Semicrystalline Polymers via Ring-Opening Polymerization: Preparation and Polymerization of Alkylene Phthalate Cyclic Oligomers

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ABSTRACT: Preparation of cyclic oligomeric alkylene phthalates via pseudo-high dilution condensation of alkylene diols with iso- and terephthaloyl chlorides and conversion to high molecular weight polyesters via ring-opening polymerization is described. Sterically unhindered amines such as quinuclidine or 1,4-diazabicyclo[2.2.2]octane (DABCO) catalyze the condensation significantly faster than other tertiary amines and are useful for carrying out this conversion in high yield, in the first direct reaction of diol and diacid chloride to form cyclic polyesters. The mixtures of oligomeric cyclics melt at 150−200° C, providing liquids of low viscosity. Ring-opening polymerization using tin or titanate catalysts affords high molecular weight polymers within minutes. Complete polymerization of PBT oligomeric cyclics can be achieved at 180−200 °C, significantly below the polymer's melting point of 225 °C, and with molecular weights as high as 445×10^3. Polymers formed via such a process are more crystalline than conventionally prepared polyesters.

Introduction

Several years ago, a research program into the preparation and polymerization of cyclic oligomers of engineering thermoplastics was initiated.[1] It was anticipated that the low melt viscosities of such reactive cyclic oligomers would provide an opportunity for reactive processing via methods not available with conventionally prepared polymers. Until our work on Bisphenol A (BPA) carbonate oligomers, most research had concentrated on the preparation and characterization of discrete cyclic oligomers (e.g., BPA carbonate tetramer[2]) via *classical* high dilution chemistry.[3] In contrast, our work has concentrated on the development of selective and efficient *pseudo*-high dilution reactions, in which only the reactive intermediates need be dilute. Such reactions allow high product concentrations and are much more amenable to scaling to commercial quantities, since large volumes of solvent are not necessary. This work has been extended to include many other types of polycarbonates, and in recent years, several groups have investigated the preparation and polymerization of aryl esters,[4] poly(ether imides),[5] poly(ether sulfones),[6] poly(ether ketones),[7] cyclic aramides,[8] and cyclic phenylene disulfides.[9] Several authors have recently reported the preparation of either pure, single-sized cyclics or mixtures of cyclic oligomers via high dilution reactions, with certain advantages cited for each. Although pure, multiply recrystallized single-sized cyclics may have purity advantages, typically low yields and purification considerations preclude commercial applications; melting points of pure, discrete cyclic oligomers are also often very high (>300 °C). Preparation of mixtures can provide significant melting point depression, allowing melt processing during ring-opening polymerization at lower temperatures, but purification can often be difficult; linear oligomeric impurities will limit the ultimate molecular weight achievable. We have therefore concentrated on identifying *selective,* high yielding reactions that afford mixtures of cyclics to the *near total exclusion* of linear oligomers. Such reactions provide the advantages of both approaches and allow the possibility of scaling to commercial quantities. In summary, we have concentrated on using *kinetic reaction control* to prepare cyclic oligomers, while relying on *thermodynamic* reaction control for the polymerization of the cyclics, since it is known that the levels of cyclics in melt polycondensation reactions of the polymers of interest are low.

Applications in the composites area were particularly appealing, since the low molecular weight cyclic oligomers should flow and wet-out fibers better than high molecular weight polymers and because the ring-opening polymerization of such oligomers should afford extremely high molecular weights without formation of byproduct volatiles. Because large volume applications for thermoplastic composites were envisioned primarily in the automotive or aeronautic markets, solvent-resistant thermoplastic matrixes were sought. Although certain polycarbonates showed some solvent resistance,[10] a fast-crystallizing, semicrystalline polymer such as poly(butylene terephthalate) [PBT] was of more interest. We now wish to report the efficient preparation of alkylene phthalate cyclic oligomers via a novel *pseudo*-high dilution condensation reaction catalyzed by unhindered amines. We also report that butylene phthalate cyclic oligomers can be efficiently polymerized using tin or titanate catalysis well below the melting point of the resulting polymer, leading to formation of high molecular weight polyester, which subsequently crystallizes at the reaction temperature. Such processing allows the fabrication of thermoplastic composites without the need for thermal cycling of a molding tool (Scheme 1).

Results

Cyclic oligomers of polyesters such as PBT or poly(ethylene terephthalate) [PET] have been known for some time, being formed in the parent polymers at concentrations of 1−3%, as characterized by several groups.[11] However, alkylene phthalate cyclics have been prepared only in low productivity reactions (yields <50% at <0.01 M monomer concentration) via multistep

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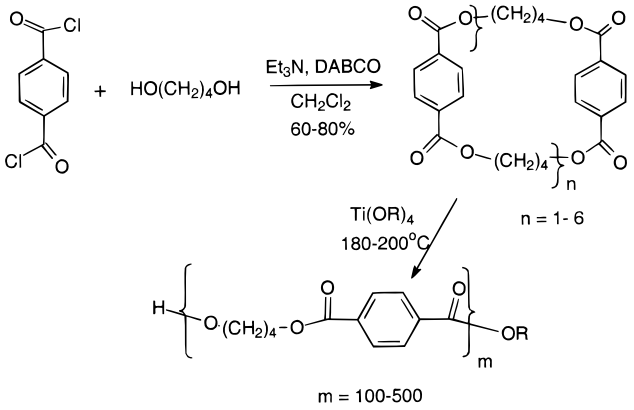
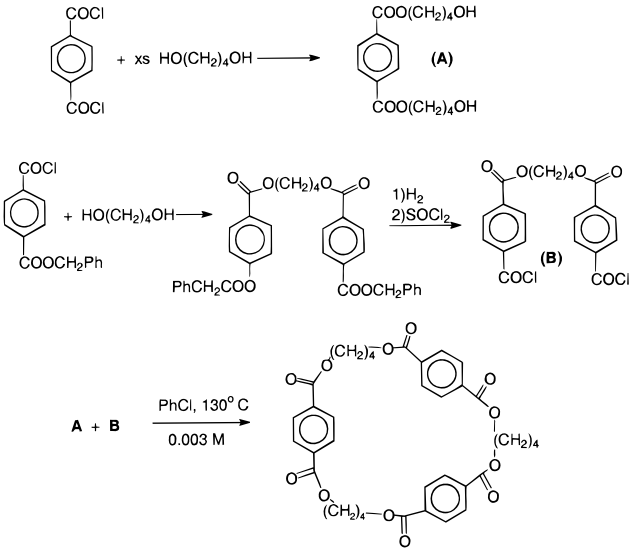
Scheme 1. Preparation and Polymerization of Butylene Terephthalate Oligomeric Cyclics



