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Polymerization of 2,6,7-Trioxabicyclo[2.2.1]Heptane with Either Contraction or Expansion

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SUMMARY

2,6,7-Trioxabicyclo[2.2.1]heptane (I) polymerizes to poly ortho ester (Poly-I) at -78°C with opening of one ring and volume shrinkage. Heating Poly-I with acid isomerized it to an open chain poly-ether formate (Poly-II); this occurred with a large volume expansion. Direct conversion of I to Poly-II by heating with acid occurred with net moderate increase. Monomer I is the first reported monomer which can be polymerized with either shrinkage or expansion as desired. Saponification of Poly-II gave Poly-III, a new water-soluble copolymer.

INTRODUCTION

It has been shown that, under vigorous conditions, spiro ortho esters (Bailey et al., 1976a) or ketal lactons (Bailey, 1975) polymerize with essentially no shrinkage during polymerization, but spiro ortho carbonates (Bailey et al., 1976b) undergo polymerization with simultaneous opening of both rings with large expansion. These are the only known monomers which polymerize with volume expansion. Brief mention was made that the atom-bridged bicyclic ortho esters 1,4-diethyl-(Bailey et al., 1978) and 4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane (Bailey et al., 1977) polymerized with a slight volume expansion, but details are not yet available.

We showed that the atom-bridged bicyclic ortho ester 2,6,7-trioxabicyclo[2.2.1]heptane (1) undergoes cationic polymerization under mild conditions (dichloromethane solution, -78°C) with opening of a single ring (Poly-I) (Yokoyama et al., 1979). In this Communication we show that (1) Polymerization of monomer to Poly-I under mild conditions occurs with shrinkage, (2) When heated with acids, Poly-I isomerizes to a completely ring-opened ether formate polymer with a large expansion in volume, (3) Direct

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polymerization of monomer to Poly-II can be carried out under vigorous conditions and occurs with a net expansion in volume, (4) Poly-II undergoes saponification to form a new water-soluble copolymer.

EXPERIMENTAL

^{1}H-NMR spectra were obtained using Varian NMR spectrometer Model EM-360L. Infrared spectra were recorded using Perkin Elmer 337 spectrophotometer. The number average molecular weight of polymer was determined using Hewlett Packard Vapor Pressure Osmometer Model 302B on solution of DMF at 37°C.

Polymerization was carried out as follows: The required amounts of monomer and trifluoromethanesulfonic acid were weighed into a small glass ampoule under argon atmosphere, and the ampoule was cooled and sealed off. Polymerization was terminated with a few ml of triethylamine-methanol (vol. ratio 1:4) and polymer was precipitated into a large amount of methanol or n-pentane. Polymer was purified by reprecipitation.

The specific volume (ml/g) of monomer and polymers were determined as follows: At each temperature, 2 ml of monomer and polymer was collected into a 2 ml cylindrical calibrated volumetric KIMAX flask used as a pycnometer and weighed at room temperature. Volume change in polymerization was calculated with use of the specific volume at each temperature.

Polymer prepared at 80°C was hydrolyzed as follows: Polymer (0.336g, 3.29×10^{-3} mol for monomer unit; MW, 2100) was dissolved in IN potassium hydroxide aqueous solution (20 ml) and the solution was refluxed for 6 hours. After neutralization, some water was evaporated and the hydrolyzed polymer was extracted with n-butanol (50 ml x 5). The n-butanol was evaporated and the residual polymer was dried under vacuum to constant weight. Yield, 0.228g, 93%; MW, 1200 (VPO, DMF, 37°C).

RESULTS

Table 1 shows results of the polymerizations and Fig. 1 shows the NMR spectra with assignments of the resulting polymers I, II, and III. From these data we propose that the known Poly-I isomerizes to Poly-II, a copolymer of 65% of [formyloxy methyl]-ethylene oxide units IIa and 35% of [2-formyloxy]trimethylene oxide units. This structural assignment is established by (1) disappearance of orthoformate proton at δ5.8 ppm, (2) appearance of formate ester peak at δ8.1 ppm (NMR) and 1735 cm^{-1} (IR), (3) methinyl absorption in IIb was visible at δ5.2 ppm and allowed the ratio IIb/II to be determined from the ratio of peak area at δ5.2 ppm:peak area at δ8.1 ppm.

The data in Table I also indicate that the main formation path of Poly-II occurs via prior formation of Poly-I.

