BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1687—1689 (1968)

Ring-opening Polymerization of the Macrocyclic Ester

Kentaro YODA and Kazuyuki KIMOTO

Katata Research Institute, Toyobo Co., Ltd., Honkatata-cho, Otsu

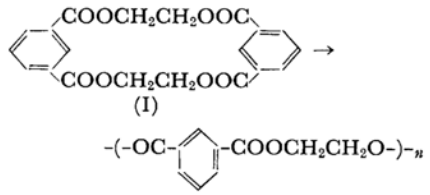
(Received January 10, 1968)

The ring-opening polymerization of cyclic bis(ethylene isophthalate) (I) was carried out in the presence of various metallic compounds as catalysts. Among the polycondensation catalysts for ethylene terephthalate, antimony and tin compounds were very effective in the ring-opening polymerization of I. On the other hand, titanium, zinc, calcium, and aluminum compounds did not show high catalytic activity. The polymerization of I proceeded even at temperatures below the melting point of I. As the melting point of the resulting poly(ethylene isophthalate) was much lower than the polymerization temperature, the reaction system gradually melted in consequence of the progress of the polymerization reaction.

With regard to the macrocyclic esters of aliphatic carboxylic acids, many investigations[1,2] have been carried out. Recently, the presence of families of macrocyclic oligoesters containing aromatic nuclei has been demonstrated in a number of technically important synthetic polyester resins.[3-6] On the other hand, it is well known that some cyclic esters with more than two ester groups, such as lactide, glycolide, and salicylide, can be polymerized to produce linear polyesters by the use of a metallic compound as the catalyst.[7-11]

Goodman and Nesbitt[5] obtained poly(ethylene terephthalate) by the ring-opening polymerization of macrocyclic oligo(ethylene terephthalates).

The present paper will be concerned with the ring-opening polymerization of cyclic bis(ethylene isophthalate)[4] (I) by various catalysts.



(I)

Experimental

The melting points were determined on a Yanagimoto electric micromelting-point apparatus. All the melting points are uncorrected. The infrared absorption spectra were obtained in a KBr disk using a Hitachi EPI-S2 infrared spectrophotometer. The NMR spectra were taken in trifluoroacetic acid, using tetramethylsilane as the external reference, on a Varian A-60 NMR spectrometer; their chemical shifts are presented in terms of δ values. All the solvents were purified and dried according to the ordinary methods.

Catalysts. Calcium acetate and zinc acetate, G. R. grade, were obtained from Nakarai Chemicals. Antimony trioxide, G. R. grade, was obtained from E. Merck AG. Di-*n*-butyltin oxide and di-*n*-butyltin dibenzoate were supplied by Yoshitomi Pharmaceutical Industries. Aluminum butoxide, triphenyl stibine, and titanium tetraglycoxide were prepared according to known procedures.[12-14]

Cyclic Bis(ethylene isophthalate) (I). The ring dimer of ethylene isophthalate was prepared by a procedure described in the literature[4] and was purified by vacuum sublimation, followed by recrystallization from dimethylformamide; mp 326—328°C (lit. 325—327°C).

Found: C, 62.75; H, 4.19%. Calcd for $C_{20}H_{16}O_8$: C, 62.50; H, 4.20%.

The infrared spectrum and the NMR spectrum of I are shown in Figs. 1 and 2 respectively. A fine powder (smaller than 200 mesh) of I was used as the starting material in the polymerization experiments.

The General Procedure for the Polymerization of I. A mixture of I and a catalyst was placed in a glass ampoule under a nitrogen atmosphere. Then the system was evacuated twice and sealed under a nitrogen flow. The polymerization was carried out

1) H. Mark and G. S. Whitby, "Collected Papers of W. H. Carothers on High Polymeric Substances," Interscience Publishers, Inc., New York (1940), pp. 141, 212, 221, 248, 259, 265.
2) J. Dale, *J. Chem. Soc.*, **1965**, 72.
3) S. D. Ross, E. R. Coburn, W. A. Leach and W. B. Robinson, *J. Polymer Sci.*, **13**, 406 (1954).
4) C. E. Berr, *ibid.*, **15**, 591 (1955).
5) I. Goodman and B. F. Nesbitt, *Polymer*, **1**, 384 (1960).
6) S. Hashimoto and J. Sakai, *Kobunshi Kagaku (Chem. High Polymers)*, **23**, 422 (1967).
7) C. E. Lowe, U. S. Pat. 2668162 (1954).
8) J. Kleine and H. H. Kleine, *Makromol. Chem.*, **30**, 23 (1959).
9) T. Turuta, K. Matsuura and S. Inoue, *ibid.*, **75**, 211 (1964).
10) K. Hirono, G. Wasai, T. Saegusa and J. Furukawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 604 (1964).
11) A. K. Schneider, U. S. Pat. 2696481 (1954).
12) W. G. Young, W. H. Hartung and F. S. Crossley, *J. Am. Chem. Soc.*, **58**, 100 (1936).
13) G. S. Hiers, "Organic Syntheses," Coll. Vol. I, p. 550 (1956).
14) D. F. Herman, U. S. Pat. 2654770 (1953).

