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# A Facile Synthesis of Oxetane Derivatives for Preparing Cross-Linked Polyoxetane Resins Bearing the Bromide at the Spacer End

Masatoshi MOTOI,* Hiroshi SUDA, Katsuhiko SHIMAMURA, Shinsuke NAGAHARA, Mitsuru TAKEI, and Shigeyoshi KANOH
Department of Chemistry and Chemical Engineering, Faculty of Technology, Kanazawa University, Kodatsuno, Kanazawa-shi 920
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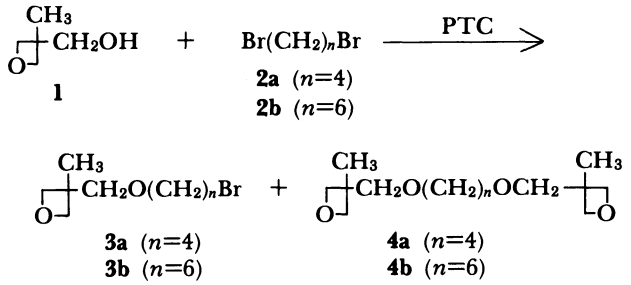
3-(6-Bromo-2-oxahexyl and 8-bromo-2-oxaoctyl)-3-methyloxetanes, and 1,8- and 1,10-bis(3-methyl-3-oxetanyl)-2,7-dioxaoctane and -2,9-dioxadecane were readily prepared in fairly good yields by the reaction of 3-hydroxymethyl-3-methyloxetane (**1**) with tetra- and hexamethylene dibromides in the presence of a phase-transfer catalyst. The formation of the mono- and disubstituted products depends upon the molar ratios of the dibromide to **1**. The optimum reaction conditions for the etherification of **1** with tetramethylene dibromide were searched. The (ω-bromo-2-oxaalkyl)oxetanes were polymerized to give soluble polyoxetanes ($\bar{M}_n$ 3500—5500) by cationic ring-opening polymerization. The use of the bisoxetanes, a new cross-linking agent, as a comonomer gave insoluble elastic polyoxetane resins having a pendant bromide at the spacer end.

In the course of our studies on the polymerization of the oxetanes and other cyclic ethers,[1-7] we hoped to synthesize oxetane derivatives for producing soft, somewhat polar polyoxetane resins; we found that the oxetane derivatives **3a**, **3b**, **4a**, and **4b** can be readily prepared by the etherification of 3-hydroxymethyl-3-methyloxetane (**1**) with α,ω-dibromoalkanes **2a** and **2b** in the presence of a phase-transfer catalyst (PTC).




So far, several chemical reactions of the substituents attached to the oxetane rings have been reported. Chlorine of the chloromethyl group at the C-3 position of the oxetane ring was replaced into alkoxyl, aryloxyl, acetoxyl, and azido groups by displacement reactions.[8-11] Macroheterocycles bearing one or two spiro-oxetane rings were synthesized from base-induced condensations of 3,3-bis(chloromethyl)oxetane with heteropolymethylene glycols.[12] Recently, several preparation methods for the oxetane ring with various substituents have also been reported.[13-19]

Oxetanes **3a** and **3b** seem to be very useful for designing a variety of the functional polyethers since the polymers possess long spacers of oxapolymethylenes, $-CH_2O(CH_2)_n-$ where $n$=4 or 6, and the terminal bromine that can be readily converted into various other functional groups. It is also known that lengthening the spacers having catalytic sites is important for realizing improved catalytic activities.[20] Furthermore, the bisoxetanes **4a** and **4b** are expected to react as bifunctional monomers to give insoluble polyoxetane resins. In this paper, we describe a facile preparation of new oxetane derivatives, which give their soluble and insoluble polymers by cationic ring-opening polymerization; we also discuss reaction courses for obtaining the optimum conditions for preparing such oxetanes by phase-transfer catalysis. Related to the present study, compounds containing two oxetane rings were reported: bis[(3-methyl- and 3-ethyl-3-oxetanyl)methyl] hexanedioates[21] and 2,6-dioxaspiro[3.3]heptane.[22]

## Results and Discussion

**Preparation of Monomers.** The monomers, **3a** and **3b**, carrying ω-bromo-2-oxaalkyl groups were synthesized by the reaction of **1** with α,ω-dibromoalkanes **2a** and **2b** in the presence of tetrabutylammonium bromide (TBAB) or hydrogen sulfate (TBHS) as PTC. **3a** and **3b** reacted further with **1** to give bisoxetanes **4a** and **4b** under the same reaction conditions. The formation of these oxetane derivatives as a main product depends on the mole ratio of the dibromide to **1**. The etherification reaction was examined under several conditions concerning the mole ratio, the PTC, and the solvent. The yield of the product was determined at a given reaction time by gas chromatography (GC) using hexadecane as an internal standard. The results are summarized in Table 1. When the reaction of **1** with a threefold molar equivalent of **2a** was carried out under refluxing in hexane and 50% aqueous NaOH with TBAB (5% molar respect to **1**), **3a** and **4a** were produced in 81.1 and 14.6% yields, respectively, indicating that more than 96% of **1** was consumed to produce the two products (Run no. 7). **2a** remained unchanged in a 29% recovery, suggesting that a considerable amount of **2a** is consumed by side reactions (vide infra). The decrease in the mole ratio was favorable for the formation of **4a**. The reaction at

