*Macromolecules* **2000,** *33,* 5053−5064

# Synthesis of Cyclic Oligoesters and Their Rapid Polymerization to High Molecular Weight[†]

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*Received February 17, 2000; Revised Manuscript Received March 30, 2000*

ABSTRACT: We report advances for both synthesizing cyclic oligoesters and tailoring their physical properties to make ring-opening polymerization more practical for polyester manufacturing. Solution and suspension methods provide cyclic oligoesters rapidly with high yield and purity. Both methods can be adapted to continuous process operation using simple, inexpensive raw materials. Synthesis methodology influences the distribution of cyclic ring sizes. Nonequilibrium cyclic oligomer distributions produce variant crystal morphologies. Some kinetic cyclic oligoester mixtures have melting points remarkably reduced from those previously reported for the pure components. New mixed solvent syntheses, cyclic cooligomers, and ring-opening copolymerizations are demonstrated. The kinetics and efficiencies of cyclic oligoester polymerization to high molecular weight for homopolymer and copolymers are characterized. A new approach for a continuous, melt-phase ring-opening polymerization is demonstrated which avoids the high temperatures normally required to melt cyclic oligomers.

## Introduction

Ring-opening polymerization of cyclic oligoesters could be a revolutionary, new means to manufacture polyesters which are now typically manufactured by polycondensation of linear oligomers. In polycondensation linear oligomers are linked together while producing a small molecule byproduct. These polycondensation, forward-reaction rates in linear oligoester melts are intrinsically fast, but unfortunately, the reverse reaction rates are also fast and about equal in magnitude. Thus, the observed rates in commercial melt polycondensations are most often limited by the mass transport required to remove the condensation byproduct from the polymerizing melt itself.[1] In contrast, the same polyesters can be produced by ring-opening polymerization, ROP, of cyclic oligoesters without producing a condensation byproduct. If ROP reactions are fast, then we would anticipate that cyclic oligoesters could quickly polymerize to high molecular weight linear polymer in a closed vessel, without the mechanical energies required to remove a polymerization byproduct molecule. Practical implementation of ROP should enable many new specialty and commodity manufacturing methods and polymeric materials.

Practical, widespread application of ROP is hindered by the limited efficiencies for synthesizing and isolating many types of cyclic oligoesters. It is most common to obtain cyclic oligomers from their respective linear oligomers or polymers. Cyclic oligoesters are equilibrium components of linear polyesters,[2] but typically the cyclics compose less than 5 wt %, depending on the polyester. These cyclics can be isolated from linear polymer by extraction;[3] however, this method is slow and requires a large amount of polymer to acquire appreciable quantities of cyclics. Carothers demonstrated that cyclic oligoesters readily distill from molten polyesters at elevated temperatures under high vacuum, although these methods are limited to aliphatic oligoesters.[4] Cyclics can be produced directly from their monomeric components. Direct reaction of acid chlorides with glycols in dilute solution gives high yields of cyclic oligoesters.[5] Synthesis of aliphatic cyclic oligoesters in high yield on a solid support is also known.[6] Other known synthesis methods for cyclic oligoesters take advantage of the ring-chain equilibria which favors cyclic oligomer formation when diluting a mixture of cyclic and linear oligomers.[7] The ring-chain equilibration reaction is rapid, and new synthetic methods for poly(ethylene terephthalate), PET, take advantage of this rapid ring-chain equilibration.[8] For example, dissolving linear PET in dilute solution gives the cyclic oligomers in good yields at temperatures for which transesterification is a rapid reaction.[8] In a variation of this procedure, Semlyen and Bryant have shown that dissolving the linear PET in 1-methylnaphthalene at 240 °C at 10 wt % concentration gives a 30% yield of the cyclic oligomer.[8]

Practical, widespread application of ROP is also hindered by the unfavorable physical properties of the cyclics themselves. Once one has isolated a quantity of a cyclic oligoester, there still remains the issue of how to execute the ROP. Many cyclic oligoesters melt at relatively high temperatures. This is especially problematic for the cyclic oligo(alkylene arylate)s. For example, the cyclic oligo(ethylene terephthalate), COET, trimer is by far the most abundant and readily synthesized cyclic oligomer from PET. This oligomer is known to melt at 321 °C,[9] substantially higher than the practical thermal stability of its polymer.

We now report advances in both synthetic methods and physical properties that may make ROP more practical. Our solution and suspension methods provide cyclic oligoesters rapidly with high yields and purities. Furthermore, each of these methods can be adapted to continuous process operation using simple, inexpensive raw materials. We report that synthesis methodology can influence the distribution of cyclic ring sizes. Nonequilibrium cyclic oligomer distributions produce variant crystal morphologies. In fact, we find some cyclic oligoester mixtures have melting points remarkably

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[†] Publication Number 7864.

10.1021/ma000278b CCC: $19.00

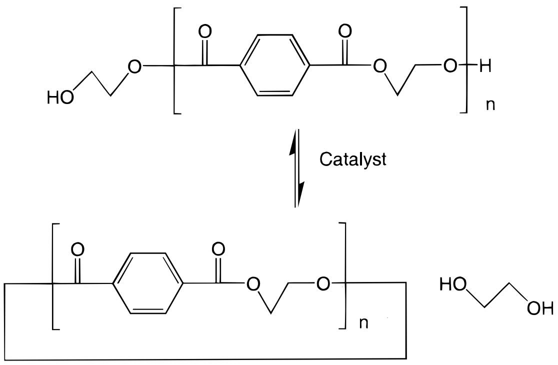


**Figure 1.** Ring–chain equilibration. Equilibration between linear polyesters and polyester cyclic oligomers is fast compared to the time scale of conventional polycondensation.

reduced from those previously reported for the pure components. Finally, we discuss the kinetics and efficiencies of cyclic oligoester ROP to high molecular weight. Under optimal conditions, the COETs polymerize to a number-average degree of polymerization greater than 80 in under 10 min at 285 °C, even in closed vessels. We also propose and demonstrate a new approach for a continuous, melt-phase ROP process which avoids the high temperatures normally required to melt cyclic oligomers.

## Results

Our methods for synthesizing cyclic oligoesters from linear precursors and polymerizing cyclics to high MW polyesters exploit the basic, rapid equilibria between linear and cyclic species, as illustrated for COET and PET in Figure 1. Cyclics are favored under dilution and with sparse concentrations of hydroxy groups.[7] This still allows several degrees of freedom to optimize synthesis methodology. The linear terephthaloyl starting material can range from bis(2-hydroxyethyl) terephthalate, BHET, to high molecular weight PET. Cyclization of the starting material can occur in a medium which is a good solvent either for both linear and cyclic oligoesters, for only cyclic oligoesters, or for only linear oligoesters. The choice of solvent medium has a surprising effect on the cyclic oligoester distribution equilibration kinetics. In many cases, nonequilibrium cyclic oligoester size distributions can be obtained easily. The melting temperatures of some distributions are observed to be much lower and much more practical than the melting temperature of the equilibrium cyclic oligoester distribution. We will illustrate these considerations with two example methods: suspension synthesis and solution synthesis. We further illustrate these techniques can produce a variety of cyclic oligoester compositions using different starting materials. High polymer is favored in concentrated systems, and the degree of polymerization is determined by the number of hydroxy end groups present to initiate ROP. We illustrate the most important considerations required to produce conversions to high molecular weight polyester.

**Suspension Synthesis of Cyclic Oligo(ethylene terephthalate).** This section illustrates the conversion of high polymer droplets to cyclic oligomers which become dissolved into the continuous suspension fluid. PET and linear oligomer remain immiscible in hydrocarbons even at temperatures in excess of 300 °C. COETs readily dissolve in saturated hydrocarbons, such as hexadecane at temperatures over 200 °C, but crystallize out of solution as the hydrocarbon is either cooled or titurated with nonsolvent. This is the basis for a new cyclic oligomer synthesis strategy that yields the cyclic oligomers quantitatively and free of linear impurities. The resulting cyclic oligomers are sufficiently pure for direct polymerization to high molecular weight with no need for subsequent purification. The polymerization of these materials is described later in this section.

Suspended PET droplets in hexadecane refluxing at 287 °C rapidly forms cyclic oligomer in the hexadecane phase. The melt droplets are easily formed and suspended by adding up to 5 wt % PET pellets (nominally 0.6 IV, $M_w = 44\,000$) into lab glassware accommodated with rapid stirring. The reaction is catalyzed by adding 20 ppm tetraisopropyl titanate catalyst to the hexadecane. Other solvents are also known[10] and could be used. Removing and cooling aliquots of the hexadecane phase causes precipitation of COET. The COET is a mixture of various ring sizes but free of linear impurities. Returning the purified hexadecane to the suspension causes more cyclic to form and dissolve as the PET melt continues to reequilibrate with cyclic components. Repetition of this process ultimately brings about nearly complete conversion of the PET to cyclic oligomer. This demonstration constitutes a batchwise, laboratory-scale model of a continuous process for COET production. The equilibrium concentration of COET in molten PET is ca. 1.7%. Therefore, the complete conversion of PET to COET is a remarkable achievement. Similarly, we find other conventional industrial monomers such as BHET work well using this synthesis strategy.

