 1.85 mol). When the temperature of the reaction mixture reached ~140 °C, 210 μL of titanium(IV) isopropoxide catalyst was injected into the kettle. The temperature during the first stage of reaction was 202 °C. After 2.5 h, the reaction temperature was raised to 242 °C to drive off any remaining methanol. At this time, the distillation adapter was removed from the kettle. Using a 25 mL glass pipet, 8–18 mL aliquots of prepolymer were removed. During this procedure, N_2 was continually flushed through the reactor. The clear, colorless prepolymer samples were placed in vials which were capped and placed in a desiccator. The reactor was resealed for the second stage of polymerization. A heated vacuum line was used to prevent crystallization of EMPD. The second stage of polymerization was conducted at 245 ± 1 °C and a vacuum of 1.2 ± 0.2 mmHg. After 2 h, the reactor kettle was opened to the atmosphere. The clear, colorless polymer was placed into a large Petri dish and stored in a vacuum desiccator.

Twenty grams of this polyester was purified by dissolving in 100 mL of chloroform followed by filtration through a 4–8 μm fritted glass funnel. The polymer was recovered by dropwise precipitation into 1000 mL of methanol under vigorous mixing. The recovered sample was washed with 2 × 200 mL aliquots of fresh methanol. The polymer was placed in a Petri dish and dried in an oven at 90–100 °C for 48 h. This single precipitated polymer from the bulk synthesis was designated PEMPT 7-OH. The "OH" indicates the polymer has hydroxyl end groups.

Synthesis of Poly(2-ethyl-2-methylpropylene terephthalate) of Varying M_n. By varying the second-stage reaction time, the prepolymer samples removed at the end of the first stage of the bulk reaction were polymerized to obtain PEMPT of different molecular weights. A typical synthesis is described below. To a 100 mL trap tube was added ~18 mL of prepolymer. The reactor tube was sealed, purged with N_2, and then placed into an oil bath at 250 °C and magnetic stirring begun. The tube outlet was again connected to a heated vacuum line. The mixture was allowed to react for the appropriate time (see Table 1). When the specified time was reached, the reactor tube was removed from the oil bath and cooled. The polyester was removed from the reactor tube by dissolution into 50 mL of chloroform, filtered through a 4–8 μm fritted glass funnel, and recovered by dropwise precipitation into 500 mL of vigorously stirred methanol. The recovered sample was washed with 2 × 100 mL aliquots of fresh methanol. The single precipitated sample was placed in a Petri dish lined with Teflon film and dried for several hours under vacuum (~300 mmHg). Additional drying was carried out in an oven at 90–100 °C for 48 h. Six PEMPT samples were synthesized/purified in this manner and are identified as PEMPT 1-OH through PEMPT 6-OH.

Each of the precipitated and dried polymers above was further purified. Three grams of each polymer was redissolved (20 mL of chloroform) and recovered by dropwise precipitation (200 mL of methanol). The twice-precipitated polymers were placed in lined Petri dishes and dried 1 h at 100 °C under vacuum (~300 mmHg). The temperature of the oven was lowered to 78 °C, and the polymers were dried under vacuum, <1 mmHg, for 4 days. These six samples were designated as PEMPT 1A-OH through PEMPT 6A-OH. All the PEMPT samples, including PEMPT 7-OH, were stored in a vacuum desiccator.

End-Capping of Poly(2-ethyl-2-methylpropylene terephthalate). All end-capping reactions used the PEMPT 1-OH through PEMPT 6-OH series of polyesters. End-capping reactions were carried out in solution. Chloroform (40 mL) was transferred via cannula to a nitrogen-purged, septum-capped 100 mL round-bottom flask containing 0.8 g of PEMPT and a magnetic stir bar. Three hours was allowed for the polymer to dissolve at ambient temperature. HFBCl (0.65 mL, 4.4 mmol) was then added via syringe while the solution was vigorously stirred. Two samples for each polyester were prepared in this manner. After 18 h at room temperature, one set of polymer samples was recovered by precipitation into 400 mL of methanol. The precipitated polymers were rigor-