Scheme 2. Preparation of PBT Cyclic Trimer As Reported by Meraskentis and Zahn[12]



pathways, for example by reaction of an oligomeric diol with an oligomeric acid chloride under classical high dilution conditions (0.003 M; Scheme 2); increasing the reaction concentration to 0.01 M decreased the cyclic yield to 1.5−7.9%.[12] No reports of direct formation of cyclics via reaction of monomeric iso- or terephthalate derivatives with monomeric diols could be found. Initially, it was anticipated that PBT cyclics could be prepared by a routine extension of earlier *pseudo*-high dilution chemistry, since the reaction of terephthaloyl chloride (TPC) with diols such as 1,4-butanediol was expected to be fast. Thus, slow addition of equimolar amounts of TPC and butanediol to an amine base under anhydrous conditions should form cyclic oligomers. However, using triethylamine, pyridine, or even 4-(dimethylamino)pyridine as bases in such reactions led to only small amounts of cyclic oligomers (<5% by HPLC analysis, with products identified by comparison to authentic materials isolated from commercial PBT by the method of Wick[11]).

Further investigation in model reactions revealed that the reaction of aromatic acid chlorides with diols such as butanediol or ethylene glycol was surprisingly slow. For example, reaction of butanediol with benzoyl chloride using stoichiometric pyridine or triethylamine as base provided only 5% or 11% butylene dibenzoate, respectively, after 1 h at ambient temperature. Although monobenzoate formed fairly rapidly, complete conversion to dibenzoate required 24 h of reaction, even using a 2-fold excess of pyridine. A number of experiments were carried out using this model system, which showed that most conventional amines gave poor yields of dibenzoate (Table 1). However, it was noticed that less hindered amines gave higher yields. In fact, very unhindered amines such as diazabicyclo[2.2.2]octane (DABCO) or quinuclidine gave very fast reactions and a quantitative yield of dibenzoate within 15 min at ambient temperature.

Table 1. Reaction of Benzoyl Chloride with Butanediol Using Amine Bases[a]

$2PhCOCl + HO(CH_2)_4OH + 2\ amine \rightarrow PhCOO(CH_2)_4OCOPh + 2\ amine\text{-}HCl$

amine	solvent	time	% dibenzoate
Et_3N	THF	24 h	30
	CH_2Cl_2	3 h	30
pyridine	CH_2Cl_2	3 h	46
	THF	3 h	12
	dioxane	3 h	22
	EtOAc	3 h	21
4-DMAP	CH_2Cl_2	3 h	22
Me_2N-octyl	CH_2Cl_2	3 h	67
Me(pyrrolidine)	CH_2Cl_2	1 h	75
DABCO	CH_2Cl_2	15 min	99
quinuclidine	CH_2Cl_2	15 min	97

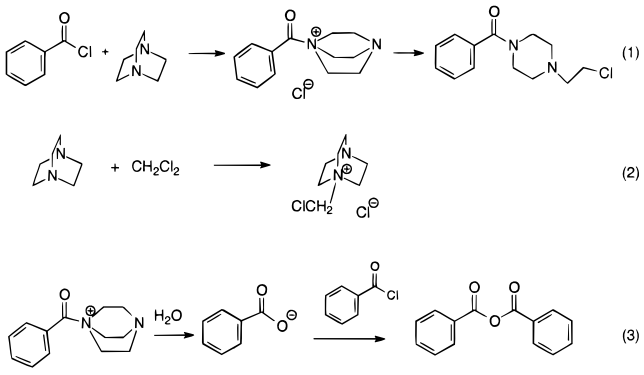
[a] Benzoyl chloride was added to a stirred solution of amine and butanediol in solvent at 0.5 M diol concentration at ambient temperature, sampling after the time shown and analyzing by VPC vs internal standard.

The amine can serve two purposes, to neutralize the HCl liberated in the reaction, and to serve as a nucleophilic catalyst. As a nucleophilic catalyst, the amine attacks the acid chloride to form an intermediate acylammonium salt, which is then attacked by the nucleophilic alcohol. Apparently, triethylamine is too sterically hindered to attack the carbonyl of a benzoyl chloride. Although one might expect 4-DMAP to be less hindered, its acylammonium salt would be electronically stabilized (by delocalization of the positive charge in the 4-DMAP ring), and thus less reactive. Only the acylammonium salts from DABCO or quinuclidine give both highly activated and sterically uncrowded acylammonium intermediates.

Using the results of the model experiments as guidelines for choice of solvent and amine, cyclization reactions were carried out by concurrent addition of equimolar amounts of isophthaloyl chloride (IPC) or TPC in CH_2Cl_2 and butanediol in dry THF to a slight stoichiometric excess of DABCO or quinuclidine in CH_2Cl_2 over 1 h, with a final product concentration of 0.2 M. HPLC analysis of the THF-soluble portion of the product indicated cyclic oligomers as the major products, with small amounts of linear oligomers also present. Isophthalate cyclics were isolated in 45% yield, and PBT cyclics in 30% yield, by far the highest yields of cyclics from a direct reaction of monomeric diacid chlorides and diols. The mixtures of oligomeric cyclics were separated by filtering the crude reaction products that contained insoluble polymer through Celite, washing with HCl, filtering again, and then subjecting the product to flash chromatography over silica gel to remove linear oligomers. The major cyclic formed in both cases was the 2+2 dimer, which accounted for 40−65% of the total cyclic yield, with diminishing amounts of higher cyclics. Linear oligomers were present in amounts of 0.1−2%. Cyclic dimer, trimer, and tetramer were separated by column chromatography and were shown to be identical to authentic cyclics that had been isolated from com-

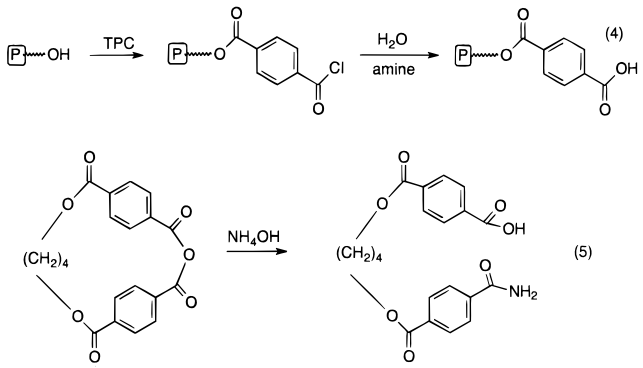
mercial PBT using literature techniques.[11] Linear oligomers were compared to oligomers prepared by reaction of dimethyl terephthalate with excess butanediol.

