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Thermal polymerization of uniform macrocyclic ethylene terephthalate dimer

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Abstract

Thermal ring-opening polymerization of uniform macrocyclic ethylene terephthalate dimer was examined at various temperatures above its melting point. From SEC study, it can be indicated that the polymerization proceeded through chain reaction, not through a typical polycombination reaction. Maximum molecular weight of the polymer obtained under optimum reaction conditions reached to a sufficiently high level of more than 20,000 (M_w). It is noteworthy that this new reaction for synthesizing poly(ethylene terephthalate) progresses without any catalyst under atmospheric pressure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Macrocyclic oligomer; Ring-opening polymerization

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1. Introduction

Cyclic oligomers have been of much interest as starting materials for entropically driven ring-opening polymerization [1–3]. Polymers thus obtained are expected to contain no monomer moiety which sometimes lowers the physical or optical properties of polymers. In addition ring-opening polymerization of some cyclic oligomers could lead to ultrahigh molecular weight polymers with M_w more than two million which is about 20 times higher than that obtained by conventional polycondensation [4–9].

Poly(ethylene terephthalate) (PET) is one of the most important thermoplastic polymers for synthetic fibers and plastics. It is reported that the commercial PET prepared by conventional step-growth polycondensation without solvent contains typically 1–3% of cyclic oligomer fractions which are composed of a mixture of $(CO–C_6H_4–CO–O–CH_2–CH_2–O)_n$ with $n = 2–10$ [10–22]. These macrocyclic oligomers are generated, as is commonly known, by: (1) the cyclization of the linear oligomers; (2) cyclodepolymerization proceeding from the chain ends, or “back-biting”; and (3) by exchange–elimination reactions occurring randomly within or between polymer chain ester groups, or “pinch-out”. The macrocyclic ethylene terephthalate trimer is particularly stable and it is a major component of the cyclic oligomer mixture. Most of the reports about cyclic oligomers of PET have focused on quantities and characterizations of the oligomers above the trimer ($n \geq 3$). Thus, except for few reports, presence of cyclic dimer is not a matter of common knowledge [17]. In the extract, dimer is present in very small quantities, however, to our knowledge sublimate obtained from the products or inside of the production equipment is mostly dimeric.

In 1960, Goodman and Nesbitt [11] reported that polymerization of ethylene terephthalate macrocyclic trimer catalyzed by antimony oxide at 306°C resulted in a polymer ($[\eta] = 0.67$), in 15 min. They also polymerized the macrocyclic dimer with an excess diethylene glycol unit for 1 h at 275°C using the same catalyst and obtained a high melting polymer. In 1998, in a similar investigation, Brunelle et al. [23,24] reported that polymerization of mixtures of alkylene phthalate macrocyclic oligomers using tin or titanium catalysts affords high molecular weight polymers within minutes. However, because melting point of homo-oligocyclic ethylene terephthalate mixture was observed as high as above 300°C, most of the studies are focused on melt polymerization of oligocyclic butylene terephthalate mixture (melting point 185°C) or cocyclics with oligoethylene terephthalate (melting point 175°C). Recently,

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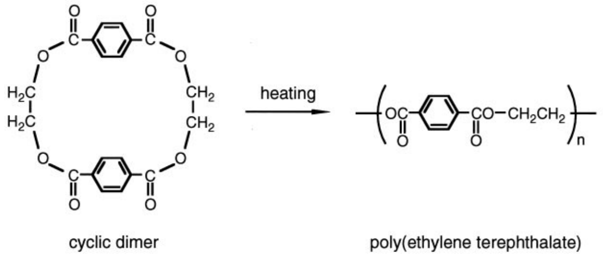

Scheme 1.

Youk et al. [25] reported that an ethylene terephthalate macrocyclic oligomer mixture ($n = 3$–7) can be polymerized without adding any catalyst resulting in a polymer of M_n 4800. This was considered to be caused by the presence of residual catalyst, which is impossible to remove completely. Furthermore, to our knowledge there is no report on investigation about ring-opening polymerization of uniform macrocyclic ethylene terephthalate dimer.