Table 2. Molecular Weight and Distribution Data of PEMPT

polyester	M_n(GPC)	M_w(GPC)	M_z(GPC)	M_n(fluoride)	M_n(NMR)
PEMPT 1A-OH	3 100	7 300	11 700	4 100	4 500
PEMPT 2A-OH	4 600	11 900	18 500	6 100	5 800
PEMPT 3A-OH	11 600	21 000	31 700	9 500	8 600
PEMPT 4A-OH	13 500	25 200	38 100	11 500	12 000
PEMPT 5A-OH	17 800	34 500	52 500	18 200	17 100
PEMPT 6A-OH	21 400	42 600	65 400	37 500	42 300
PEMPT 7-OH				17 700	21 500

ously washed with 3 × 40 mL aliquots of fresh methanol and dried under vacuum at 80 °C for 5 days. The other set of samples was recovered in a similar fashion after 94 h of reaction at ambient temperature. The main variation to the procedure for BZCl end-capping was that a smaller scale was employed (0.2 g of polyester, 10 mL of chloroform, and 0.37 g (3.2 mmol) of BZCl) and pyridine (0.26 mL (3.2 mmol)) was added as a catalyst/acid acceptor. After 48 h, the reaction was terminated by dropwise precipitation of the solution into 100 mL of methanol followed by washing with 3 × 10 mL aliquots of methanol. Samples were dried under vacuum, <1 mmHg, for 5 days at 80 °C. In addition to these samples, control samples of PEMPT varying in molecular weight were also prepared. The controls were 0.2 g of polyester dissolved in 10 mL of chloroform which were then recovered by the identical precipitation procedure described above for BZCl end-capping. The three sets of six polyesters, HFBCl end-capped, BZCl end-capped, and the controls, are designated as PEMPT 1-HFB through PEMPT 6-HFB, PEMPT 1-BNZ through PEMPT 6-BNZ, and PEMPT 1B-OH through PEMPT 6B-OH.

Characterization. Unless otherwise stated, characterization of the polyesters of varying molecular weight was conducted on the PEMPT 1A-OH through PEMPT 6A-OH series of samples. Molecular weight determination by GPC analysis employed a Waters Model 590 pump combined with a Waters WISP Auto Injector Model 710B. The detector was a Perkin-Elmer Model LC90 variable-wavelength UV detector operated at 254 nm. Three Waters Ultra Styragel columns of 10^5, 10^4, and 10^3 Å were used. A Nelson Analytical data collection system with series 2600 software was used for data collection/analysis. Chloroform at 1 mL/min was used as the solvent. Narrow molecular weight polystyrene (PS) standards were used for calibration. The absolute number-average molecular weight (M_n) was determined by fluoride analysis of the HFBCl-terminated PEMPTs. Fluoride analysis was conducted at the University of Massachusetts Microanalysis Laboratory. The procedure involves combustion of the sample utilizing the Schöniger oxygen flask technique with capture of the fluoride ions in an aqueous solution.[46] Fluoride concentration was then determined using a calibrated, fluoride-selective electrode. Four samples each of PEMPT 2-HFB and PEMPT 6-HFB were analyzed to obtain an average value for the weight percent fluoride while two samples of each of the remaining HFBCl-terminated polyesters were used. The end-group concentrations determined in this manner were adjusted for the presence of acid end groups. Acid end-group content is determined by titration under nitrogen of ~0.5 g of polymer in chloroform with a standardized 2.310 × 10^{-3} M KOH/methanol solution using phenolphthalein as the indicator. M_ns were also determined by proton NMR. The procedures and resonances used for determination are discussed later in this paper.

Proton NMR was conducted on a Varian 300-XL spectrometer (300 MHz). Sample solutions were approximately 1% w/v with deuterated chloroform as solvent and TMS used as an internal reference. The pulse angle was 67.7° with an acquisition time of 3.725 s and a delay time between pulses of 7.0 s. Sixty-four scans per sample were recorded. Carbon-13 NMR was conducted on a Varian 200-XL spectrometer (200 MHz). The sample, PEMPT 7-OH, was dissolved in deuterated chloroform (9.5% w/v). Several drops of TMS (Aldrich 99.9+% NMR grade) were added as an internal reference. The number of scans was 2048 with proton decoupling applied. A ^{13}C–^{1}H COSY experiment was also conducted on the Varian 200-XL spectrometer. The PEMPT 7-OH sample prepared for the ^{13}C experiment above was used in this experiment. The full carbon and hydrogen spectral widths of the polyester were scanned.

Infrared spectroscopy was conducted on an IBM 38 FTIR under nitrogen at room temperature. The frequency range was 400–4000 cm^{-1} with 4 cm^{-1} resolution. One hundred scans were recorded on samples that had been cast from a chloroform solution (~1% w/v) onto NaCl plates and annealed 24 h under vacuum at 76 °C. Samples were stored in a vacuum desiccator prior to scanning.

Differential scanning calorimetry (DSC) employed a Perkin-Elmer DSC-7. Indium and recrystallized dimethyl isophthalate were used for calibration standards. All runs were heating scans conducted at 20 °C/min with a sample size of ~6 mg. Reported T_gs are midpoint values averaged from 2–3 separate runs per sample. Thermogravimetric analysis was carried out in a Perkin-Elmer TGS-2 with the controller and data station described above. Nitrogen at ~45 mL/min was used as a purge gas. Calibration employed four ferromagnetic standards; alumel, nickel, Nicoseat, and Perkalloy. All heating scans were conducted at 20 °C/min with a sample size of ~5 mg. The reported decomposition temperature, T_d, is the temperature at which the maximum rate of weight loss occurred.