Although the yield of cyclic oligomers was much higher than any previous attempts at a single step reaction of which we are aware, a significant amount of work was carried out in order to increase the reaction yield and to eliminate unwanted linear oligomers. Three side reactions were identified that interfere with synthesis, all of them involving the unhindered amine: reaction of the amine with acid chloride to form an acylammonium salt, followed by decomposition to an amide (eq 1); reaction with CH_2Cl_2 to form a salt (eq 2); and hydrolysis of the acid chloride, forming carboxylate via catalysis with the amine via the acylammonium salt (eq 3). The first two reactions could be avoided by



minimizing contact time between the reagents, and the third by carefully drying all reagents. Use of dry CH_2Cl_2 was found to be particularly important, since even 100 ppm of water in the solvent will hydrolyze 3.7% of the acid chloride in a reaction carried out at 0.2 M monomer concentration, forming either anhydride or carboxylic acid-containing polymers, and also damaging control of balanced stoichiometry. Eventually, we found that only catalytic amounts (2.5−10%) of unhindered amine were necessary, with Et_3N making up the remainder of the organic base, minimizing unwanted reactions of the very reactive unhindered amines. Finally, a means for delivering neat butanediol was devised, avoiding the need to use THF, which was also a potential source of water. Incorporating these changes into the process allowed the formation of PBT cyclics in 0.25 M reactions carried out in 1 h, with yields as high as 85%. The remainder of material was higher molecular weight polymer, which was removed by filtration through Celite.

Initially, polymerization reactions were found to be slow, or to require high levels of catalyst. This effect was traced to the presence of low levels of anhydride-containing cyclics in the reaction products. A workup procedure that removed both hydroxybutyl-terminated and acid-terminated linear oligomers, as well as anhydride containing cyclics, was developed. At the end of the reaction, HPLC analysis was used to detect the presence of hydroxybutyl-terminated oligomers. If linears were present, small portions of additional TPC were added, converting the alcohols either to cyclics or to acid chloride-terminated oligomers (eq 4). Quenching with water effectively hydrolyzed all acid chlorides (in the presence of excess amine), and addition of a small amount of ammonium hydroxide converted any anhydrides present to amide−acid oligomers (eq 5). Filtration through Celite removed all the insoluble acid-terminated oligomers. HPLC analyses indicated the level of linear oligomers in typical reactions to be less than 0.5%, testifying to the selective formation of cyclic oligomers over linears. A representative HPLC trace of the crude product from the cyclization reaction is shown in Figure 1. The identity of the PBT cyclics was confirmed by separation of the cyclics into individual oligomers and comparison with those reported in the literature.[11,12] Linear oligomers were compared to those produced via conventional polymerization of dimethyl terephthalate with excess butanediol, producing hydroxybutyl-terminated linear oligomers. Only the linear monomer (BHBT), dimer, trimer, and tetramer were soluble enough in THF for HPLC analysis, while the cyclics were soluble up to the heptamer. Once optimized, the reaction of terephthaloyl chloride with butanediol was easily scaled to several liters, and then to a 100-gal reactor, which was capable of producing 10 kg of cyclic PBT oligomers per batch.



Using similar procedures, a variety of alkylene phthalate cyclics were prepared in high yields via direct reaction of diols with diacid chlorides (Table 2); other than 100% PBT and 5% PET/PBT (molar) cocyclic oligomers (see below), these reactions were not optimized. The yields of cyclic oligomers from terephthaloyl chloride were somewhat lower than those from isophthaloyl chloride using either ethylene glycol or neopentylene glycol. In the former case, only a trace of cyclic (2+2) dimer was present, due to ring strain, and cyclic (3+3) trimer was the predominant species; a correspondingly higher amount of polymer was formed. It is not surprising that the isophthalates, which have a bent conformation, were formed more readily than the terephthalates.

With a supply of cyclics readily available, attention was turned to polymerization. Because reactive processing applications were most appealing, melt polymerization was the method of choice. Visually, the mixture of PBT cyclic oligomers began to melt at about 140 °C and was completely molten at 160−190 °C. DSC showed a broad melting range (100−175 °C), with peaks at 130 and 160 °C; the total melting endotherm was 68 J/g. The second heating showed some crystallization occurring before remelting with a peak temperature of 163 °C ($\Delta H = 32$ J/g). The melt viscosity of PBT cyclics was about 30 cP at 190 °C;[13] molten cyclics could be stirred easily with a magnetic stirrer.

Initially, difficulties with incomplete polymerization were encountered, which were linked to impurities. Control polymerizations indicated that either carboxylic acids (e.g., monomethyl terephthalate) or anhydrides (benzoic anhydride or the anhydride from monomethyl