We characterized the COETs produced from suspension cyclization in hexadecane by fast atom bombardment mass spectrometry, FAB-MS; NMR; elemental analyses; high-performance liquid chromatography, HPLC; differential scanning calorimetry, DSC; and scanning electron microscopy, SEM. Similar results are obtained using BHET monomer, oligomer, and PET as starting materials. FAB-MS shows a distribution of cyclic oligomers with M + H parent ion peaks at 385, 577, 769, and 961 amu with a very weak parent ion peak at 1153 amu. The $^1$H NMR shows an aromatic resonance at 8.04 ppm (singlet, with small singlets at 8.03 and 8.02 ppm, with a total intensity for 1H) and an aliphatic resonance at 4.63 ppm (singlet, 1H) ($CD_2Cl_2$ solution). No other resonances were detectable in the $^1$H NMR. The $^{13}C\{^1H\}$ NMR spectra show a carbonyl carbon resonance at +166 ppm, aromatic resonances at +134.7 and +130.3 ppm, and aliphatic carbon resonances at +63.5 ppm. Precision elemental analysis on the cyclics found: 62.51% C, 4.15% H, 0.24% N. This composition agrees with the theoretical compositions for $(C_{10}H_8O_4)_n$: 62.50% C, 4.17% H, 0.0% N.

We find that COETs prepared in suspension cyclizations have relatively narrow molecular weight distributions. In this example the COETs were crystallized from hydrocarbons slowly cooled over 3 h, and molecular weight distributions were characterized from both FAB-MS and HPLC-MS. FAB-MS is approximate for the distribution of rings sizes.[11] The integrations of FAB-MS peak areas indicate ca. 8% dimer, 78% trimer, and 8% tetramer with the remaining 6% being pentamer and hexamer. Because of the very large differences in volatility between COETs and the plurality of crystal structures formed, FAB-MS alone is difficult to calibrate accurately to actual sample composition. We believe HPLC analysis is a more accurate, quantitative tool.

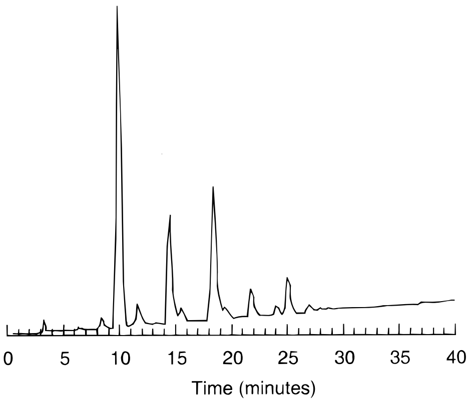


**Figure 2.** High-pressure liquid chromatogram (HPLC) for a high melting COET mixture, prepared in saturated hydrocarbons. This chromatogram reveals the narrow ring size distribution for the composition prepared in saturated hydrocarbon medium.

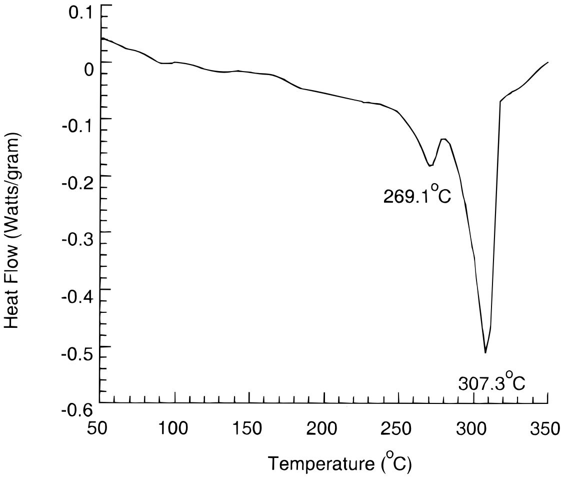


**Figure 3.** Differential scanning calorimetry (DSC) trace for a high melting COET mixture, prepared in saturated hydrocarbons.

Figure 2 illustrates a liquid chromatograph for this composition. Mass spectrometry of isolated fractions confirmed that each peak corresponds to a discrete ring size. Interestingly, the small peaks at approximately 15.5 and 19.5 min retention correspond to oligomers containing a diethylene glycol unit in addition to ethylene glycol units. Integration of the chromatograph indicates our COETs are composed of ca. 0.9% dimer, 39.6% trimer, 14.9% tetramer, 22.1% pentamer, and 4.4% hexamer with the remaining comprising higher COETs and cyclics containing diethylene glycol linkages. Since these compositions are so dominated by the COET trimer, we would expect these product mixtures to melt at high temperatures, over 300 °C.

This synthesis method does normally produce high melting COET mixtures, although the melting points are greatly influenced by both the crystallization process and the molecular weight distribution. In fact, we have extensively characterized how the crystallization processing affects melt behavior. We can offer the following overview as we compare processing method with DSC and SEM observations. Figure 3 illustrates the DSC trace for COETs obtained by slowly cooling the hexadecane suspending solvent. This sample's SEM reveals large hexagonal prism morphologies in addition to small amounts of other crystalline morphologies; see Figure 4. The COET trimer crystals are mainly hexagonal prisms, and these correspond to the highest DSC melting endotherm at 307 °C. Slow cooling can also create multiple prisms at a single-crystal nucleation site, such as the starlike crystal habits illustrated in Figure 5. These stars correlate with a melting DSC peak near 304 °C. The "surfboard-like" habits illustrated in Figure 8 are identified with DSC melting peaks between 186 and 189 °C, as seen in hot-stage experiments. Small amounts of "cauliflower-like" crystal habits are also observed which exhibit a DSC melting peak near 206−210 °C and other peaks between 255 and 276 °C. Titurating the hot hexadecane suspension phase with cold saturated hydrocarbons reduces the quantity of high-temperature melting crystals. Greater amounts of cauliflower-like habits are formed in place of the prisms. SEM images of these habits are reproduced in Figure 8. Additional low-temperature endotherms, as low as 186−190 °C, appearing in the DSC traces arise from the habits formed by quick tituration.

**Solution Synthesis of Cyclic Oligo(ethylene terephthalate).** This section illustrates the syntheses of COETs in a single-phase solution from the conversions of either high polymer or linear oligomer. In this case PET, linear oligomer, cyclic oligomer, and catalyst are each soluble and dissolved in the same solvent. Pure cyclics are unavailable until the cyclization reactions are complete. Furthermore, the linear species must remain dilute, nominally less than 5%, to favor cyclic oligomers over linear oligomers. However, since even the cyclics are dilute, the process conditions create a kinetic cyclic molecular weight distribution which requires several additional hours to converge to the equilibrium distribution. This slow equilibration between cyclics is very advantageous, however, because we find that the isolated, kinetic COET distributions can be melted at temperatures that are greatly reduced from the melting points of the equilibrium cyclic distributions.

We synthesize COETs in 1 h by heating BHET in 1-methylnaphthalene solvent while distilling the ethylene glycol/solvent azeotrope. The solvent contained 20 ppm tetraisopropyl titanate catalyst. Similar results are found using diphenyl ether as the solvent. Once the solution is cooled to room temperature, we find the COETs with only trace quantities of linear polymer. This methodology is inherently batchwise. However, a continuous methodology can be implemented and COET purity can be further improved by adding cold saturated hydrocarbons to the hot solution. This precipitates the cyclic oligomers nearly free of linear polymer in high overall yield. At 2.5% solids or lower, the total isolated yield is greater than 90%. Even at 5% solids, the isolated yield is 65%. At higher concentrations, the linear polyester dominates. Depolymerizing high molecular weight PET under the same conditions yields similar results. For example, PET in either 1-methylnaphthalene or phenyl ether provides greater than 90% yield of cyclic oligomers at 2% solids and gives up to 65% yields even at 5% solids.

