Synthesis and Ring-Opening Polymerization of Poly(alkylene 2,6-naphthalenedicarboxylate) Cyclic Oligomers

Patricia Hubbard and William J. Brittain*

Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

William J. Simonsick, Jr., and Charles W. Ross, III

Marshall R&D Laboratory, DuPont, Philadelphia, Pennsylvania 19146

Received June 11, 1996; Revised Manuscript Received October 4, 1996[⊗]

ABSTRACT: Cyclic oligomers of poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) and poly(butylene 2,6-naphthalenedicarboxylate) (PBN) were prepared by reaction of 2,6-naphthalenedicarbonyl dichloride with the corresponding diol. The structures of the cyclic oligomers were confirmed by a combination of GPC, mass spectrometry, and NMR analysis. The PEN cyclics were obtained in 57% yield with a preponderance of the cyclic trimer. The PBN cyclics were obtained in 75% yield with a preponderance of the cyclic dimer. Ring-opening polymerization of either cyclic material was performed in the melt using either a tin or titanium catalyst. The inherent viscosity of PBN or PEN prepared via ring-opening polymerization was lower than that of commercial samples.

Background

Polyesters based on 2,6-naphthalenedicarboxylate have gained commercial importance in recent years because of their good mechanical properties including high tensile strength and high modulus. Similar in structure to poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), the corresponding naphthalate polyesters offer the added advantage of higher glass transition (T_g) and melt (T_m) temperatures; for example, the T_g for poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) is 120 °C, which is 40 °C higher than PET. The higher T_gs make naphthalate polymers more useful for a broad range of applications, such as magnetic tape, medical parts requiring steam sterilization, and hot food containers.

Polyesters based on 2,6-naphthalenedicarboxylate are typically prepared either by solution polymerization[1] or by ester interchange in the melt.[2] The resulting polymers can be difficult to process, with melting points of 246 °C for poly(butylene 2,6-naphthalenedicarboxylate) (PBN) and 260 °C for PEN[3] and high melt viscosities. An alternative to these processes would be the ring-opening polymerization of cyclic oligomers under solvent-free conditions. The ring-opening polymerization of cyclic oligomers has the advantage that the naphthalate polymer can be prepared from low-viscosity precursors. Extensive work by Brunelle has shown the utility of cyclic oligomers for the synthesis and processing of Bisphenol A polycarbonate.[4] Similarly, Brunelle and co-workers[5,6] have developed reliable methods to prepare polyester and polyarylate cyclic oligomers with yields up to 85% at final concentrations >0.5 M using an amine-catalyzed reaction under pseudo-high-dilution conditions. We have initiated a program[7] to define the synthetic scope and utility of cyclic 2,6-naphthalenedicarboxylate oligomers. Our first goal was to produce laboratory quantities of the cyclic oligomers and test their viability as low-viscosity precursors to PEN and PBN.

Results

Poly(butylene 2,6-naphthalenedicarboxylate). Adapting the method of Brunelle and co-workers,[5] PBN cyclics were prepared by reaction of 2,6-naphthalenedicarbonyl chloride with 1,4-butanediol using diazabicyclo[2.2.2]octane (DABCO) as an acid acceptor and catalyst, as shown in Scheme 1. The PBN polymer is insoluble in dichloromethane and can be separated from the oligomers by filtration. The yield of PBN cyclics was 75%; we attribute the remainder of the mass balance to polymer. GPC analysis of the cyclic oligomers reveals several individual peaks with the largest observed at the highest elution volume (Figure 1A).

Confirmation of the cyclic nature of the products was based on the absence of end groups in the ^{1}H NMR and mass spectrometry (MS) (Figure 2A). Potassium ionization of desorbed species (K^+IDS) with mass spectrometric detection is a soft ionization technique affording pseudomolecular ions in the form of $[M]K^+$ with little or no fragmentation.[8] Intact organic molecules are desorbed by rapid heating. In the gas phase the organic molecules are ionized by potassium attachment. Little energy is imparted to the ions, thereby producing exclusively molecular ions. Potassium ions are produced by thermionic emission of K^+ from an aluminosilicate matrix that contains K_2O. Recently, we have found that K^+IDS is useful for the characterization of polyfunctional alkoxysilanes. Both linear and cyclic species produced during a synthesis were characterized in a single K^+IDS experiment.[9] K^+IDS analysis of the cyclic PBN sample revealed cyclic dimer (m/z = 579, $[M]K^+$) as the most abundant material, with a small peak for cyclic trimer (m/z = 849, $[M]K^+$) also observed. Traces of linear oligomers were observed at m/z = 597 (cyclic dimer plus H_20) and m/z = 669 (cyclic dimer plus 1,4-butanediol). Based upon peak area measurements in the mass spectrum, we estimate that the cyclic dimer is accompanied by ≈3% linear oligomers. Based on the MS analysis, we have assigned the peaks in the GPC so that we can estimate the distribution of cyclic oligomers (Table 1). This approach has been successfully applied to the analysis of low molecular weight poly(ethylene oxide) oligomers. The cyclics begin to melt near 150 °C and form a clear, homogeneous liquid at 220 °C (Figure 3A).

