Thermal Tranesterification of Bis(hydroxymethyl)propane-1,3-diyl Units in (Poly(ethyl terephthalate) and Poly(butylene terephthalate): A Route to Thermoset Polyesters

Robert M. Kriegel,[†] David M. Collard,[*,†] Charles L. Liotta,[†] and David A. Schiraldi[‡]

School of Chemistry and Biochemistry and the Polymer Education and Research Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, and Trevira Corporation, P.O. Box 5750, Spartanburg, South Carolina 29304-5750

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ABSTRACT: Copolymerization of 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane with dimethyl terephthalate and either ethylene glycol or 1,4-butanediol affords polyesters with pendant ketals. Acid-promoted debenzalation provides 2,2-bis(hydroxymethyl)propane-1,3-diyl structural units. Thermal transesterification to afford rigid, adhesive thermosets is controlled by the composition of the copolymer and curing conditions (temperature and time).

Introduction

The commercial production of poly(ethylene terephthalate), PET, for use as a semicrystalline polymer in film, fiber, and packaging applications exceeds 3.9 × 10^9 lb/year in the United States.[2] The additional flexibility of the repeat units of poly(butylene terephthalate), PBT, allows for the greater crystallinity and crystallization rates desirable for injection molding operations, but most of these applications require that the polymer be reinforced with glass fiber or mineral fillers.[3] End groups of polyesters consist of alcohols or carboxylic acids. The reactivity of these end groups is responsible for chain extension by thermally induced solid-state polymerization[4] or by reaction with difunctional reagents (e.g., diisocyanates).[5] The functional end groups have also been used to modify polymers with fluorescent tags to probe surface chemistry,[6] immobilize biomolecules to polyesters,[7] impart biocompatibility,[8] enhance blending,[9] and improve adhesion.[10] The identity of the end groups also has a large influence on chemical and physical properties. A number of approaches to incorporate pendant hydroxyl groups into polyesters have been reported which allow for further control of physical properties and chemical modification.

Attempts to incorporate pendant hydroxyl or carboxyl functional groups in polyesters by use of trifunctional reagents in polycondensation reactions inevitably leads to branched and cross-linked polymers at high conversion.[11] Incorporation of as little as 1 mol % of glycerol or trimellitic acid into a standard PET or PBT synthesis can lead to an intractable thermoset copolyester.[12] However, smaller amounts of a polyfunctional monomer are added to enhance the properties of polyesters. Alternative methods for the synthesis of polyesters substituted with reactive groups are limited in their applicability. The nucleophilic ring-opening of diepoxides with dicarboxylates produces polyesters with a pendant hydroxyl group on each repeat unit.[13] For example, ring-opening polymerization of diglycidyl terephthalate with terephthalic acid affords a polymer containing both 2-hydroxypropane-1,3-diyl and (hydroxymethyl)ethane-1,2-diyl structural units.[14] In a different approach, interfacial polycondensation between isophthaloyl chloride in an organic solvent and a carboxylic acid-substituted diol in basic aqueous solution affords polyesters bearing carboxylic acid pendants.[15] Neither of these synthetic approaches is amenable to the preparation of poly(alkylidene terephthalate)s from α,ω-alkanediols and terephthalic acid derivatives.

Reaction of diacid derivatives with diols which contain a masked (i.e., protected) alcohol, followed by deprotection, would constitute a general procedure for the preparation of hydroxyl-substituted polyesters.[16] In particular, this approach would allow for the preparation of copolyesters which contain a small amount of a hydroxyl-bearing comonomer. Once unmasked, the pendant hydroxyl groups are capable of undergoing thermal transesterification to afford branched, and ultimately cross-linked, polymers. Such thermoset polyesters[17] might find use as structural adhesives, protective coatings, foamed structures, and insulators for electronics.