COETs produced from solution cyclization and quickly isolated are typically found to have a broad, kinetic molecular weight distribution. These products were characterized by the same methods described in the previous section; here we will only summarize our findings relevant to the molecular weight distribution, crystallization, and melting point. FAB-MS indicates considerably broader cyclic distributions, with much lower trimer composition. Integration of the FAB-MS

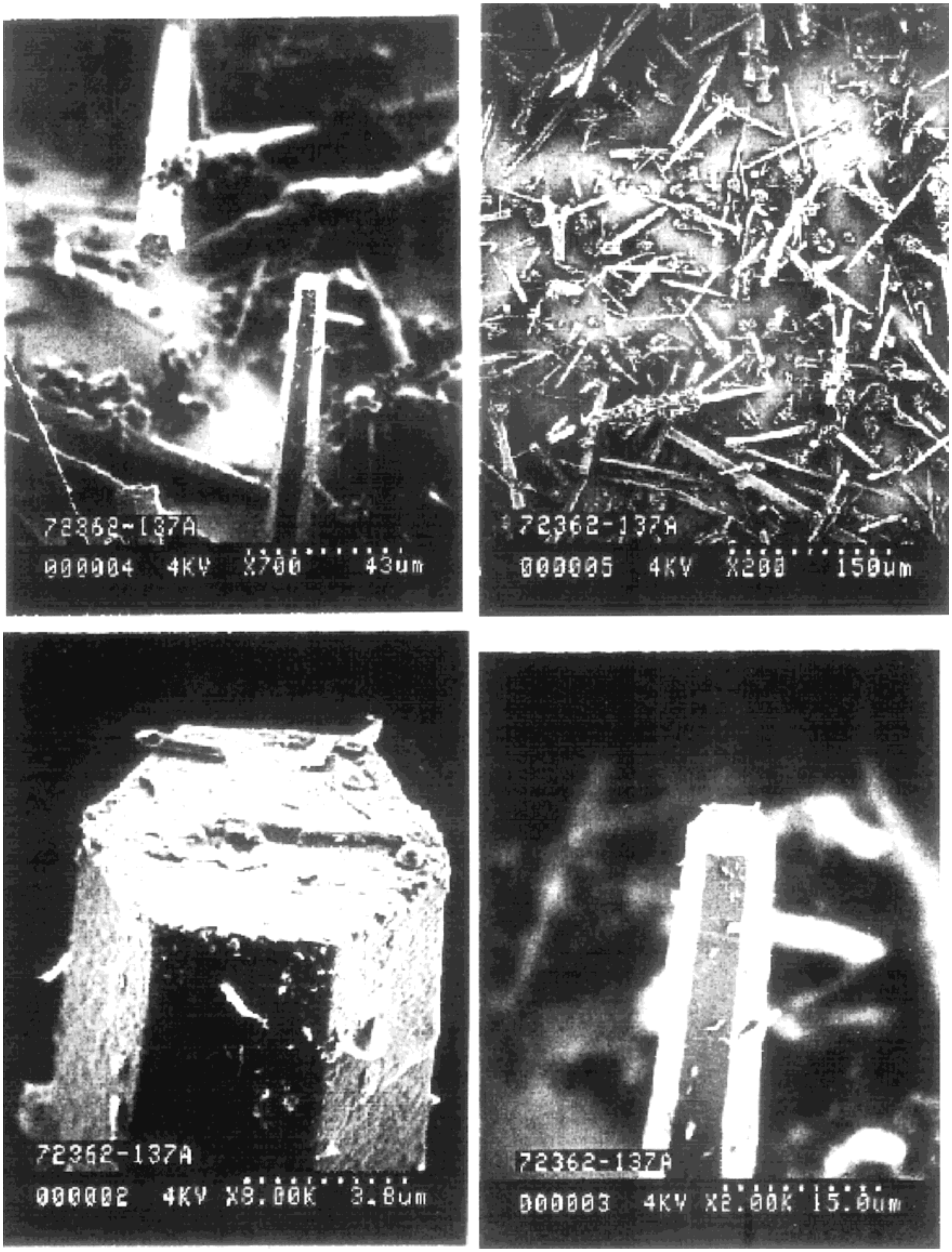


**Figure 4.** Scanning electron microscopy (SEM) revealing the particle morphologies of the high melting COET mixture, prepared by slow cooling of a hexadecane solution.

peak areas indicate ca. 13.2% dimer, 54.3% trimer, 11.0% tetramer, 10.6% pentamer, 5.9% hexamer, 3.3% heptamer, 1.3% octamer, and 0.3% nonamer. Figure 6 illustrates a liquid chromatograph for this composition. Integration of the chromatograph indicates our COETs are composed of ca. 25.0% trimer, 12.7% tetramer, 15.3% pentamer, 14.0% hexamer, 12.0% heptamer, 8.6% octamer, 6.6% nonamer, and 1.8% decamer with the remaining mass comprising cyclics with diethylene glycol linkages. Mass spectrometry of isolated fractions confirmed that each peak corresponds to a discrete ring size. The small peaks at approximately 15.5 and 19.5 min retention correspond to oligomers containing a diethylene glycol unit in addition to ethylene glycol units.

More importantly, these broad compositions *melt at temperatures less than 290 °C*. DSC traces for representative samples prepared in this way are given in Figure 7. Scanning electron microscopy reveals an array of crystalline morphologies, all of relatively small particle size; see Figure 8. For comparison, pure COET trimer melts at 321 °C. Temperatures greater than 300 °C are generally impractical for PET polymerization and processing because thermal degradation reactions be-

**Figure 5.** Scanning electron microscopy revealing the particle morphology of COET mixture prepared in hexadecane and crystallized by slow cooling to room temperature. These morphologies melt at ca. 304 °C.

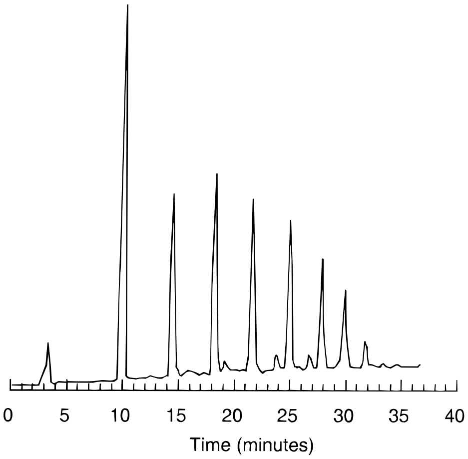


**Figure 6.** HPLC trace for a low melting COET mixture, prepared in diphenyl ether solution. This chromatogram illustrates the broad ring size distribution of polyester cyclic oligomers prepared in phenyl ether solution.

come active. These results suggest that it might be industrially feasible to use these relatively low-temperature melting cyclics for ROP while manufacturing resins, composites, and shaped parts.

We find that the broad distributions of cyclic oligomers are initial kinetic products, while the narrow distributions are the ultimate thermodynamic composition of the oligomers. These findings are consistent with previous literature.[12,13] We followed the product distribution vs time in an experiment in which we converted BHET to cyclic oligomer in 1-methylnaphthalene solution. We found that the initial products were broad distributions of cyclic oligomer ring sizes and over time became narrow in distribution. Previous researchers have described routes to broad, kinetic distributions of polycarbonate cyclic oligomers and also of poly(butylene terephthalate) cyclic oligomers.[12]

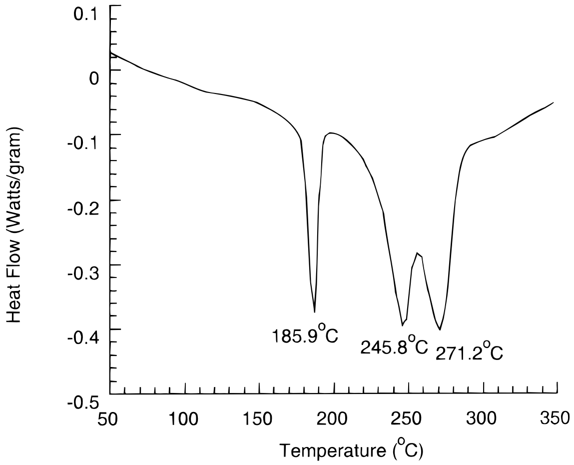


**Figure 7.** DSC trace for a low melting COET mixture, prepared in diphenyl ether solution, illustrating the broad, low-temperature thermal events.

We considered the possibility that the low melting temperature of the broad COET distributions might be the result of the linear polymer being present as an impurity in the mixtures prepared from 1-methylnaphthalene or diphenyl ether. However, experiments in which the high melting cyclic oligomers were purposely coprecipitated or cocrystallized with linear oligomers from solution did not cause melting point depression. Instead, the DSC traces and X-ray scattering patterns are a superposition of each component. This suggests that the linear impurities do not influence the melting point significantly and that the ring size distributions dictates the melting point. This is consistent with other reports.[12]

**Mixed-Solvent Synthesis of Cyclic Oligo(ethylene terephthalate).** A possible process enhancement results from using a mixture of saturated and aromatic hydrocarbons, such as hexadecane/diphenyl ether. In this solvent system, the linear oligomer used as a precursor to the cyclic oligomer is fully soluble and the cyclics form in high conversion. However, the cyclic oligomers then precipitate on cooling the solvent system to room temperature, without additional treatment with a nonsolvent. These mixtures give products which exhibit DSC endotherms as follows: 187 °C (12 J/g) and 301 °C (46 J/g), with a large shoulder on the DSC peak at ca. 277 °C.

