

**University of Massachusetts Amherst**

---

**From the Selected Works of William MacKnight**

---

2000

## Polymerization of Ethylene Terephthalate Cyclic Oligomers with Antimony Trioxide

William MacKnight, *University of Massachusetts Amherst*

Ji Ho Youk

Roger P. Kambour



Available at: [https://works.bepress.com/william\\_macknight/222/](https://works.bepress.com/william_macknight/222/)

# Polymerization of Ethylene Terephthalate Cyclic Oligomers with Antimony Trioxide<sup>†</sup>

Ji Ho Youk, Roger P. Kambour, and William J. MacKnight\*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received November 1, 1999; Revised Manuscript Received March 4, 2000

**ABSTRACT:** Conditions for polymerizing ethylene terephthalate cyclic oligomers (ETCs) with the catalyst antimony trioxide were investigated with the ultimate goal in mind of using ETCs to produce high-performance poly(ethylene terephthalate) (PET) composites. The ETCs used were prepared both by a direct synthesis method and by cyclodepolymerization (CDP) in dilute solution. ETCs prepared exhibited a distribution of oligomeric species displaying a broad melting range, the uppermost end of which lies at 290 °C. In the case of ETCs prepared by CDP, purified ETCs (p-ETCs) were prepared by eliminating remaining impurities including linear oligomers and cyclic oligomers containing the diethylene glycol (DEG) unit using dichloromethane and tetrahydrofuran. A homogeneous mixture of ETCs prepared by the direct synthesis method or p-ETCs with antimony trioxide was successfully polymerized to high molecular weight (MW) PET ( $M_n \geq 25\,000$ ) at 293 °C within 15 min. The lower the contents of remaining impurities, the higher the MW of the resultant PET. The PET of highest MW ( $M_n = 32\,000$ ) was obtained from polymerization of p-ETCs with bismuth trioxide at 293 °C for 15 min. PET polymerized from p-ETCs showed the same thermal behavior as did the commercial one. In this research, a useful method of PET recycle by using ETCs was successfully established.

## Introduction

It is well-known that poly(ethylene terephthalate) (PET) has valuable characteristics including strength, toughness, solvent resistance, and heat resistance. However, during the past few decades the growth in the commercial use of PET has brought with it an increasing opportunity for its reuse. In previous research,<sup>1</sup> we have established a method for PET recycle by converting it into ethylene terephthalate cyclic oligomers (ETCs) for low-viscosity precursors with a yield of 50 wt % for 1.5 h. The ring-opening polymerizations of reactive cyclic oligomers such as these have been the subjects of interest for a large area of polymer science and technology over several decades because the low melt viscosities of reactive cyclic oligomers provide an opportunity for reactive processing such as reaction injection molding (RIM) and composite reaction injection molding (CRIM).<sup>1–12</sup> The melt viscosity of ETCs at 295 °C where all ETCs can be melted was as low as about 30 cP initially, which is low enough for these melts to be applied to processes such as RIM and CRIM.<sup>1</sup> However, unfortunately, when ETCs were polymerized at 230 °C using a cyclic organostannoxane as a polymerization initiator (one which is known to be an effective initiator capable of producing a coordinated ring expansion polymerization<sup>12–15</sup>), the resultant PET had enough crystallinity for a good composite matrix, but the molecular weight (MW) was not sufficient for the products to form matrices sufficiently strong and tough to be useful in composites.<sup>1</sup>

Goodman and Nesbitt<sup>16–18</sup> separated individual cyclics from ETCs extracted from PET chip and polymerized them with antimony trioxide ( $\text{Sb}_2\text{O}_3$ ). However, the preparation and polymerization of ETCs are not suitable

for a commercial scale operation because only 1.3–1.7 wt % of ETCs can be extracted from PET chip and because only the cyclic trimer melt can be polymerized to high MW linear PET at 306 °C in a reasonably practical period of time, e.g., in ca. 15 min. Recently, the cyclodepolymerization (CDP) of PET was reported, but the yield and reaction time are still not suitable for a commercial scale production.<sup>19</sup> Also, we found that ETCs extracted from PET or prepared by the CDP method need special purification to be polymerized.

In this research, conditions for the effective purification and polymerization of ETCs mixture prepared by the CDP from PET waste using antimony trioxide were established. We believe that this research enhanced the possibility of PET recycle via the commercial scale preparation and polymerization of ETCs. Also, another effective catalyst for the ETCs polymerization was discovered.