Density measurements were carried out in a density gradient column at 23.1 °C. The column was composed of a sodium bromide deionized, degassed aqueous solution. Beads of known density, ranging from 1.0600 to 1.2700 g/cm^3, were used for calibration. Reported values are averages of 3–5 samples per polyester. Samples were allowed to equilibrate 12 h in the column prior to measurement.

The solubility of PEMPT was determined in a variety of solvents at room temperature. All solvents were ≥99% pure, except for 1,1,2,2-tetrachloroethane, which was 98%. To a 2 mL vial were added ~0.020 g of PEMPT 7-OH and 1.0 mL of solvent. The vials were covered with Teflon tape and then capped. The solubility of the polyester was visually observed after 75 h in solvent.

Characterization Results and Discussion

Poly(2-ethyl-2-methylpropylene terephthalate). Molecular Weight. The hydroxyl (from fluoride analysis) and acid end-group concentrations of the synthesized PEMPTs are displayed in Table 1. At all but the longest reaction time, the number of acid end groups are <2% of the total concentration. Proton NMR analysis of the HFBCl-terminated PEMPTs indicates that the reaction had only proceeded to 90% completion; thus, the hydroxyl concentrations in Table 1 have been adjusted accordingly. Table 2 displays the molecular weight data from GPC analysis (relative to PS standards) and the M_ns from fluoride analysis of HFBCl end-capped PEMPTs and from ^{1}H NMR analysis. The M_ns determined from GPC, fluoride, and NMR analysis all increase with polymerization time, as expected. M_ns calculated from fluoride analysis and ^{1}H NMR are in agreement and range from 4000 to 40 000. M_ns determined from GPC range between 3100 and 21 000. The identification of end-group resonances used to calculate M_ns from ^{1}H NMR and to determine end-capping reaction completion is discussed with the NMR results below. Further interpretation of GPC data will be included in the discussion of end-capped PEMPTs.

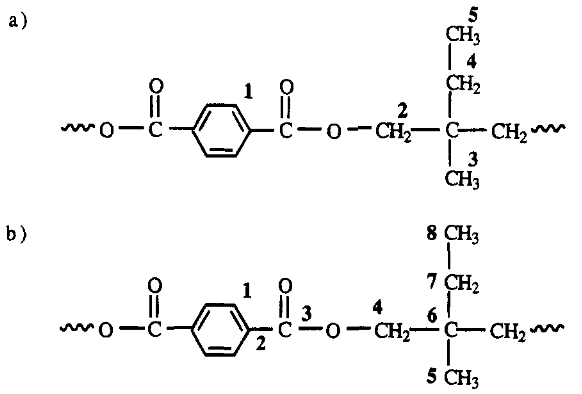

Figure 1. Chemical structure of PEMPT with numerically coded (a) hydrogen atoms and (b) carbon atoms.

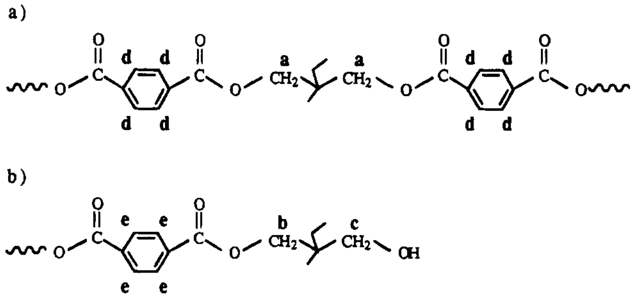

Figure 2. Substitution of the propylene group of PEMPT with alphabetically coded hydrogen atoms: (a) dual aromatic ester; (b) aromatic ester/hydroxyl.

NMR. Figures 1a and 1b show the repeat unit of PEMPT with numerically coded hydrogen and carbon atoms, respectively. Proton assignments were unambiguous due to chemical shift and splitting considerations: H(1) $\delta = 8.081$ ppm (s), H(2) $\delta = 4.290$ ppm (s), H(3) $\delta = 1.118$ ppm (s), H(4) $\delta = 1.591$ ppm (q), and H(5) $\delta = 0.979$ ppm (t). The ^{13}C$-^{1}$H COSY experiment was used to assign carbon atoms C(1) $\delta = 129.62$ ppm, C(4) $\delta = 68.50$ ppm, C(5) $\delta = 18.85$ ppm, C(7) $\delta = 27.29$ ppm, and C(8) $\delta = 7.71$ ppm. Carbon C(3), a carbonyl carbon, corresponds to a resonance at $\delta = 165.49$ ppm.[47] Hence, C(2) is assigned to the final observed resonance characteristic of an aromatic group, $\delta = 133.95$ ppm. Quaternary carbon C(6) corresponds to a peak observed at $\delta = 37.88$ ppm. The hydrogen and carbon resonances of the terephthalate ring and the methylene sequences adjacent to the carbonyl in PEMPT agree with values of similar compounds.[10,12,48-51]