**Synthesis of Other Cyclic Oligoester Compositions.** Cyclic oligomer compositions other than COET can also be prepared by these suspension and solution methods. Table 1 provides a partial list of the various ester compositions we have synthesized from diacids and diols. The table also provides an example synthesis fluid and the corresponding product melting point(s) measured by DSC. The concentration at which the cyclic oligomers form is dependent on the choice of diacid and diol. The Supporting Information for this article provides details of these syntheses. Although the majority of these experiments on cyclic oligomer formation have been run on scales yielding less than 10 g of cyclic oligomer, these synthetic methods have been successfully scaled up to yield approximately 450 g of cyclic oligomer per experiment.

The cyclic oligo(ethylene isophthalate), COEI, distribution of ring sizes and their melting points depend on

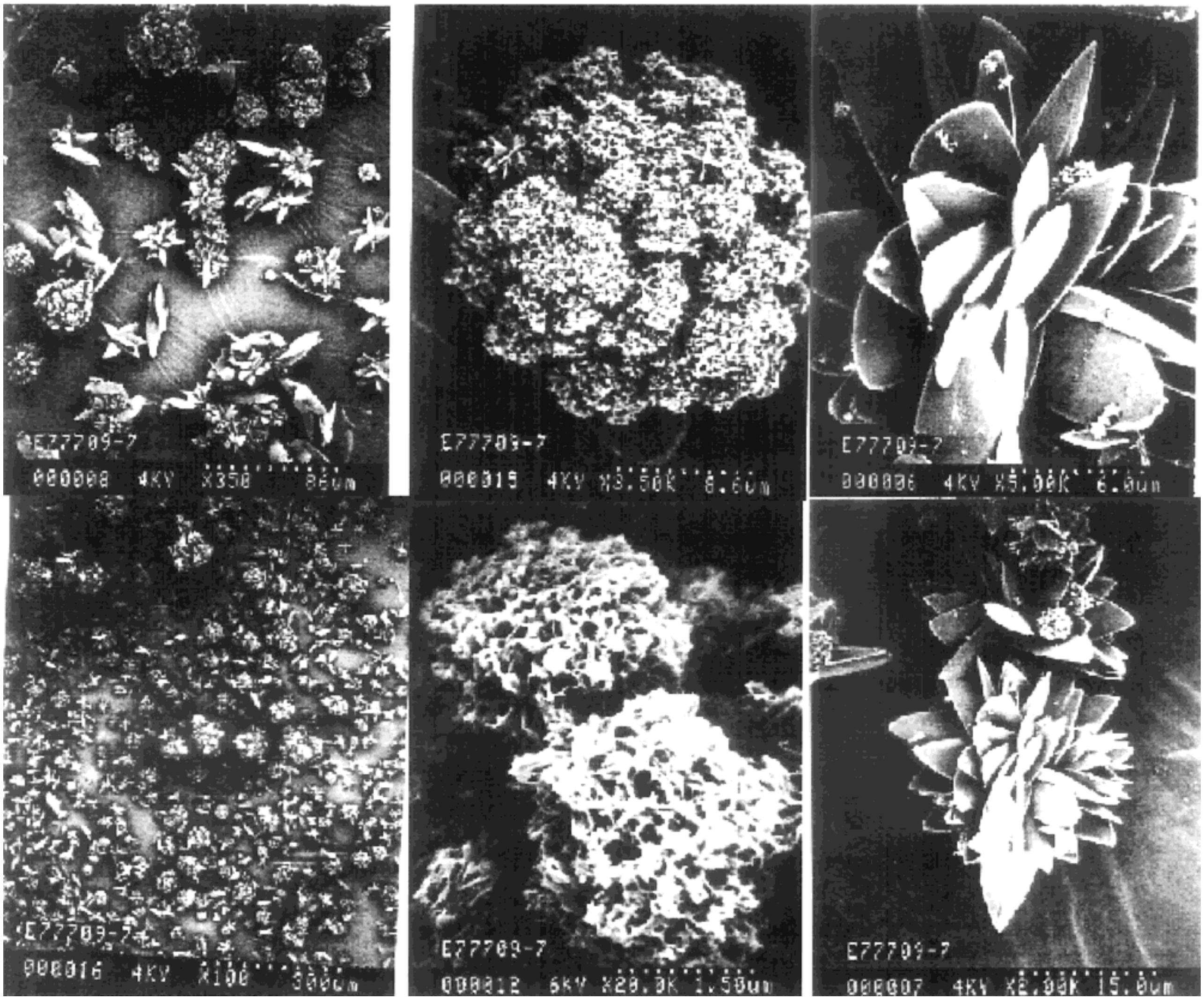


**Figure 8.** SEM revealing the particle morphologies of the low melting COET mixture, prepared by slow cooling of a diphenyl ether solution.

**Table 1. Scope of the Cyclic Oligomer Compositions Synthesized from Diacids and Diols**

| diacid | diol | synthesis fluid | melting point, °C |
|---|---|---|---|
| terephthalic | 1,4-butanediol | diphenyl ether | 125, 188, 236 |
| terephthalic | 1,3-propanediol | hexadecane | 243 |
| terephthalic | 1,3-propanediol | diphenyl ether | N.A.[a] |
| isophthalic | ethylene glycol | hexadecane | 331 |
| isophthalic | ethylene glycol | diphenyl ether | 321 |
| terephthalic | neopentyl glycol | hexadecane | 278 |
| terephthalic | neopentyl glycol | diphenyl ether | 278 |
| isophthalic | neopentyl glycol | diphenyl ether | N.A.[c] |
| 1,4-cyclohexanedicarboxylic acid | ethylene glycol | tetradecane | 80 |
| chloroterephthalic[b] | ethylene glycol | tetradecane | 200 |

[a] NA = measurement is not available. [b] Data from A. G. Anderson, personal communication. [c] Impure with linear oligomers.

synthesis solvent and preparation method. In hexadecane, the conversion to cyclics is 21% at 12% solids and 53% at 3.8% solids. The sole detectable species isolated from this system is the COEI dimer, which has a sharp melting point at 331 °C. In phenyl ether the yield is quantitatively complete at 3.8% solids. These cyclic oligomers have a broader distribution of ring sizes. FAB-MS indicates 66% dimer, 22% trimer, 10% tetramer, and 3% pentamer. Concomitantly, the melting temperature spans a broader melting range, and the final melting point of ca. 321 °C is also reduced.

Chemical structure greatly influences the conversion of linear to cyclic species at a given loading concentration. The synthesis of the COEIs occurs at higher concentrations than does the synthesis of COETs. This indicates that the isophthaloyl residues in the polyester backbone cause a strong tendency to form cyclic oligomers. The meta-aromatic linkage permits much more favorable free energy of backbiting reactions than does the para-aromatic linkage. The reaction of neopentyl glycol with isophthalic acid gives a high yield of the corresponding cyclic oligomer in phenyl ether at 8.4% solids, a very high concentration. This observation also reflects the favorable free energetics for interconversion of cyclic oligomer and linear polymer for neopentyl glycol and isophthalic acid.

**Cyclic Co-oligomers.** A particularly interesting variation on our previous work is the synthesis of a cyclic oligomer containing more than one type of diol. In principle, cocyclic compositions can be synthesized by either cocyclization of a mixture of linear precursors or transcyclization of a mixture of cyclic precursors. In one particular illustration of the former method, we coesterified both ethylene glycol and 1,4-butanediol in the same ring with terephthalic acid. These cyclics melt at a temperature that is suppressed compared to that of the pure COET and the pure cyclic oligo(butylene terephthalate), COBT. To illustrate the latter method, we also attempted to find conditions in which ester–ester interchange between cyclic oligomers of two different compositions was a significant reaction. First we ultrapurified COET and COBT so that end groups were below detectable limits. We combined COET and COBT in a melt and mixed for various periods up to 5 min. Analysis did not show evidence for the formation of the cyclic oligomer containing both the ethylene glycol and the 1,4-butanediol residue, in either the presence or the absence of catalyst, by mass spectroscopy. This experiment indicates that direct ester–ester interchange is not a significant reaction in the absence of species containing hydroxyl end groups.