Table 1. Etherification of **1** with **2a** by Phase-Transfer Catalysis[a)]

| Run no. | Mole ratio, **2a**/**1** | PTC[b)] | Solvent | | Product and yield/%[c)] Reaction time/h 0.5 | 1.0 | 1.5 | 2.0 |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.5 | TBAB | Hexane | **3a**: | 0.2 | 0 | 0 | |
| | | | | **4a**: | 34.7 | 35.5 | 35.2 | |
| 2 | 0.8 | TBAB | Hexane | **3a**: | 0.8 | 0 | 0 | |
| | | | | **4a**: | 49.4 | 52.3 | 52.0 | |
| 3 | 1.0 | TBAB | Hexane | **3a**: | 5.8 | 0.2 | 0[d)] | |
| | | | | **4a**: | 56.8 | 62.0 | 63.1 | |
| 4 | 1.2 | TBAB | Hexane | **3a**: | 19.4 | 11.0 | 5.7 | |
| | | | | **4a**: | 50.8 | 58.6 | 61.3 | (63.7) |
| 5 | 1.5 | TBAB | Hexane | **3a**: | 39.5 | 33.3 | 28.1 | |
| | | | | **4a**: | 33.0 | 41.0 | 43.2 | |
| 6 | 2.0 | TBAB | Hexane | **3a**: | 60.9 | 60.8 | 59.3 | |
| | | | | **4a**: | 19.4 | 22.1 | 23.0 | |
| 7 | 3.0 | TBAB | Hexane | **3a**: | 83.0[e)] | 81.1 | (76.2) | |
| | | | | **4a**: | 14.6 | 14.6 | | |
| 8 | 3.0 | TBAB | Ether | **3a**: | 74.0 | 82.8 | 80.2 | |
| 9 | 3.0 | TBAB | Benzene | **3a**: | 68.1 | 67.7 | | |
| 10 | 3.0 | TBHS | Hexane | **3a**: | 74.5 | 76.1 | 77.3 | |
| 11 | 3.0 | TBHS | Ether | **3a**: | 69.1 | 67.9 | 73.8 | |
| 12 | 3.0 | None | Hexane | **3a**: | 2.6 | 3.4 | 4.9 | |

a) **1**, 2.06 mmol; PTC, 5% molar respect to **1**; $n$-$C_{16}H_{34}$ (as internal standard), 1.06 mmol; volume of organic layer was adjusted to 3 ml by adding hexane; 50% NaOH, 2.7 g; under reflux. b) Phase-transfer catalyst (PTC): TBAB and TBHS refer to tetrabutylammonium bromide and hydrogen sulfate, respectively. c) Determined by GC. Value in parenthesis indicates isolated yield of reaction using 10 or 30 g of **1**. d) After 1.5 h, **2a** was not detected and **5** was formed in 17.0% yield. e) After 0.5 h, 29.2% of **2a** fed was left unchanged and no **5** was detected.

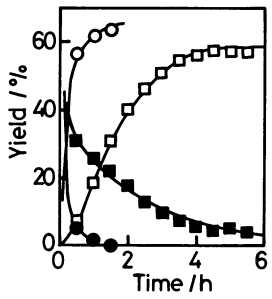
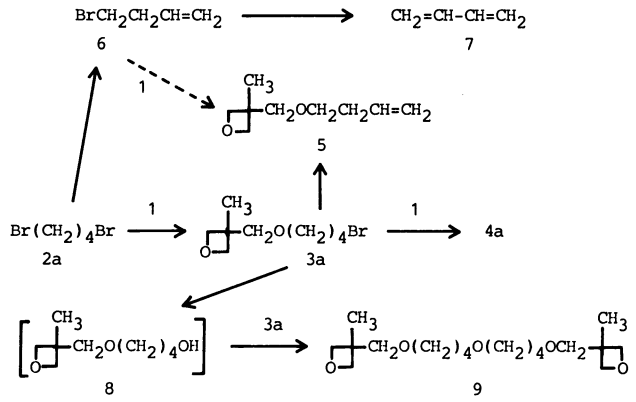


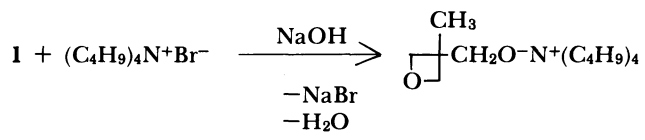

Fig. 1. Time-yield curves of **3a** (●, ■) and **4a** (○, □) in the reaction between **1** and **2a** at a 1:1 mole ratio in the presence of TBAB: (■, □) 0.7; (●, ○) 5.0 mol% to **1**.