The PBN cyclics were polymerized using dibutyltin oxide catalyst. As expected, the resulting polymer was insoluble in THF, so GPC analysis in this solvent was

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

S0024-9297(96)00850-9 CCC: $12.00

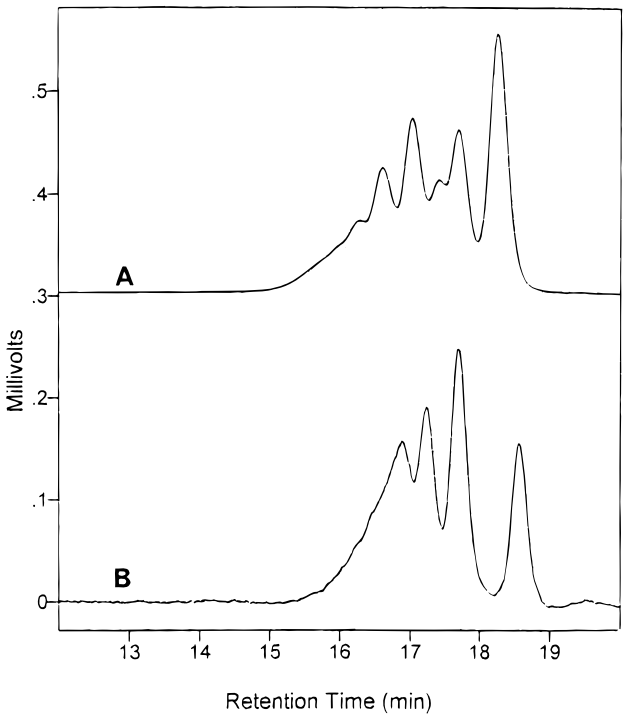
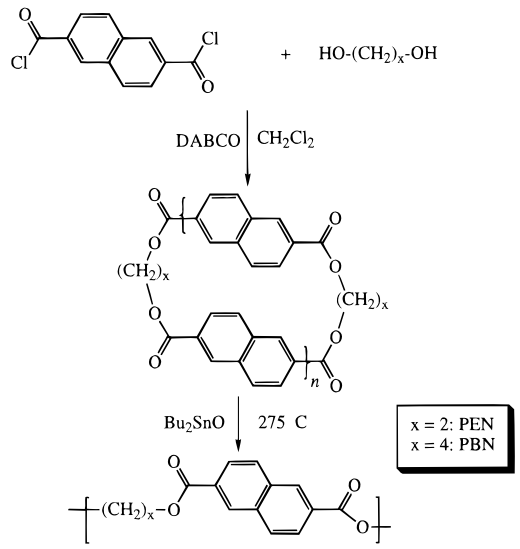


Figure 1. Gel permeation chromatography traces of PBN (A) and PEN (B) cyclic oligomers.

Scheme 1



not possible. The change in solubility and thermal properties (T_g and T_m) are consistent with conversion to polymer (Figure 3A). The polymer showed a melt endotherm near 240 °C, comparable to a commercial PBN polymer. The inherent viscosity of the PBN prepared from cyclic oligomers was 0.28 dL/g, which is lower than the commercial sample (0.69 dL/g). The lower viscosity of PBN prepared from cyclics may originate from two possible sources: (1) traces of linear oligomers in the cyclic PBN which act as chain-transfer agents, and (2) decomposition of the tin catalyst during ring-opening polymerization.