## Experimental Section

**General Information.** The intrinsic viscosities of PETs were measured in phenol/1,1,2,2-tetrachloroethane (6/4 w/w) at  $25 \pm 0.01$  °C. The number-average molecular weights ( $M_n$ ) of PETs were determined by using  $[\eta] = 3.72 \times 10^{-4} (M_n)^{0.73}$ .<sup>20</sup> High-pressure liquid chromatography (HPLC) analysis was performed by using a Waters liquid chromatograph equipped with an ultraviolet detector (wavelength 254 nm) and a Supelco LC-Si 5  $\mu\text{m}$  column. In the case of cyclic oligomer analysis, the chromatograph was run at a flow rate of 2.0 mL/min at 25 °C. The solvent was 1,4-dioxane, and the eluent was 1,4-dioxane/hexane (3/7 v/v). A 2 mg sample of cyclic oligomers was dissolved in 2 mL of 1,4-dioxane, and then 20  $\mu\text{L}$  of solution was injected. In the case of linear oligomer analysis, the chromatograph was run at a flow rate of 1.0 mL/min at 25 °C using the same column. The solvent was 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/chloroform (1/20 v/v), and the eluent was ethanol/chloroform (4/96 v/v). A 4 mg sample of linear oligomers was dissolved in 0.1 mL of HFIP, and then 2 mL of chloroform was added. A 15  $\mu\text{L}$  aliquot of solution was injected. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were

<sup>†</sup> This paper is dedicated to Dr. Karel Dusek on the occasion of his 65th birthday.

\* To whom correspondence should be addressed.

**Table 1. Molecular Weight of PET Polymerized from Various ETCs with 0.5 mol % Antimony Trioxide at 293 °C for 15 min**

entry	ETCs	yield (wt %)	cyclics <sup>b</sup> (%)	trimer in ETCs <sup>b</sup>	DEG unit (mol %) <sup>c</sup>	IV (dL/g)	$M_n$	polymer color
1	direct synthesis method		99.9	57.0		0.61	25 300	white
2	soluble in DCM <sup>a</sup>	92	92.7	52.1		0.46	17 200	gray
3	soluble in dioxane <sup>a</sup>	96	97.4	46.2		0.46	17 200	gray
4	soluble in DCM, insoluble in acetone <sup>a</sup>	61	94.2	38.6		0.47	17 700	gray
5	soluble in DCM, insoluble in THF <sup>a</sup>	28	98.8	33.0	1.8	0.60	24 800	white
6	soluble in DCM, soluble in THF <sup>a</sup>	72	91.0	32.1	5.9	0.34	11 400	yellow

<sup>a</sup> Cyclodepolymerization. <sup>b</sup> From HPLC peak area. <sup>c</sup> From NMR.

obtained on a Bruker AMX-2 500 MHz spectrometer using CF<sub>3</sub>-COOD as a solvent to determine the content of diethylene glycol (DEG) units in the ETCs. The contents of Sb and Ti in ETCs were measured using a Direct Reading Echelle inductively coupled plasma (ICP) spectrometer (Leeman Labs Inc., DRE). A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to study the thermal behaviors of the PETs. All PETs were melted at 290 °C for 3 min, cooled to room temperature at a cooling rate of -20 °C/min, and then heated to 300 °C at a heating rate of 20 °C/min under a nitrogen atmosphere.

**Preparation of ETCs via Ring/Chain Equilibration in Dilute Solution (Cyclodepolymerization, CDP).** A 2 gal reactor was charged with about 50 g of PET ( $M_n \approx 20\,000$ ) and 5.5 L of *o*-dichlorobenzene to produce a solution 0.05 M in ethylene terephthalate residues. The solution was heated to 240 °C with 3 mol % of titanate catalyst. After 1.5 h the product solution was cooled to 100 °C to induce the precipitation of any unreacted linear polymer. The latter was then removed by filtration. ETCs were subsequently recovered from the resultant filtrate by vacuum evaporation of the solvent, followed by recrystallization from hexane and filtration. The yield of ETCs was 50%. ETC trimer is the most predominant cyclic. The ETCs prepared had a distribution of oligomeric species and displayed a broad melting range.

**Preparation of ETCs by Direct Synthesis.** The direct synthesis of ETCs from ethylene glycol and terephthaloyl chloride was carried out via a method of Brunelle.<sup>12,21</sup> The yield of ETCs was 60%.

**Preparation of PET Linear Oligomers and Bis(2-hydroxyethyl) Terephthalate (BHET).** To prepare PET linear oligomers, a mixture of dimethyl terephthalate (DMT), 1,2-ethanediol (ED), and zinc acetate with a mole ratio of 1:3:0.005 was melted and reacted at 190 °C for 3 h under a nitrogen atmosphere. The reaction product was dried in a vacuum oven at 60 °C for 3 days to eliminate excess ED. BHET (mp 109 °C)<sup>22</sup> was extracted from the dried product with distilled water at 70 °C and then recrystallized three times from distilled water.

