Oxetane Derivatives and Their Polymers for Designing Functional Polymers Containing a Soft, Somewhat Polar Polyether Network as a Polymer Support

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Several oxetane derivatives having functional groups, such as ester, ketone, ether, acetal, and azo, at the end of 2-oxapolymethylene spacers which were linked to the C-3 carbon of an oxetane ring were readily prepared by a substitution reaction of the corresponding bromide of the oxetane. These oxetanes were polymerized by cationic ring-opening polymerization to give their polymers with molecular weights ranging from 16000 to 1000, depending on the structure of the functional group of the monomer used. When using bisoxetanes as a cross-linking agent in the above polymerization, insoluble resins containing soft, somewhat polar polyether networks as a polymer support were obtained. Some chemical reactions of the pendant functional groups were also examined for the oxetane derivatives and their polymers.

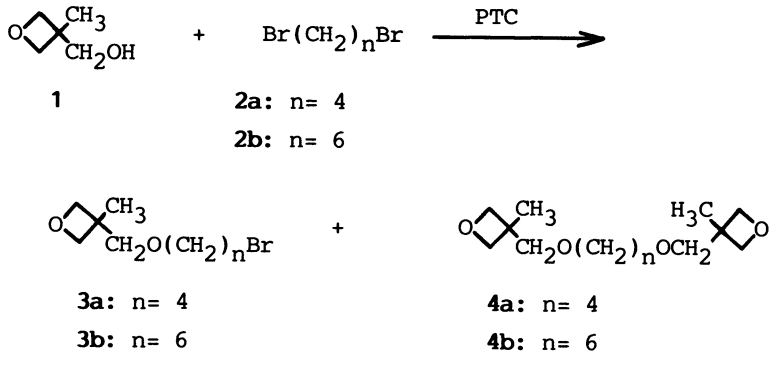
Since the mid-1960s, synthesis of functional polymers has been increasingly recognized to be one of the most interesting subjects in polymer chemistry. So far, a variety of monomers and their polymers have been prepared in order to design polymers which realize respective functionalities desired in using those polymers under applied conditions.[1-3] However, there have been few studies on the use of polyethers as materials for producing the functional polymers, particularly as polymer supports. In the course of our investigations of cationic ring-opening polymerization of oxetanes, we hoped to utilize oxetane derivatives for preparing various functional polymers which possess functional groups in the pendant groups of a soft, somewhat polar, polyether network. Accordingly, we have prepared oxetanes **3a** and **3b**, which have a bromine atom at the end of 2-oxapolymethylene spacers, as well as bisoxetanes **4a** and **4b**, which were used successfully as a cross-linking agent capable of forming polyether networks by cationic ring-opening copolymerizations with **3a** and **3b**.[4]

In the ordinary way of obtaining oxetanes with functional substituents, chlorine atoms of 3,3-bis(chloromethyl)oxetane were replaced with acetoxyl, alkoxyl, cyano, and azido groups.[5-8] Substitution reactions on the chloromethyl groups of poly[3,3-bis(chloromethyl)oxetane] were also examined to form ester, ether, thioether, and cyano groups at the side chain end of the uncross-linked polyoxetane.[9] In this article, we report the preparation and chemical reactions of oxetane derivatives and their polymers which will be used conveniently for designing various functional polyethers.