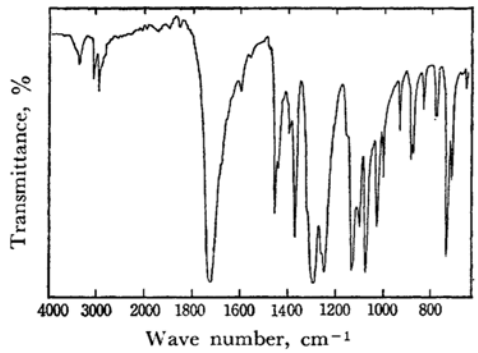


Fig. 1. Infrared spectrum of cyclic bis(ethylene isophthalate).

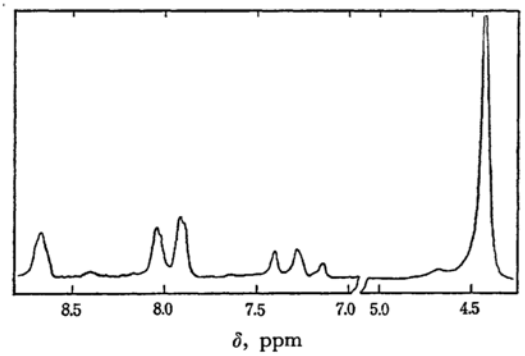


Fig. 2. NMR spectrum of cyclic bis(ethylene isophthalate).

at a given temperature for a definite period. The polymer produced was dissolved in chloroform, and the insoluble, unpolymerized I was filtered off. *n*-Heptane was added to the chloroform solution to precipitate the polymer. Then the separated polymer was dried under reduced pressure. The intrinsic viscosity of the polymer was measured by an Ubbelohde's viscometer in a mixed solvent composed of phenol and tetrachloroethane (6 : 4) at 30°C.

Results and Discussion

The experimental results are shown in Table 1. The polymerization of I proceeded even at temperatures below the melting point of I. However, no polymeric material was obtained by heating I at 265°C for 120 min.

Among the polycondensation catalysts[15,16] for ethylene terephthalate, antimony and tin compounds were very effective in the ring-opening polymerization of I. However, titanium, zinc, calcium, and aluminum compounds did not show any high catalytic activity.

When antimony trioxide was used as a catalyst, a white, powder-like polymer was obtained, while a slightly brownish polymer was obtained by the use of the di-*n*-butyltin oxide catalyst. These polymers were confirmed to be poly(ethylene isophthalate) by comparing their melting points, solubilities, infrared spectra, and NMR spectra with those of the poly(ethylene isophthalate) prepared by the melt polycondensation of bis-β-(hydroxyethyl isophthalate). The infrared spectrum and the NMR spectrum of the polymer are shown in Figs. 3 and

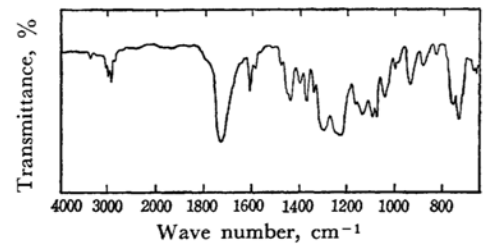


Fig. 3. Infrared spectrum of poly(ethylene isophthalate).

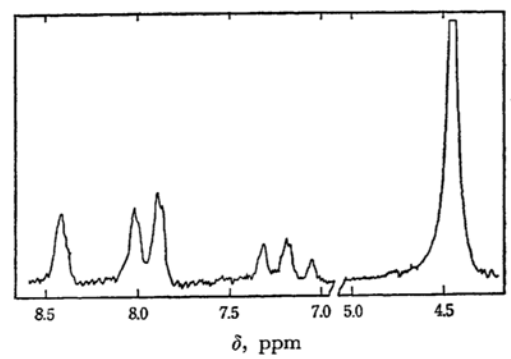


Fig. 4. NMR spectrum of poly(ethylene isophthalate).

4 respectively. In the NMR spectrum of poly(ethylene isophthalate), the complicated signals which appear at 8.42, 8.02, 7.88, 7.32, 7.20, and 7.06 ppm are due to the four protons attached to the benzene nucleus.[17] The singlet at 8.42 ppm may be due to the proton on C-2 surrounded by two ester groups. It should be noted that this singlet in the NMR spectrum of linear poly(ethylene isopthalate) shifts to 8.67 ppm in the spectrum of I (Fig. 2). The difference in the chemical shift of the proton on C-2 between linear and cyclic structures suggests that the structural conformation of a resonance system including two carbonyl groups and a benzene nucleus is different in poly(ethylene isophthalate) and in I, and that, therefore, the anisotropic effect of the resonance system is different in the linear polymer and in I.