Here we describe the incorporation of 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane into PET and PBT, followed by acid-promoted deprotection (debenzalation) to afford linear polymers with 2,2-bis(hydroxymethyl)-propane-1,3-diyl units. Thermal transesterification to afford rigid thermosets is controlled by the amount of comonomer in the polymer and the curing conditions (temperature and time).

Experimental Section

Materials. Ethylene glycol and 1,4-dioxane were dried over sodium, pyridine was dried with CaH_2, and chloroform was dried over P_2O_5, prior to distillation. Trifluoroacetic acid and *N*,*N*-dimethylformamide were used as received from the Aldrich Chemical Co. All materials were obtained from Aldrich, with the following exceptions: dimethyl terephthalate and ethylene glycol were obtained from Hoechst Celanese Corp. and pentaerythritol was received from Eastman Chemical. All reactions were performed under a nitrogen atmosphere unless otherwise noted.

Characterization. Nuclear magnetic resonance (NMR) spectra were obtained on 300 MHz Varian Gemini 2000,

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[*] To whom correspondence should be addressed.
[†] Georgia Institute of Technology.
[‡] Trevira Corporation.

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Table 1. Quantities of Reagents for Solution-Phase Polymerization of PET/1

theoretical mol % **1**	5%	10%	15%	20%
ethylene glycol/g (mol)	8.883 (0.1432)	8.710 (0.140)	6.943 (0.112)	7.385 (0.1187)
terephthaloyl chloride/g (mol)	30.667 (0.1511)	33.221 (0.164)	28.952 (0.143)	30.191 (0.1487)
5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane, **1**/g (mmol)	1.768 (7.90)	4.032 (18.0)	6.994 (31.0)	6.724 (30.0)
reaction time/h	30	24	24	22
yield/g (%)	15.633 (51)	28.508 (83)	13.169 (40.5)	24.66 (73.8)

Table 2. Reagents for Thermal Transesterification Polymerization of PET/1 and PBT/1

	PBT/**1**			PET/**1**	
mol % **1**	0.75	1	3	1	3
1 /g (mmol)[a]	6.76 (30)	8.96 (40)	26.88 (120)	8.96 (40)	26.88 (120)
catalyst		Ti(OBu)$_4$ (0.376 g)		Mn(OAc)$_2$ (277 mg), Sb$_2$O$_5$ (358 mg), polyphosphoric acid, 10% w/w in ethylene glycol (1.679 g)	

[a] Based on 4 mol of dimethyl terephthalate.

Bruker AMX 400 MHz, or Bruker DMX 500 MHz instruments. Samples were dissolved in either deuterated trifluoroacetic acid (TFA-*d*) or a 50:1 (v/v) mixture of $CDCl_3$ and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Infrared characterization was performed using a Nicolet 520 FTIR spectrophotometer. Melting points were collected using a Thomas-Hoover Melting Point Apparatus. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Series 7 differential scanning calorimeter under nitrogen. The temperature program provided heating and cooling cycles between 50 °C and 290 °C at 10 °C/min. Samples were analyzed for T_g, T_c, and T_m, as appropriate.

Dilute solution viscometry was performed at 25 °C using a 4% polymer solution in *o*-chlorophenol. Run down times were measured for five trials and averaged. Intrinsic viscosities were extrapolated from infinite dilution curves.

5,5-Bis(hydroxymethyl)-2-phenyl-1,3-dioxane (1). The title compound was prepared according to the method of Bograchov.[18] Recrystallization from toluene gave 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane as a colorless solid (46%): mp 135−137 °C (lit.[14] 134−135 °C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.22 (d, $J_{\mathrm{HCOH}} = 5$ Hz, 2H, axial exocyclic CH$_2$), 3.70 (d, $J_{\mathrm{HCOH}} = 5$ Hz, 2H, equatorial exocyclic CH$_2$), 3.80 (d, $J_{\mathrm{gem}} = 12$ Hz, 2H, C4,6 axial H), 3.90 (d, $J_{\mathrm{gem}} = 12$ Hz, 2H, C4,6 equatorial H), 4.55 (t, $J_{\mathrm{HOCH}} = 5$ Hz, 1H, axial OH), 4.62 (t, $J_{\mathrm{HOCH}} = 5$ Hz, 1H, equatorial OH), 5.40 (s, 1H, benzylic H), 7.40−7.55 (m, 5H, aryl H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 139, 129, 128, 126 (aromatic C); 100 (C2), 69 (C4,6), 61, 59 (exocyclic CH$_2$); IR (KBr): 3289 cm^{-1} (OH str.), 1453 (aromatic C−C), 1038 (C−O str.).