Scheme 1.

mole ratios of 1.0 to 1.2 gave **4a** in maximum yield of about 63% (Run nos. 3 and 4), which is higher than the yield of the reaction at the stoichiometric mole ratio of 0.5 (Run no. 1). At mole ratios below 1.0, all of the **2a** fed was consumed to form **4a** and by-products within at least 1.5 h. However, **1** remained, even when **2a** was completely consumed, as indicated from the following fact: when **2a** (half the amount used in the original reaction) was added into the reaction mixture upon the complete consumption of **2a** and was then allowed to react for 2 h, the yield of **4a** increased from 52 to 68% (Run no. 2). The etherification of **1** with **2a** proceeded very slowly in the absence of PTC: the yield of **3a** was only 5% after 1.5 h (Run no. 12). Therefore, PTC is obviously required for preparing oxetane derivatives. Figure 1 shows the time-product yield curves in the reaction of **1** with **2a** at a **2a**/**1** mole ratio of 1.0 in the presence of TBAB in 0.7 and 5.0 mol% to **1**. As shown in the curve of the reaction with 0.7 mol% TBAB, the yield of **4a** increases with an increase of the reaction time, while the yield of **3a**, which is produced as a main product in the early period of the reaction, decreases. This fact indicates that **3a** is an intermediate in the formation of **4a**, the rate of which can be lowered by decreasing the amount of PTC.

3-Methyl-3-(2-oxa-5-hexenyl)oxetane (**5**) was obtained as a low-boiling fraction of the reaction mixture from **1** and **2a**. Therefore, it should be considered that the such bromides as **2a** and **3a** are led to elimination products under applied phase-transfer catalytic condi-




tions. The alkoxide anion of **1**, formed in a concentrated alkaline solution, transfers to an organic layer, together with a quarternary ammonium countercation. In the organic layer the alkoxide anion acts not only as a nucleophile in the substitution but also as a base in the elimination of the bromides. Actually, the odor of 1,3-butadiene (**7**) came out from the top of a water-cooled condenser during the early stage of the reaction of **1** with **2a**.

To investigate the material balance, reactions of the bromides as a substrate were carried out in hexane and 50% aqueous NaOH in the presence of TBAB (Table 2). In reactions at **3a**/**1** mole ratios of 0.5 and 1.0 (Run nos. 13 and 14), **4a** was detected in about 55% yield together with **5** in 32% yield after 1.5 h, at which time the starting material, **3a**, disappeared completely. The reaction between **3a** and **1** at a ratio of 2.0 gave **4a** in a 80.7% yield (40.4% conversion of **3a**) after 1.5 h; an additional 1-h reaction resulted in an increase of only 2% yield of **4a**, while the **3a** recovery decreased from 14.4 to 8.3% (Run no. 15). In these reactions of **3a** with **1** (Run nos. 13, 14, and 15), therefore, 13 to 21% of **3a** was consumed to produce unknown products. When **3a** was heated in a concentrated alkaline solution, no **3a** and a 32% yield of **5** were detected after 14 h, although at an early stage of the 0.5-h reaction, **5** was hardly detectable in spite of the consumption of 21% of the **3a** which was fed (Run no. 16). A pot residue of distillation from this reaction mixture was identified as being 1,13-bis(3-methyl-3-oxetanyl)-2,7,12-trioxatridecane (**9**). This product is probably formed from an etherification reaction of **3a** with the alcohol **8** derived from the bromide **3a** by its hydrolysis (Scheme 1). On the other hand, 98% of **3a** was left unchanged after heating a mixture of **3a** and threefold molar equivalent of **2a** under the same conditions as above (Run no. 17). In the absence of **1**, **2a** itself was stable under the present conditions (Run no. 18). The oxetane ring was also found to be stable under the present conditions, because the structure of 3-methyl-3-(2-oxadecyl)oxetane (**10**) was not altered upon treatment with the alkaline solution (Run no. 19). These findings lead to the following: (1) The existence of a sufficient amount of **2a** under phase-transfer catalytic conditions seems to prevent side reactions of bromide **3a**, though it is difficult at this point to explain why **2a** prevents the side reactions. (2) The reaction of **1** with 4-bromo-1-butene (**6**) is unimportant, since **5** is not produced in the reaction at a **2a**/**1** mole ratio of 3.0. Presumably, **6** is almost exclusively consumed to give **7** by an elimination reaction, but not to form **5** by a substitution reaction from **1** and **6**. (3) The elimination reaction of **3a**, which occurs during the existence of **1** (or its alkoxide anion), is also restrained by using a sufficient amount of **2a**. (4) In the reaction for preparing the bisoxetanes, the existence of an adequate amount of **2a** is required in