**Polymerization of ETCs.** A 0.5 g sample of ETCs and a small amount of catalyst were introduced into a vial and mixed by dissolving in dichloromethane (DCM). The DCM was slowly evaporated with vigorous stirring using a magnetic stirrer. All samples were dried in a vacuum oven at 80 °C for 12 h. The vial containing ETCs and catalyst was purged with nitrogen to avoid degradation and then put in a salt bath controlled at predetermined temperature. The polymerizations of ETCs were carried out at this temperature under a nitrogen atmosphere. The resulting PET was removed from the vial and quenched in an ice-water bath.

**Preparation of ETC/PET Blends and Polymerization.** A 0.5 g sample of PET and ETCs and 0.3 mol % antimony trioxide were dissolved in 10 mL of HFIP. The solution was slowly dried at room temperature. This blend and others like it were dried in a vacuum oven at 60 °C for 24 h before polymerization.

## Results and Discussion

Goodman and Nesbitt<sup>16-18</sup> separated cyclic trimer, tetramer, and pentamer from ETCs extracted from PET chips with boiling dioxane by using their solubility

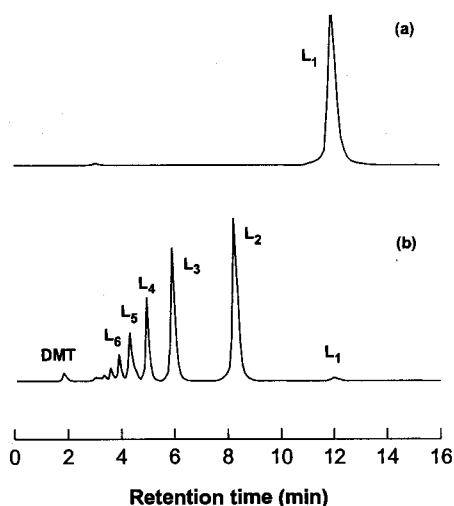
differences. The melting temperatures of cyclic trimer, tetramer, and pentamer determined by them were in the range 314–316, 225–229, and 247–250 °C, respectively. These separated oligomers were each polymerized with antimony trioxide to high MW PETs. Interestingly, polymerization conditions for each cyclic were quite different. To obtain high MW PET, cyclic trimer, tetramer, and pentamer were each polymerized at 306 °C for 15 min, 275 °C for 45 min, and 306 °C for 60 min with 0.05 wt % antimony trioxide, respectively. It appears that the polymerization conditions are strongly dependent on the species.

On the other hand, ETCs prepared by CDP in dilute solution consist of a distribution of oligomeric species displaying a broad melting range, the uppermost end of which lies at 290 °C. Actually, the CDP product consists of a distribution of ETCs of various sizes, together with a small amount of cyclic oligomers containing the DEG unit. This melting range is lowered as a result of a significant depression of the melting points of the high-melting oligomers by the presence of the lower-melting ones. Therefore, in this study, most ETCs were polymerized at 293 °C to melt all cyclic oligomers and to minimize thermal degradation of the resultant PET.

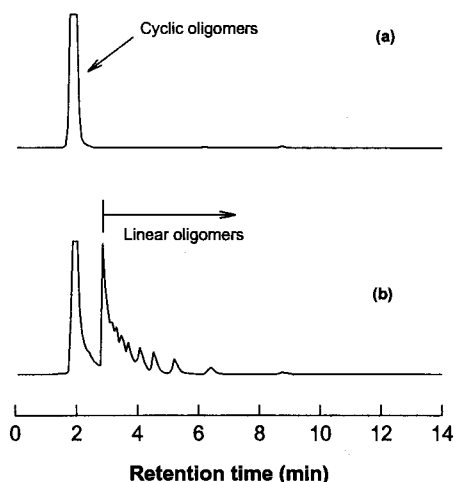
Table 1 shows the polymerization results of various ETCs prepared by different preparation and purification methods. Although the polymerization conditions for each cyclic oligomer were very different, ETCs were successfully polymerized with 0.5 mol % antimony trioxide within a reasonably practical period of time for a RIM or CRIM process. The melting and polymerization temperature of cyclic tetramer, the second major component in ETCs, determined by Goodman and Nesbitt,<sup>16-18</sup> is much lower than this polymerization temperature. However, it was successfully polymerized. There are other reports that its melting temperature is in the range 324–329 °C.<sup>23,24</sup>

The MWs of the resultant PETs were dependent on the preparation and purification methods of the particular batches ETCs. These various batches of ETCs have different contents of linear oligomers and distributions of cyclic oligomers. The contents of linear oligomers and distributions of cyclic oligomers were determined by HPLC analysis. Figure 1 shows the HPLC analysis of PET linear oligomers. The retention time of BHET is about 12 min (Figure 1a). As the MW of linear oligomer increases, the retention time decreases. A small amount of DMT unreacted monomer was detected at the retention time of about 2 min, and this time was confirmed by injecting pure DMT.