2-Phenyl-5,5-bis(phenylcarboxymethyl)-1,3-dioxane (2). Benzoyl chloride (3.00 g, 22.0 mmol) was added via an addition funnel over 2 h to a solution of 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane (2.17 g, 10.0 mmol) and pyridine (1.80 g, 22.6 mmol) in dry 1,4-dioxane (22 mL). The solution was stirred for 24 h, diluted with chloroform (50 mL), and washed with 5% aqueous $NaHCO_3$ (2 × 50 mL) and distilled water (1 × 50 mL). The chloroform was removed under reduced pressure and the pale yellow solid residue was recrystallized from toluene (100 mL) and dried under vacuum at room temperature to afford 2-phenyl-5,5-bis(phenylcarboxymethyl)-1,3-dioxane as a white solid (2.30 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.1 (d, $J = 12$ Hz, 2H, C4,6 CH$_{2,\mathrm{ax}}$), 4.33 (s, 2H, axial exocyclic CH$_2$), 4.36 (d, $J = 12$ Hz, 2H, C4,6 CH$_{2,\mathrm{eq}}$), 4.90 (s, 2H, equatorial exocyclic CH$_2$), 5.6 (s, 1H, benzylic H), 7.3−8.0 (m, 15H, aryl H).

Solution-Phase Polymerization PET Containing 1 (PET/1). Terephthaloyl chloride was added to a mixture of ethylene glycol, **1**, and pyridine (27 mL) in 1,4-dioxane (300 mL) by Soxhlet extraction (Table 1). The dioxane solution was heated at reflux for an additional 6 h after the addition was complete. The heterogeneous mixture was cooled to room temperature and poured into water (400 mL). The precipitated solid was collected by gravity filtration and washed with water (3 × 100 mL). The white solid was washed with methanol in a Soxhlet extractor for 12 h and dried under reduced pressure (2 mmHg) at room temperature for 24 h to give benzal-protected copolymers PET/**1** as colorless solids. Spectral data (^{1}H NMR, IR) collected were consistent with the structure of the copolymer and allowed for determination of the ratio of repeat units (see Results and Discussion).