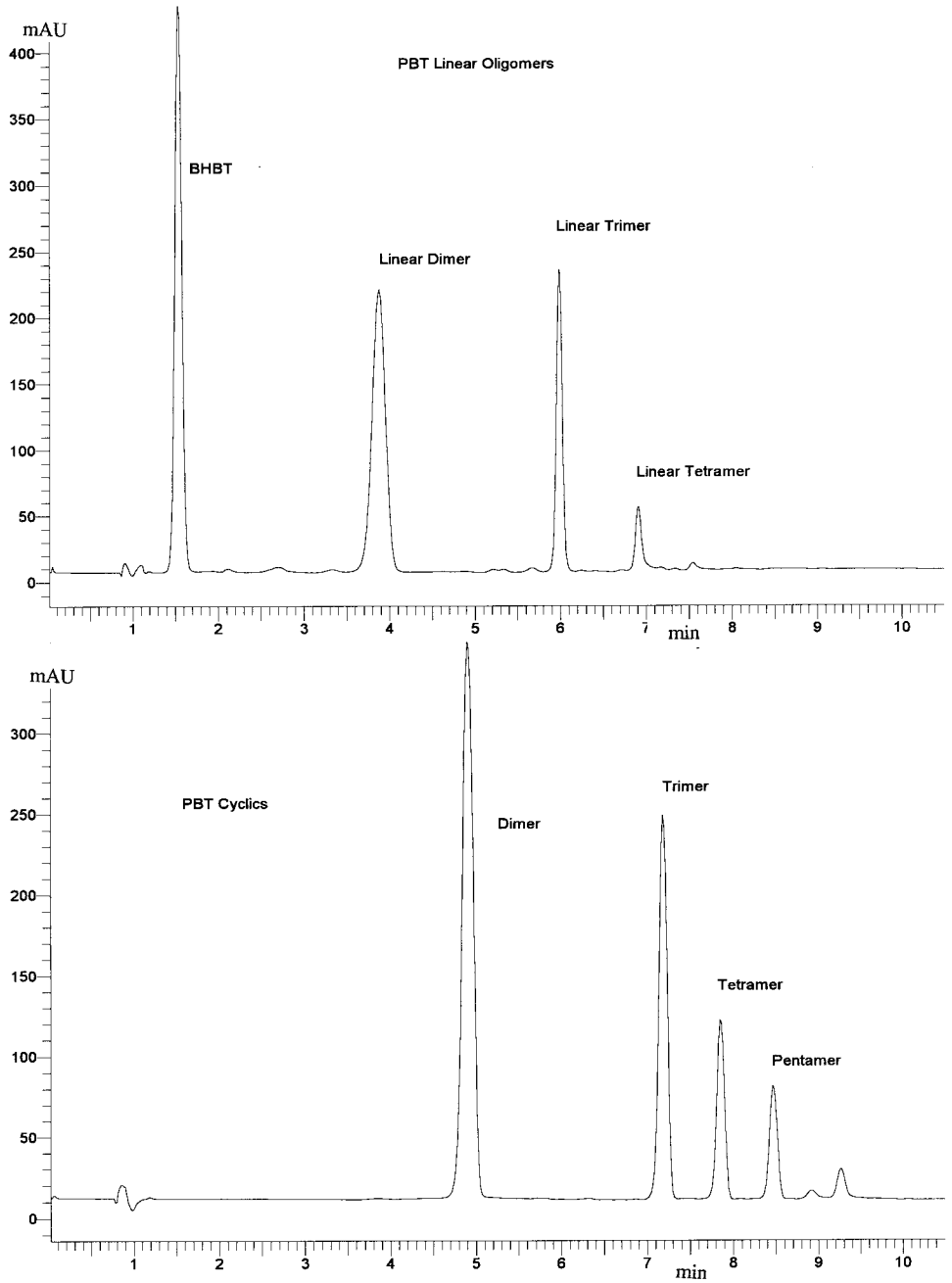
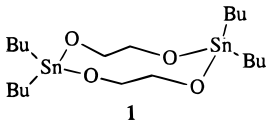


Figure 1. HPLC traces of PBT oligomers (5μ C-8 column, THF/H_2O gradient, 255 nm detection): linear oligomers (above; BHBT = 1,4-bis(4-hydroxybutyl) terephthalate) and cyclic oligomers (below). Assignments made by comparison to authentic materials.

terephthalate) interfered with catalysis by tin or titanate, presumably by forming tin or titanium carboxylates that were ineffective initiators at 190 °C. Since hydrolysis reactions during preparation of cyclics could lead to either of these products, their presence seemed likely. A very small peak corresponding to the anhydride was noted in the FTIR at 1800 cm^{-1}, and thin-layer chromatography (TLC) analysis showed a small amount of material that did not elute from the origin in crude samples. The issue was resolved simply by stirring cyclics in CH_2Cl_2 with silica, followed by filtration and evaporation. Removal of these impurities by adsorption on silica gel allowed complete and rapid polymerization. TLC was developed as a quick method to check the cyclic purity. TLC chromatography on silica gel plates using 5% acetone in CH_2Cl_2 as the eluent showed the cyclics as a series of spots with $R_f \sim 0.3-0.6$. Polar impurities such as acids or anhydrides remained at or near the origin.

Although many types of compounds can initiate polymerization of oligomeric cyclic esters, certain tin and titanium initiators were most effective (Table 3). Either commercially available titanates [tetrakis(2-ethylhexyl)-titanate {TOT} or Ti(O-*i*-Pr)$_4$] or cyclic stannoxanes such as **1** were effective initiators for polymerization at



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levels of 0.05−1.0 mol % based on monomer units. These initiators are thought to operate by Lewis acid activation of the ester group and then transferring a ligand and forming a new ester and an active chain end

Table 2. Preparation of Alkylene Phthalate Cyclic Oligomers[a]

cyclic type[b]	% yield[c]	FTIR[d] (cm^{-1})	^1H NMR[e] (ppm)	cyclic ratio[f]
PEI	80	3021, 1725, 1296, 1206	4.17−4.73 (4H) 8.11−8.14 (4H)	74, 13, 6, 2
PET	60	3021, 1725, 1286, 1209	4.65−4.77 (4H) 7.51−8.93 (4H)	39, 21, 14, 10, 7, 3, 1
PBI	85	3021, 1720, 1306, 1212	1.93−2.08 (4H) 4.39−4.50 (4H) 7.49−8.65 (4H)	63, 19, 8, 7, 3, 1
PBT	82	3022, 1718, 1274, 1206	1.96−2.18 (4H) 4.34−4.42 (4H) 7.83−8.11 (4H)	51, 26, 11, 8, 2, 2
PHI	75	3021, 1718, 1307, 1216	1.56−1.86 (8H) 4.34−4.42 (4H) 7.47−8.65 (4H)	59, 23, 11, 6
PHT	55	3025, 1717, 1274, 1209	1.55−1.85 (8H) 4.35−4.42 (4H) 8.07−8.11 (4H)	33, 18, 9, 5, 3, 1
PNI	80	3022, 1721, 1278, 1208	1.06−1.34 (6H) 4.25−4.38 (4H) 7.19−8.60 (4H)	62, 26, 12
PNT	53	3021, 1721, 1278, 1208	1.14−1.46 (6H) 4.27−4.97 (4H) 7.67−8.21 (4H)	68, 10, 2
PDI	53	3024, 1724, 1306, 1206	3.81−3.94 (4 H) 4.42−4.44 (4H) 7.18−8.47 (4H)	83, 14, 1
PDT	49	3021, 1719, 1278, 1216	3.78−3.87 (4H) 4.43−4.49 (4H) 7.95−7.98 (4H)	58, 26, 8

[a] Cyclic oligomers prepared from IPC or TPC and diol; purified by filtration through Celite to remove polymer and flash chromatography to remove linears. [b] I = isophthalate, T = terephthalate, E = ethylene, B = butylene, H = hexylene, N = neopentylene, D = diethylene glycol. [c] Isolated yield after removing polymer and linears. [d] Solution FTIR in $CHCl_3$. [e] $CDCl_3$ solvent. [f] Ratio of peaks on HPLC.