Figure 2 shows the HPLC analysis of the soluble and insoluble parts of ETCs as-prepared in dioxane. ETCs prepared by the CDP and purification described in Experimental Section were referred to as ETCs as-



**Figure 1.** HPLC traces of (a) BHET and (b) PET linear oligomers.  $L_1$ – $L_6$  indicate the number of repeating units in the linear oligomers.

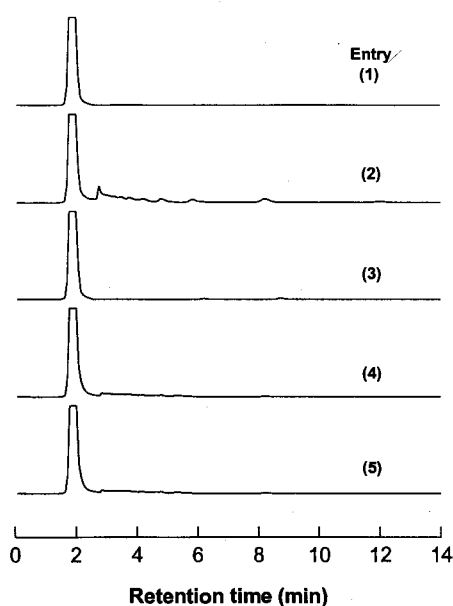


**Figure 2.** HPLC traces of (a) soluble and (b) insoluble part of ETCs as-prepared in 1,4-dioxane.

prepared. Many studies on ETCs have been carried out by extracting them with dioxane.<sup>16–18,24</sup> The soluble part (96 wt %) consists of almost pure cyclics. In this HPLC analysis, cyclic oligomers could not be separated from each other.

The insoluble part (4 wt %) consists of cyclics and linear oligomers. In the preparation of ETCs, linear oligomers were eliminated twice by precipitation at 100 °C and recrystallization. However, in the insoluble part in dioxane, linear oligomers were still detected by HPLC analysis. If all linear oligomers have hydroxyl end groups, high MW linear oligomers having short retention times could be more easily eliminated owing to the solubility difference. However, at short retention times, a higher concentration of linear oligomers was detected. Therefore, it seems that most linear oligomers in the soluble part are low MW oligomers having nonpolar end groups. Practically, the commercial PET has other end groups such as carboxyl and vinyl groups formed by thermal degradations and side reactions during the polycondensation of PET.<sup>25</sup>

Figure 3 shows that HPLC analysis of various ETCs (entries 1–5 in Table 1) confirms the presence of linear oligomers. ETCs prepared by the direct synthesis method show no linear oligomer peaks. DCM and dioxane were used to eliminate linear oligomers from the ETCs as-



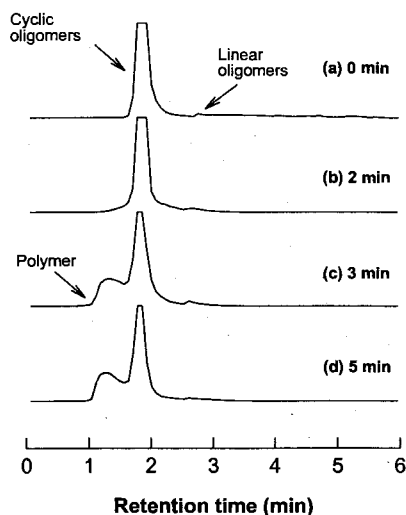
**Figure 3.** HPLC traces of various ETCs in Table 1 for analysis of linear oligomers.

prepared. As can be seen, DCM could not eliminate all the linear oligomers from the ETCs as-prepared, but after the second purification with acetone or tetrahydrofuran (THF), just a small amount of linear oligomers was still detected.