In addition to the main-chain resonances, assignment of proton resonances associated with the hydroxyl end-group structure of PEMPT is also desired. End-capping reactions allow unambiguous identification and confirmation of these resonances; thus, what follows is a joint discussion of the NMR of the hydroxyl-terminated and end-capped polyesters. Figures 2a and 2b show the substitutions on the propylene group of PEMPT including dual aromatic ester and aromatic ester/hydroxyl, respectively. The protons are alphabetically coded to prevent any confusion with the previous discussion, H(1) $\equiv$ H(d) and H(2) $\equiv$ H(a). The ^{1}H NMR spectra of PEMPT OH with varying molecular weight are shown in Figure 3. The region displayed corresponds to the backbone methylene protons, H(a), H(b), and H(c) in Figures 2a and 2b. The large singlet at 4.290 ppm has been assigned to the methylene protons with dual aromatic ester substitution, protons H(a). Two additional resonances, a singlet at $\delta = 4.231$ ppm and a multiplet centered at $\delta = 3.423$ ppm, decrease with increasing molecular weight. With the number of end groups decreasing with increasing M_n, these resonances are tentatively assigned to the methylene protons of a hydroxyl-terminated propylene group, H(b) and H(c).

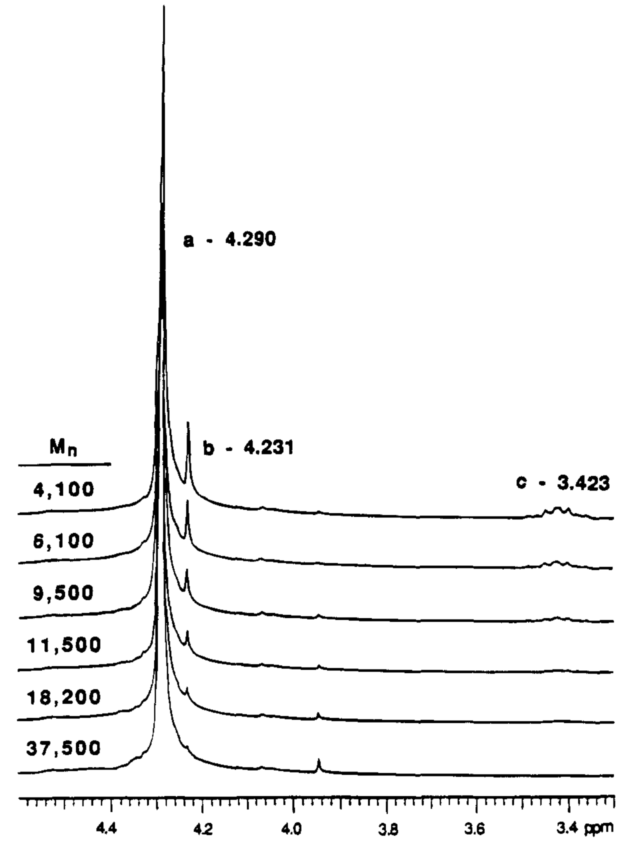

Figure 3. 300 MHz ^{1}H NMR spectra displaying the backbone methylene region of PEMPT at the indicated molecular weights.

Examining the hydroxyl end-group structure (Figure 2b), the resonance associated with the methylene protons adjacent to the remaining aromatic ester, protons H(b), is expected to remain a singlet and be shifted slightly upfield. This is caused by the removal of the other deshielding aromatic ester. The 4.231 ppm resonance is assigned to these protons. Methylene protons adjacent to a hydroxyl group are known to be multiplets due to splitting associated with the adjacent hydroxyl proton.[52] This fact, combined with the large upfield shift expected with the removal of the aromatic ester, enables the multiplet at 3.423 ppm to be assigned to the methylene protons adjacent to the hydroxyl end group, H(c). The relative shift of H(b) downfield from H(c) agrees with the shifts seen in model compounds studied by Judas et al.[48] The resonance of the hydroxyl proton is observed as a triplet, $\delta = 2.174$ ppm. This has been verified by the addition of deuterium oxide to the NMR sample solution. A decrease in intensity of the 2.174 ppm resonance as well as a collapse of the multiplet at 3.423 ppm to a quartet is observed. This behavior is expected for hydrogen$-$deuterium exchange of an alcohol, providing additional confirmation for the above peak assignments.

