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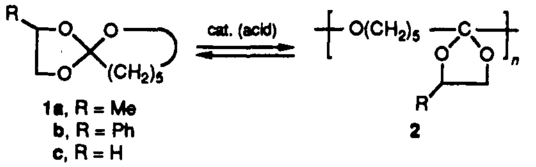
A Novel Polymerization Behavior of Spiroorthoester: An Equilibrium Polymerization

The monomers undertaking equilibrium polymerization via cationic ring-opening and ring-closing processes are exemplified by tetrahydrofuran (THF).[1,2] Recently we have found that spiroorthoester (SOE) undergoes a novel equilibrium polymerization involving cationic ring-opening and ring-closing processes. SOE is known as one of the monomers showing no shrinkage in volume on polymerization, which yields poly(ether-ester) through a double ring-opening isomerization process.[3] The equilibrium polymerization consists of a cationic single ring-opening polymerization without such an isomerization process and competitive depolymerization of poly(SOE) to the spiroorthoester. This paper describes the characterization of the equilibrium polymerization.

Polymerization of SOE (**1a**) was carried out with a cationic catalyst $SnCl_4$ (2 mol %), at 0 °C for 1 h under an argon atmosphere to afford viscous polymer as an *n*-hexane-insoluble fraction [yield: 77%, $\bar{M}_w$ 26 400, $\bar{M}_n$ 12 600: estimated by gel permeation chromatography (GPC) with THF as a solvent]. The obtained polymer was identified as poly(cyclic orthoester) (**2a**) (eq 1), which was the same polymer as that obtained by the polymerization with Al(acac)$_3$.[4] The cationic polymerization of SOE at low temperature, therefore, gives poly(cyclic orthoester),[5] in contrast to that at high temperature, which forms poly(ether-ester).



(1)

When the obtained polymer **2a** was treated with a catalytic amount of anhydrous HCl in CH_2Cl_2 at 25 °C, **2a** was converted unexpectedly to the starting monomer SOE (**1a**, 82% by GLC), which could be easily isolated by vacuum distillation in 52% yield [bp 59.5 °C (1.6 mmHg); lit.[6] bp 45 °C (0.6 mmHg)] and identified by IR and NMR spectra. Its depolymerization process was monitored by GPC, as shown in Figure 1.

Noteworthy is the depolymerization to the spirocyclic monomer, since the polymerization of SOE is considered so far to proceed through the advantageous release of the strain of the spirocyclic structure. The consecutive changes of the GPC profile appear to be indicative of a stepwise depolymerization, which would proceed by the zipping mechanism.[7] This polymerization-depolymerization process is strongly suggested as a typical behavior of the equilibrium polymerization, in which no essential change is observed by changing the substituent from a methyl (**1a**) to a phenyl (**1b**) or hydrogen (**1c**) group.

Figure 2 shows the temperature-conversion curves in the solution of polymerizations of **1a**-**c** with $SnCl_4$ (2 mol %) in CH_2Cl_2 (concentration: [SOE] = 2 M) for 1 h. The conversion of **1** decreased with a rise of temperature, suggesting another typical behavior of the equilibrium polymerization.

To this type of the equilibrium polymerization, generally Dainton's equation[2] (eq 2) can be applied

$$T = \Delta H^\circ/(\Delta S^\circ + R \ln [M_l]) \qquad (2)$$

or

$$\ln [M_l] = \Delta H^\circ/RT - \Delta S^\circ/R \qquad (2')$$

where T, $[M_l]$, ΔH°, and ΔS° are polymerization temperature, concentration of monomer at an equilibrium, enthalpy change in appropriate standard state, and entropy change in appropriate standard state, respectively.

If eq 2 is operative in the polymerization of **1**, plots of $\ln [M_l]$ vs $1/T$ should give a straight line and both values of ΔH° and ΔS° can be calculated. For this calculation, the conversions higher than 50% were not used to exclude the viscosity effect. The linear relation between $\ln [M_l]$ and $1/T$ ($r > 0.98$) was obtained for each SOE (Figure 3). ΔH° and ΔS° values are listed in Table I. The value ΔH° increases with an increase of the size of the substituent,

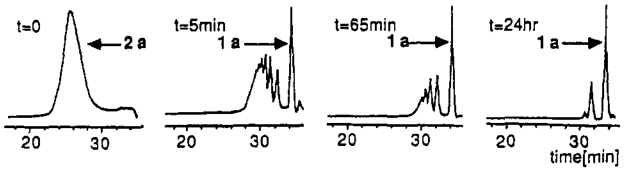


Figure 1. GPC change of the depolymerization of poly(cyclic orthoester) **2a**.