Table 2. Analysis of Reaction of Bromides under Phase-Transfer Catalytic Conditions[a]

| Run no. | Reactant | | Mole ratio, A/B | Time/h | Yield or recovery/%[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | A | B | | | **3a** | **4a** | **5** | **2a** |
| 13 | **3a** | **1** | 0.5 | 0.5 | (0.0) | 57.1 | | |
| | | | | 1.0 | (0.0) | 57.0 | | |
| | | | | 1.5 | (0.0) | 54.9 | 31.8 | |
| 14 | **3a** | **1** | 1.0 | 0.5 | (1.9) | 55.3 | | |
| | | | | 1.0 | (0.0) | 55.4 | | |
| | | | | 1.5 | (0.0) | 55.6 | 31.6 | |
| 15 | **3a** | **1** | 2.0 | 0.5 | (24.8) | 75.8 | | |
| | | | | 1.5 | (14.4) | 80.7 | | |
| | | | | 2.5 | (8.3) | 83.1 | 29.6 | |
| 16 | **3a** | None | — | 0.5 | (78.9) | | 0.0 | |
| | | | | 1.0 | (71.4) | | 0.5 | |
| | | | | 5.0 | (42.3) | | | |
| | | | | 14.0 | (0.5) | | 32.0 | |
| 17 | **3a** | **2a** | 3.0 | 0.5 | (99.0) | | | |
| | | | | 1.0 | (97.6) | | | |
| | | | | 2.0 | (96.8) | | 0.0 | (90.4) |
| 18 | **2a** | None | — | 0.33 | | | | (90.0) |
| | | | | 0.66 | | | | (88.1) |
| 19 | **10** | None | — | 0.5 | (99.7)[c] | | | |
| | | | | 1.0 | (97.7)[c] | | | |
| | | | | 2.0 | (99.7)[c] | | | |

a) Reactant A, 2.11 mmol; PTC, TBAB in 5% molar respect to reactant B (to reactant A in Run nos. 16, 18, and 19); 50% NaOH, 2.7 g; volume of organic layer was adjusted to 3 ml by addition of hexane; under reflux. b) As internal standard of GC determination, $n$-$C_{16}H_{34}$ (1.05 mmol) was used for **3a** and **4a**, and $n$-$C_{10}H_{22}$ (3.15 mmol) for **2a** and **5**. Value in parenthesis indicates recovery of the reactants. c) Value for remaining **10**.

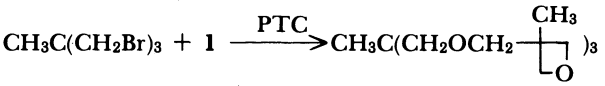
order to avoid an elimination reaction of **3a**, until **1** is completely consumed to give **4a** from **3a** as an intermediate.

The use of ether as a solvent gave a yield of **3a** comparable to that in a reaction using hexane, though the use of benzene resulted in a lower yield (Run nos. 8 and 9). With TBHS, a slightly lower yield of **3a** was determined by GC, even when using hexane and ether (Run nos. 10 and 11).

Thus, **3a** and **4a** were isolated in 76.2 and 63.7% yields, respectively, from reactions at mole ratios of 3.0 and 1.2 on a preparative scale using 10 or 30 g of **1** and hexane as a solvent (Run nos. 7 and 4). The preparation results concerning the other ocetane derivatives are indicated in Table 3. In the same way as above, **3b** and **4b** were isolated, respectively, in 73.4 and 62.8% yields from the reactions at mole ratios of 3.0 and 1.0. Octyl bromide (**11a**) and benzyl chlorides **12a** and **12b** are used well as halides for the etherification of **1**. With the bromide **11a**, **10** was isolated in 92.9% yield, although the reaction with the chloride **11b** gave **10** in only 2% yield. The reaction of **1** with benzyl chlorides should be performed at a mole ratio of 1.0 to give sufficient yields. The use of a molar excess of benzyl chlorides toward **1** resulted in the formation of a considerable amount of dibenzyl ethers, which could hardly be removed from the desired products by fractional distillation.

**11a** R=*n*-$C_8H_{17}$, X=Br **10** R=*n*-$C_8H_{17}$
**11b** R=*n*-$C_8H_{17}$, X=Cl **13a** R=$C_6H_5CH_2$
**12a** R=$C_6H_5CH_2$, X=Cl **13b** R=(*p*)-$CH_3C_6H_4CH_2$
**12b** R=(*p*)-$CH_3C_6H_4CH_2$, X=Cl

An etherification reaction of **1** with tribromide **14** did not take place to give the desired product **15**, resulting in a 86% recovery of **14**, isolated by distillation. This indicates that a nucleophilic attack of the alkoxide anion of **1** onto the $\alpha$-carbon of the bromide **14** is difficult, since this $\alpha$-carbon is quite similar to that of neopentyl bromide which has difficulty in being susceptible to the $S_N2$ reaction.