Supporting evidence for these end-group assignments comes from the ^{1}H NMR spectra of PEMPT 2-OH reacted with HFBCl for 0, 18, and 94 h, respectively. Both the 4.231 and 3.423 ppm resonances decrease in intensity with increasing end-capping time. The decrease in intensity represents the conversion of the

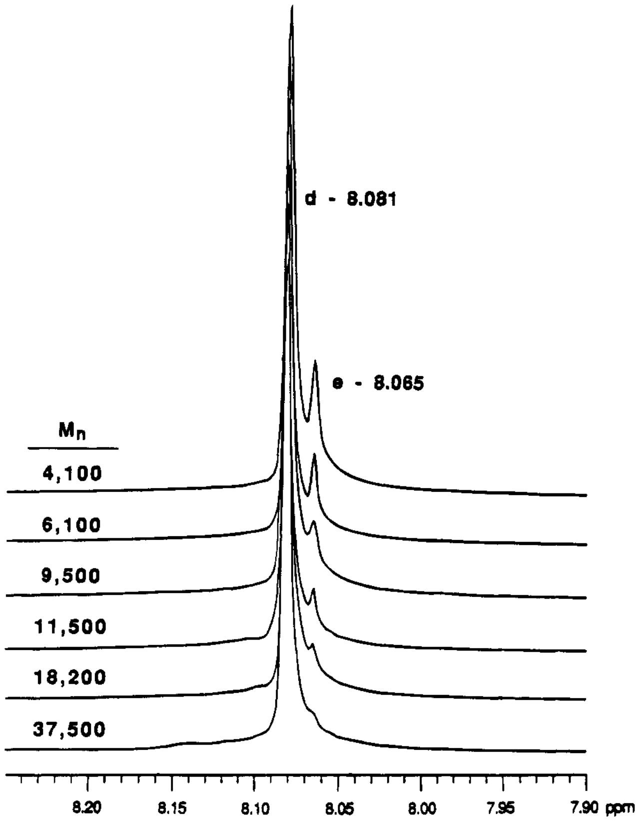

Figure 4. 300 MHz ^{1}H NMR spectra displaying the aromatic region of PEMPT at the indicated molecular weights.

hydroxyl groups to heptafluorobutyrate esters and confirms that these resonances correspond to the methylene protons of the hydroxyl-terminated propylene end group. Additionally, ^{1}H NMR results of PEMPT 2-OH after reaction with BZCl reveal that both the 4.231 and 3.423 ppm resonances are no longer present in the spectrum. It should be noted that the areas corresponding to the H(a) and H(b) resonances were used to calculate the M_ns from ^{1}H NMR and to calculate the correction used in the determination of M_ns from fluoride analysis (Table 2).

Similarly, Figure 4 displays the aromatic region associated with the ^{1}H NMR of the non-end-capped PEMPT samples. The large resonance at 8.081 ppm has been assigned to the protons of a terephthalate ring with dual aliphatic–aromatic ester substitution, H(d) in Figure 2a. The smaller resonance at 8.065 ppm decreases with increasing M_n. This peak will be assigned to the protons of a terephthalate ring adjacent to the aliphatic-hydroxyl end group, H(e) in Figure 2b. This assignment is confirmed once again by NMR examination of the end-capped PEMPTs. As end-capping reaction time increases, the resonance at 8.065 ppm decreases. This corresponds to the conversion of the hydroxyl groups to heptafluorobutyrate groups and verifies the assignment of this resonance. In the ^{1}H NMR of PEMPT 2-BNZ, this resonance is absent and a new resonance at 8.070 ppm appears. It is apparent that the terephthalate group adjacent to the terminal propylene group is magnetically nonequivalent to a midchain terephthalate group.

FTIR. The infrared spectra agree with literature values of similar polyesters.[34,53–55] Results focus on the hydrogen-bonding region of the spectrum which is of particular interest. The FTIR spectra of PEMPT 1A-OH and PEMPT 5A-OH in the region of 2800–3800 cm^{-1} have been examined. Three resonances appear in this frequency region, commonly related to hydrogen bonding. Broad resonances at 3430 and 3550 cm^{-1} are observed in both spectra, while an additional sharp resonance at 3585 cm^{-1} is observed in the PEMPT 5A-OH sample. This resonance is not apparent in the low-M_n sample, although it may be obscured by a higher intensity 3550 cm^{-1} peak. Self-associated hydrogen bonds have been observed in phenoxy resins as broad peaks at 3450 cm^{-1}, while the free hydroxyl is found at 3570 cm^{-1}.[56] In the current samples, the sharp resonance at 3585 cm^{-1} is assigned to the unassociated hydrogens, while the broad resonance at 3430 cm^{-1} is assigned to the self-associated hydroxyl–hydroxyl interaction. The remaining broad peak at 3550 cm^{-1} is assigned to a hydroxyl–carbonyl hydrogen bond. A resonance in this frequency region has been assigned to this interaction in a Phenoxy/poly(ϵ-caprolactone) blend.[56] As expected, the intensity of these hydrogen-bonding resonances is higher in the low molecular weight sample (high hydroxyl content).