**Cyclization Catalysis.** The catalysts we have explored for cyclic oligomer formation include titanium alkoxides, antimony glycoxide, aluminum butoxide, and zirconium ethoxide. These coordinated metal compounds are significantly rate enhancing relative to the catalyst-free composition. In principle, any conventional polytransesterification catalyst should suffice; however, we have not thoroughly investigated the effect of catalyst choice on product attributes. Conversion is enhanced by catalysis, especially in aromatic solvents. Additional synthetic details are given in the Experimental Section and in the Supporting Information.

**Ring-Opening Polymerization of COET.** The intent of this study is to provide a road map for the important variables affecting ROP conversion, rather than to provide a detailed kinetic and mechanistic investigation. Here we illustrate that low molecular weight, linear species in the ROP mixture affect the ROP kinetics qualitatively and can serve to limit the final molecular weight. We also illustrate a new process concept where high molecular weight, linear species in the ROP mixture can be used to dissolve the cyclic oligomers at temperatures well below the melting temperature for the pure cyclic oligomers.

First we illustrate that low molecular weight linear species in the ROP mixture affect the kinetics qualitatively by creating two distinct kinetic regimes. We created a mixture of cyclic and linear oligo(ethylene terephthalate) which contains 15 wt % linear species. A series of samples of this mixture were brought to 280 °C in 1 atm of dry nitrogen sweep. Samples were permitted to react in the melt state over times spanning 1–120 min. Then each sample is quenched and submitted for molecular weight and viscosity analyses. These data are illustrated in Figure 9. The initial, fast polymerization stage is first-order with time. This stage is dominantly ROP with fast disappearance of cyclics conserving the number of reactive linear ends. The first-order rate constant from these data is 0.7 min$^{-1}$, correlating to a half-life for the first-order portion of this reaction of about 60 s. The second and final, slower stage is second-order with time. The second-order rate constant is $2 \times 10^{-3}$ M$^{-1}$ min$^{-1}$. This stage is dominantly condensation polymerization, involving esterification of residual hydroxyl and carboxyl end groups and transesterification between glycol end groups. Only in this stage is there an appreciable reduction in the concentration of reactive linear ends.

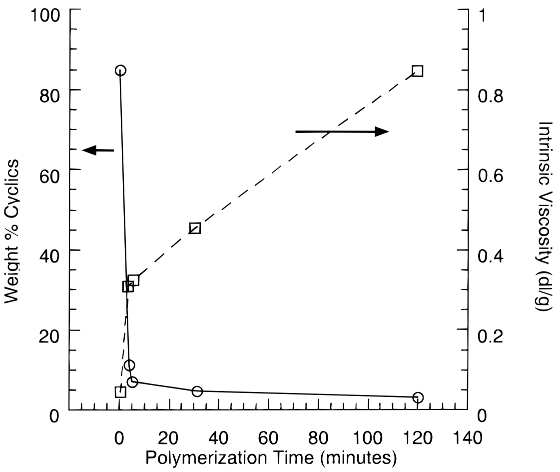


**Figure 9.** Typical two-stage polymerization behavior observed for COET polymerizations, showing rapid polymerization by ring-opening of the cyclic oligomer followed by slower, diffusion-limited, polycondensation.

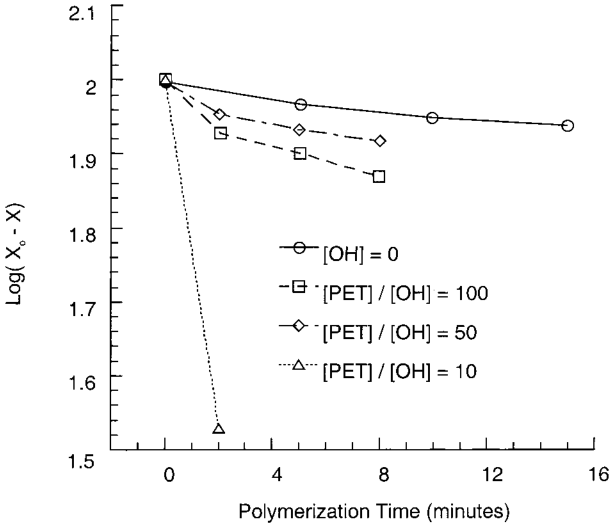


**Figure 10.** Semilogarithmic plot of cyclic concentration change, $X_0 - X$, for a first-order reaction describing initial polymerization of COET trimer at various [cyclic oligomer]/[hydroxyl group] ratios.

Hydroxyl end groups function as initiating species and therefore dramatically affect polymerization rates. Rigorously purified and dried COET trimer, separated from the other components of the mixture by means of chromatography, polymerizes extremely slowly, even at temperatures up to 300 °C. This reaction likely requires trace hydroxyl impurities such as moisture. However, when controlled amounts of 1-butanol as an hydroxyl-containing initiating species are added to the COET trimer, rapid polymerization is restored, illustrating the necessity for the hydroxyl-containing compound as an initiating species. Figure 10 illustrates the large rate enhancement due to the linear species.

To illustrate further the effect of end groups, we polymerized a COET composition which contained 180 mequiv/kg of acid end groups and approximately 480

**Table 2. Polymerization of COET in an Equal Weight of PET Linear Polymer at 280 °C, 1 atm Pressure**

| run | polym time (min) | IV (dL/g) | $M_n$[a] | $M_w$[a] | residual cyclic[b] (%) | comment |
|---|---|---|---|---|---|---|
| | | 0.68 | 13200 | 32 200 | 1.7 | control: linear polymer used in the cyclic polymerization |
| A | 10 | 0.54 | 6570 | 24 200 | 8.3 | did not predry polymer or cyclic |
| B | 30 | 0.58 | 9760 | 26 000 | 3.3 | did not predry polymer or cyclic |
| C | 10 | 0.57 | 4920 | 26 600 | 5.3 | predried polymer and cyclic |
| D | 30 | 0.89 | 9890 | 38 900 | 1.8 | predried polymer and cyclic |
| E | 10 | 0.67 | 6240 | 27 400 | 3.3 | replicate of run C |
| F | 30 | 0.71 | 8260 | 31 600 | 2.5 | replicate of run D |

[a] SEC data are uncorrected for the contribution from cyclic oligomer, giving artificially high polydispersities. [b] These numbers are uncorrected for SEC response factors.

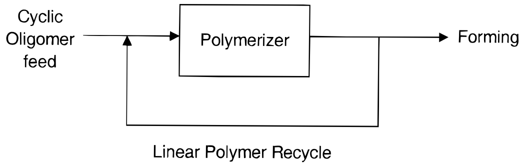


**Figure 11.** Process for polymerizing cyclic oligomers in the presence of linear polymer. This process could be carried out at conventional PET processing temperatures, bypassing issues of the high melting points of the COET mixtures.

mequiv/kg of hydroxyl end groups. The theoretical Flory molecular weight distribution for a condensation polymer with this end group concentration would have a number-average molecular weight, $M_n$, ca. 3000 and a weight-average molecular weight, $M_w$, ca. 6000. We polymerized two samples at 280 °C, at 1 atm pressure, using 100 ppm Ti as titanium(IV) isopropoxide. One sample polymerized for 10 min, and a second sample polymerized for 30 min. Size exclusion chromatography on the 10 min sample indicated $M_n = 2810$ and $M_w = 8630$, with ca. 3.1% unconverted cyclic. After 30 min the resulting polymer had the following characteristics: $M_n = 4280$ and $M_w = 12\,400$, with ca. 2.1 wt % unconverted cyclic. The difference in molecular weight between the 10 min run and the 30 min run, despite only a small difference in the amount of cyclic oligomer, is due to a secondary polymerization step in which transesterification results in glycol being evolved from the melt. This is the conventional polycondensation reaction: two linear chain ends react together, extend the molecular weight, and release a condensation byproduct.

A major practical limitation of melt-phase ROP schemes could be the excessively high melting temperatures of the cyclic oligomers. This is especially true for the narrow cyclic molecular distributions which tend to have melting temperatures much higher than the thermal stability of most polymers. Clearly a more practical approach would be to dissolve the cyclic oligomers in a preexisting melt, rather than having to melt the pure cyclic feeds themselves. For example, one process option would be ROP in the presence of high molecular weight, linear polymer product. In this scenario, cyclic oligomer is fed into a polymerizer together with a recycled stream of product linear polymer; see Figure 11. In this process, even high melting cyclic oligomeric mixtures could be rapidly dissolved and polymerized at temperatures appropriate for polyester manufacturing. We tested this idea by polymerizing COET in the presence of an equal amount of linear high molecular weight PET. These were reacted in the presence of 100 ppm Ti catalyst in a test tube at 280 °C at 1 atm pressure under nitrogen. This experiment yielded promising results as indicated in Table 2. These results support the proposition that cyclics can be polymerized in polyester melts. Effects of residual moisture, polymerization times, and end group concentration are as of yet unexplored. Runs A and B suggest that the COET can be polymerized without predrying and still obtain good molecular weight.