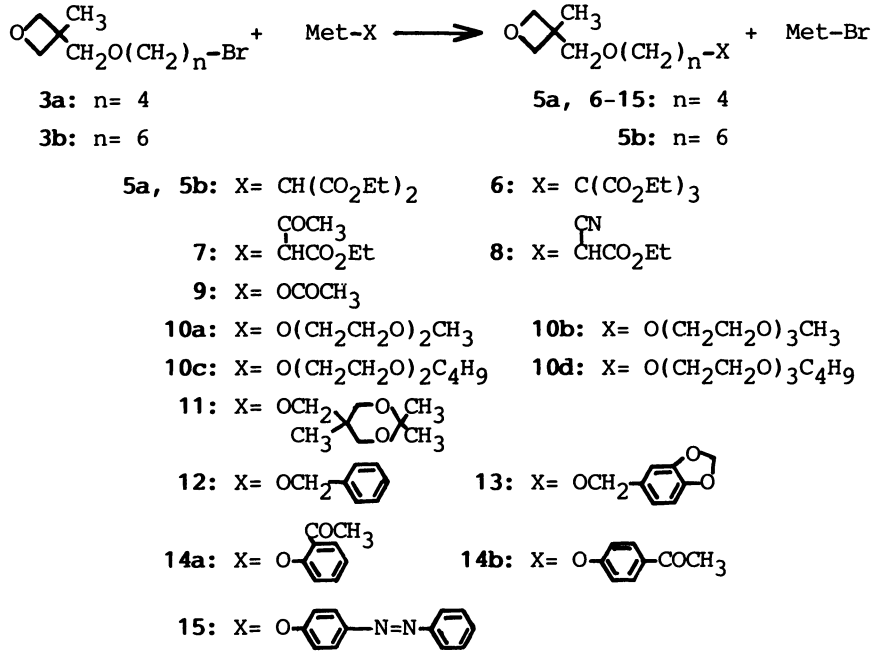
Results and Discussion

Oxetane Derivatives. Bromine atoms in oxetanes **3a** and **3b**, which were readily obtained by a reaction between **1** and **2** in the presence of tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst (PTC), were replaced with several nucleophiles to give the corresponding functional groups at the C-3 position of an oxetane ring in fairly good yields. Results of the substitution reactions are summarized in Scheme 2 and Table 1.

The ^{1}H NMR spectrum of **5b** is exemplified in Fig.



Scheme 1.



Scheme 2.

Table 1. Preparation of Oxetane Derivatives by Substitution Reaction of **3a** with Nucleophilic Reagents

Nucleophilic reagent	Conditions	Product	
	Base or PTC/solvent/temp	No.	Yield/%
$CH_2(CO_2Et)_2$	NaOEt/EtOH/reflux	**5a**	88
$CH_2(CO_2Et)_2$	NaOEt/EtOH/reflux[a)]	**5b**	75
$NaC(CO_2Et)_3$	TBAB/PhMe/reflux	**6**	74
$AcCH_2CO_2Et$	NaOEt/EtOH/reflux	**7**	54
$NCCH_2CO_2Et$	NaOEt/EtOH/reflux	**8**	52
KOAc	TBAB/PhH/reflux	**9**	84
$HO(CH_2CH_2O)_2Me$	TBAB/hexane-50%NaOH/rt[b)]	**10a**	69
$HO(CH_2CH_2O)_3Me$	TBAB/hexane-50%NaOH/rt	**10b**	68
$HO(CH_2CH_2O)_2Bu$	TBAB/hexane-50%NaOH/rt	**10c**	59
$HO(CH_2CH_2O)_3Bu$	TBAB/hexane-50%NaOH/rt	**10d**	67
HTMDO[c)]	TBAB/hexane-50%NaOH/reflux	**11**	58
$HOCH_2Ph$	TBAB/hexane-50%NaOH/rt	**12**	73
MDOBA[d)]	TBAB/hexane-50%NaOH/rt	**13**	72
(*o*)-HOArAc	TBAB/PhH-50%NaOH/reflux	**14a**	81
(*p*)-HOArAc	TBAB/PhH-50%NaOH/reflux	**14b**	88
(*p*)-HOArN=NPh	TBAB/PhMe-50%NaOH/70°C	**15**	41

a) **3b** was used in place of **3a**. b) Room temperature. c) HTMDO refers to 5-hydroxymethyl-2,2,5-trimethyl-1,3-dioxane. d) MDOBA refers to 3,4-methylenedioxybenzyl alcohol.

1(A) to demonstrate the characteristic signals of these oxetane derivatives. Generally, methylene protons (H_a) of an oxetane ring show an AB quartet around δ 4.5—5.3, and methylene protons (H_b) adjacent to the oxetane ring and methyl protons (H_g) on the oxetane ring exhibit their singlets at about δ 3.5 and 1.3, respectively. Furthermore, in the IR spectra of oxetane derivatives, cyclic and acyclic ethers possess absorption bands due to a C-O-C stretching vibration, respectively, at 980 and 830, and 1100 cm^{-1}, as described in our previous report.[4)]

In *C*-alkylation reactions of malonic and acetoacetic esters with the bromide of **3a** or **3b**, their oxetane rings were not susceptible to the attack of carbanions, derived from the esters with sodium ethoxide as a base, while it is known that an oxirane ring is attacked by such carbanions to give a γ-lactone ring.[10,11)] *C*-Alkylation products of triethyl methane-1,1,1-tricarboxylate have been obtained by Newkome and coworkers by a reaction between alkyl bromide and triethyl sodiomethane-1,1,1-tricarboxylate in a benzene/*N*,*N*-dimethylformamide (DMF) mixture (1 : 1).[12)]