**14** **15**

The etherification of **1** with **2a** gave a remarkably low yield by the Williamson synthesis using dry solvents, since the sodium alkoxide of **1**, which was prepared from **1** and sodium metal or sodium hydride, was hardly soluble in tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and ether. On the contrary, the desired ethers were obtained in fairly good

Table 3. Preparation of Oxetane Derivatives from **1** and Halides[a]

| Run no. | Halide | Mole of **1** | Mole ratio, halide/**1** | Time/h | Product | |
|---|---|---|---|---|---|---|
| | | | | | | Yield/%[b] |
| 20 | **2b** | 0.14 | 3.0 | 2.0 | **3b** | 73.4 |
| 21 | **2b** | 0.098 | 1.0 | 2.0 | **4b** | 62.8 |
| 22 | **11a** | 0.098 | 3.0 | 12.0 | **10** | 92.9 |
| 23 | **11b** | 0.098 | 3.0 | 10.0 | **10** | 2 |
| 24 | **12a** | 0.20 | 1.0 | 3.0 | **13a** | 85.7 |
| 25 | **12b** | 0.20 | 1.0 | 2.0 | **13b** | 73.9 |

a) For 98 mmol of **1**, TBAB (4.9 mmol), 50% NaOH (130 g), and hexane (100 ml) were used under reflux. b) Isolated yield.

Table 4. Cationic Ring-Opening Polymerization of Oxetane Derivatives in DCM at 0 °C for 20 h

| Monomer | (mole ratio) | $BF_3$–THF[a] mol% | $[M]_0$[b] mol $l^{-1}$ | Polymer Yield/% | $\overline{M_n}$[c] |
|---|---|---|---|---|---|
| **3a** | | 0.5 | 3.8 | 92 | 5480 |
| **3a**+DMOX[d] | (49/51) | 1.0 | 3.2 | 91 | 8380 |
| **3a**+**4a** | (79/30) | 1.0 | 3.5 | 95 | |
| **4a** | | 1.0 | 2.2 | 87 | |
| **3b** | | 0.5 | 1.8 | 86 | 3460 |
| **3b**+**4b** | (79/21) | 1.0 | 1.9 | 99 | |
| **4b**+OX[d] | (32/68) | 0.9 | 4.1 | 84 | |
| **13a** | | 0.5 | 2.7 | 98 | 3850 |
| **13a** | | 1.0 | 2.5 | 97 | 1970 |
| **13a**+**10** | (78/22) | 1.0 | 2.2 | 100 | 2400 |
| **13b** | | 1.0 | 2.6 | 93 | 2890 |

a) Percentage to mole of ether group of oxetane ring. b) Total monomer concentration at initial time. c) By VPO (solvent, acetone) of methanol-insoluble part of product polymer. d) DMOX refers to 3,3-dimethyloxetane and OX does to oxetane.

yields by a facile operation using less expensive reagents under the present phase-transfer catalytic conditions.

**Polymerization.** Oxetanes, thus obtained, were polymerized to give their polymers ($\bar{M}_n$2000—5500) via a cationic ring-opening polymerization in dichloromethane (DCM) at 0 °C with trifluoroborane ($BF_3$)–THF complex as an initiator (Table 4). The polyoxetanes were viscous oily materials soluble in DCM, chloroform, ether, acetone, benzene, toluene, and DMF, and reprecipitated from a solution of the polymer in DCM by adding it into methanol. The IR spectra of **3a**, poly(**3a**), and poly(**4a**) are shown in Fig. 2. In Fig. 2A, the bands at 980 and 835 $cm^{-1}$ are assignable to the cyclic ether linkage of the oxetane ring. These bands disappear in the spectra of poly(**3a**) and poly(**4a**), in which the band due to the acyclic ether linkage of the resultant polyether chain appears at 1100—1120 $cm^{-1}$. Methylene protons of the oxetane ring of **3a** show signals of an AB qualtet in $\delta$ 4.25—4.65; however, the signals disappear in the spectrum of poly(**3a**) (Fig. 3). Use of bisoxetanes **4a** and **4b** as a comonomer in the polymerization of **3a** and **3b** gave gel products which were insoluble in the solvents, indicating that these polymeric products have the cross-linked structures of a polyether network. These polyoxetane resins are considered to be soft, somewhat polar polymer supports bearing a bromide at the spacer end, which will be used for preparing functional polyethers according to the way employed for the functionalization of a hard, less polar, crosslinkd polystyrene having a chloromethyl group.[23–25]

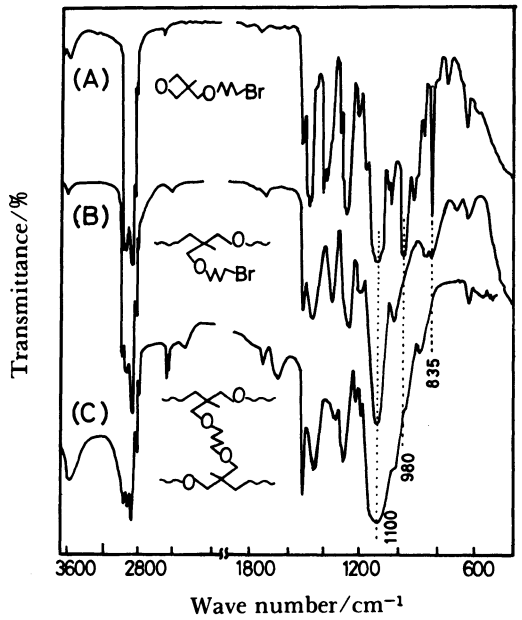



Fig. 2. IR spectra of (A) **3a**, (B) poly(**3a**), and (C) poly(**4a**).