Table II and Fig. 2 show the specific volume of monomer and polymers and the calculated volume change during the polymerization.

At temperature lower than 100°C, the specific volume of monomer is higher than that of Poly-I and lower than that of Poly-II, showing that I undergoes polymerization to form Poly-I with shrinkage at lower temperature and to form Poly-II with expansion in volume at 80°C. Maximum shrinkage for Poly-I and expansion for Poly-II are -9.8 (at 120°C) and +4.0% (at 25°C), respectively.

TABLE I

Polymerization of 2,6,7-Trioxabicyclo[2.2.1]heptane[a]

No.	Monomer g (x 10^3 mol)	Temp., °C	Time, hr	Yield, g (%)	MW	Structure of polymer
14[b]	0.894 (8.76)	-78	4	0.747 (83.6)	8300[c]	I[e] (100%)
20	0.531 (5.20)	22.5	3	0.474 (89.2)	3000	I[e] (100%)
21	0.571 (5.59)	22.5	8	0.462 (80.9)	3100	I[e] (100%)
22	0.544 (5.32)	22.5	48	0.309 (56.9)	2500	I[e] (100%)
23	0.468 (4.58)	22.5	6 days	0.210 (44.8)	1300	II[f] (100%)
24	0.503 (4.93)	80	0.5	----- (57[d])	----	I-II[f] (75-25%)
25	0.503 (4.93)	80	1	----- (100[d])	----	II[f] (100%)
26	2.604 (25.5)	80	3	2.186 (83.9)	2100	II[f] (100%)

[a] Bulk; CF_3SO_3H, 1 mol-% to monomer. [b] In CH_2Cl_2, 2 ml.

[c] 1,2-$C_2H_4Cl_2$. [d] Calculated from ^{1}H-NMR spectrum. [e] Colorless semisolids. [f] Pale tan semisolids.

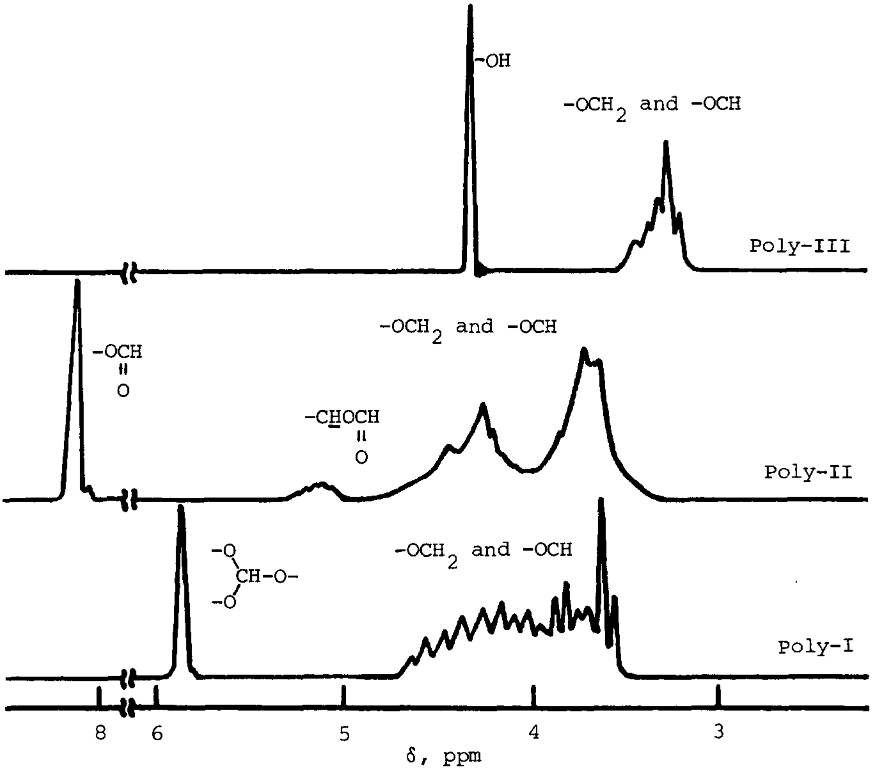


Fig. 1. NMR spectra of Poly-TOH (I). Solvent: Poly-I (sample no. 14 in Table I) and Poly-II (sample no. 26 in Table I), $CDCl_3$; Poly-III, D_2O

TABLE II

Specific Volume and Calculated Volume Change During the Polymerization

Temp., °C	Specific Volume, ml/g			Volume Change, %[a]		
	M	Poly-I	Poly-II	M→Poly-I	M→Poly-II	Poly-I→Poly-II
25	0.80	0.75	0.83	-6.2	+4.0	+9.7
50	0.82	0.76	0.84	-7.4	+2.5	+9.8
80	0.84	0.78	0.85	-7.1	+1.9	+8.2
100	0.85	0.78	0.85	-8.4	-0.3	+8.1
120	0.87	0.79	0.86	-9.8	-1.4	+8.6

[a] +, expansion; -, shrinkage.