Poly(ethylene 2,6-naphthalenedicarboxylate). PEN cyclics were prepared in an analogous manner to PBN cyclics (Scheme 1). The yield of the cyclic PEN was 57%. GPC analysis was consistent with low molecular weight oligomers (Figure 1B). Laser desorption Fourier transform mass spectrometry (LD/FTMS) con-

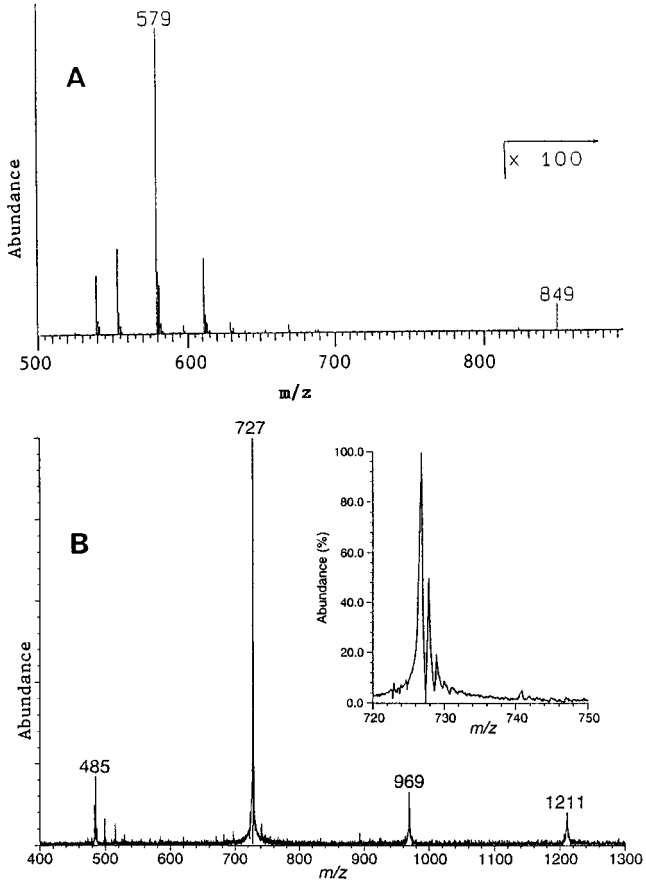


Figure 2. Mass spectrometry analysis for PBN (A) and PEN (B) cyclic oligomers.

Table 1. Molecular Weight Analysis and Ring Size Distributions[a] for Cyclic Oligomers

	PEN	PBN
% cyclic dimer	19	37
% cyclic trimer	34	19
% cyclic tetramer	27	21
% cyclic pentamer	20	14
% cyclic hexamer		9
M_n [b]	640	510
M_w [b]	840	630

[a] Ring size distribution based on GPC peak heights, distribution normalized to 100%. [b] Measured by GPC and calibrated against polystyrene standards, units in g/mol.

firmed the presence of cyclic oligomers. Under LD/FTMS conditions, ions are seen as protonated molecular ions. Figure 2A presents these data and shows the presence of cyclic dimer (m/z = 485, $[M]H^+$) through pentamer (m/z = 1211, $[M]H^+$). The inset of Figure 2A expands the region around the protonated trimer; the isotopic pattern corroborates our structural assignment. There were no peaks attributable to linear oligomers present in the MS analysis (see the Figure 2A inset for absence of peak at 745, which would correspond to the parent peak plus water); the level of detection is less than 1%. The most abundant oligomer in the PEN cyclics is cyclic trimer. Based on the MS analysis, we can assign the peaks in the GPC trace to individual oligomers and estimate the ring size distribution (Table 1). The calibration of GPC using LD/FTMS data has been previously suggested,[10] and we used this approach for the cyclic naphthalates. Thermal analysis of the PEN cyclics shows a small T_g peak near 35 °C and a crystallization exotherm near 125 °C, followed by a broad melt endotherm from 250 to 285 °C.

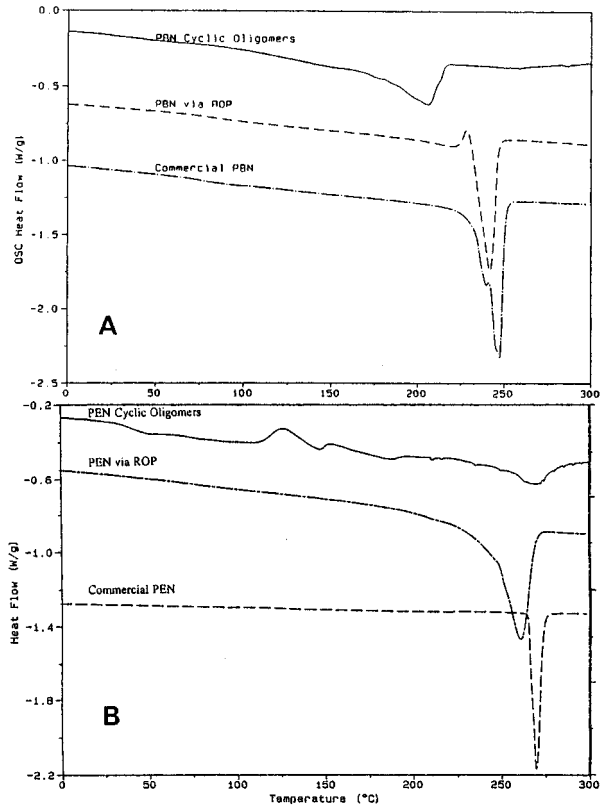


Figure 3. Differential scanning calorimetry analysis of PBN cyclics and polymer (A) and PEN cyclics and polymer (B).