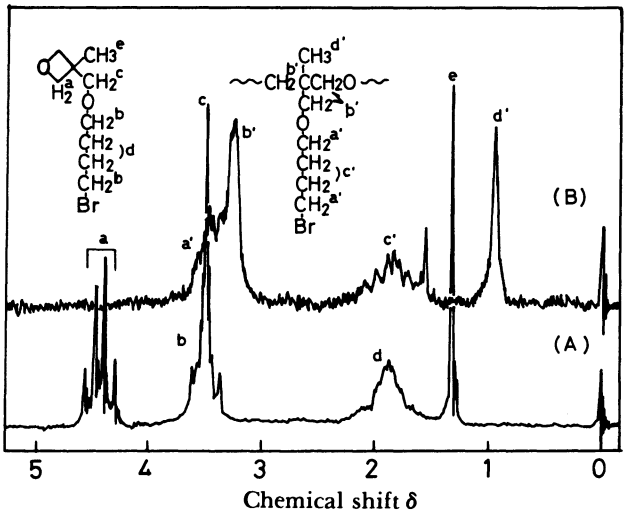



Fig. 3. $^1H$ NMR spectra of (A) **3a** and (B) poly(**3a**).

## Experimental

**Materials.** 3-Hydroxymethyl-3-methyloxetane (**1**) was prepared in 60—62% yield according to a method described in the literature.[14] Oxetane (OX) and 3,3-dimethyloxetane (DMOX) were synthesized according to a method reported in the literature.[26] Halides **2a**, **2b**, **11a**, **11b**, **12a**, and **12b**, and hexane of extra pure grade reagents were used without further purification. DCM as a solvent of polymerization was twice distilled over calcium hydride in a nitrogen atmosphere. A $BF_3$–THF complex was obtained by passing $BF_3$ gas into dried THF, followed by distillation of the saturated solution: bp 87.8 °C (1.60 kPa) [lit,[27] 79.0 °C (0.96 kPa)]. Commercially available TBAB and TBHS (Tokyo Kasei Kogyo) were used as PTC without further purification.

**3-(6-Bromo-2-oxahexyl)-3-methyloxetane (3a):** In a three-necked flask, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, a 50% aqueous NaOH solution (390 g), TBAB (4.7 g, 14.7 mmol), and hexane (300 ml) were placed and cooled in an ice-bath. A mixture of **1** (30.0 g, 0.29 mol) and **2a** (190 g, 0.88 mol) was added into it with efficient stirring and cooling. It was kept at room temperature for 30 min and then refluxed for 1.5 h. It was cooled below 5 °C and 600 ml of water was added. The organic layer, which was separated by means of separatory funnel, was dried over anhydrous $Na_2SO_4$. After removing the solvents and recovering **2a** (52 g) by distillation, the residue was distilled to give 53.1 g (76.2%) of **3a**: bp 110—112 °C (63—64 Pa); IR (neat) 1115 (acyclic ether), 980 and 835 (cyclic ether) $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=1.32 (3H, s, $CH_3$), 1.5—2.3 [4H, m, $OCH_2(C\underline{H}_2)_2CH_2Br$], 3.3—3.7 [4H, m, $OC\underline{H}_2(CH_2)_2C\underline{H}_2Br$, containing a singlet (2H) of $CH_2$ adjacent to oxetane ring at $\delta$ 3.49], and 4.25—4.65 (4H, q, $J$=6 Hz, $CH_2$ of oxetane ring).

Found: C, 45.77; H, 7.45; Br, 33.43%. Calcd for $C_9H_{17}BrO_2$: C, 45.58; H, 7.24; Br, 33.69%.

**3-(8-Bromo-2-oxaoctyl)-3-methyloxetane (3b): 3b** was prepared from **1** (14.0 g, 0.14 mol) and **2b** (100 g, 0.41 mol) in a 73.4% yield in the same way as that described for preparing **3a**: bp 95—97 °C (67 Pa); IR (neat) 1120 (acyclic ether), 985 and 840 (cyclic ether) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.22—2.22 [8H, m, $OCH_2$ $(C\underline{H}_2)_4CH_2Br$, containing a singlet (3H) of

$CH_3$ at $\delta$ 1.32], 3.30—3.70 [4H, m, $OCH_2(CH_2)_4CH_2Br$, containing a singlet (2H) of $CH_2$ adjacent to oxetane ring at $\delta$ 3.52], 4.33—4.63 (4H, q, $J$=6 Hz, $CH_2$ of oxetane ring).

