Preparation and Polymerization of Ethylene 2,6-Naphthalenedicarboxylate Cyclic Oligomers[†]

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ABSTRACT: Ethylene 2,6-naphthalenedicarboxylate cyclic oligomers (ENCs) were prepared by the ring/chain equilibration (cyclodepolymerization) of poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) in dilute solution of biphenyl and polymerized with antimony trioxide. ENCs thus prepared consisted of a distribution of oligomeric species displaying a broad melting range from 330 to 370 °C. ENC trimer (C_3) was recrystallized from ENCs solution in 1,4-dioxane, and its purity was assessed by the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric analysis. C_3 is the main component in ENCs, and its melting temperature is 370 °C. ENCs containing the diethylene glycol (DEG) unit were detected in the high-pressure liquid chromatography and MALDI-TOF analysis. ENCs and ENCs/ethylene terephthalate cyclic oligomers (ETCs) blends were polymerized with 0.5 mol % antimony trioxide at temperatures ranging from 320 to 365 °C for 5 min under a nitrogen atmosphere. The highest molecular weight (MW) (IV = 0.41 dL/g) was obtained from the polymerization of ENCs at 355 °C for 5 min. In the case of ENCs/ETCs blends, although the polymerization temperatures were decreased by adding ETCs, high MW polyesters were not obtained due to polymerization temperatures that nevertheless were still too high. PEN polymerized from ENCs showed the same thermal behaviors as the commercial product. Consequently, it was found that antimony trioxide is an effective catalyst for ENCs polymerization, but the melting and polymerization temperatures of ENCs need to be decreased to obtain PEN of higher MW.

Introduction

The polymerization of reactive cyclic oligomers of thermoplastic resins could provide an opportunity for reactive processing such as reaction injection molding (RIM) and composite reaction injection molding (CRIM) because of the low melt viscosities of these oligomers.[1−6] The ethylene terephthalate cyclic oligomers (ETCs) were prepared successfully from the ring/chain equilibration (cyclodepolymerization) of poly(ethylene terephthalate) (PET) in dilute solution of *o*-dichlorobenzene.[7,8] 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 to be applied to RIM and CRIM. Moreover, ETCs were successfully polymerized with antimony trioxide to high molecular weight (MW) PET ($M_n > 24\,000$) at 293 °C within 10 min.[9] These results have encouraged us to investigate the preparation and polymerization of other polyester cyclic oligomers with antimony trioxide.

One of the important high-performance polyesters, poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), has drawn attention for its good thermal stability, excellent mechanical properties, and outstanding gas barrier properties.[10−15] However, its high melting temperature and high melt viscosity are unfavorable for processing. Hubbard et al.[16] prepared ethylene 2,6-naphthalenedicarboxylate cyclic oligomers (ENCs) by reaction of 2,6-naphthalenedicarbonyl dichloride with 1,2-ethanediol and polymerized them with a titanium catalyst to test their possible use as low-viscosity precusors to PEN. ENCs prepared in this manner consisted of a distribution of oligomeric species displaying a broad melting range from 250 to 285 °C, in which ethylene 2,6-naphthalenedicarboxylate cyclic (ENC) trimer (C_3) was the most predominant cyclic. Unfortunately, the intrinsic viscosity of the PEN from the ENCs polymerization was 0.24 dL/g, which is approximately half the value of the intrinsic viscosity for commercial PEN. These authors suggested that changes in catalyst structure and the removal of linear oligomers would produce high MW PEN. Recently, Brunelle et al.[17] polymerized cyclic oligomeric alkylene phthalates to high MW polyesters with either tin or titanium initiators. However, these initiators are sensitive to moisture and are thermally unstable at high temperature (>230 °C) so that only polyester cyclic oligomers having low melting temperatures can be polymerized with such initiators.

In this research, ENCs were prepared by the cyclodepolymerization of PEN in dilute solution of biphenyl and analyzed. ENCs thus prepared were polymerized with antimony trioxide, and thermal properties of the resultant polymer were investigated.

Experimental Section

General Information. The intrinsic viscosities (IV) of PENs were measured by using a mixed solvent of phenol/1,1,2,2-tetrachloroethane (6/4 w/w) at 25 ± 0.01 °C. High-pressure liquid chromatography (HPLC) analysis was performed using a Waters 600 liquid chromatograph equipped with an ultraviolet detector (wavelength 254 nm) and a Supelco LC-Si 5 μm 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 μL 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 with 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

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[†] This paper is dedicated to Dr. Karel Dusek on the occasion of his 65th birthday.