Thermal Analysis. The only observed transition in the DSC heating scan (30–250 °C) of PEMPT 7-OH is a single, sharp T_g at 62.3 °C. With its 2-ethyl-2-methyl substitution on the propyl group, PEMPT has the potential to form an atactic structure and would be expected to be amorphous, as observed. If long enough sequences of a regular crystallizable structure had been formed, the melting point would likely be no greater than that of poly(propylene terephthalate), 227 °C.[57]

Table 3 summarizes the DSC and TGA data of PEMPT 1A-OH through PEMPT 6A-OH and PEMPT 7-OH. The T_g increases with molecular weight. Fox and Flory[58,59] have shown, using free volume arguments, that the observed T_g should increase with increasing molecular weight according to the functional form

$$T_g = T_{g,\infty} - K/M_n \qquad (1)$$

where T_g is the observed glass transition temperature, $T_{g,\infty}$ is the glass transition temperature at infinite molecular weight, M_n is the number-average molecular weight, and K is the constant related to the thermal expansion coefficients of the glassy and rubbery states. Least squares analysis shows that the data fits the above functional form well with the $T_{g,\infty}$ equal to 66.3 °C and the constant K equal to 8.85×10^4 °C g/mol. T_gs were determined at a heating rate of 20 °C/min with no extrapolations to zero scanning rate.

The TGA data of Table 3 show several features including that the temperature of the maximum rate of decomposition, T_d, is relatively insensitive to molecular weight, the average value for the six polyesters being 468 °C. This value is ~40 °C higher than the T_d of several aliphatic–aromatic polyesters, poly(1,5-pentylene terephthalate), poly(1,7-heptylene terephthalate), and poly(1,9-nonylene terephthalate), as previously reported.[44] The improved thermal stability is associated with the replacement of the β-hydrogens by ethylmethyl substitution, which eliminates a common decomposition mechanism of esters similar to the Chugaev reaction.[60,61] Also reported is the percent weight loss at 300 °C. There is a general increase in the weight loss with decreasing molecular weight. This is most likely caused by more low molecular weight polymer in the distribution of the PEMPT samples having smaller M_ns. At 300 °C, some of the low molecular weight species that make up the distribution

Table 3. Thermal Analysis and Density Data of PEMPT

polyester	T_g, °C	ΔC_p, J/(g °C)	T_d,[a] °C	% wt loss at 300 °C	density, g/cm^3
PEMPT 1A-OH	55	0.26	470	1.11	1.190
PEMPT 2A-OH	58	0.26	470	0.90	1.190
PEMPT 3A-OH	61	0.24	470	0.76	1.192
PEMPT 4A-OH	62	0.28	470	0.28	1.190
PEMPT 5A-OH	64	0.24	467	0.48	1.194
PEMPT 6A-OH	65	0.25	466	0.12	1.194
PEMPT 7-OH	62	0.25			1.190

[a] Temperature of the maximum rate of thermal decomposition.

Table 4. Solubility of PEMPT

solvent	δ (cal/cm^3)$^{1/2}$	solubility[a]
hexane	7.3	I
heptane	7.45	I
decane	7.75	I
cyclohexane	8.2	I
methanol	14.5	I
ethanol	12.7	I
1-propanol	11.9	I
1-butanol	11.4	I
benzene	9.15	S
toluene	8.9	S
p-xylene	8.8	S
dichloromethane	9.7	S
chloroform	9.3	S
carbon tetrachloride	8.6	S
1,2-dichloroethane	9.8	S
1,1,2,2-tetrachloroethane	10.4	S
dimethyl sulfoxide	13.4	I
N,N-dimethylformamide	12.1	P
acetonitrile	11.9	P
acetone	10.0	P
tetrahydrofuran	9.9	S
methyl ethyl ketone	9.3	S

[a] I, insoluble; S, soluble; P, partially soluble (solvent plasticized PEMPT).

may indeed be volatile or more prone to thermal degradation and lead to the observed weight loss.