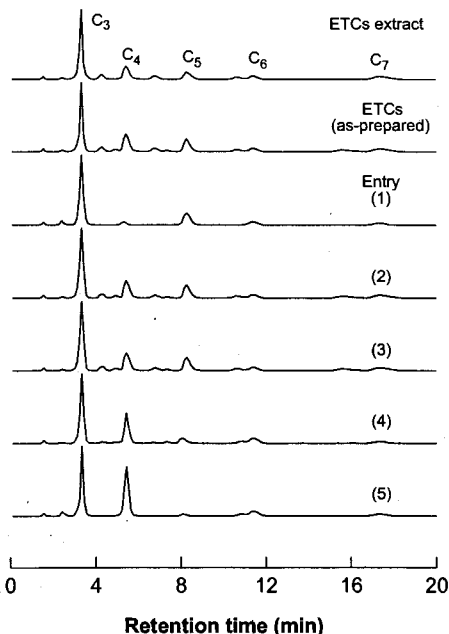
Goodman and Nesbitt<sup>16–18</sup> suggested that the initiating substances in the polymerization of ETCs may be water, or mono- or polyhydric alcohols, or any other compound providing molecular fragments that will combine terminally with the polymer chain. Experimentally, these investigators showed that an initiating substance additional to the catalyst is apparently also required, since they found that, when cyclic trimer was intensively dried and then heated with antimony oxide under dry nitrogen, no polymerization occurred.

In our study, a small amount of linear oligomers remained in our purified ETCs. Assuming that cyclic and linear oligomers have the same detector response per unit weight, the amount of cyclic oligomers was determined from HPLC peaks (Table 1).

PETs of high MW were polymerized from the ETCs listed as entries 1 and 5 in Table 1, ETC batches each of which contained a small amount of linear oligomers. However, in the case of entry 3, even though the content of linear oligomers was low, the MW of the resultant PET was not higher than that of entry 4, and the polymer color was gray. If these linear oligomers can initiate the polymerization, the MW of the resultant PET should be inversely proportional to the content of linear oligomers, but this was not observed. It seems from these results that most of these linear oligomers do not have reactive end groups providing molecular fragments and that they could not be completely eliminated during the purification process. Figure 4 shows the changes of HPLC traces of ETCs (entry 5) polymerized at 293 °C without the catalyst to delay the polymerization. When these ETCs were polymerized for 10 min at 293 °C, an  $M_n$  of 10 000 was achieved in the product. After 3 min, the polymer peak clearly appeared in the HPLC trace. However, the quantity of linear oligomers was unchanged up to 5 min, indicating that these remaining linear oligomers could not initiate the polymerization to yield higher MW PET.



**Figure 4.** Changes of HPLC traces of ETCs (entry 5 in Table 1) polymerized at 293 °C without the catalyst.



**Figure 5.** HPLC traces of various ETCs for cyclic oligomer analysis. C<sub>3</sub>–C<sub>7</sub> refer to the number of repeating units in the cyclic oligomers.

Therefore, it is very likely that there are other factors affecting the polymerization of ETCs. To identify these other factors, the distributions of various ETCs were investigated. Figure 5 shows HPLC traces of ETCs obtained in order to determine cyclic distributions. To confirm the distribution of ETCs prepared by CDP, ETCs were Soxhlet extracted from PET chip with 1,4-dioxane for 24 h. Cyclic trimer is the most predominant cyclic for all ETCs as is the case for those in the commercial PET.<sup>19,23,26</sup> Other peaks are assigned as cyclic tetramer, pentamer, hexamer, and heptamer from a linear relationship assumed between log(retention time) and ring size for these peaks. (This assumption should be valid for a homologous series of cyclic oligomers under the separation conditions used.<sup>27</sup>) Assuming all the cyclic oligomers have the same detector response per unit weight, the contents of cyclic trimer were determined. The contents of cyclic trimer varied with the preparation and purification methods for the ETCs. ETCs prepared by direct synthesis contained the largest

amount of cyclic trimer. The resultant MW of PET was independent of the content of cyclic trimer. However, it should be noted that according to the purification method for ETCs the sizes of the small peaks between the main ETC peaks were changed and high MW PETs were obtained from ETCs not showing small peaks between main ETC peaks, i.e., entries 1 and 5. THF eliminated effectively cyclic oligomers corresponding to these small peaks. As reported,<sup>28</sup> these small peaks between the main peaks correspond to ETCs containing the DEG unit.

Goodman and Nesbitt<sup>17,18</sup> separated and characterized ETC containing the DEG unit (compound D in their report) and then obtained a crystalline, fiber-forming polymer (mp = 177–180 °C) showing an X-ray pattern quite different from that of PET from its polymerization at 275 °C for 1 h. The commercial PET generally contains about 2–5 mol % DEG unit, which is incorporated by side reactions during the esterification and the subsequent polycondensation.<sup>29–31</sup> The amount of the DEG unit in PET depends on reaction conditions such as temperature, duration, and type of catalyst employed. The amount of DEG units influences the physical and chemical properties of PET. Hergenrother<sup>30</sup> reported that the presence of DEG units in the PET chain increases the thermal decomposition rate in the melt, in proportion to the concentration of DEG units. The increased acidity of the  $\beta$  hydrogens and the lack of interference from the opposing ester group in the DEG unit accelerate the ester scission.