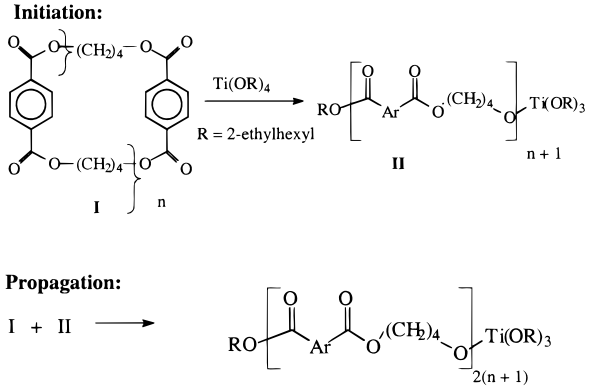
Table 3. Polymerization of 5% Molar Ratio PET/PBT Cocyclic Oligomers[a]

initiator[b] (mol %)	temp (°C)	time (min)	% polym	$M_w \times 10^{-3}$ (vs PS)	$M_n \times 10^{-3}$ (vs PS)	M_w/M_n
$Bu_2Sn{=}O$ (0.5)	275	10	97	58.9		
Ti(O-*i*-Pr)$_4$ (0.2)	190	6	98	115	55	2.1
TOT (0.1)	190	20	99	352	167	2.1
TOT (0.2)	190	20	98	117.1	52	2.25
TOT (0.3)	190	6	95	95	39.7	2.4
TOT (0.3) + 0.5% linear[c]	190	6	96	75.6	26.7	2.8
TOT (0.3) + 1.0% linear[c]	190	6	95	61.2	22.1	2.8
TOT (0.3) + 2.0% linear[c]	190	10	98	25.4	11.4	2.2
TOT (0.4)	190	20	97	62.1	19.6	3.2
TOT (0.5)	190	6	99	53.2	22.7	2.3
stannoxane **1** (0.05)	190	20	91	401	303	1.3
stannoxane **1** (0.1)	190	20	95	344	177	1.9
stannoxane **1** (0.2)	190	20	95	445	286	1.55
stannoxane **1** (0.4)	190	20	98	330	171	1.9
stannoxane **1** (0.2)	*d*	10	97	117	51.9	2.25
NaOEt (1.0)	225	10	41	5.3		
Sn(OMe)$_2$ (1.0)	250	10	54	36		
comm (Valox 315)	NA	NA		111	48.7	2.3

[a] Polymerizations were carried out neat by adding catalyst in a minimum amount of solvent to molten cyclic oligomers at the temperature shown. [b] Mole percent relative to monomer units. [c] Bis(4-hydroxybutyl) terephthalate added at level shown. [d] Polymerization carried out in DSC, heating from 50 to 250 °C at 20 °C/min.

(initiation, Scheme 3). Propagation continues until all the cyclic oligomers are depleted and the ring-chain equilibration becomes degenerate; the initiator becomes

Scheme 3. Polymerization of Poly(butylene terephthalate) Cyclics via Ring-Opening Utilizing Titanium Alkoxide Catalysis: Initiation and Propagation Steps



built into the polymer and is not terminated unless quenched. Because the cyclic oligomers are nearly strain-free, the polymerization is almost thermoneutral and leads to complete equilibration of ester groups (i.e., initiation, propagation, and chain transfer have nearly the same rates). Polydispersities therefore approach 2.0 and were typically in the range 2.0−3.0, as in conventional polycondensation of DMT with butanediol (Commercial Valox 315 has $M_w/M_n \sim 2.3$). GPC traces are typically monomodal, with a small amount (1−3%) of cyclics remaining, presumably the equilibrium amount (See Figure 3). DSC analysis of a mixture of cyclic oligomers containing stannoxane **1** showed only the melting endotherm ($\Delta H = 68$ J/g) (Figure 2a), with no exotherm evident. Cooling showed the crystallization of the polymer, and the second heating showed only the melting point of the PBT polymer at 213 °C ($\Delta H = 54$ J/g; Figure 2b); the polymer had $M_w = 117\,000$ and was 97% polymerized by GPC.

The molecular weight of the polymer can be controlled by the molar ratio of cyclic esters to linear functionalities. Low molecular weight linear oligomers such as 1,4-bis(4-hydroxybutyl) terephthalate or its oligomers limited the ultimate molecular weight achieved. Furthermore, some initiators (such as TOT) introduced nonpolymerizable monomers (2-ethylhexanol) which also limited the molecular weight. Thus, as the level of titanate initiator (which contains four alcohol groups) was decreased, higher molecular weights were observed. Conversely, as the amount of linear oligomers was decreased, the polymer molecular weight increased. When cyclic stannoxane **1** was used as the initiator, no decrease in molecular weight was observed with increasing catalyst level, because no end groups were introduced; the tin should be built into a macrocyclic polymer that is stable to GPC conditions (Scheme 4). The GPC characteristics of the stannoxane-initiated polymerizations were quite different from those of the titanate-initiated systems (much higher M_w's, lower apparent dispersities). These effects are delineated in Table 3.