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linear oligomers was dissolved in 0.1 mL of HFIP, and then 2 mL of chloroform was added. A 15 μL aliquot of solution was injected. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AMX-2 500 MHz spectrometer using CF_3COOD as a solvent. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Reflex III (Bruker Daltonics, Billerica, MA) mass spectrometer equipped with a standard nitrogen laser and a double-plate microchannel detector. The accelerating voltage was 20 kV. The samples were dissolved in chloroform to 3 mg/mL and mixed with the standard solution of matrix dithranol (1,8,9-trihydroxyanthracene) in chloroform at a 1/1 v/v ratio. The content of Sb in ENCs was measured using a Direct Reading Echelle inductively coupled plasma (ICP) spectrometer (Leeman Labs Inc., DRE). The thermal behavior of cyclic oligomers and the resulting polymers were analyzed using a Perkin-Elmer differential scanning calorimeter (DSC-7) at a heating rate of 20 °C/min under a nitrogen atmosphere. Thermal stability was measured using a thermogravimetric analyzer (TGA) (TA instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere.

Separation of ENCs from PEN. A precipitation method was used for the effective separation of ENCs in PEN.[18] A 1 g sample of PEN was dissolved in 10 mL of HFIP and then precipitated by successive addition of 20 mL of chloroform, 5 mL of acetone, and 20 mL of distilled water to give a fine precipitate over a period of 6 h. The whole mixture was stirred rapidly in an ice bath during the precipitation. After filtration of PEN using a fine glass funnel, the filtrate composed of aqueous and organic phase was transferred to a 125 mL separation funnel, and the bottom organic phase containing some oligomeric components was drawn off. The aqueous phase was extracted with 10 mL of chloroform, and the extract was combined with the other oligomer-containing organic phase. The solvents in the oligomer-containing phase were evaporated by using a rotary evaporator, and a solid oligomeric residue was obtained. To remove the linear oligomeric components, it was dissolved in 50 mL of dichloromethane (DCM) and the insoluble part was filtered off. After evaporation of the DCM, the residue was dried in a vacuum oven at 80 °C for 12 h and its weight measured.

Preparation of ETCs and ENCs via Ring/Chain Equilibration in Dilute Solution (Cyclodepolymerization). Pure ETCs were prepared by the cyclodepolymerization method and purified with DCM and tetrahydrofuran (THF) as reported in our previous research.[9] ENCs were also prepared by the same method. A 1000 mL reactor was charged with PEN (IV = 0.54 dL/g) and biphenyl as a solvent according to the concentrations of 1/20, 1/40, and 1/80 PEN/biphenyl by weight. Each mixture was heated to 240 °C with 3 mol % (based on moles of ethylene 2,6-naphthalenedicarboxylate residues) 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxyacyclodecane as a depolymerization catalyst.[8] After 2 h, the product solution was cooled to room temperature. Biphenyl was removed by Soxhlet extraction with methanol (yield > 96 wt %). ENCs were subsequently extracted from the remaining reactants with DCM. The insoluble part of the ENCs extracted in THF was filtered off to eliminate linear oligomers. The ENCs as-prepared consisted of a distribution of oligomeric species displaying a broad melting range.

Recrystallization of ENC Trimer (C_3). C_3 was separated from the ENCs solution of 1,4-dioxane. A 1 g sample of ENCs was dissolved in 200 mL of 1,4-dioxane at 70 °C, and the C_3 was then recrystallized by slowly evaporating the solvent. This recrystallization was repeated three times to obtain pure C_3.

Polymerization of ENCs and ENCs/ETCs with Antimony Trioxide. ENCs obtained at a cyclodepolymerization concentration of 1/40 (w/w) and 0.5 mol % antimony trioxide for every PEN unit were mixed by dissolving in HFIP, and then the HFIP was slowly evaporated with vigorous stirring using a magnetic stirrer. The blends of ENCs and ETCs were also prepared by dissolving in HFIP with 0.5 mol % antimony trioxide for every PEN and PET unit, in which ENCs obtained at a cyclodepolymerization concentration of 1/40 (w/w) were also used. The solution was slowly dried at room temperature with vigorous stirring. All samples were dried in a vacuum oven at 80 °C for 12 h before polymerizaton. The polymerizations of cyclic oligomers were carried out under a nitrogen atmosphere.