Found: C, 50.07; H, 8.12; Br, 30.20%. Calcd for $C_{11}H_{21}BrO_2$: C, 49.81; H, 8.00; Br, 30.13%.

**1,8-Bis(3-methyl-3-oxetanyl)-2,7-dioxaoctane (4a):** Bis-oxetane **4a** was prepared from **1** (10.0 g, 97.9 mmol) and **2a** (25.4 g, 0.12 mol) in the same way as that described for the **3a** preparation. Working up the reaction mixture followed by distillation of the crude product gave pure **4a** in a 63.7% yield: bp 124—126 °C (69—71 Pa); IR (neat) 1110 (acyclic ether), 985 and 840 (cyclic ether) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.32 (6H, s, $CH_3$), 1.53—2.02 [4H, m, $OCH_2(CH_2)_2CH_2O$], 3.33—3.76 [4H, m, $OCH_2(CH_2)_2CH_2O$, containing a singlet (4H) of $CH_2$ adjacent to oxetane ring at $\delta$ 3.50], and 4.31—4.62 (8H, q, $J$=6 Hz, $CH_2$ of oxetane ring).

Found: C, 65.12; H, 10.20%. Calcd for $C_{14}H_{26}O_4$: C, 65.07; H, 10.16%.

**1,10-Bis(3-methyl-3-oxetanyl)-2,9-dioxadecane (4b):** This compound was prepared from **1** (10.0 g, 97.9 mmol) and **2b** (23.9 g, 97.9 mmol) using the same procedure as above: yield, 62.8%; bp 129—130 °C (55 Pa); IR (neat) 1110 (acyclic ether), 980 and 830 (cyclic ether) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.15—1.95 [8H, m, $OCH_2(CH_2)_4CH_2O$, containing a singlet (6H) of $CH_3$ at $\delta$ 1.31], 3.25—3.75 [4H, m, $OCH_2(CH_2)_4CH_2O$, containing a singlet (4H) of $CH_2$ adjacent to oxetane ring at $\delta$ 3.49], 4.25—4.65 (8H, q, $J$=6 Hz, $CH_2$ of oxetane ring).

Found: C, 66.80; H, 10.74%. Calcd for $C_{16}H_{30}O_4$: C, 67.08; H, 10.58%.

**3-Methyl-3-(2-oxadecyl)oxetane (10):** In the presence of TBAB (4.9 mmol), **1** (10.0 g, 97.9 mmol) and **11a** (56.7 g, 0.29 mol) were heated for 12 h in a 50% NaOH solution (130 g) and hexane (100 ml) with stirring under reflux. The ordinary work-up and distillation gave pure **10** in a 92.9% yield: bp 152.5—153.0 °C (2.4 kPa); IR (neat) 1110 (acyclic ether), 980 and 830 (cyclic ether) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.72—1.97 [total 18H, $CH_3$ adjacent to oxetane ring and $OCH_2(CH_2)_6CH_3$], 3.31—3.71 [total 4H, a singlet of $CH_2$ adjacent to oxetane ring and multiplet of $OCH_2(CH_2)_6CH_3$], and 4.31—4.61 (4H, q, $J$=6 Hz, $CH_2$ of oxetane ring).

Found: C, 72.68; H, 12.40%. Calcd for $C_{13}H_{26}O_2$: C, 72.83; H, 12.25%.

**3-Methyl-3-(3-phenyl-2-oxapropyl)oxetane (13a):** **1** (20.0 g, 0.196 mol) and **12a** (24.8 g, 0.196 mol) were allowed to react under reflux for 2 h in hexane (200 ml) and 50% NaOH in the presence of TBAB (9.8 mmol). The desired product **13a** boiling at 82—86 °C (72—83 Pa) was obtained in a 85.7% yield by fractional distillation: IR (neat) 3060, 3030, 1600, 1585, 1500 (aromatic CH and C=C), 1100 (acyclic ether), 980, 840 (cyclic ether), 740 and 700 (monosubstituted aromatic ring) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.34 (3H, s, $CH_3$), 3.56 (2H, s, $CH_2OCH_2Ph$), 4.31—4.61 [4H, q, $J$=5.5 Hz, $CH_2$ of oxetane ring, containing a singlet (2H) of $CH_2Ph$ at $\delta$ 4.59], and 7.38 (5H, s, aromatic).

Found: C, 74.95; H, 8.41%. Calcd for $C_{12}H_{16}O_2$: C, 74.95; H, 8.40%.