The polymerization reaction was typically carried out at 180−200 °C, well below PBT's melting point of ~225 °C. Regardless, complete polymerization with only 1−3% cyclic remaining (by GPC) could be achieved. Figure 3 shows gel permeation chromatography of the starting cyclics, the polymer resulting from ring-opening polymerization, and a typical commercial PBT. Three factors controlled the completeness of polymerizations:

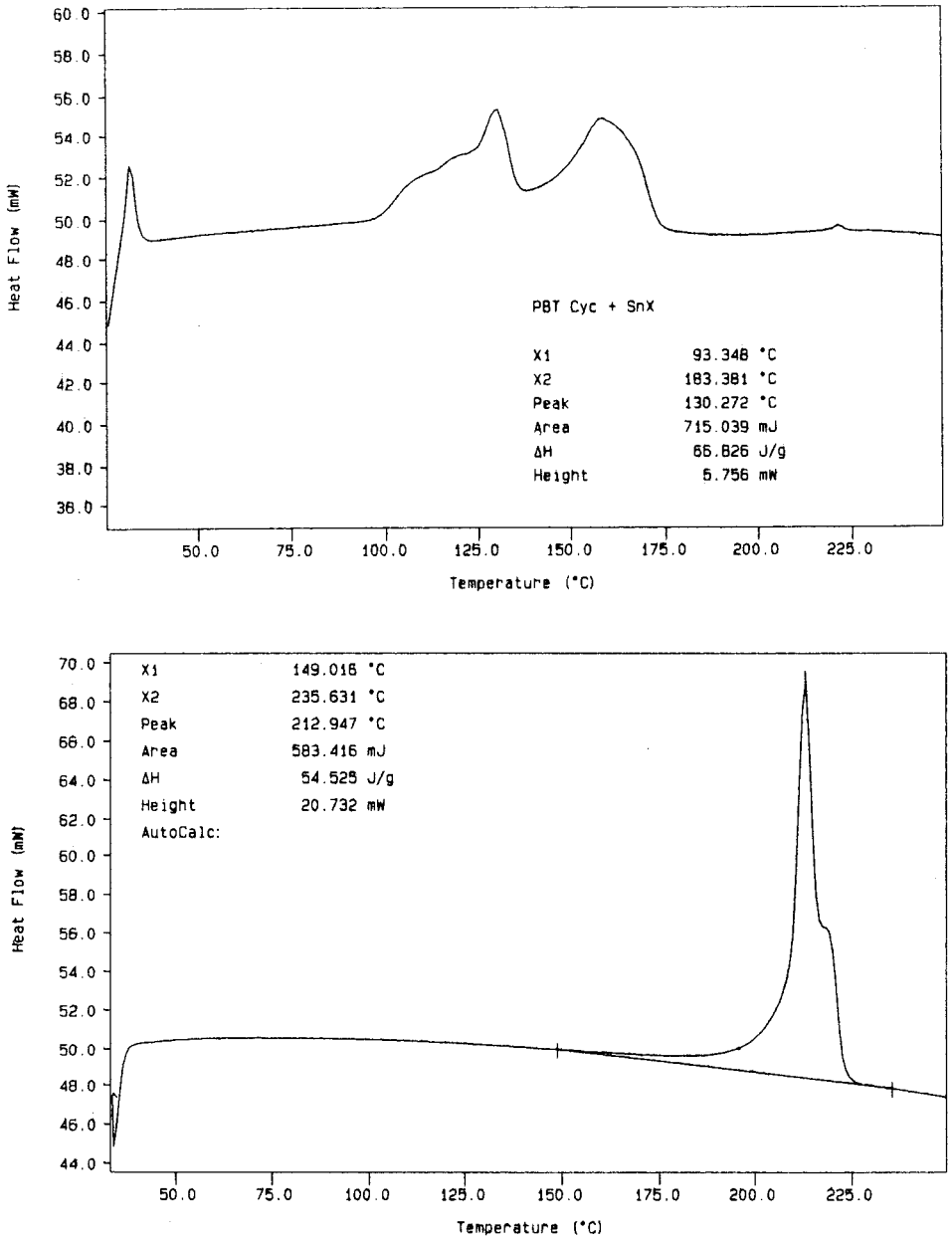


Figure 2. (a) DSC trace of PBT cyclic oligomers containing 0.3% stannoxane **1**. (b) Second heating after polymerization reaction.

(1) purity of the monomers (see above), (2) complete mixing of initiator before polymerization causing the viscosity to increase to the point where mixing stopped (the initiator needs to be intimately mixed with the molten cyclic), and (3) polymerization at a high enough rate that polymerization was essentially complete before crystallization occurred. For most fast initiators, polymerization at 190 °C using mechanical stirring at 300−500 rpm was ideal for effecting complete conversion to polymer. In some cases, premature crystallization (temperatures below 185 °C) or inefficient mixing of the initiator led to incomplete polymerization and recovery of cyclics along with polymer.

Polymers prepared from cyclic oligomers showed higher levels of crystallinity than conventionally prepared polyester (60−80 J/g vs 35−50 J/g for commercial materials of similar molecular weights; see Table 4, entries 1 and 11). The cause of such excess crystallinity is under investigation.[14] One possibility is that more order exists in the polymer since polymerization only requires breaking and making ester bonds, rather than removal of condensation byproducts such as methanol or butanediol and the vigorous mixing which that process requires. The crystallinity of the polymer could be controlled by incorporation of low levels of another monomer (such as ethylene glycol) into the cyclics. Table 4 shows the changes in cyclic and polymer thermal properties when prepared from various molar mixtures of ethylene and butylene glycols. Note that a cocyclic prepared by mixing reactants melted at a significantly lower temperature than a physical mixture of PET and PBT cyclics which had been prepared separately (entries 8 and 9). Much of our processing work was carried out using the 5% (molar) PET/PBT cocyclics.

Conversion of cyclic oligomers to composite structures via resin transfer molding (RTM) and reaction injection molding (RIM) techniques has been demonstrated and will be the subject of subsequent publications. Glass loadings as high as 70% and composite tensile moduli of 3 million psi are routinely achieved.[15]