The concentrations of DEG units before and after separation from ETCs with THF and the resultant MWs of the PETs polymerized with 0.5 mol % antimony trioxide are listed in Table 1. The concentrations of DEG units were determined from NMR analysis.<sup>32</sup> During the CDP, ETCs containing DEG unit are inevitably produced because DEG units are already incorporated in the PET chain. As can be seen, cyclic oligomers containing the DEG unit could not be completely eliminated from ETCs by purifying with THF. A plausible reason for this may be that the larger cyclic rings containing one DEG unit might have very similar solubility properties to those of the pure ETC rings. ETCs prepared by the direct synthesis method have no cyclic oligomers containing the DEG unit, and ETCs purified by DCM and THF (entry 5, designated p-ETCs) have a small amount of them. As can be seen, high MW PET was obtained from polymerization of these two ETCs. The lower the content of the DEG unit in ETCs, the higher the MW of the resultant PET. However, the DEG content may not be the only reason for this result since other unknown impurities affecting the resulting MW of PET can be eliminated during the separation of cyclics containing the DEG unit.

For reasons of practicality, all ETCs produced by the CDP reaction should be susceptible to polymerization without further purification. ETCs (entry 2) were polymerized at 270 and 280 °C with 0.5 mol % antimony trioxide for 15 min (Table 2). Although 270 and 280 °C are not high enough to melt all ETCs, higher MW PETs were obtained at these temperatures. As the polymerization proceeds, lower melting cyclic oligomers start polymerizing easily and apparently then dissolve the remaining, higher melting ones. These MWs are higher than that of PET polymerized from ETCs at 293 °C. To examine which cyclic oligomers have been reacted first,

**Table 2. Effects of Polymerization Conditions on the Molecular Weight of PET Polymerized from Various ETCs with Antimony Trioxide**

cyclic oligomers	Sb <sub>2</sub> O <sub>3</sub> (mol %)	temp (°C)	time (min)	IV (dL/g)	M <sub>n</sub>	polymer color
ETCs (entry 2)	0.5	270	15	0.55	22 000	yellow
	0.5	280	15	0.51	19 800	yellow
p-ETCs	0.05	293	15	0.42	15 200	white
	0.3	293	15	0.63	26 500	white
	0.5	293	10	0.61	25 300	white
	0.5	293	15	0.60	24 800	white
	0.5	293	20	0.60	24 800	white
	0.5	293	25	0.56	22 500	white
	0.5	303	5	0.53	20 900	gray
	0.5	303	15	0.54	21 400	gray
	0.7	293	15	0.59	24 200	white
	1.0	293	15	0.63	26 500	white

**Table 3. Effect of the Preparation Method of ETCs and Antimony Trioxide Mixture on the Molecular Weight of PET; Polymerization with 0.5 mol % Antimony Trioxide at 303 °C for 5 min**

method	IV (dL/g)	M <sub>n</sub>
slow dry	0.53	20 900
fast dry	0.17	4 400

**Table 4. Polymerization of ETCs/PET and p-ETCs/PET Blends with 0.3 mol % Antimony Trioxide at 270 °C for 15 min under Nitrogen Atmosphere**

blend	composition	IV (dL/g)	M <sub>n</sub>
ETCs/PET	25/75	0.55	22 000
	50/50	0.51	19 800
	75/25	0.44	16 200
p-ETCs/PET	25/75	0.69	30 000
	50/50	0.46	17 200
	75/25	0.37	12 800

ETCs were melted at 230 °C for 10 min, and then the remaining solids were extracted with DCM. A large amount of cyclic trimer and a small amount of ETC trimer containing the DEG unit and ETC tetramer were detected in the HPLC analysis of the extracted material.

Table 2 also shows the effect of polymerization conditions on the MW of PET polymerized from p-ETCs with antimony trioxide. It is shown that using this lower temperature is important in that it minimizes the thermal degradation of the PET produced. Therefore, for reasons of thermal stability, it is a great advantage to use an oligomer mixture of ETCs because the upper end of the melting endotherm of ETCs is reduced to 290 °C from 306 °C, the temperature at which ETC trimer was polymerized in the work of Goodman and Nesbitt. The highest MW was obtained at 0.3 mol % antimony trioxide concentration, and the resultant MWs seem to be independent of the catalyst concentration above a critical concentration. Moreover, it was found that homogeneous mixing of ETCs and antimony trioxide is a more important factor than any other for obtaining high MW PET since high MW PET was not obtained when p-ETCs and antimony trioxide were mixed by fast drying from DCM (Table 3).