The best results for the ring-opening polymerization of PEN cyclics were obtained using 1 mol % titanium(IV) propoxide and heating the mixture in the melt at 295−300 °C for 25 min. Thermal analysis of the PEN produced from ring-opening polymerization revealed a melting endotherm at 261 °C, which is nearly identical to the value for a commercial sample of PEN (Figure 3B). The inherent viscosity of the PEN from ring-opening polymerization was 0.24 dL/g, which is approximately half the value of the inherent viscosity for commercial PEN (0.50 dL/g).

Discussion

We have demonstrated the feasibility of using the ring-opening polymerization of cyclic oligomers to produce PEN and PBN. These preliminary experiments produced good yields of the cyclic oligomers without a serious effort to optimize the preparative conditions. Ring-opening polymerization produced the corresponding polymers.

A motivation for using cyclic oligomers to produce PEN and PBN is the potential advantage of reactive processing. Ring-size distributions in the PEN and PBN cyclics are dominated by smaller rings (trimer and dimer, respectively). Interestingly, the most abundant oligomer for PEN cyclics was trimer while the dimer was the most abundant for PBN cyclics. As has been discussed in the literature,[11,12] the ring-size distribution of cyclic oligomers has a direct effect on the processing window. For example, the cyclic dimer, trimer, tetramer, and pentamer of poly(ethylene terephthalate) have individual melting points of 228, 318, 324, and 252 °C.[13] Likewise, the individual cyclic oligomers of poly(butylene terephthalate) have melting points of 193, 168, and 248 °C for the cyclic dimer, trimer, and tetramer.[14] Consequently, the preponderance of one cyclic oligomer can have the effect of increasing the required processing temperature for the ring-opening polymerization of cyclic oligomers.

In our study of PBN and PEN, we have found it necessary to perform the ring-opening polymerizations in the range of 275−300 °C. We believe that this may reflect the high proportion of dimer and trimer present in the cyclic oligomer mixtures. For example, the PEN cyclics show a melting endotherm near 260 °C. Nevertheless, the viscosity of the cyclics is low at these elevated temperatures (based on visual observations using a hot stage), which still makes them promising as low-viscosity precursors. One element of our larger research effort in the cyclic oligomers is understanding the relationship between macrocyclization conditions and ring-size distribution. In the present case, it is possible that changes in the feed rate will alter the partitioning between intermolecular (chain extension) and intramolecular (cyclic oligomer formation) reactions.

While we obtained PEN and PBN with lower values for inherent viscosity compared to commercial samples, we believe that changes in catalyst structure[15] and the removal of linear oligomers from the cyclics will produce polymers with higher inherent viscosities. Part of our current effort is directed toward this goal as well as expanding the synthetic scope of cyclic oligomers to other polyester families.

Experimental Section

General Procedures and Materials. IR spectra were recorded in dichloromethane with a Nicolet System 730 spectrometer. Mass spectral data were obtained using K^+IDS, potassium ionization of desorbed species (Finnigan 4615B GC/MS System), or LD/FTMS, laser desorption Fourier transform mass spectrometry (Finnigan FTMS 2001 System equipped with a Tachisto CO_2 laser). DSC scans were made on a TA Instruments 2920 DSC with a heating rate of 15 °C/min and a nitrogen purge. Reported data are from second heating scans, where the first heating scans were run to establish uniform thermal histories. ^{1}H NMR spectra were taken in $CF_3COOD/CDCl_3$. Gel permeation chromatography (GPC) was performed with a Waters system using two PLgel 5 mm MIXED-D columns with THF eluent at a flow rate of 1 mL/min. Melting points were measured using a Haake Buchler melting point apparatus. Inherent viscosities (η_{inh}) were measured in 60/40 (w/v) phenol/tetrachloroethane.

Commercial samples of PEN and PBN were obtained from Amoco Chemical Co. Dichloromethane was distilled from P_2O_5. Tetrahydrofuran was distilled from benzophenone/sodium. Unless noted otherwise, all other reagents were used as received.