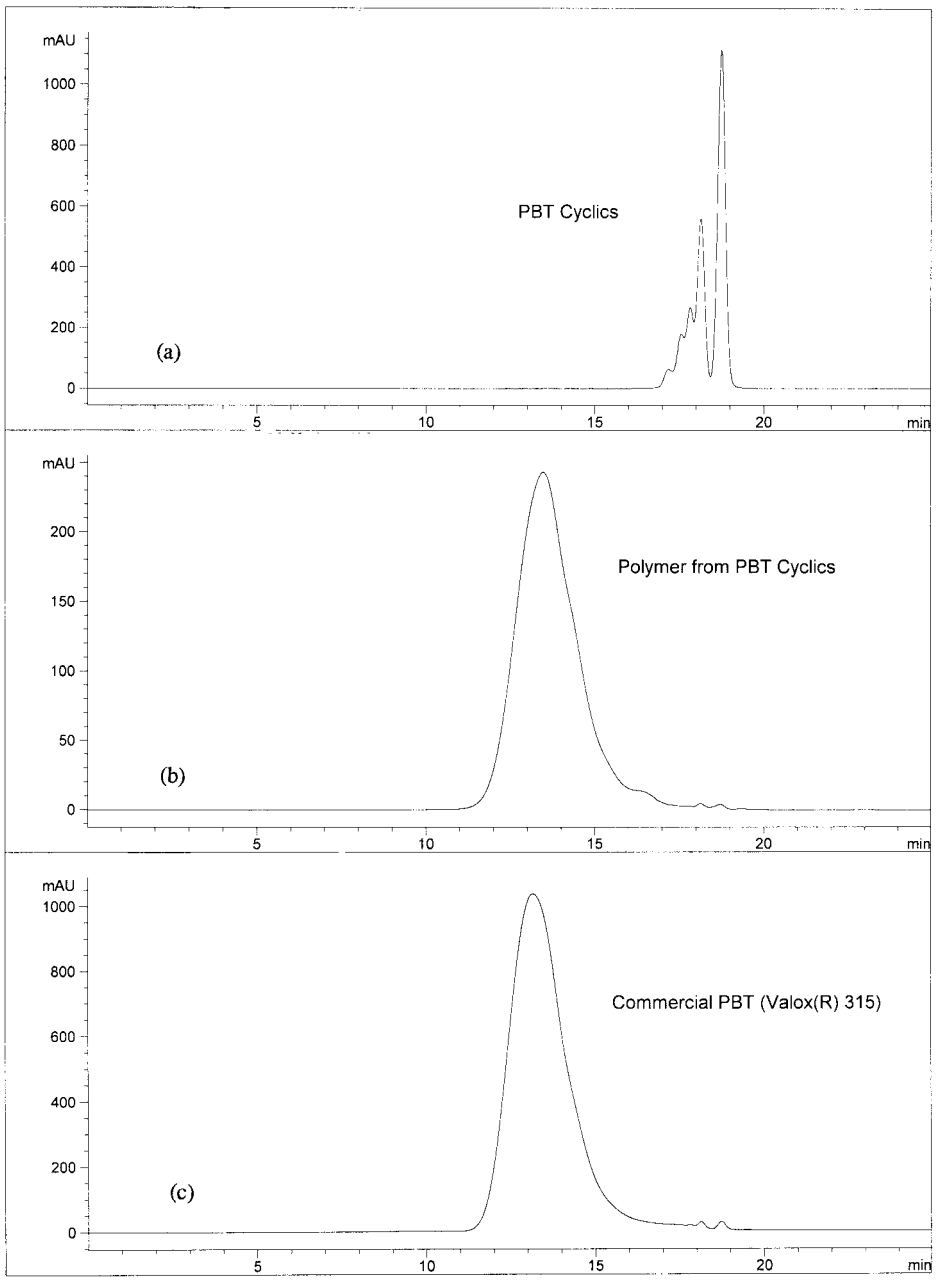
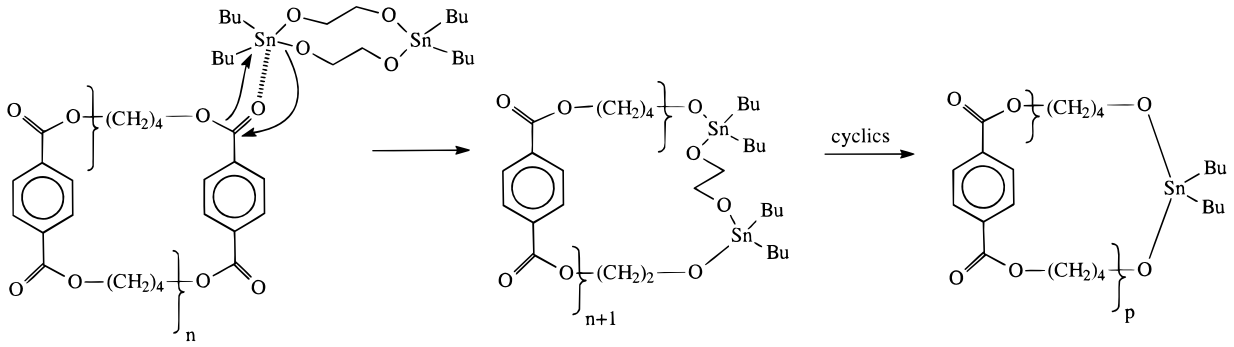


Figure 3. GPC traces of (a) PBT cyclic oligomers, (b) polymer resulting from polymerization of cyclics, and (c) commercial PBT (Valox 315).

Scheme 4. Incorporation of Cyclic Stannoxane Initiator into a Macrocycle



Conclusion

A new method for preparation of polyesters from glycols and aromatic acid chlorides has been developed and optimized. The technique affords a convenient, high yield method for preparation of large quantities of oligomeric cyclics with very high selectivity of cyclic oligomers over linear oligomers. Purification to polymerization quality has been simply achieved. The cyclic

Table 4. Mixed Cyclic Alkylene Oligomer[a] Properties and Polymerizations[b]

entry	PET/PBT molar ratio	soften T (°C)	flow point (°C)	mp (°C)	% polym	$M_w \times 10^{-3}$	polym mp (°C)	polym ΔH (J/g)
1	0/100	150	167	185	96	104.1	228	72.1
2	1/99	140	160	175	100	90.4	226	68.6
3	2/98	140	156	176	99	132.7	224	67.3
4	3/97	140	160	177	98	113.0	224	64.4
5	5/95	140	158	175	98	121.1	220	59.0
6	7/93	140	155	177	99	110.0	217	57.4
7	8/92	140	155	172	99	96.6	217	57.1
8	10/90	140	155	175	94	79.7	214	47.8
9	10/90[b]	140	170	>225				
10	100/0	230	270	>300				
11	Valox 315	na	na	na	98	98.0	226	45.8

[a] All compositions (except where noted) are cocyclics prepared by reacting a mixture of ethylene glycol and butanediol with TPC. [b] Polymerizations were carried out by drying the cyclics under vacuum at 100 °C and then melting at 190 °C under vacuum. With efficient stirring, 0.3 mol % of TOT was added, polymerizing for 20 min at 190 °C. [c] 10/90 mixture of PET and PBT cyclics, prepared independently and mixed in solution and then evaporated.

oligomers melt at 130−180 °C and have very low melt viscosities. Polymerization of the cyclic oligomers has been achieved with a variety of initiators, most notably tin and titanium esters. Polymerization can be complete within minutes and leads to very high molecular weight polyesters that have a high degree of crystallinity. Further work on the development of new initiators, the mechanism of ring-opening polymerization, and fabrication of composites will be reported in due course.