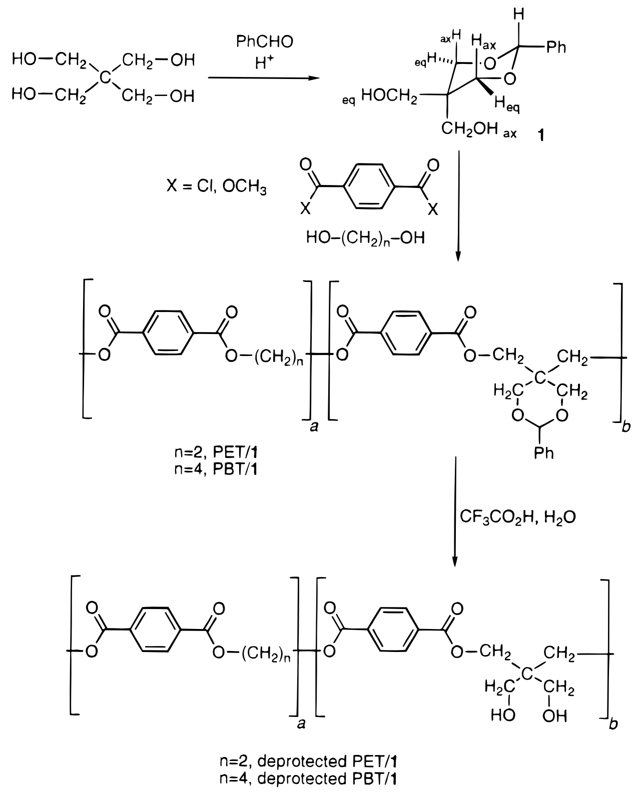
Thermal Transesterification Polymerization of PET, PBT, PET/1, and PBT/1. Dimethyl terephthalate (776.8 g, 4.004 mol) and either ethylene glycol or 1,4-butanediol with appropriate catalyst (Table 2) were added to a 1-L stainless steel reaction vessel equipped with a mechanical stirrer, distillation head, and condensor. The mixture was heated for 2 h at 180−210 °C, during which methanol was removed by distillation. 5,5-Bis(hydroxymethyl)-2-phenyl-1,3-dioxane was added to the mixture, and the pressure was slowly reduced over 40 min to $\leq$1 mmHg. The reaction mixture was heated to 250−260 °C for an additional 2 h for polymerization of PBT and PBT copolymers, or 285−290 °C for PET and PET copolymers, during which ethylene glycol or 1,4-butanediol was removed by distillation. The progress of the reaction was monitored by current drawn by the mechanical stirrer. The polymer was extruded from the reaction vessel under a positive pressure of N_2 to yield PET, PBT, PET/**1**, or PBT/**1** as white solids.

Debenzalation of PET/1 and PBT/1. The polymers were added to trifluoroacetic acid (4 mL/g of polymer) at room temperature and stirred until all of the solid material was dissolved. The solution was stirred for an additional 2−3 h. The polymer solution was then slowly poured into water (500 mL) whereupon a solid precipitated. The solid was removed by filtration, washed with water (300 mL), washed with hot methanol for 24 h using a Soxhlet extractor, and vacuum-dried at room temperature to afford 2,2-bis(hydroxymethyl)-propane-1,3-diyl containing copolymers, deprotected PET/**1** and PBT/**1**, as white solids.

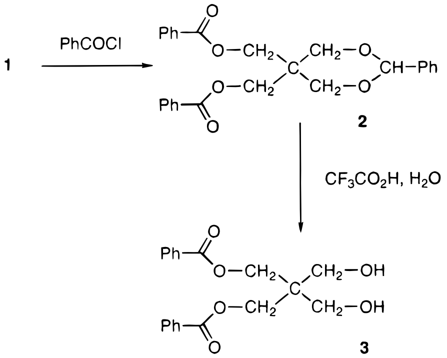
Results and Discussion

Monomer Synthesis. The synthesis of 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane, (**1**) was accomplished by the condensation of benzaldehyde and pentaerythritol in acidic aqueous solution.[14] Precipitation of the monobenzalated product from the reaction mixture minimizes the formation of the dibenzal. The ^{1}H NMR spectrum of **1** is consistent with the dioxane ring in a chair conformation with the phenyl group locked

Scheme 1



Scheme 2



in an equatorial position (Scheme 1). The complete assignment of the spectrum of **1** aids in the determination of the structure of the copolymers. In DMSO-d_6, the hydroxyl protons appear as triplets ($J_{\mathrm{HOCH}} = 5$ Hz) at 4.62 ppm (equatorial) and 4.55 ppm (axial) owing to the coupling with the exocyclic methylene protons. Selective decoupling of the hydroxyl protons aided in the assignment of the doublets at 3.70 and 3.20 ppm to the exocyclic methylenes. The dioxane ring protons appear as doublets with a large coupling constant ($J_{\mathrm{gem}} = 12$ Hz) at 3.80 ppm (equatorial) and 3.90 ppm (axial). The benzylic proton (C2) appears as a sharp singlet at 5.40 ppm.