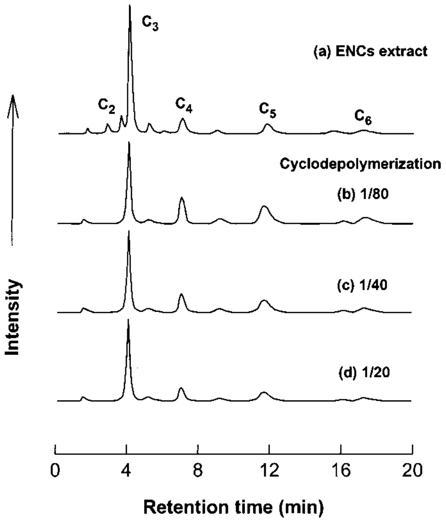

Figure 1. HPLC traces of ENCs extract and ENCs prepared by the cyclodepolymerization at different concentrations. The numbers in the figures indicate the number of repeating units in the cyclic oligomers.

Results and Discussion

Figure 1a shows the HPLC trace of ENCs extracted from PEN by using the precipitation method. The equilibrium content of ENCs in PEN was 1.44 wt %. Aoki[19] reported that the equilibrium content of ENCs is 1.16 wt % except for ENCs containing the diethylene glycol (DEG) unit, in which C_3 (66 wt %) is the most predominant cyclic. The equilibrium content of ENCs in PEN is smaller than the content of ETCs in PET (2.01 wt %)[20] probably due to the naphthalene groups providing added rigidity to the PEN backbone.[19] Assuming all the ENCs have the same detector response per unit weight, the content of the most predominant cyclic, C_3, in the ENCs was 56 wt %. Other peaks are assigned to the ENC dimer (C_2), tetramer (C_4), pentamer (C_5), and hexamer (C_6) using a linear relationship between log(retention time) and ring size for these peaks, which should be the case for a homologous series of cyclic oligomers under the separation conditions used.[21] The presence of all the ENCs was also confirmed by the MALDI-TOF mass spectrometric analysis in this study, the results of which will be discussed in detail later. In the case of ENCs extracted from PEN, the C_2 containing one DEG unit and other ENCs containing the DEG unit were clearly detected between the main peaks. This was also confirmed by the MALDI-TOF mass spectrometric analysis. In the HPLC analysis of ETCs, small peaks between main peaks correspond to ETCs containing the DEG unit.[18] The DEG unit in PET is incorporated by side reactions during the esterification and the subsequent polycondensation.[22−27] The concentration of DEG units in PEN determined from NMR analysis is 3.7 mol %.[26] Hence, it is considered that the DEG unit in PEN was incorporated during the polymerization and that ENCs containing the DEG unit occurred as a result. Figure 1b−d shows HPLC traces of ENCs prepared by the cyclodepolymerization of PEN in various solution concentrations. The distributions of these ENCs were obtained from ENCs extracted from the reactants with

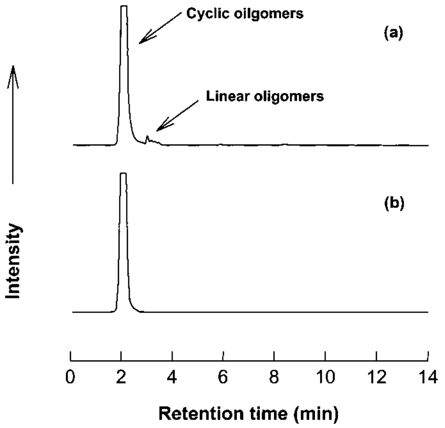

Figure 2. HPLC traces of (a) insoluble and (b) soluble part of ENCs extracted with DCM after the cyclodepolymerization in THF.

Table 1. Effect of Dilution in the PEN Ring/Chain Equilibrium Reaction on the Yield of ENCs

PEN/solvent (w/w)	yield of ENCs (wt %)
1/20	22.6
1/40	31.3
1/80	38.1

DCM, in which small amounts of linear oligomers were present. Although the content of each cyclic oligomer was changed according to the preparation conditions, C_3 was the most predominant cyclic for all ENCs. As the concentration of PEN used for the cyclodepolymerization was increased, the fraction of C_3 increased. This was also observed in the preparation of ETCs from the cyclodepolymerization of PET.[28] ENCs prepared by the cyclodepolymerization did not show the peaks of C_2 and C_2 containing one DEG unit. It is assumed that they were extracted during the Soxhlet extraction of biphenyl with methanol.