Table 4 shows the polymerization results of ETCs (entry 2)/PET and p-ETCs/PET blends using 0.3 mol % antimony trioxide at 270 °C for 15 min under a nitrogen atmosphere. This is very important in manufacturing of PET composites because ETCs can lower the melt viscosity of PET and because greater amounts of reinforcing material can be used in such PET composites. In the case of p-ETCs, a PET of MW higher than that of the starting PET ( $M_n = 24\,200$ ) was obtained when a 25/75 w/w blend of p-ETCs and PET was used.

**Table 5. Effect of Catalysts on the Molecular Weight of PET Polymerized from p-ETCs at 293 °C for 10 min**

catalyst (0.5 mol %)	melting point of catalyst (°C)	IV (dL/g)	M <sub>n</sub>
without catalyst added <sup>a</sup>		0.18	4 800
without catalyst added		0.31	10 000
Sb <sub>2</sub> O <sub>3</sub>	655	0.61	25 300
Zn(CH <sub>3</sub> COO) <sub>2</sub>	237	0.26	8 000
CH <sub>3</sub> COONa	58	0.32	10 500
CH <sub>3</sub> COOK	292	0.43	15 700
GeO <sub>2</sub>	1115	0.22	6 300
MgO	2852	0.21	5 900
Bi <sub>2</sub> O <sub>3</sub> <sup>b</sup>	825	0.73	32 400

<sup>a</sup> ETCs prepared by direct synthesis method. <sup>b</sup> At 293 °C for 15 min.

**Table 6. Thermal Properties of Commercial PET and PET Polymerized from p-ETCs**

IV (dL/g)	Sb <sub>2</sub> O <sub>3</sub> (mol %)	T <sub>g</sub> (°C)	T <sub>cc</sub> (°C)	-ΔH <sub>c</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>f</sub> (J/g)
0.59 (Aldrich Co.)		72	191	36	251	40
0.42	0.05	73	191	28	245	29
0.53	0.5	69	194	39	250	41
0.56	0.5	71	200	43	255	46
0.61	0.5	72	190	34	247	39

The hydroxyl end groups in PET can initiate the polymerization of ETCs so that to obtain high MW PET the polymerization condition should be carefully controlled. The lower MWs of PETs obtained from p-ETCs/PET = 50/50 and 75/20 appear to result from lower polymerization temperature and short polymerization time. Indeed, we believe this can be extended to mixtures of ETCs with other polymers.

We tested other catalysts for p-ETC polymerization. Table 5 shows the effect of these catalysts on the MW of PET polymerized from p-ETCs at 293 °C for 10 min. Interestingly, we found that p-ETCs can be polymerized without adding any catalyst. This result is considered to be the effect of the presence of residual catalyst, antimony trioxide, added in the original polymerization process. p-ETCs contain 0.2 wt % of Sb and 0.01 wt % of Ti. In the case of some catalysts, lower MW PETs were obtained than the PET polymerized without catalyst. It appears that the thermal stability of the catalyst used can affect the MW of PET in this polymerization system. It is worth noting that the PET of highest MW ( $M_n = 32\,100$ ) was obtained from polymerization of p-ETCs with bismuth trioxide (Bi<sub>2</sub>O<sub>3</sub>) at 293 °C for 15 min.

Goodman and Nesbitt<sup>16-18</sup> showed that PET polymerized from PET cyclics with antimony trioxide had infrared absorption and X-ray diffraction characteristics identical to those of commercial PET.

In this study, the thermal behavior of PET polymerized from ETCs was investigated by DSC and compared with the thermal behavior of commercial PET (Table 6). The two materials displayed almost the same thermal behaviors.

## Conclusion

ETCs were prepared by the direct synthesis method and by CDP of PET in dilute solution. In the case of ETCs prepared by the CDP route, purified ETCs (p-ETCs) were prepared by eliminating remaining impurities including linear oligomers and cyclic oligomers containing the DEG unit using DCM and THF. A homogeneous mixture of ETCs prepared by the direct synthesis method or p-ETCs was successfully polymer-

ized within 15 min to high MW PET ( $M_n \geq 25\,000$ ) using antimony trioxide at 293 °C. The lower the content of linear oligomers and the cyclic oligomers containing the DEG unit in the ETCs used, the higher was the MW of the resultant PET. The highest MW was obtained at 0.3 mol % antimony trioxide concentration, and the resultant MWs seem to be independent of the catalyst concentration above a critical concentration. However it was found that homogeneous mixing of ETCs and antimony trioxide is a more important factor than any other. Higher MW PET than that of the starting PET was obtained from the blend of p-ETCs/PET = 25/75 at 270 °C for 15 min, indicating that ETCs can lower the melt viscosity of PET and thus greater amounts of reinforcing material can be used in PET composites. The PET of highest MW was obtained from polymerization of p-ETCs with bismuth trioxide at 293 °C for 15 min. PET polymerized from ETCs showed almost the same thermal behavior as did the commercial one.