In the present work, we attempted the ring-opening polymerization of ethylene terephthalate macrocyclic dimer without any catalyst with the aim of developing a new synthetic process for advanced PET (Scheme 1). Dimer used in this study was obtained from the polymer sublimate received from a PET production site. Presently, PET is generally produced by direct esterification of terephthalic acid or transesterification of dimethyl terephthalate with metal catalysts in vacuo. However, synthesis by our method does not need vacuum as no side-products are formed during this process. In addition, this method is expected to yield a polymer with improved physical properties since it will not contain any residual monomers.

2. Experimental

2.1. Materials and measurements

The crude dimer was obtained from a tenter at the PET films production site of a domestic company and purified by fractional crystallization using benzene, methanol, and chloroform. From gas chromatography analysis purity was confirmed to be more than 99.99%. The structure was determined by electrospray ionization time-of-flight (ESI-TOF) mass spectrometry and X-ray crystallographic analysis [26]. ESI-TOF mass spectrometry: calcd. for $C_{20}H_{16}O_8H^+$ (monoisotopic), 385.0918 $[M + H]^+$ m/z; found, 385.0927 $[M + H]^+$ m/z. Crystal data for the macrocyclic dimer: $C_{20}H_{16}O_8$, $M_w = 384.34$, crystal size $0.6 \times 0.6 \times 0.3$ mm^3, monoclinic, space group $P2_{1/c}$ $a = 8.5383(6)$, $b = 12.666(2)$, and $c = 7.9787(6)$ Å $\beta = 90.714(4)°$, $V = 862.8(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.464$ g/cm^3. The intensity data were collected on a Rigaku R-AXIS-RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation, λ(Mo Kα) = 0.71069 Å, ω-scan, $\mu = 1.15$ cm^{-1}, 10,952 measured ($-10 \leq h \leq 11$, $-16 \leq k \leq 15$, $-9 \leq l \leq 10$, $2\theta(\max) = 55.0°$) and 2050 unique reflections ($R_{int} = 0.031$). The structure was solved by direct method (SIR92) [27]. $F(000) = 392.00$; 1170 observed reflections ($I \leq 3\sigma(I)$) were used for the

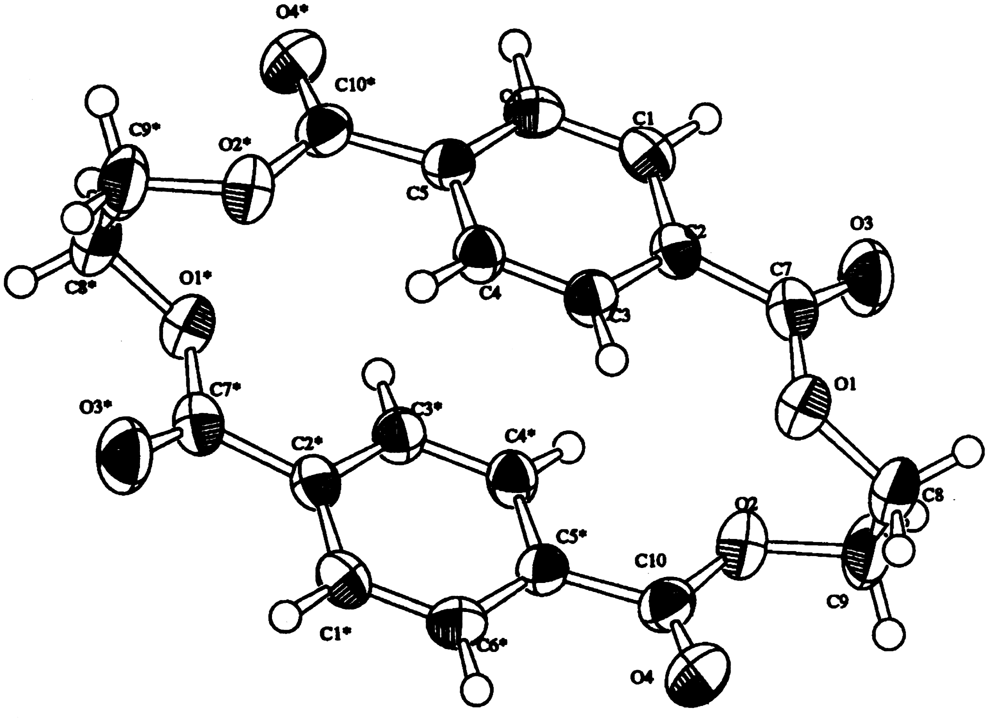

Fig. 1. X-ray structure of macrocyclic ethylene terephthalate dimer.