Experimental Section

General Information. Reagent CH_2Cl_2 was dried using activated 3 Å molecular sieves and checked by Karl Fischer titration using a Mettler DF-37 coulometric titrator. The purity of freshly received TPC was checked by dissolution in dry CH_2Cl_2; if clear solutions did not result, it was distilled under high vacuum. Et_3N was distilled from CaH_2, and DABCO was sublimed. Freshly opened bottles of butanediol were stored under Ar. HPLC analysis was carried out using a THF/water gradient on a Zorbax 5μ C-8 column. Gradient: (Step 1) Program from 40 to 88% THF with curvature exponent of −2 at flow rate of 1.75 mL/min. (Step 2) Program from 88 to 100% THF over 0.1 min (linear). (Step 3) Hold at 100% and flow = 2.0 mL/min for 1 min. (Step 4) Program from 100% to 40% THF over 1 min at flow = 1.75 mL/min. (Step 5) Reequilibrate at 40% THF for 6 min. GPC analyses were carried out by dissolving samples in 15% hexafluoro-2-propanol/chloroform and analyzing 0.5% (w/v) samples on a Polymer Labs Mixed C-5μ column, eluting at 0.75 mL/min with 3% 2-propanol/$CHCl_3$; molecular weights were calibrated relative to polystyrene standards. Integration of the cyclics peaks relative to the polymer peak revealed the extent of reaction.

Preparation of Cyclic Oligomers. 1,4-Butylene Terephahalate Cyclics. A three-neck 5-L flask was fitted with a mechanical stirrer, nitrogen purge, and a pair of calibrated peristaltic pumps for controlled addition of reagents. The reactor was charged with 3 L of dry CH_2Cl_2 (<20 ppm water), 1.7 mol of Et_3N (235 mL), and 40 mmol of DABCO (4.48 g). A 1.0 M solution of terephthaloyl chloride in CH_2Cl_2 (800 mL) and neat 1,4-butanediol (72 g; 0.80 mol) were added at a constant rate over 30 min to 1 h, using the peristaltic pumps to maintain stoichiometry in the reactor. The reaction was mildly exothermic, reaching reflux temperature in about 20 min. Five minutes after the reaction was complete a small sample was quenched with water, washed with HCl, filtered, and analyzed by HPLC. If hydroxybutyl linear oligomers were detected, a small portion of TPC was added to the reactor to convert them to acid chloride-terminated oligomers. When linears were no longer detected, the reaction was quenched with a small amount of water (10 mL), followed by addition of aqueous NH_4OH (10 mL). Polymer was removed by filtration through Celite, and the CH_2Cl_2 solution was worked up by washing sequentially with 3 N HCl, 1 N HCl, and water (3×). Filtration and evaporation provided the crude PBT cyclics in 82% yield. Cyclics could be further purified by stirring a CH_2Cl_2 solution with silica gel, to remove trace polar impurities. The cyclics could be fractionated by column chromatography into individual oligomers. Thus, 3.68 g of mixed cyclics was eluted over silica gel using 4% acetone/CH_2Cl_2 to afford 1.337 g of cyclic dimer (mp = 196 °C; lit.[11] = 194, 196 °C), 660 mg of cyclic trimer (mp = 167−168 °C; lit.[11] mp = 168 °C), 227 mg of cyclic tetramer (mp = 245−246 °C; lit.[11] mp = 247−249 °C), 218 mg of cyclic pentamer, and 65 mg of cyclic hexamer. HPLC, ^{1}H NMR, and FTIR were identical to those of the authentic cyclics, separated from commercial PBT according to Wick et al.:[11] A 2-lb sample of cryogenically ground Valox 315 was extracted with 3 L of hot dioxane, stirring for 16 h, followed by filtration and evaporation. The 8 g of soluble semisolid was subjected to flash chromatography on silica gel to produce a mixture comprising 49% cyclic dimer, 26% trimer, 12% tetramer, 8% pentamer, and 2% hexamer. The individual cyclics were isolated by medium-pressure chromatography over silica gel.

The preparations of mixed PET/PBT cocyclics were carried out by using the same procedure, but feeding a mixture of ethylene glycol and butanediol instead of the pure butanediol. All ratios shown in Table 4 are molar ratios.

The preparations of cyclics from TPC or IPC using ethylene glycol, neopentylene glycol, diethylene glycol, or 1,6-hexanediol were carried out according to the following procedure: A three-neck round-bottom flask was fitted with a mechanical stirrer, nitrogen purge, and a septum. The flask was charged with 100 mL of CH_2Cl_2 and cooled to 0 °C, at which time 50 mmol of 1,4-diazabicyclo[2.2.2]octane was added. Solutions of 20 mmol each of the appropriate diol (dissolved into 10 mL of THF) and either TPC or IPC (in CH_2Cl_2) were added simultaneously at 0 °C over 30 min, with addition carried out at subsurface, using a syringe pump. Five minutes after complete addition of the two reagents, the reaction was quenched at 0 °C with 2 mL of water. The slurry was stirred for 5 min, at which time it was treated with 50 mL of 1 M HCl. The solution was allowed to stir for another 5 min, after which it was diluted with 50 mL of CH_2Cl_2 and was filtered through Celite to remove solids, when necessary, before washing. Washing of the filtrate with 50 mL of 0.1 M HCl, water, and finally brine, followed by drying with $MgSO_4$, filtration, and evaporation gave the crude products, typically white solids. Further purification to remove linears could be carried out by passing CH_2Cl_2 solutions of the cyclics through a short column of silica gel, eluting with 1−2% acetone/CH_2Cl_2. Results, HPLC analyses, and spectral characteristics are shown in Table 2.

Polymerization of PBT Cyclic Oligomers. Cyclic PBT oligomers (10.0 g; 45.5 mmol) were placed in a 25-mL round-bottomed flask and heated at 100 °C under vacuum for 10 min to dry the powder. Heating under vacuum was continued at 190 °C with stirring until all the material was molten. When

the vacuum was released with nitrogen, the temperature was adjusted, if necessary, and then initiator was added as a 1 M solution in *o*-dichlorobenzene, causing the stirrer to stop, usually within seconds, as the material polymerized. Within 2−5 min the sample typically crystallized. Samples were quenched by immersion in ice water and then were analyzed by GPC.

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