### References and Notes

- (1) Youk, J. H.; Boulares, A.; Kambour, R. P.; MacKnight, W. J. *Macromolecules*, in press.
- (2) Schnell, H.; Bottenbruch, L. *Makromol. Chem.* **1962**, *57*, 1–11.
- (3) Brunelle, D. J.; Shannon, T. G. U.S. Patent 4,829,144, 1989.
- (4) Brunelle, D. J.; Bradt, J. E. U.S. Patent 5,039,783, 1991.
- (5) Brunelle, D. J.; Bradt, J. E. U.S. Patent 5,214,158, 1993.
- (6) Brunelle, D. J. In *Ring Opening Polymerization: Mechanism, Catalysis, Structure, Utility*; Brunelle, D. J., Ed.; Hanser Verlag: Munich, 1993; Chapter 11.
- (7) Ganguly, S.; Gibson, H. W. *Macromolecules* **1993**, *26*, 2408–2412.
- (8) Brunelle, D. J.; Garbaskas, M. F. *Macromolecules* **1993**, *26*, 2724–2729.
- (9) Hubbard, P.; Brittain, W. J.; Simonsick, W. J., Jr.; Ross, C. W., III *Macromolecules* **1996**, *29*, 8304–8307.
- (10) Jiang, H.; Chen, T.; Xu, J. *Macromolecules* **1997**, *30*, 2839–2842.
- (11) Krabbenhoft, H. O.; Brunelle, D. J.; Pearce, E. J. *J. Appl. Polym. Sci.* **1997**, *66*, 2251–2255.
- (12) Brunelle, D. J.; Bradt, J. E.; Serth-Guzzo, J.; Takekoshi, T.; Evans, T. L.; Pearce, E. J.; Wilson, P. R. *Macromolecules* **1998**, *31*, 4782–4790.
- (13) Kricheldorf, H. R.; Lee, S.-R. *Macromolecules* **1995**, *28*, 6718–6725.
- (14) Kricheldorf, H. R.; Lee, S.-R.; Bush, S. *Macromolecules* **1996**, *29*, 1375–1381.
- (15) Kricheldorf, H. R.; Lee, S.-R. *Macromolecules* **1996**, *29*, 8689–8695.
- (16) Goodman, I.; Nesbitt, B. F. Br. Patent 843,356, 1960.
- (17) Goodman, I.; Nesbitt, B. F. *Polymer* **1960**, *1*, 384–396.
- (18) Goodman, I.; Nesbitt, B. F. *J. Polym. Sci.* **1960**, *48*, 423–433.
- (19) Bryant, J. J. L.; Semlyen, J. A. *Polymer* **1997**, *38*, 2475–2482.
- (20) Hergenrother, W. L.; Nelson, C. J. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2905–2915.
- (21) Brunelle, D. J. General Electric Corporate, Research & Development, Schenectady, NY, private communication.
- (22) Krzikalla, R. *Angew. Chem.* **1955**, *67*, 108–110.
- (23) Shiono, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 4123–4127.
- (24) Peebles, L. H., Jr.; Huffman, M. W.; Albett, C. T. *J. Polym. Sci., Part A-1* **1969**, *7*, 479–496.
- (25) Besnoin, J.-M.; Choi, K. Y. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 55–81.
- (26) Cooper, D. R.; Semlyen, J. A. *Polymer* **1973**, *14*, 185–192.
- (27) Cimecioglu, A. L.; Zeronian, S. H.; Alger, K. W.; Collins, M. J. *J. Appl. Polym. Sci.* **1986**, *32*, 4719–4733.
- (28) Hudgins, W. R.; Theurer, K.; Mariani, T. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1978**, *34*, 145–155.
- (29) Hovenkamp, S. G.; Munting, J. P. *J. Polym. Sci., Part A-1* **1970**, *8*, 679–682.
- (30) Hergenrother, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 875–883.
- (31) Fakirov, S.; Segonov, I.; Kurdowa, E. *Makromol. Chem.* **1981**, *182*, 185–197.
- (32) Frank, W. P.; Zachmann, H. G. *Prog. Colloid Polym. Sci.* **1977**, *62*, 88–92.

MA991838D