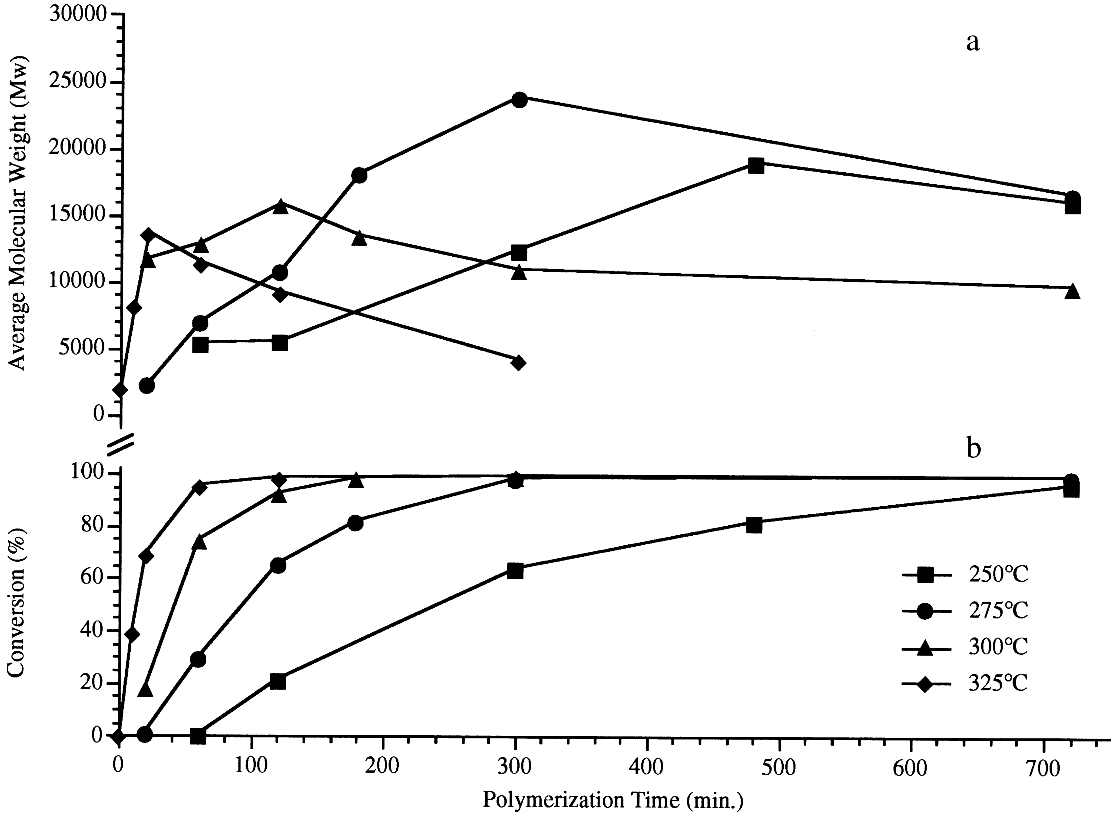

Fig. 2. Effect of polymerization time on: (a) average molecular weight; (b) conversion.

refinement. Refinement on F, number of parameters = 127. The positions of the hydrogen atoms were calculated in ideal positions and their positions were not refined. $R = 0.036$ ($R_w = 0.042$, $w = 1/\sigma^2(F_o)$). Residual electron density: 0.17, $-0.29e$ Å^{-3}. All calculations were performed using the teXsan 1.9 (crystallographic software package of Molecular Structure Corporation (1985 and 1992)).

2.2. Instruments

ESI-TOF mass spectrometer (PE Biosystems Mariner) was used for the molecular weight analysis of macrocyclic dimer. A matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer (Shimadzu/Kratos Kompact MALDI III) was used for the molecular structure analyses of the polymerization products using 2,5-dihydroxybenzoic acid as a matrix, and hexafluoro-2-propanol (HFIP) as a solvent. Crystal data for macrocyclic dimer was collected on a Rigaku R-AXIS-RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. Size exclusion chromatography (SEC) analyses were performed with a JASCO GULLIVER system coupled with a Shodex K-804L column and a ultraviolet detector set at 254 nm. The mobile phase was chloroform and data was recorded at 35°C at a flow rate of 1 ml/min. Weight-average molecular weights (M_w) were estimated by comparison with polystyrene standards. Polymer samples were dissolved in 50% (v/v) HFIP/chloroform and 2% (v/v) samples were injected.