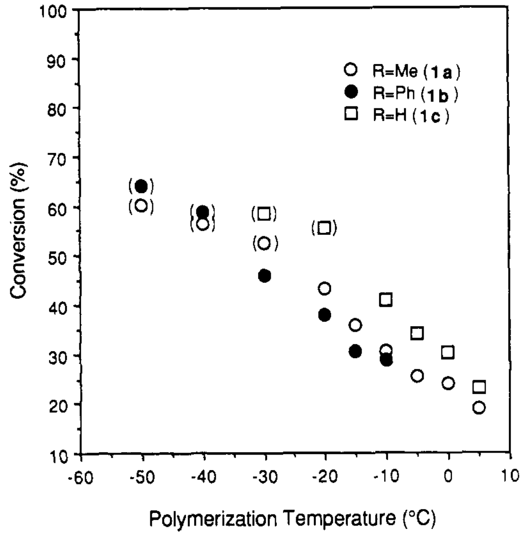


Figure 2. Polymerization temperature-conversion curves of the polymerizations of **1a**-**c**.

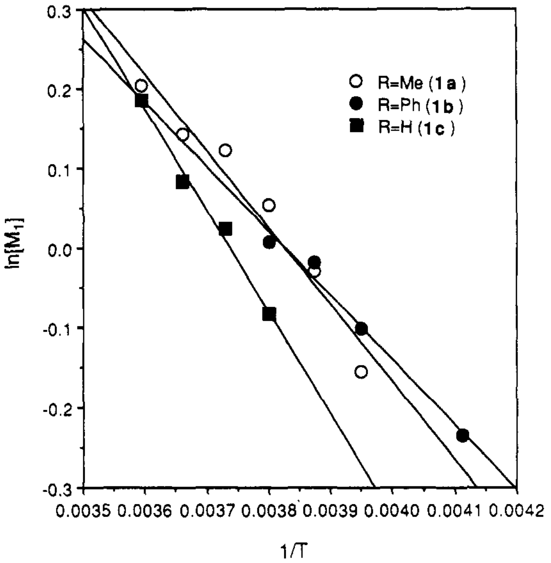


Figure 3. Relationship between $\ln [M_l]$ and $1/T$.

Table I
$\Delta H°$ and $\Delta S°$ for Polymerization of 1

	1a (R = Me)	**1b** (R = Ph)	**1c** (R = H)
$\Delta H°$, kJ/mol	-8.0	-6.7	-10.6
$\Delta S°$, J/mol·deg	-30.7	-25.7	-39.6
T_c,[a] °C	254	258	172

[a] Values for bulk polymerization, which are obtained by extrapolation.

H < Me < Ph, at the 2-position of 1. The order can be explained by less stability of the polymer state by steric repulsion between the substituents and/or between the substituent and polymer main chain. The $\Delta S°$ value decreases similarly, indicating that the entropy difference between polymer and monomer is in reverse proportion to the size of the substituent. Ceiling temperatures, which are calculated for bulk condition by using $\Delta H°$ and $\Delta S°$, are also listed in Table I. In the calculation change of solvent from CH_2Cl_2 to monomer was neglected. **1c** had its ceiling temperature of 172 °C, whereas 2-substituted derivatives (**1a** and **1b**) had rather higher ceiling temperature over 250 °C.

As mentioned above, we have found a novel equilibrium polymerization by the use of SOE (**1**). It is of special interest that the polymer **2** depolymerizes to the spirocyclic monomer, despite the fact that SOE (**1**) has sufficient strain to polymerize via a ring-opening process. This might be explained by the enthalpy effect due to the high potential of polymer **2**. This new equilibrium polymerization of SOE is of interest not only because of its mechanistic features but also because of its potential application to polymer synthesis.

References and Notes

(1) (a) Sims, D. *J. Chem. Soc.* **1964**, 864. (b) Dreyfuss, M. P.; Dreyfuss, P. *J. Polym. Sci., Part A-1* **1966**, *4*, 2179.

(2) Dainton, F. S.; Ivin, K. *Quart. Rev.* **1985**, *12*, 61.

(3) (a) Bailey, W. J. *J. Elastplast.* **1973**, *5*, 142. (b) Endo, T. *Polym. Prepr. Jpn.* **1984**, *33*, 39. (c) Endo, T.; Ogasawara, T. *Netsu Kokasei Jushi* **1984**, *5*, 30. (d) Tagoshi, H.; Endo, T. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 77.

(4) Chikaoka, S.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3101.

(5) Chikaoka, S.; Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1989**, *38*, 1437.

(6) Suzuki, S.; Yoshida, H.; Ogata, T.; Inokawa, S. *Nippon Kagaku Zasshi* **1968**, *89*, 988.

(7) (a) Kern, W.; Gherdon, H. *Makromol. Chem.* **1960**, *40*, 101. (b) Meerwein, H.; Delfs, D.; Morshel, H. *Angew. Chem.* **1960**, *72*, 927.

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Registry No. 1a, 21511-66-0; **1b**, 130904-43-7; **1c**, 13043-49-7; **2a** (homopolymer), 130572-36-0; **2a** (SRU), 130547-89-6; $SnCl_4$, 7646-78-8.