5,5-Bis(phenylcarboxymethyl)-2-phenyl-1,3-dioxane (**2**) was synthesized as a model compound for the copolymers and for investigation of the hydrolysis of the benzal protecting group (Scheme 2). Reaction of **1** with benzoyl chloride in a mixture of pyridine and 1,4-dioxane gave **2**. The ^{1}H NMR of **2** in $CDCl_3$ shows doublets ($J_{\mathrm{gem}} =$ 12 Hz), which are characteristic of the axial and equatorial ring protons, and two proton singlets for each of the exocyclic methylene groups. The benzal-protecting group is subject to hydrolysis under acidic conditions.[19] The ^{1}H NMR of **2** in TFA-*d* shows the presence of benzaldehyde (δ 7.59 (2H), 7.76 (1H), 7.99 (2H), 9.89 (1H)). The signals due to the ring protons of **2** collapse into a sharp singlet at δ 4.33, corresponding to the hydroxymethyl protons of the debenzalated product, 2,2-bis(phenylcarboxymethyl)propane-1,3-diol (**3**).

Polymerization. Solution-phase reaction of terephthaloyl chloride (**1**) and ethylene glycol in 1,4-dioxane/pyridine under anhydrous conditions gave the copolymer PET/**1**. Terephthaloyl chloride was slowly added to a mixture of the diols in solution via extraction from a Soxhlet extractor by refluxing dioxane. Several different compositions of copolymer were synthesized by using an appropriate mixture of **1** and ethylene glycol (Table 1). Both PET and PBT containing **1** were synthesized from dimethyl terephthalate by a thermal transesterification melt polymerization in a stainless steel high-temperature reactor.

The compositions of the copolymers were determined by integration of the peaks in the ^{1}H NMR spectrum corresponding to the structural units derived from **1**. Due to the acid-sensitive nature of the protected repeat unit, a mixture of $CDCl_3$/HFIP (2–5% HFIP) was used to acquire NMR spectra under neutral conditions. In addition to the signals for the ethylene (δ 4.8) and 1,4-phenylene (δ 8.2) units, a 500-MHz spectrum of PET/**1** clearly shows doublets at 4.33 and 4.81 ppm, consistent with the successful incorporation of the benzal-containing repeat units derived from **1**. In common with the spectrum of the model diester **2**, the exocyclic methylene of these units appear as singlets (4.33 and 4.80 ppm) and the benzylic proton appears at 5.50 ppm. Integration of the peaks at δ 8.10 (1,4-phenylene) and δ 5.50 (benzylic) allowed for determination of the comonomer ratio in the polymer. The amount of **1** incorporated into the polymer by thermal polymerization was consistently lower than the monomer feed ratio, owing to loss of volatile monomer under the reaction conditions. NMR spectra of PET/**1** in TFA-*d* shows the presence of benzaldehyde as well as singlets for the deprotected hydroxymethyl (4.33 ppm) and 2,2-disubstituted 1,3-propanediyl units (4.66 ppm).

Polymer Deprotection. The benzal-containing polymers were deprotected on a preparative scale by dissolving the polymers in TFA (4 mL/g of polymer) and stirring for several hours with the solution exposed to the atmosphere, and subsequent precipitation in water. The ^{1}H NMR spectra of the polymers in $CDCl_3$/HFIP showed that the diol is deprotected and that the benzaldehyde is completely removed from the polymer after Soxhlet extraction. Measurements of intrinsic viscosity before and after deprotection (Table 3) indicate that there is a decrease in molecular weight as a result of ester hydrolysis during this process.