Table 1 shows the yield of ENCs. The yield increased with increasing dilution. The presence of linear oligomers after purification with THF was investigated using HPLC. Figure 2 shows HPLC traces of the (a) insoluble and (b) soluble parts of ENCs extracted with DCM after the cyclodepolymerization in THF. Ten weight percent was insoluble in THF. As shown in Figure 2a, small amounts of linear oligomers were detected at longer retention times. The detection of linear oligomers by this analysis was already discussed in our previous research.[9] (Goodman and Nesbitt [29−31] suggested that the initiating substances in ETCs polymerization may be water, or mono- or polyhydric alcohols, or any other compound providing molecular fragments.) To obtain high molecular weight PEN, reactive linear oligomers should be eliminated. Figure 2b shows that linear oligomers are eliminated successfully after purification with THF, which was also confirmed by the absence of end groups in the ^{1}H NMR results.

Figure 3a shows HPLC traces of ENCs. The distribution of ENCs was changed after the elimination of linear oligomers with THF. A large amount of C_4 was insoluble in THF so that the content of C_4 decreased after purification. The ENCs were further purified with acetone to eliminate ENCs containing the DEG unit (yield = 80 wt %). As shown in Figure 3b, the sizes of the small peaks between the main ENCs peaks decreased. A certain amount of ENCs containing the DEG unit was eliminated with acetone. Figure 3c shows the HPLC trace of pure C_3. C_3 was successfully separated by recrystallization from the dioxane solution of ENCs.

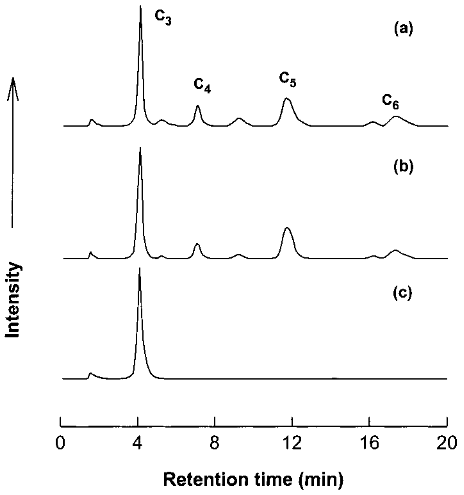

Figure 3. HPLC traces of (a) ENCs, (b) ENCs insoluble in acetone, and (c) ENC trimer (C_3).

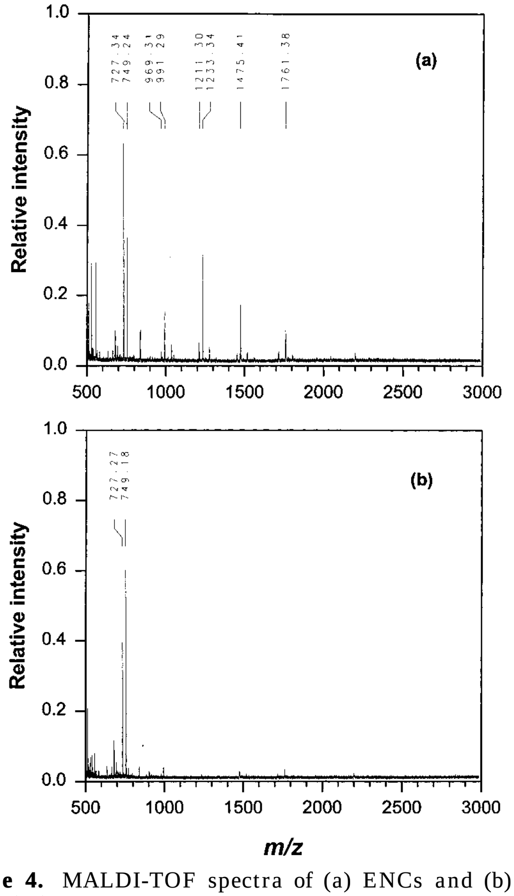

Figure 4. MALDI-TOF spectra of (a) ENCs and (b) ENC trimer (C_3).