Density. Since variations in T_g can be described in terms of free volume, one might anticipate a systematic change in density with polyester M_n. Table 4 also contains density data for the PEMPT samples. A slight increase in density is observed with increasing molecular weight. However, the span is only ±0.002 g/cm^3, which is within experimental error. The population as a whole has a density of 1.191 ± 0.003 g/cm^3. This value agrees with reported densities of aliphatic side-chain-substituted PETs having nearly the identical composition of PEMPT, poly(1,2-pentylene terephthalate) and poly(1,2-hexylene terephthalate).[62]

Solubility. Table 4 identifies the solubility of PEMPT in a variety of solvents. The table is divided by solvent type including aliphatic, alcoholic, aromatic, and chlorinated and includes the solubility parameter of each solvent.[63] In addition, some other common solvents are also tested. PEMPT is insoluble in both aliphatic and alcoholic type solvents. On the other hand, PEMPT is completely soluble in all the aromatic and chlorinated solvents tested. These solvents have solubility parameters in the range of 8.5–10.5 (cal/cm^3)$^{1/2}$. PEMPT exhibits complete solubility in ten of the solvents tested, and their average solubility parameter, 9.4 ± 0.6 (cal/cm^3)$^{1/2}$, will be taken as a rough estimate for the solubilty parameter of PEMPT itself. This value agrees with a value calculated from the molar attraction constants of Van Krevelen, 9.4 (cal/cm^3)$^{1/2}$.[64] Overall, compared to the semicrystalline PET and PBT,[65] the amorphous PEMPT shows improved solubility in a wide variety of solvents.

End-Capped Poly(2-ethyl-2-methylpropylene terephthalate). Characterization of PEMPT HFB, PEMPT BNZ, and PEMPT B-OH (control samples) centers primarily on GPC and DSC analysis. Limited proton NMR is also conducted; however, NMR is mainly used to monitor the end-capping reaction and these results were discussed.

Molecular Weight. Table 5 displays the molecular weight data obtained from GPC for PEMPT 1B-OH, PEMPT HFB, and PEMPT BNZ. The molecular weights and polydispersities of the PEMPT HFB and PEMPT BNZ samples are in good agreement. At the high molecular weights, the polydispersity, M_w/M_n, approaches 2.0, which is the theoretical prediction for polyesters synthesized by a step growth mechanism.[66] It is noted that as the M_n of the two end-capped polymers is decreased, the polydispersity also decreases. This is thought to be associated with the precipitation procedure used in polyester recovery. Polymers/oligomers of low molecular weight will be soluble in the recovery solvent, especially at the low polymer concentrations employed. The consequence is a decrease in polydispersity with a decrease in molecular weight.

Comparing the M_ns of the two hydroxyl-terminated polyesters PEMPT 1A-OH (Table 2) and PEMPT 1B-OH (Table 5), the values agree, indicating that the slightly different precipitation procedures (PEMPT/chloroform ratios of 15% vs 2%) did not significantly alter the molecular weights/distributions of these two sets of polyesters. The low M_ns of hydroxyl-terminated polyesters show significant differences compared to the PEMPT HFB and PEMPT BNZ results. The decrease in the polydispersity with decreasing molecular weights is not observed in the hydroxyl-terminated samples. The two lowest molecular weights have polydispersities significantly greater than 2.0. Thus, it appears that at the low molecular weights (high hydroxyl content), the PEMPT 1A-OH and PEMPT 1B-OH samples are interacting with the GPC columns. Interaction with the columns may slow the travel of the polyesters, making the calculated M_ns lower and the polydispersity greater, as is observed. The molecular weight averages that are less dependent on low molecular weight species, M_w and M_z, are in much better agreement with the end-capped PEMPTs at all molecular weights. This would also indicate that the low molecular weight species are responsible for the discrepancy.

Thermal Analysis. Table 6 displays the thermal analysis data of PEMPT B-OH, PEMPT HFB, and PEMPT BNZ. No significant differences are observed in the ΔC_ps at T_g relative to molecular weight and end-group modifications. All three sets of data show decreasing T_gs as the M_n (calculated from fluoride analysis of PEMPT HFB samples) decreases. Figure 5 shows a plot of T_g vs $1/M_n$ for all three sets of polyesters. The T_gs of the two end-capped samples are nearly identical