Thermal Transesterification. The thermal-phase transitions of the protected polymer samples are shown in Table 3. The polymers are thermally stable to cycling up to 300 °C with the collection of reproducible thermograms upon repeated thermal cycling. Treatment of polyesters PET/**1** and PBT/**1** with acid results in the deprotection of the benzal group to afford bis(hydroxymethyl)propane-1,3-diyl units. Differential scanning thermograms of PET samples containing > 5 mol % of the repeat unit derived from **1** showed a glass transition temperature and melting endotherm only in the first heating cycle. No crystallization was observed upon cooling and subsequent cycles gave no evidence of

Table 3. Thermal Characteristics of Copolymers Containing 1

		blocked copolymers					deblocked copolymers		
polymer	method[a]	theor. mol %	calc. mol %[b]	T_m (°C)	T_g (°C)	$[\eta]^c$	T_m (°C)	T_g (°C)	$[\eta]^c$
PET/**1**	T	1	0.81	259	85	0.613	264	81	0.311
	T	3	2.22	248	84	0.792	248	80	0.249
	S	5.2	4.9	243	78		250	90	0.196
	S	10.9	9.8	228	89		240[d]	92	0.298
	S	21.7	15.2	197	88		226[d]	93	0.236
	S	20.1	18.8	199	89		211[d]	93	0.215
PBT/**1**	T	0.75	0.75	227	65		227	47	0.708
	T	1	0.57	228	62		231	57	0.655
	T	3	1.41	222	61		222	62	0.540

[a] S, solution-phase polymerization; T, thermal transesterification polymerization. [b] Calculated by integration of ^{1}H NMR signals. [c] *o*-Chlorophenol at 25 °C. [d] T_m only observed on first heating cycle.

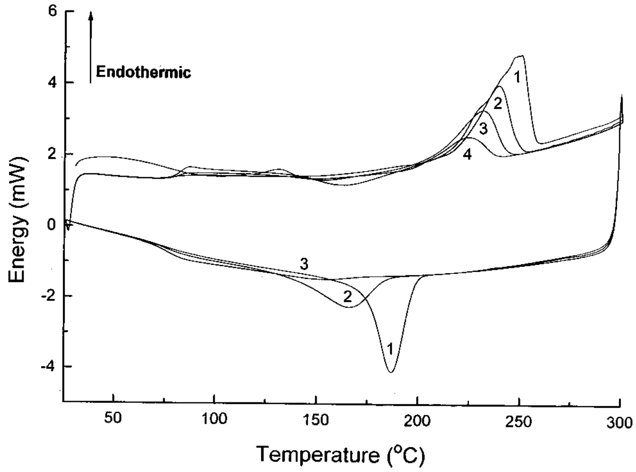


Figure 1. Differential scanning calorimetry of deprotected PET/**1** (5 mol % **1**). Four heating and three cooling cycles are shown.

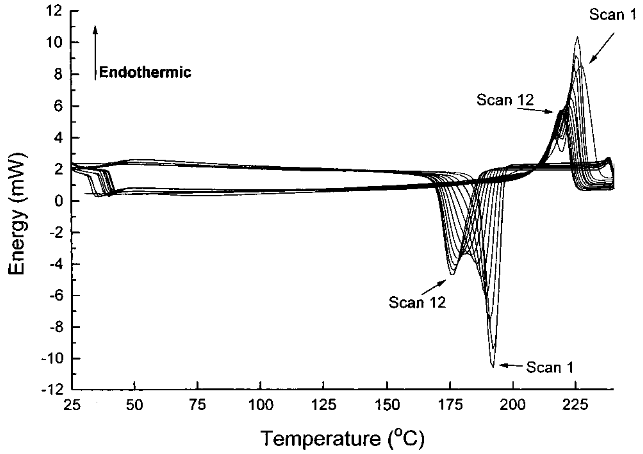


Figure 2. Differential scanning calorimetry of deprotected PBT/**1** (0.75 mol % **1**). The temperature was cycled between 25 °C and 240 °C for 12 cycles, holding the polymer at 240 °C for 1 h after the heating scan before cooling.