The cyclic nature of the ENCs was confirmed by MALDI-TOF mass spectrometry. Parts a and b of Figure 4 show MALDI-TOF spectra of ENCs and C_3, respectively. It can be easily seen that there are peaks corresponding to molecular ions of ENCs, detected as MH^+ and MNa^+, at m/z = n242 + 1 and n242 + 23. It is confirmed from Figure 4a,b that the large two peaks at m/z = 727 and 749 correspond to C_3 with $n = 3$. As analyzed by HPLC, C_3 is the most predominant cyclic in ENCs. As shown in Figure 3a, ENCs contained a smaller amount of C_4 than of C_5. This distribution was also detected by MALDI-TOF analysis. The peaks at m/z = 727 and 749, 969 and 991, 1211 and 1233, and 1453

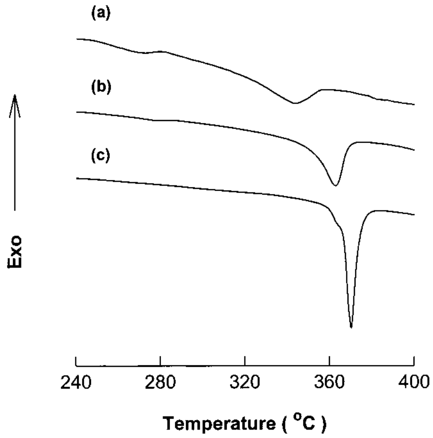

Figure 5. DSC thermograms of (a) ENCs extract, (b) ENCs, and (c) ENC trimer (C_3).

Table 2. Polymerization of ENCs and ENCs/ETCs with 0.5 mol % Antimony Trioxide for 5 min under a Nitrogen Atmosphere

cyclic oligomers	polymerization temp (°C)	IV (dL/g)	T_g (°C)	T_m (°C)
ENCs	360	0.31	120.2	269.7
ENCs (insoluble in acetone)	355	0.41	119.7	268.4
ENC trimer	365	0.39	127.5	276.7
ENCs/ETCs (90/10 w/w)	350	0.33	114.1	244.2
ENCs/ETCs (80/20 w/w)	340	0.37	109.3	
ENCs/ETCs (70/30 w/w)	320	0.28	99.1	

and 1475 correspond to C_3, C_4, C_5, and C_6, respectively. Also, ENCs containing the DEG unit were detected in the MALDI-TOF analysis as they had also been detected in the HPLC analysis. Specifically, the peak at m/z = 1761 corresponds to the ENC heptamer containing one DEG unit. Therefore, it is confirmed that the DEG unit in PEN was incorporated during the polymerization and that ENCs containing the DEG unit were produced during the cyclodepolymerization.

Figure 5 shows DSC thermograms of ENCs extract, ENCs, and C_3 obtained from the first scan. C_3 has a melting temperature of 370 °C. ENCs show a broad melting range from 330 to 370 °C. The melting temperature of ENCs is slightly lower than that of C_3 due to the presence of other ENCs. In the case of ENCs extract, the melting temperature is still more suppressed by the presence of other ENCs. However, this melting temperature is almost 85 °C higher than that reported by Hubbard et al.[16] This may result from differences in the distributions of the ENCs or their contamination with linear oligomers. In any case, to polymerize completely molten ENCs, the polymerization temperature must be about 360 °C. Although it is possible to polymerize the ENCs melt at 360 °C, the resultant PEN may be thermally unstable at this temperature. It was revealed from the previous study that the polymerization temperature of ETCs should be as low as possible in order to minimize the thermal degradation of the resultant PET.[9] Table 2 shows the results of polymerization of various ENCs and ENCs/ETCs blends with 0.5 mol % antimony trioxide for 5 min under a nitrogen atmosphere. The residual content of Sb in ENCs is 0.01 wt %. The IV of PEN polymerized from ENCs was 0.31 dL/g, which is low compared with the IV of commercial PEN (Aldrich Co., IV = 0.54 dL/g). The highest IV, 0.41 dL/g, was obtained from the polymerization of the ENCs fraction insoluble in acetone. (This was a fraction containing a smaller amount of ENCs having the DEG unit than did the ENCs as-prepared.) The IV of PEN polymerized from C_3 was 0.39 dL/g. As shown in the ETCs polymerization,[9] it appears from these results that the lower the content of the DEG unit in the ENCs, the higher the MW of the resultant PEN.