As the melting point[18] of poly(ethylene isophthalate) was much lower than the polymerization temperature, the reaction system gradually

15) H. Zimmermann, *Faserforsch. u. Textiltechn.*, **13**, 481 (1962).
16) K. Yoda, *Kobunshi Kagaku (Chem. High Polymers)*, **24**, 472 (1967).
17) M. Murano, Y. Kaneishi and R. Yamadera, *J. Polymer Sci.*, **A3**, 2698 (1965).
18) R. Yamadera and C. Sonoda, *ibid.*, **B3**, 411 (1965)

TABLE 1. POLYMERIZATION OF CYCLIC BIS(ETHYLENE ISOPHTHALATE)

Cyclic bis(ethylene isophthalate): 1.3×10^{-3} mol
Catalyst: 1×10^{-5} mol (No. 1—23), 3×10^{-6} mol (No. 24)
2×10^{-5} mol (No. 25), 3×10^{-5} mol (No. 26)

No.	Catalyst	Temp. °C	Time min	Polymer yield, %	$[\eta]$	Mp °C
1	—	308	120	0	—	—
2	Sb_2O_3	308	120	94.5	0.50	140—143
3	Sb_2O_3	273	120	15.0	—	—
4	Sb_2O_3	265	120	trace	—	—
5	Sb_2O_3	292	20	16.2	0.21	129—131
6	Sb_2O_3	292	40	33.9	0.34	134—136
7	Sb_2O_3	292	60	86.1	0.37	133—135
8	Sb_2O_3	292	80	91.6	0.49	131—132
9	Sb_2O_3	292	120	93.0	0.50	133—135
10	Sb_2O_3	292	160	92.4	0.34	132—134
11	$SbPh_3$	308	120	78.6	0.33	118—120
12	$Ti(OC_2H_4OH)_4$	308	120	trace	—	—
13	$Al(OBu)_3$	308	120	trace	—	—
14	$Zn(OAc)_2$	308	120	trace	—	—
15	$Ca(OAc)_2$	308	120	trace	—	—
16	Bu_2SnO	265	120	trace	—	—
17	Bu_2SnO	293	120	74.6	0.21	—
18	Bu_2SnO	296	120	91.7	0.21	—
19	Bu_2SnO	321	120	84.4	0.22	—
20	Bu_2SnO	308	30	72.7	0.15	—
21	Bu_2SnO	308	60	81.3	0.26	—
22	Bu_2SnO	308	120	87.4	0.29	133—134
23	$Bu_2Sn(OBz)_2$	308	120	79.9	0.20	104—106
24	Sb_2O_3	292	40	19.8	0.21	—
25	Sb_2O_3	292	40	58.0	0.35	—
26	Sb_2O_3	292	40	62.5	0.41	135—137

melted in consequence of the progress of the polymerization reaction.

In the polymerization of I by antimony trioxide at 292°C, a high-molecular-weight polymer was obtained in spite of its low rate of conversion. Such a figure would indicate that the ring-opening polymerization of I is of a rather chain-reaction type; if so, the conversion should express the rate of polymerization. The polymerization proceeded heterogeneously, and the rate of polymerization of I was slow until the reaction time of 35 min had passed, as is shown in Fig. 5. After 35 min, the reaction system changed to a liquid and the polymerization reaction proceeded rapidly.

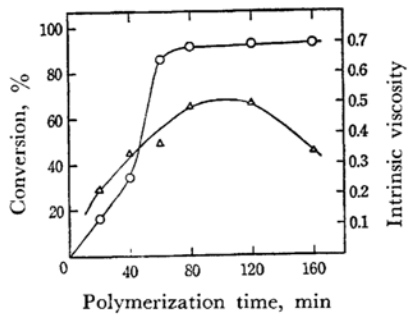


Fig. 5. Time dependences of conversion and intrinsic vicosity.
○ Conversion, △ Intrinsic viscosity
Polymerization temp. 292°C
Cyclic bis(ethylene isophthalate) 1.3×10^{-5} mol
Catalyst: Sb_2O_3 1.3×10^{-3} mol

The polymerization reaction proceeds in a heterogeneous state, and the rate of polymerization is affected by the particle size of the starting material and the degree of mixing with the catalyst. Therefore, the kinetic study is accompanied with some difficulty.

No polymeric substance was obtained by the solution polymerization of I in α-methylnaphthalene at 200°C for 600 min in the presence of diethylzinc, triethylaluminum, or triphenylstibine as a catalyst. Furthermore, an attempt at the radiation polymerization of I at room temperature by Co-60 γ-rays (total dose: 5.4×10^6R) failed.

The authors are much indebted to Mr. Murano of this Institute for the measurement of the NMR spectra.