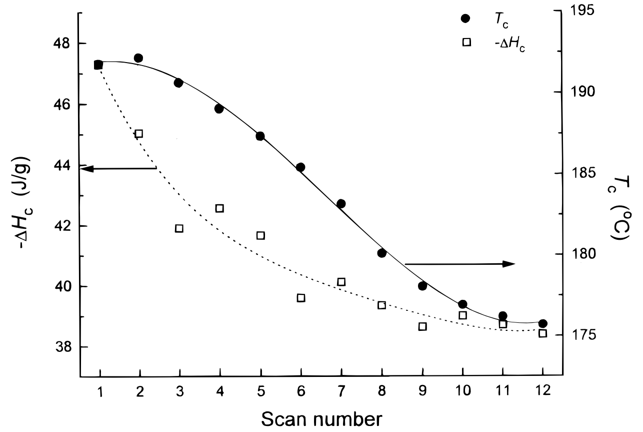


Figure 3. Plots of enthalpy of crystallization (ΔH_c) and crystallization temperature (T_c) vs cycle number for deprotected PBT/**1** copolymer (0.75 mol % **1**).

thermal transitions. The melting and crystallization temperatures of the deprotected PET containing 5 mol % **1** initially appear normal for a PET copolymers and the decrease upon each successive cycle to 300 °C (Figure 1). The enthalpy of the transitions also decreases. After five cycles no crystallization or melting transitions were observed.

The deprotected copolymers with less than 5 mol % of the bis(hydroxymethyl)propanediyl structural unit show a steady decrease in the melting (T_m) and crystallization temperatures (T_c), as well as a decrease in the melting enthalpy, ΔH_m, upon repeated cycling, indicating a lower degree of crystallization. The effect of holding deprotected PBT/**1** (0.75 mol % **1**) above its melting point (240 °C) was demonstrated by differential scanning calorimetry. A monotonic decrease in the heat of crystallization (ΔH_c) and T_c was observed over a number of hours. The melting transition initially decreases and broadens (Figure 2). However, the sample attains a new steady-state melting transition after approximately 9 h at 240 °C. Similarly, the crystallization transition attains a new steady-state value, in contrast to the polymers with a high proportion of comonomer, which do not crystallize after melting.

The decrease in the values of ΔH_c and T_c of these polymers (Figure 3) can be attributed to the thermal transesterification reaction of the hydroxymethyl groups of the pentaerythritol containing a comonomer. Transesterification would initially lead to branching and ultimately to cross-linked material with the formation of an interpenetrating network. The number of chains remains constant since the formation of a branch point produces a new end group on a shorter polymer chain. Branching or cross-linking of the copolymer retards the crystallization of the polymer.

Whereas the deprotected polymers are freely soluble in TFA prior to thermal cross-linking, the heat-treated (300 °C for several hours) deprotected PET/**1** (5 mol % **1**) copolymer is swollen in TFA by a factor of approximately 500%. Samples of deprotected polymer also show an increase in their adhesion to glass substrates after thermal treatment. PET films melted onto glass substrates could be removed with a razor blade. In contrast, similar films produced from PET/**1** copolymers under the same conditions could not be removed from the substrate without being destroyed. Polymers containing 5 mol % of the bis(hydroxymethyl)propane-1,3-diyl unit are rendered insoluble after very short times above T_m, making it difficult to provide a detailed analysis of the course of the transestification.

In conclusion, we have shown that pendant hydroxyl groups can be incorporated into commercial polyesters and that thermal transesterification can be performed to afford rigid and adhesive cross-linked materials. We also briefly investigated the chemical and physical properties of the system. The rate and extent of cross-linking of the 2,2-bis(hydroxymethyl)propane-1,3-diyl units can be controlled by the concentration of the reactive groups in the copolymer, time and temperature. Polymers with a high content of bis(hydroxymethyl)-propane-1,3-diyl units undergo cross-linking with a loss of melting and crystallization transitions upon a single excursion to high temperature (approximately 6 min above T_m). Polymers with lower levels of the reactive structural unit undergo slower cross-linking under the same conditions. Future research will include the investigation of the rate of transesterification reactions and location within the polymer microstructure.

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