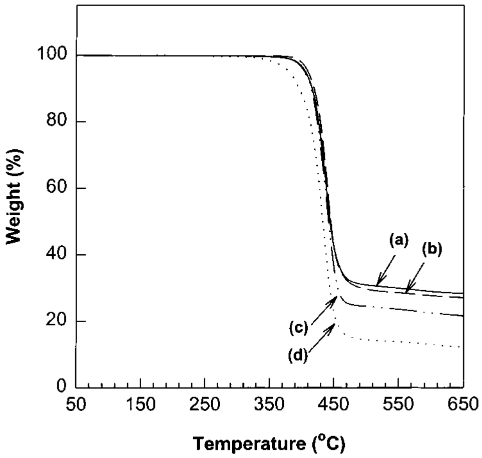

Figure 6. TGA curves of (a) ENCs, (b) commercial PEN, (c) PEN polymerized from ENCs, and (d) ETCs.

Figure 6 shows TGA curves of ENCs, ETCs, PEN, and PEN polymerized from ENCs. ENCs, PEN, and PEN polymerized from ENCs exhibited very similar thermal stability. As reported by other researchers,[32] they all start thermal degradation at about 360 °C where polymerization was conducted. To enhance the thermal stability of the ENCs and PEN, it is an advantage to use an oligomer mixture in order to depress the melting temperature of the ENCs. In this study, small amounts of ETCs (T_m = 290 °C) were added to ENCs, but it was found from DSC analysis that the melting temperature of the ENCs was not significantly lowered. As the polymerization of the ENCs/ETCs blend proceeds, the lower melting ETCs will start polymerizing first and then dissolve the ENCs. Thus, the polymerization temperatures can be decreased by increasing the ETCs content, and consequently the thermal degradation of the resultant polymers can be minimized. Unfortunately, in this study, polyesters of high MW were not obtained probably because polymerization temperatures were still too high and ETCs were not thermally stable at these temperatures as shown in Figure 6. However, we believe that high MW PEN can be obtained by changing the polymerization process of ENCs: ENCs should be melted quickly and then polymerized at temperatures at which ENCs and the resultant PEN remain stable.

The thermal behavior of PEN polymerized from ENCs was investigated by DSC and compared with the behavior of commercial PEN (Table 2). For the DSC analysis, all polymers were melted at 20 °C above their melting temperatures for 3 min and then cooled to room temperature at a cooling rate of 20 °C/min. The glass transition temperature and melting temperature of commercial PEN are 119 and 265 °C, respectively. Figure 7 shows DSC thermograms of commercial PEN and PEN polymerized from ENCs as-prepared. They show almost the same thermal behavior.

Conclusion

The equilibrium content of cyclic oligomers in PEN is 1.44 wt %, which is smaller than the ETCs content in PET. This difference may be due to the steric effects

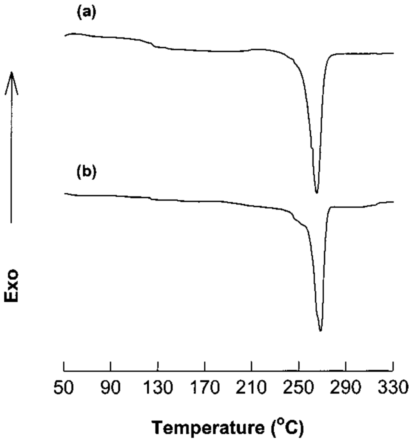

Figure 7. DSC thermograms of (a) commercial PEN and (b) PEN polymerized from ENCs with antimony trioxide.

of the naphthalene groups. ENCs were prepared by the cyclodepolymerization of PEN in various solution concentrations in yields as high as 38 wt %. ENCs showed a broad melting range, the uppermost end of which lay at 370 °C. C_3 was recrystallized from ENCs solution in 1,4-dioxane, and the purity of the resultant product was confirmed by the MALDI-TOF analysis. C_3 is the most predominant cyclic in ENCs, and its melting temperature is 370 °C. ENCs containing the DEG unit were detected in the HPLC and MALDI-TOF analysis.

ENCs and ENCs/ETCs blends were polymerized with 0.5 mol % antimony trioxide for 5 min under a nitrogen atmosphere. The PEN of IV = 0.41 dL/g was obtained from polymerization of ENCs at 355 °C treated with acetone to reduce the content of ENCs containing the DEG unit. The IV of PEN polymerized from C_3 was 0.39 dL/g. Although the polymerization temperatures could be decreased by adding ETCs, polyesters of high MW were not obtained probably due to polymerization temperatures that nevertheless were still too high. However, it is believed that high MW PEN can be obtained by melting ENCs quickly and then polymerizing them with antimony trioxide at temperatures at which the resultant PEN is stable. PEN polymerized from ENCs showed the same thermal behavior as did the commercial one.

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