**Ring-Opening Copolymerizations.** Despite their high melting points, the COEI copolymerize at high rates and moderate temperatures (275−280 °C) with either high molecular weight PET polymers or with COET. For example, COEIs react with high molecular weight PET melt to give poly(ethylene terephthalate-*co*-ethylene isophthalate), P(ET-*co*-EI), copolymers. This suggests that copolymers of ethylene glycol with both terephthalic acid and isophthalic acid could be prepared commercially by adding COEI in a postpolymerization step to PET homopolymer. Conventional P(ET-*co*-EI) copolymers are manufactured from feeding terephthalic acid, isophthalic acid, and ethylene glycol at the beginning of the polymerization. Alternatively, the copolymers can be produced by adding COEI to PET homopolymer. In each case the copolymers have similar melting points and crystallization behavior dependent on the copolymer composition. At low isophthalate content the melting point is only about 10 °C lower than PET homopolymer melting point, and the degree of crystallization is not significantly affected. This may suggest long segments of PET repeat units persist in these compositions. At higher isophthalate content the melting point is reduced by about 40 °C from the PET homopolymer, and the degree of crystallinity is significantly reduced, suggestive of a randomized structure. Similar compositions result from copolymerization of COET and COEI, through sequential addition of the cyclic oligomers. In the first step, the lower melting COETs ($T_m = 290$ °C) are homopolymerized at 280 °C, using titanate catalyst (100 ppm Ti), generating high molecular weight PET with $T_m \sim 255$ °C. In the second step, the high melting COEI ($T_m = 331$ °C) are added and dissolved in the PET melt, and polymerization is practically complete within ∼15 min at 280 °C. A low heat of fusion in the DSC suggests a relatively random structure and high molecular weight. Size exclusion chromatography confirms the molecular weight enhancement following the PEI addition in the second step.

## Discussion

We have described several advances in the science and technology of aromatic cyclic oligoesters. We have shown that cyclic oligoesters are easily prepared in high yield from simple, inexpensive raw materials, such as BHET, derived from either dimethyl terephthalate or terephthalic acid with ethylene glycol in the presence of a fluid reaction medium and a catalyst. We have shown that manipulating ring size distributions alters the melting point of cyclic mixtures. Narrow ring size distributions of COETs are easily prepared in suspensions using saturated hydrocarbons as the reaction medium. These narrow ring size distributions have melting points higher than normal PET processing temperatures and are the thermodynamic ring size distributions. Broad, low melting ring size distributions result from synthesis in solution and rapid isolation. Both synthesis approaches appear readily adaptable to continuous operation for industrial scale manufacturing.

PET could be recycled by means of cyclic oligomers. One advantage of cyclic oligomers is that these processes for making them are inherently purifying. Therefore, it should be possible to start with lower purity grade terephthalic acid or ethylene glycol. The cyclics can also be prepared directly from previously manufactured PET articles and even postconsumer recycle. We expect that these results will extend to many other polyesters and other condensation polymers.

Some ulterior ideas remain as challenges. Attempts to prepare cyclic oligoesters in dichloromethane or toluene solutions by depolymerization of high molecular weight polymer at high temperature (250−280 °C) under pressure in an autoclave have not been successful to date. Other experiments on cyclic formation in hot liquids under pressure or in supercritical media are in progress. An attempt to design a polymeric “template” for cyclic oligomer formation was unsuccessful, presumably due to insufficient intermolecular interactions between the acrylic residues of the host polymer and the polyester monomers.[14] Attempted host polymers were methacrylic acid that is highly cross-linked with ethylene glycol dimethacrylate and also polystyrene that is highly cross-linked with divinylbenzene. An attempt to make 6,6-nylon cyclic oligomers by these methods from the salt of hexamethylenediamine and adipic acid was unsuccessful.[15]

We have defined conditions that rapidly polymerize cyclic oligoesters to high molecular weight in a matter of minutes, very rapidly compared to incumbent manufacturing processes. The high polymerization rate results from the fact that ROP does not require elimination of a condensation byproduct. The conditions we described for polymerization of the cyclic oligomers leave nearly the equilibrium concentration of residual cyclic oligomer in the final polymer. Both the high melting composition or the low melting composition polymerizes rapidly at sufficient temperature in the presence of a catalyst, providing a hydroxyl-containing end group is present. The hydroxyl-containing end group functions as an initiator, and its concentration determines the qualitative kinetics and final molecular weight of the polymer. Typically, polymerization to molecular weights characteristic of PET fiber and film is complete in 3 min for the broad, low melting compositions. Either of these ring size distributions polymerizes rapidly in PET melts, enabling polymerization at temperatures typical of PET processing, thereby eliminating the concern over the high melting points.

We have scouted conditions for polymerizing the COETs, delineating the key variables determining polymerization rates and the molecular weights of the resulting polymers as described below.[16]

*1. Hydroxyl End Groups.* Hydroxyl-containing species are commonly present in the cyclics as end groups of linear oligomeric contaminants, at levels which depend on the method of synthesis and separation. Such impurities affect both polymerization rate and the molecular weight of the resulting polymer. Increasing hydroxyl concentration leads to faster polymerization rates and lower molecular weights.

*2. Catalyst Level.* Most of our investigations have been with titanium(IV) isopropoxide catalyst, with no significant difference in polymerization rate being observed over Ti catalyst concentrations ranging from 20 to 200 ppm on a metals basis. Antimony glycoxide is also effective at 250 ppm.

*3. Melting Temperature.* The melting temperature of the cyclic oligomer mixture of a given chemical composition is dependent on the ring size distribution. Typically cyclic oligoesters have higher melting points than the corresponding linear polymer, a significant limitation for some applications. We describe several approaches to melting point depression. We find that polymerization of cyclic oligomers in the presence of molten high molecular weight polymer completely circumvents the problem of high melting.

*4. Polymerization Temperature.* For a given cyclic oligomer mixture, increasing polymerization temperature brings about faster polymerization. However, the practical polymerization temperature range can be quite narrow, with the low end of the temperature range being dictated by the melting point of the cyclic oligomer mixture and the high end of the temperature range being determined by the decomposition temperature of the polymer.

*5. Chemical Composition.* The chemical compositions included in this study of polymerization are poly(ethylene terephthalate), poly(ethylene isophthalate), poly(butylene terephthalate), and poly(ethylene chloroterephthalate). Because the chemical composition determines the melting point of the cyclic oligomer and resulting polymer, the chemical composition therefore also constrains the conditions for ROP.

We anticipate that a promising opportunity for cyclic oligoesters is for on-line modification of polymers in which comonomers are added in an extruder to conventional, linear, high molecular weight polyester homopolymers. Reaction of the cyclic oligomer with polymer melts, in the extruder, yields high value polyester copolymers.

## Experimental Details

**Molecular Weight Analysis.** The inherent viscosities (IV) were determined in 0.5 wt % hexafluoro-2-propanol (HFIP) solution at 30 °C. Molecular weight was determined by size exclusion chromatography (SEC) on samples dissolved in HFIP, using PET standards. SEC measurements were carried out on a Waters 150C instrument equipped with mixed bed Shodex columns (styrene cross-linked with divinylbenzene) with porosity ranges of $2 \times 10^7$, $4 \times 10^6$, $4 \times 10^5$, and $7 \times 10^4$, using a refractive index detector. Absolute molecular weights were determined using PET standards for the SEC calibration curve.

**High-Performance Liquid Chromatography** (HPLC) analyses were used to determine the composition of various cyclic mixtures. The separations were carried out using a Hewlett-Packard 1050 liquid chromatograph with Adsorbax normal phase silica column, 25 cm length, 4.6 mm diameter. The mobile phase was chloroform/THF/hexane gradient with a flow rate of 1.0 mL/min. “Solvent A” has the composition 10% chloroform, 2.5% THF, 87.5% hexane. “Solvent B” has the composition 90% chloroform, 10% THF. A linear gradient from 30% B to 100% B over 60 min was used. Samples were prepared using methylene chloride as the solvent and a concentration range from 0.5 to 2.0% w/v. Detection was provided by a UV detector set at 254 nm, and the separation was carried out at ambient temperature.