Table 5. Molecular Weight and Distribution Data of End-Capped PEMPTs from GPC Analysis

polyester	M_n	M_w	M_z	M_w/M_n	M_z/M_w
PEMPT 1B-OH	3 400	8 100	12 200	2.34	1.51
PEMPT 2B-OH	5 600	13 300	20 500	2.40	1.54
PEMPT 3B-OH	10 200	21 200	33 000	2.09	1.56
PEMPT 4B-OH	12 200	25 400	39 500	2.08	1.55
PEMPT 5B-OH	17 100	34 100	52 700	1.99	1.55
PEMPT 6B-OH	21 100	42 300	65 200	2.01	1.54
PEMPT 1-HFB	6 300	8 800	11 900	1.39	1.36
PEMPT 2-HFB	8 800	13 400	19 100	1.51	1.43
PEMPT 3-HFB	12 500	21 300	32 000	1.70	1.50
PEMPT 4-HFB	14 400	25 400	38 600	1.76	1.52
PEMPT 5-HFB	18 400	34 200	52 300	1.86	1.53
PEMPT 6-HFB	21 800	42 400	65 300	1.94	1.51
PEMPT 1-BNZ	5 500	8 000	11 200	1.44	1.40
PEMPT 2-BNZ	8 600	13 200	18 900	1.53	1.44
PEMPT 3-BNZ	11 500	20 300	30 800	1.71	1.52
PEMPT 4-BNZ	13 500	24 500	37 300	1.81	1.52
PEMPT 5-BNZ	18 000	33 700	51 200	1.87	1.52
PEMPT 6-BNZ	21 700	42 000	64 200	1.94	1.53

Table 6. Thermal Analysis Data of End-Capped PEMPTs

	PEMPT B-OH		PEMPT HFB		PEMPT BNZ	
M_n	T_g, °C	ΔC_p, J/(g °C)	T_g, °C	ΔC_p, J/(g °C)	T_g, °C	ΔC_p, J/(g °C)
4 100	57	0.25	48	0.22	47	0.23
6 100	61	0.25	54	0.24	54	0.26
9 500	63	0.25	59	0.26	58	0.26
11 500	64	0.26	61	0.26	60	0.28
18 200	65	0.24	63	0.27	62	0.26
37 500	66	0.24	65	0.26	64	0.26

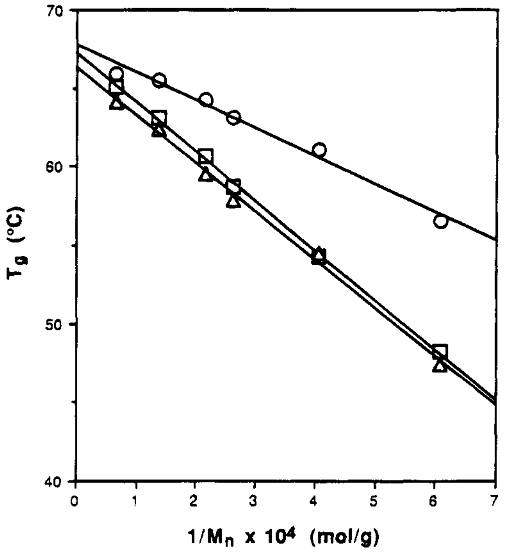

Figure 5. T_g vs $1/M_n$ of end-capped PEMPTs: (○) PEMPT B-OH; (□) PEMPT HFB; (△) PEMPT BNZ.

at all M_ns, while the T_gs of the PEMPT B-OH samples are somewhat higher. The deviation increases with decreasing M_n. The data appear to indicate that the ability of the PEMPT B-OH samples to hydrogen bond alters their properties. If hydrogen bonding is the cause of the variation, the low molecular weight polyesters with their high hydroxyl end-group concentration should exhibit the largest T_g variation. It is also expected that as the concentration of end groups decreases with increasing M_n, the difference between the T_gs should decrease. The results depicted in Figure 5 agree with these two statements. Additionally, at high molecular weights, end-group effects would be negligible and $T_{g,\infty}$ is expected to be independent of end-group type. Figure 5 shows that the three sets of data extrapolate to an identical value for $T_{g,\infty}$, 67 ± 1 °C.

Conclusions

A novel amorphous polyester, PEMPT, is conveniently synthesized at a variety of molecular weights using standard two-stage polycondensation techniques. Modification of the end-group structure of the polyester is also achieved via nucleophilic substitution reactions with acid chlorides. Characterization of the polyesters employs a large array of analytical techniques. Of particular importance is the detailed ^{1}H NMR analysis which includes the identification and assignment of midchain resonances and resonances associated with the end-group structure of PEMPT. In later blend studies, these resonances are used to identify both midchain and end-group transreactions. The ability to hydrogen bond, particularly for the low-M_n polyesters, leads to variations in their observed properties compared to end-capped PEMPTs. Hydrogen bonding produces a less mobile chain which manifests itself as an increase in the T_gs of the hydroxyl-terminated PEMPTs compared to values for the HFBCl- and BZCl-terminated polyesters. With its amorphous structure and improved solubility and thermal properties compared to PET and PBT, this well-characterized polyester is ideally suited for quantitative phase behavior and transreaction studies of polyester/polycarbonate blends.

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