2.3. Ring-opening polymerization of macrocyclic ethylene terephthalate dimer

Polymerization reaction was carried out by heating the macrocyclic dimer under nitrogen without catalysts on a programmed heating device (Seiko Instruments Inc. SSC5100). Ground macrocyclic dimer (1.3–1.6 mg) was placed on the aluminum pan with simple seal and heated from 20°C to the holding temperature at a rate of 10°C/min, then held at the final temperature for the required time. Conversion percentage and molecular weights of the polymer were determined by SEC.

3. Results and discussion

Single crystal X-ray refraction data of the macrocyclic ethylene terephthalate dimer was analyzed as shown in Fig. 1. As the crystal was found to be completely solvent free, it is assumed that aperture of the molecule center might not be large enough to trap a benzene molecule. Crystal of macrocyclic ethylene terephthalate dimer seems to be relatively stabilized because of the flexibility of ethylene glycol bonds. The mean planes of both benzene rings were parallel

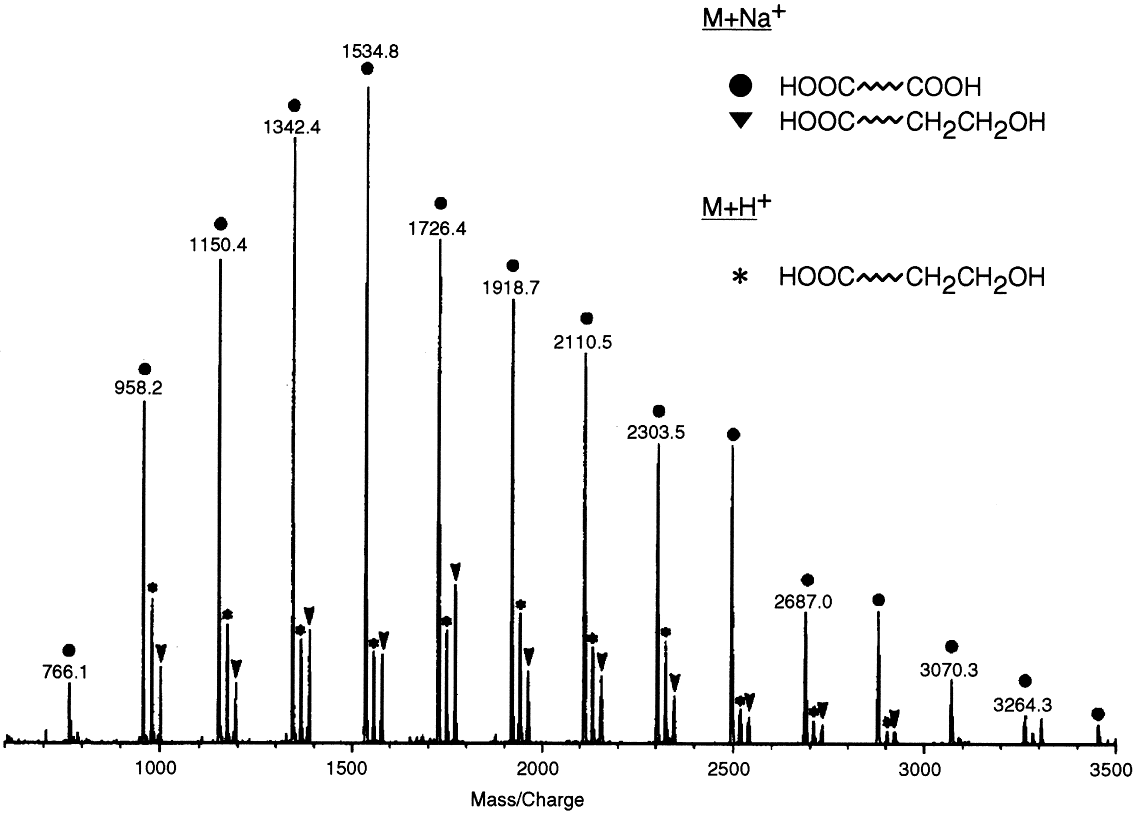

Fig. 3. MALDI-TOF mass spectrum of the polymer obtained by thermal polymerization of macrocyclic ethylene terephthalate dimer without catalyst.

and both ethylene glycols were arranged in the gauche configuration.