**Table 3. Summary of COET Formation Experiments**

| starting material | solvent | initial solvent vol (mL) | final solvent vol (mL) | time (min) | isolated yield (g) | isolation method | catalyst |
|---|---|---|---|---|---|---|---|
| 40.0 g DHET | hexadecane | 400 | 185 | 35 | n.d. | cooling | $Al(OC_4H_9)_3$ |
| 8.0 g DHET | hexadecane | 600 | n.d.[a] | 240 | 0.92 | cooling | $Ti(OC_3H_7)_4$ |
| 80.0 g DHET | hexadecane | 600 | 455 | 50 | 0.85 | cooling | none |
| 40.0 g DHET | heptadecane | 400 | 345 | 20 | 0.80 | cooling | $Ti(OC_3H_7)_4$ |
| 40.0 g DHET | octadecane | 400 | 345 | 20 | 1.08 | cooling | $Ti(OC_3H_7)_4$ |
| 10.0 g TPA oligomer | hexadecane | 400 | 400 | 180 | 0.58 | cooling | $Ti(OC_3H_7)_4$ |
| 4.0 g PET ($\eta_{inh} = 0.47$) 0.20 2G | hexadecane | 400 | 400 | 240 | 0.82 | cooling | $Ti(OC_3H_7)_4$ |
| 10.0 g DHET | 1-methylnaphthalene | 400 | 190 | 60 | 3.77 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 10.0 g PET ($\eta_{inh} = 0.9$), 0.40 mL 2G | 1-methylnaphthalene | 400 | 400 | 60 | 2.9 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 10.0 g TPA oligomer | 1-methylnaphthalene | 400 | 400 | 180 | 0.63 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 2.0 g DHET | diphenyl ether | 400 | 227 | 60 | 1.40 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 4.0 g DHET | diphenyl ether | 400 | 232 | 60 | 2.1 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 5.0 g DHET | diphenyl ether | 400 | 200 | 40 | 2.81 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 6.5 g DHET | diphenyl ether | 400 | 200 | 42 | 2.7 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 4.0 g PET, 0.20 2G | diphenyl ether | 400 | 400 | 240 | 3.50 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 8.0 g PET, 0.40 2G | diphenyl ether | 400 | 400 | 120 | 4.96 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 12.0 g PET, 0.40 mL 2G | diphenyl ether | 400 | 400 | 240 | 1.3 | pentane precipitation | $Ti(OC_3H_7)_4$ |
| 10.0 g DHET | diphenyl ether/ hexadecane (3:1) | 400 | 305 | 45 | 6.7 | cooling | $Ti(OC_3H_7)_4$ |

[a] "n.d." means not determined.

**Thermal Characterization.** Thermogravimetric analysis (TGA) and differential scanning calorimetry analyses (DSC) were carried out on a DuPont model 9900 thermal analyzer with TG and DSC modules. Standard heating rates of 20 °C/min were used, with samples of 5−20 mg, in a dry nitrogen atmosphere.

**Cyclic Oligomer Synthesis**. This experimental includes representative syntheses of polyester cyclic oligomers and cyclic oligomer polymerization in the presence of linear polymer. Other experiments are summarized in Table 3. Details of the syntheses for COETs and other polyester oligomers are given in the Supporting Information.

**Preparation of COET in Hexadecane Using Aluminum *sec*-Butoxide Catalyst**. A 1 L three-neck flask was charged with 40.0 g of catalyst-free dihydroxy ethyl terephthalate, 400 mL of hexadecane (purified by passing down a column of acidic alumina and sparging with dry nitrogen for 30 min), and 0.05 mL of aluminum *sec*-butoxide. The three-neck flask had a distillation head with nitrogen source, mechanical stirring, and a glass stopper in the necks. The reaction mixture was heated with distillation to remove a solvent volume of 215 mL over the course of 35 min. The boiling point of hexadecane is 287 °C. At the end of that time period, the stirring was turned off, and the hot mother liquor was decanted from the insoluble material, which is linear polymer (29.0 g). The hot mother liquor was allowed to cool, yielding white microcrystals, which were fully soluble in methylene chloride. The FAB-MS showed a distribution of cyclic oligomers as follows: dimer (8%), trimer (78%), tetramer (8%), pentamer (~6%), hexamer (trace). The $^1$H NMR shows an aromatic resonance at 8.04 ppm (singlet, with small singlets at 8.03 and 8.02 ppm, with a total intensity for 1H) and an aliphatic resonance at 4.63 ppm (singlet, 1H) ($CD_2Cl_2$ solution). No other resonances were detectable in the $^1$H NMR. The $^{13}C\{^1H\}$ NMR spectra show a carbonyl carbon resonance at +166 ppm, aromatic resonances at +134.7 and +130.3 ppm, and aliphatic carbon resonances at +63.5 ppm. This composition of cyclic oligomers shows melting endotherms in the DSC, as given in the Discussion section of this report. Elemental analysis: Found: 62.51% C, 4.15% H, 0.24% N (Microanalysis, Inc., Wilmington, DE). Calculated for $(C_{10}H_8O_4)_n$: 62.50% C, 4.17% H, 0.0% N.

**Preparation of COET in Hexadecane Using Titanium Propoxide Catalyst.** A 1 L three-neck flask was charged with 8.0 g of catalyst-free dihydroxy ethyl terephthalate, 600 mL of hexadecane (purified by passing down a column of acidic alumina and sparging with dry nitrogen for 30 min), and 6.0 mL of a solution of $Ti(O\text{-}i\text{-}C_3H_7)_4$ diluted 1:1000 on a weight basis with hexadecane. After a 4 h run time with distillation of hexadecane/ethylene glycol azeotrope, 2.4 g of linear polymer was isolated at the bottom of the reaction flask and 0.92 g of COET was collected by allowing the supernatant to cool to room temperature and isolating by filtration.

**Preparation of COET in 1-Methylnaphthalene**. A 1 L three-neck reaction flask was charged with 10.0 g of catalyst-free bis(2-hydroxyethyl terephthalate), 6.0 mL of a solution of $Ti(O\text{-}i\text{-}C_3H_7)_4$ diluted 1:1000 on a weight basis with hexadecane, and 400 mL of distilled 1-methylnaphthalene (boiling point 240 °C). The flask was equipped with a distillation head with nitrogen source, mechanical stirring, and a glass stopper in the remaining necks. This solution was heated to distill off 210 mL of solvent and ethylene glycol over the course of 60 min. Cooling the solution to room temperature precipitated 3.22 g of a mixture of linear polyester and cyclic oligoester as a white microcrystalline powder. Of this mixture, ca. 57% was linear, by gravimetric analysis of extracts, with $M_n = 4280$, $M_w = 5640$, and inherent viscosity = 0.12 dL/g. Treating the filtrate with 900 mL of pentane precipitated an additional 3.77 g of cyclic oligoester. The total yield of cyclics is therefore ca. 65%. Secondary ion mass spectrometry confirmed that oligomer up to cyclic nonamer was present in this product.

**Synthesis of Poly(butylene terephthalate) Cyclic Oligomer**. A 12.0 g sample of commercially available poly(butylene terephthalate) (Polysciences, Inc.) was heated in 400 mL of distilled diphenyl ether containing 0.40 mL of polymer grade 1,4-butanediol and 6.0 mL of a solution of $Ti(O\text{-}i\text{-}C_3H_7)_4$ diluted 1:1000 on a weight basis with hexadecane for 3.5 h with no distillation. The cyclic component, isolated by pentane precipitation of the supernatant, was 0.31 g and was predominantly cyclic dimer by FAB-MS.

In a related experiment, the PBT cyclic oligoester was prepared directly from dimethyl terephthalate and 1,4-butanediol, giving 9.54 g of material impure with linear and 3.3 g of linear-free cyclic starting with 7.0 g of dimethyl terephthalate and 3.25 g of 1,4-butanediol. An attempt to run this on 300 g scale resulted in product with unacceptable numbers of acid ends (119 and 119 mequiv/kg, two determinations), suggesting that decarboxylation of the intermediates to acid ends and, likely, THF is problematic.

**Formation of a Cyclic Oligomeric Mixture of Terephthalic Acid with Both Butanediol and Ethylene Glycol**. In an experiment in which 12.0 g of commercially available polybutylene terephthalate (Polysciences, Inc.) was heated in 400 mL of distilled diphenyl ether containing 0.40 mL of polymer grade ethylene glycol and 6.0 mL of a solution of Ti-

$(O\text{-}i\text{-}C_3H_7)_4$ diluted 1:1000 on a weight basis with hexadecane for 3.5 h with no distillation yielded 5.5 g of material on cooling. The product was rich in linear polymer and contained 0.90 g of fully methylene chloride soluble cyclic oligomer on precipitation with pentane. The FAB-MS of this product showed strong peaks for ions at 853 and 1073 amu for a cyclic with three PBT repeat units and one PET repeat units (in addition to $H^+$) for the 853 amu peak and four PBT repeat units and one PET repeat units for the 1073 amu peak. No other FAB-MS peaks were interpretable. This mixture shows depressed melting points and should be pursued.