Poly(butylene 2,6-naphthalenedicarboxylate) Cyclic Oligomers. A 500 mL round-bottom flask with a magnetic stirrer, addition funnel, syringe pump, and argon inlet was charged with a solution of DABCO (1.40 g, 0.0125 mol) in 100 mL of dichloromethane. A solution of 2,6-naphthalenedicarbonyl dichloride (1.27 g, 0.005 mol), prepared by reaction of the diacid with thionyl chloride, in 100 mL of dichloromethane was added via the addition funnel over 30 min at 0 °C. A solution of 1,4-butanediol (0.45 g, 0.005 mol) in 10 mL of THF was added simultaneously. After the reaction was quenched with methanol, 1 M HCl was added to the reaction flask. Any polymer formed was filtered off, the aqueous layer was extracted with dichloromethane, and the organic

layer was washed with dilute HCl and NaCl solutions and then evaporated to dryness. Crude yield = 75%; IR (CH_2Cl_2): 1716 cm^{-1} (C═O); ^{1}H-NMR (200 MHz, $CF_3COOD/CDCl_3$): δ 8.7 (2H, s), 8.1 (4H, m), 4.7 (4H, 2), 2.2 (4H, s); η_{inh} not measurable (i.e. no increase in viscosity of solvent on addition of cyclics).

PBN Polymer. In a 50 mL flask, PBN cyclics (0.50 g) were intimately mixed with dibutyltin oxide (0.0048 g, 1.9×10^{-5} mol) in dichloromethane. After removal of the solvent, the flask was heated for 15 min at 275 °C to afford polymer; η_{inh} = 0.28 dL/g (compared with 0.69 dL/g for commercial PBN received from Amoco).

Poly(ethylene 2,6-naphthalenedicarboxylate) Cyclic Oligomers. PEN cyclic oligomers are prepared according to the method used for PBN cyclics, with a final yield of 57%; IR (CH_2Cl_2): 1716 cm^{-1} (C═O); ^{1}H-NMR (200 MHz, $CF_3COOD/CDCl_3$): δ 8.8 (2H, m), 8.2 (4H, m), 5.0 (4H, 2), 4.2 (4H, s); η_{inh} not measurable (i.e. no increase in viscosity of solvent on addition of cyclics).

PBN Polymer. In a 50 mL flask, PEN cyclics (0.1624 g) were intimately mixed with titanium(IV) propoxide (6.7×10^{-6} mol) in dichloromethane. After removal of the solvent, the flask was heated for 25 min at 295−300 °C using a salt bath (1:1 (w/w) $NaNO_3$/KNO_3) to afford polymer; η_{inh} = 0.24 dL/g (compared with 0.50 dL/g for commercial PBN received from Amoco).

References and Notes

(1) Kato, T.; Kabir, G.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1447.
(2) Wiener, M. V. U.S. Patent 3 377 319, 1968.
(3) Duling, I. N. U.S. Patent 3 436 376, 1969.
(4) *Ring-Opening Polymerization/Mechanisms: Catalysis, Structure, Utility*; Brunelle, D. J., Ed.; Carl Hanser Verlag: Munich, 1993; Chapter 11.
(5) Brunelle, D. J.; Bradt, J. E. U.S. Patent 5 039 783, 1991. Brunelle, D. J.; Bradt, J. E. U.S. Patent 5 214 158, 1993.
(6) Brunelle, D. J.; Shannon, T. G. U.S. Patent 4 757 132, 1988. Guggenheim, T. L.; McCormick, S. J.; Kelly, J. J.; Brunelle, D. J.; Colley, A. M.; Boden, E. P.; Shannon, T. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30 (2)*, 579.
(7) Wilson, P. A.; Brittain, W. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36 (2)*, 136. Hubbard, P. A.; Brittain, W. J.; Simonsick, W. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37 (1)*, 238.
(8) Simonsick, W. J., Jr. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1989**, *43*, 257.
(9) Michalczyk, M. J.; Simonsick, W. J., Jr.; Sharp, K. G. *J. Organomet. Chem.*, in press.
(10) Nuwaysir, L. M.; Wilkins, C. L.; Simonsick, W. J., Jr. *J. Am. Soc. Mass. Spectrom.* **1990**, *1*, 66.
(11) Brunelle, D. J. *Makromol. Chem., Macromol. Symp.* **1992**, *64*, 65.
(12) Mullins, M. J.; Woo, E. P.; Murray, D. J.; Bishop, M. T. *CHEMTECH* **1993**, 25.
(13) Shiono, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 4123.
(14) East, G. C.; Girshab, A. M. *Polymer* **1982**, *23*, 323.
(15) Brunelle, D. J.; Takekoshi, T. U.S. Patent 5 407 984, 1995.

MA960850S