Purified uniform macrocyclic dimer was dried completely under vacuum at 70°C overnight. The dried dimer was ground as fine as possible using a pestle and mortar and the ground powder was then kept in an aluminum pan generally used for DSC analysis. The pan was simply sealed with the exclusive sample sealer, and heated from 20°C to the required temperature at a rate of 10°C/min in a furnace under nitrogen atmosphere. When an open pan was used, some part of the starting material sublimed during the heating process. Different reports have quoted different melting points of the dimer ranging from 175 to 229°C [13,17,26]. In the present work we estimated its melting point as 225°C on the basis of DSC analysis, therefore melt polymerization was carried out at or above 250°C.

At 250°C, polymerization progressed very slowly, and after 8 h of heating, a polymer of M_w 19,200 could be obtained in 83% yield. In order to see the effect of reaction time on polymer yield and molecular weight, when reaction time was extended to 12 h, conversion increased to 100% but a drop in M_w (16,300) was observed. On increasing the reaction temperature to 275°C, complete conversion could be attained in approximately 5 h and a polymer of M_w 24,000 and M_w/M_n 1.8 was obtained. When the reaction temperature was raised to 300°C, reaction became much faster and a polymer of M_w 16,000 and M_w/M_n 1.7 could be obtained in as high yield as 93% within 2 h. Further increase in reaction temperature to 325°C increased the reaction rate and 70% conversion could be attained in a short span of only 20 min. However, simultaneous pyrolysis reaction decreased the molecular weight of the final product to a level of M_w 13,700 ($M_w/M_n = 1.6$). Therefore, it can be concluded that extremely high temperatures are unsuitable for present polymerization reaction. All the products were yellow-colored solids and soluble in HFIP or 50% (v/v) HFIP/chloroform. Longer reaction times imparted more yellow color to the product and resulted in decrease in M_w, probably due to degradation.

Dependence of molecular weight and percent conversion on the reaction temperature and time are shown in Fig. 2. At lower reaction temperatures comparatively longer reaction times were required to achieve high molecular weight and high conversion, whereas at high reaction temperatures reaction progressed at very fast rate. Maximum M_w of 24,000 was obtained at 275°C in 5 h. Any further increase in reaction temperature or reaction time at the same temperature resulted in a decrease in the M_w. Polymer molecular weights attained by this route are in the practically usable range, and there is a possibility of further improvement if appropriate catalysts are used. Such efforts are currently underway.

SEC traces of the polymers obtained in different reaction times exhibited only two separate peaks; one for the starting material (dimer) and other for the polymer. With increased reaction times, as the polymerization proceeded, the polymer peak grow, while the area of peak corresponding to the dimer kept decreasing. Thus, it can be indicated that the polymerization proceeded through chain reaction, not through typical polycombination reaction. Detailed investigation about the mechanism of this reaction was not carried out. However, presumably the alkoxide ion generated by scission of the ester linkage of the cyclic dimer initiates the reaction by attacking the ester carbonyl of other macrocyclics or linear chains. Fig. 3 shows the MALDI-TOF mass spectrum of the polymer obtained by polymerization at 325°C for 120 min. Spectra of the various products obtained by using different conditions were indistinguishable. Sodium adducts and protonated positive ions were detected within the mass range of $m/z < 5000$. Although SEC analysis confirmed that the products of M_w higher than 5000 were main components, corresponding molecular ions-related peaks could not be detected in the MALDI spectra under present analytical conditions. In the MALDI spectrum, it was observed that transesterification and/or degradation after polymerization resulted in components of even and odd repeat units equally. The spectrum also showed peaks corresponding to two types of oligomeric series differing in their end groups. One series had –COOH groups at both the chain terminals whereas the other series had –COOH at one end and $-CH_2CH_2OH$ at the other. Components with –COOH groups at both the chain ends might be caused by chain scission at the ester linkage of resulting polymer. Moreover, since this spectrum belongs to low molecular weight fraction, effect of degradation i.e. polymer chains with –COOH group at both ends appear to be dominant and this might not be the case for high molecular weight polymer.

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