**3-[3-(4-Methylphenyl)-2-oxapropyl]-3-methyloxetane (13b):** An equimolar mixture of **1** and **12b** in hexane was refluxed for 3 h under phase-transfer catalytic conditions. The ordinary work-up gave pure **13b** boiling at 86—88 °C (43 Pa) in a 73.9% yield: IR (neat) 1620, 1520 (aromatic C=C), 1100 (acyclic ether), 985, 840 (cyclic ether), 810 and 755 (para-substituted aromatic ring) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.27 (3H, s, aliphatic $CH_3$), 2.30 (3H, s, aromatic $CH_3$), 3.44 (2H, s, $CH_2$ adjacent to oxetane ring), 4.22—4.70 [4H, q, $J$=6 Hz, $CH_2$ of oxetane ring, containing a singlet (2H) of $CH_2Ar$ at $\delta$ 4.99], and 7.28 (4H, s, aromatic).

Found: C, 75.58; H, 9.08%. Calcd for $C_{13}H_{18}O_2$: C, 75.68; H, 8.81%.

**3-Methyl-3-(2-oxa-5-hexenyl)oxetane (5):** This compound was contained in a low-boiling fraction of the reaction mixture from **1** and **3a**. Repeated fractional distillation of this fraction gave **5** (98% purity by GC analysis): bp 75—80 °C (2.53 kPa); IR (neat) 1640 (C=C), 1110 (acyclic ether), 980 and 830 (cyclic ether) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.30 (3H, s, $CH_3$), 2.13—2.57 (2H, m, $CH_2CH_2CH=CH_2$), 3.44—3.65 (2H, t, $CH_2CH_2CH=CH_2$, containing a singlet (2H) of $CH_2$ adjacent to oxetane ring at $\delta$ 3.50), 4.27—4.57 (4H, q, $J$=6 Hz, $CH_2$ of oxetane ring), 4.89—5.36 (2H, m, $CH=CH_2$), and 5.52—6.25 (1H, m, $CH=CH_2$).

**1,13-Bis(3-methyl-3-oxetanyl)-2,7,12-trioxatridecane (9):** **3a** (2.07 g, 8.73 mmol) was heated under reflux for 8 h in hexane (20 ml) and 50% NaOH (11 g) in the presence of TBAB (0.44 mmol). The contents was mixed with water (50 ml) and extracted with ether. The organic layer was separated from the aqueous layer and 0.96 g of **9** was obtained as a pot residue by distilling the organic layer at 200 °C (muximum temperature of bath)/33 Pa: IR (neat) 1115 (acyclic ether), 980 and 835 (cyclic ether) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.32 (6H, s, $CH_3$); 1.45—1.90 [8H, m, $OCH_2(CH_2)_2CH_2O$], 3.20—3.70 [8H, m, $OCH_2(CH_2)_2CH_2O$, containing a singlet (4H) of $CH_2$ adjacent to oxetane ring at $\delta$ 3.48], and 4.28—4.57 (8H, q, $J$=6 Hz, $CH_2$ of oxetane ring).

**2-Bromomethyl-2-methyl-1,3-dibromopropane (14):** Into powdered 1,1,1-tris(hydroxymethyl)ethane (5.96 g, 49.6 mmol) in a three-necked flask, phosphorus tribromide (20.1 g, 74.3 mmol) was added drop by drop at 80 °C and the mixture was heated at 170 °C for 10 h. After adding ice (30 g) into the reaction mixture and standing overnight, a volatile fraction was collected by steam-distillation. An organic layer of the distillate was separated and distilled to obtain **14** boiling at 105—108 °C (1.60 kPa) in 31—37% yield: IR (neat): 1460, 1420, 1375, and 1270 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=1.29 (3H, s, $CH_3$) and 3.52 (6H, s, $CH_2Br$).

**Cationic Ring-Opening Polymerization of Oxetanes.** In a ground-glass test tube, dried and flashed with dry nitrogen gas, an oxetane was introduced by using a hypodermic injection under a nitrogen atmosphere. The monomer was diluted with DCM, and chilled at −50 °C, and mixed with a catalytic amount of $BF_3$-THF (as a 0.27 mol $l^{-1}$ solution in DCM). After being closed with a ground-glass stopper, the test tube was transferred to an ice-bath and allowed to stand for 20 h. The contents, in the case of soluble polymer, was poured into methanol, and, in the case of gel product, filtered and washed with 10% aqueous methanol and methanol successively. The polymer was collected and dried at 80 °C for 8 h in vacuo.

**Measurement.** GC analysis of the products was performed in a Shimadzu GC-8A apparatus: glass column (3.2$\phi$×1 m) packed with Silicone High Vaccum Grease (30%)/celite (80—100 mesh); carrier gas, He (66 ml $min^{-1}$); temp, 140 or 250 °C. The IR spectra were recorded on a JASCO A-202 spectrometer and $^1H$ NMR on a 60 MHz instrument (Hitachi R-24B) using TMS as an internal

standard. Molecular weight measurements were made by VPO in a Corona molecular weight apparatus (model 117).

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