**Preparation of Cyclic Oligo(ethylene isophthalate).** BHEI was converted to COEI by heating 10.0 g of BHEI in 400 mL of purified hexadecane in the presence of 6.0 mL of a solution of $Ti(O\text{-}i\text{-}C_3H_7)_4$ diluted 1:1000 on a weight basis with hexadecane for 30 min, while approximately 140 mL of the hexadecane/ethylene glycol azeotrope distilled over. The yield of COEI was approximately 7.0 g (93% isolated yield), with approximately 70% cyclic dimer and 30% cyclic trimer by FAB-MS and no detectable higher oligomers. This cyclic oligomeric mixture melts in excess of 300 °C. In an analogous preparation in diphenyl ether, the cyclic oligomer was isolated in 84% yield by pentane precipitation with the ratio of cyclic dimer to cyclic trimer being approximately the same as in hexadecane.

In a related experiment using 15.0 g of BHEI and all other variables being the same, the cyclic was isolated in 10.0 g yield, with the following end group analysis: 164.4 and 66.4 mequiv/kg glycol ends (replicate determinations) and no detectable acid ends.

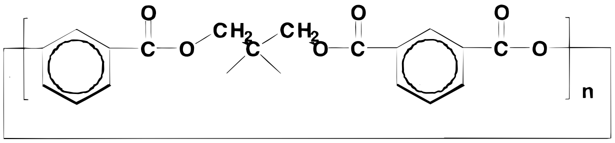
In larger scale experiment, 251 g of COEI was made using 450 g of BHEI in 14 L of distilled diphenyl ether containing 0.5 g of tetrapropyl titanate. The end group analysis showed 2.1 and 2.9 mequiv/kg of acid ends in replicate determinations and 138.2 and 137.7 mequiv/kg of glycol ends in replicate determinations.

**Preparation of the Cyclic Oligomer of Terephthalic Acid with Diethylene Glycol.** A 0.30 g sample of the cyclic oligomer of terephthalic acid with diethylene glycol was prepared by heated 8.0 g of bis(diethylene glycol terephthalate) in 400 mL of purified hexadecane containing 6.0 mL of a solution of $Ti(O\text{-}i\text{-}C_3H_7)_4$ diluted 1:1000 on a weight basis with hexadecane. $^1H$ NMR spectra indicate the sample was impure with linear polymer.

**Preparation of the Cyclic Dimer of Terephthalic Acid with Neopentyl Glycol.** This, and related experiments, started directly with dimethyl terephthalate and the glycol going directly to the cyclic without isolation of intermediates. A 7.0 g (36.1 mmol) sample of polymer grade dimethyl terephthalate, 3.75 g (36.1 mmol) of neopentyl glycol, and 12.0 mL of the 1:1000 weight basis dilution of tetrapropyl titanate were heated in 400 mL of distilled diphenyl ether. After distillation of ca. 80 mL of solvent in 60 min, the solution was allowed to cool to room temperature. No solids precipitated until the solution was treated with 3× pentane, giving 2.9 g of the cyclic dimer of terephthalic acid with neopentyl glycol. The melting point is 270 °C, and the FAB-MS shows only one ion, that at 469 amu for the cyclic dimer + $H^+$.

**Preparation of the Cyclic Oligomers of Isophthalic Acid with Neopentyl Glycol.** A 21.0 g sample of dimethyl isophthalate reacted in 400 mL of distilled diphenyl ether with 11.3 g of neopentyl glycol and titanate catalysis after distillation of ~150 mL of phenyl ether and phenyl ether/ethylene glycol azeotrope yielded 6.0 g of solids upon treatment of the mother liquor with pentane. These solids were the cyclic oligomer impure with linear polymer, methyl ester ended oligomers, and the "anhydride cyclic" with the structure shown below.

A variation of this experiment was run by direct reaction of isophthaloyl chloride (4.00 g) with neopentyl glycol (1.87) in NMP solution (60 mL), followed by hydrolysis with water. The FAB-MS revealed three series of compounds in this mixture: cyclic oligomer down to cyclic unimer, linear polymer with acid ends, and the "anhydride cyclic" with the following structure:



**Cyclic Oligomer of 1,4-Cyclohexanedicarboxylic Acid and Ethylene Glycol.** A 5.00 g sample of this diester was heated with 6 mL of the 1:1000 volumetric dilution of tetrapropyl titanate in 400 mL of tetradecane for 35 min with distillation of 115 mL of the tetradecane. At the end of the run, the heat source was removed and the agitation was stopped, revealing a brown polymeric layer adhered to the inside of the flask. After the vessel cooled 3 min, the tetradecane was transferred to a Schlenk flask by means of a cannula. White precipitate formed as it cooled to room temperature. FAB-MS suggested the following distribution of cyclics: 27.8% dimer, 62.3% trimer, 7.4% tetramer, 2.0% pentamer, and 0.5% hexamer. This cyclic oligomeric mixture has a broad melting endotherm in the DSC centered at 80 °C. The TGA showed onset of weight loss at 205 °C with complete weight loss by 454 °C.

**Cyclic Oligomer Polymerization in the Presence of Linear Polymer.** In these experiments the cyclic was polymerized in the presence of linear polymer. The linear polymer was prepared in an autoclave using 42 ppm Zn and 292 ppm Sb with no other additives. The polymer had 0.68 dL/g inherent viscosity with the following SEC numbers: $M_n$ = 13 200, $M_w$ = 32 200, $M_z$ = 50 200. The polymerizations with cyclic oligomer were run at 50:50 cyclic oligomer/linear polymer with 100 ppm Ti added as 30 $\mu$L of a concentrate of $Ti(OC_3H_7)_4$ in hexadecane. The cyclic oligomer had the following end group analysis: 161 and 184 mequiv/kg of glycol ends (duplicate determinations) and 1 mequiv/kg of acid ends. In some of these experiments, the glassware, polymer, and cyclic were predried at 100 °C in a vacuum oven overnight.

**Isolation Methods.** "Cooling" means simply allowing the solution to cool to room temperature and isolating the product on a fritted glass funnel. "Pentane precipitation" means adding pentane to the solution after allowing it to cool to room temperature. The amount of pentane is sufficient (usually 3 times the solution volume) such that further pentane addition causes no additional precipitation. Typically, the experiments in 1-methylnaphthalene and diphenyl ether yielded a crop of cyclic that was impure with linear material when cooling to room temperature. This fraction was separated by filtration, and the filtrate is then treated with pentane to yield cyclic free of linear byproduct.

**Polymerization Reactions.** In a typical polymerization, 0.50 g of cyclic oligomer was charged into a test tube reaction vessel equipped with an overhead stirrer and a sidearm for nitrogen inlet, the charging operation being carried out in an inert atmosphere drybox. The reaction vessel was transferred into the fume hood, placed under nitrogen, and heated at the desired reaction temperature using a Wood's metal bath. After the reactants melted, the desired amount of catalyst was added by syringe, using a catalyst solution in $Ph_2O$, and the polymerization was carried out under nitrogen. For most polymerizations described in this study, $Ti(O\text{-}i\text{-}C_3H_7)_4$ was used as the catalyst, at 100 ppm Ti level. Samples were removed from the reaction vessel as a function of time for analysis by gel permeation chromatography and differential scanning calorimetry.

Conversion in the polymerization reactions are calculated from the area under the corresponding SEC peaks, by applying a response factor. The response factor ($R_f$) provides the correction for the difference in the detector response for COETs and high molecular weight PET linear chains. To determine $R_f$, a constant volume of 0.01 M solution of the COET trimer and high molecular weight PET in HFIP were injected into the SEC columns, and the areas under the corresponding elution peaks were measured. The response factor was obtained as the ratio of the two areas and was used in all conversion calculations, using $R_f = A_{PET}/A_{COET} = 1.394$.

**Acknowledgment.** We thank J. E. Marshall and W. M. Gray for experimental contributions to this work, E. Ling and Dr. R. E. Fuller for SEC analyses, D. B. Healey and Dr. H. G. Barth for HPLC analyses, Dr. J. Lazar and Dr. J. Bletsos for mass spectral analyses, and P. Turner for solution viscosity determinations. We acknowledge helpful discussions with Dr. A. G. Anderson, Dr. W. Memeger, Dr. J. A. Rakestraw, and Dr. F. G. Gallagher.

**Supporting Information Available:** Variations on preparation of COET's. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA000278B