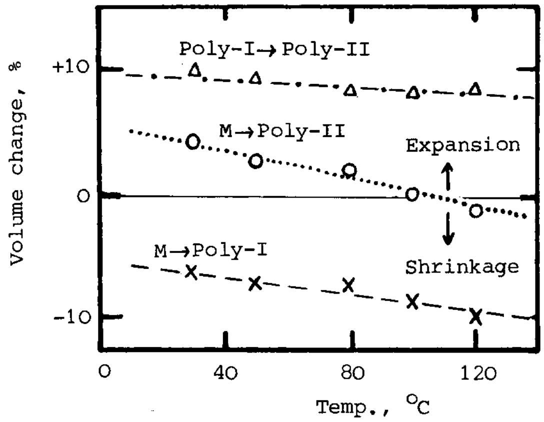
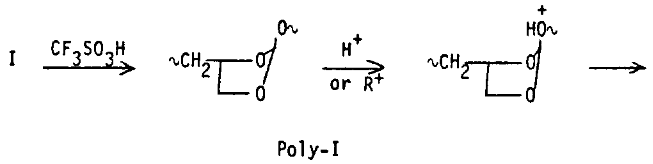


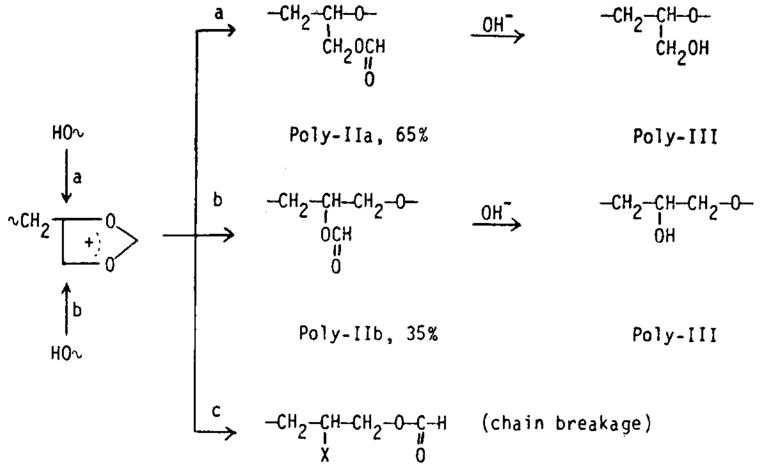
Fig. 2. Volume change during the polymerization, as a function of temperature

Finally, Poly-II is very easily base-hydrolyzed to form a water-soluble poly-ether with hydroxy substituent (Poly-III). Poly-III is soluble in polar organic solvents such as DMSO, DMF, and MeOH, also.

MECHANISM OF POLYMERIZATION AND ISOMERIZATION

From the results shown in Table I, the following mechanism of polymerization and isomerization is suggested. Protonation (or alkylation) occurs preferentially on the exo chain oxygen and 1,3-dioxolan-2-ylium ion is generated. This then opens to the formate group. A small amount of protonation may occur on the ring oxygen, and chain cleavage occurs. That this happens is shown by loss in molecular weight in going from Poly-I to Poly-II.





$X=SO_3CF_3$, O^+ (polymer chain), and OH (generated from contaminated water).

VOLUME CHANGE

Conversion of monomer to Poly-I occurs as usual with shrinkage; this is the normal consequence of combining monomers from van der Waal's covalent distance. Conversion of Poly-I to Poly-II occurs with expansion. Again, this is the expected increase in van der Waal's distance accompanying conversion of two σ bonds to a π bond.

As far as we know, this is the first case that one monomer is useful for both the purpose of shrinkage and expansion by the selection of the polymerization conditions. Similar consideration may also be applicable to the spiro monomers cited above.

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