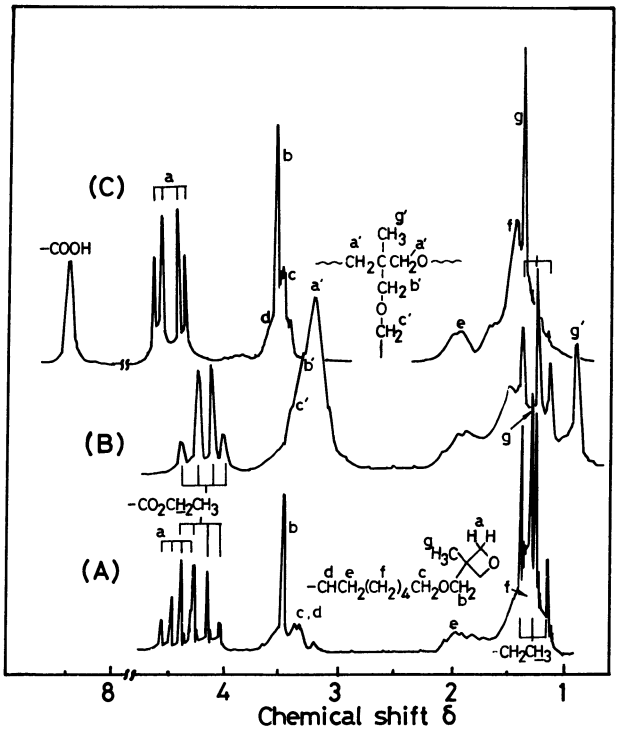
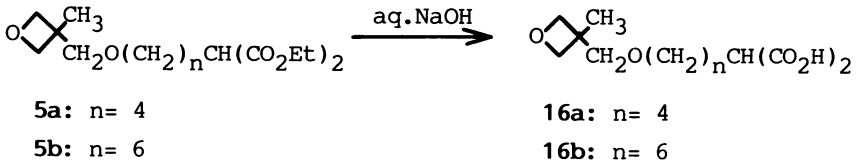


Fig. 1. ^{1}H NMR spectra of (A) **5b**, (B) poly (**5a**), and (C) **16b** (hydrolysis product from **5b**).

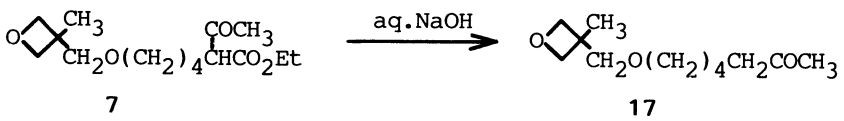
However, we have found that the *C*-alkylation product **6** was more readily prepared in an isolated yield of 74% by a phase-transfer catalytic equimolar reaction between the sodium salt of the triester and the bromide **3a** using TBAB as a PTC in toluene at 100 °C.

In connection with the further conversion of diesters **5** and **7** into other oxetane derivatives, some of their chemical reactions were examined. 1,1-Dicarboxylic esters in **5** were converted into the corresponding dicarboxylic acid of **16**, but not to a monocarboxylic acid, on hydrolysis of **5** with an aqueous sodium hydroxide (NaOH) solution in methanol at reflux temperature. As shown obviously from the ^{1}H NMR spectrum of **16b** in Fig. 1(C), a signal due to a carboxyl proton at δ 8.58 and an AB quartet due to methylene protons of the oxetane ring at δ 4.3—4.7 appear in an integral intensity ratio of 2:4, indicating that a decarboxylation reaction of **5** is difficult to achieve under the hydrolysis conditions applied. However, heating keto ester **7** in 1.0 mol dm^{-3} NaOH at 90 °C gave the corresponding ketone **17** via a decarboxylation of the sodium carboxylate formed from **7**. The ^{1}H NMR spectrum of **17** showed a distinct singlet due to an acetyl group and an AB quartet due to methylene protons of the oxetane ring, respectively, at δ 2.12 and 4.4—4.7, but did not show any signals due to the ester group or to a carboxyl proton.

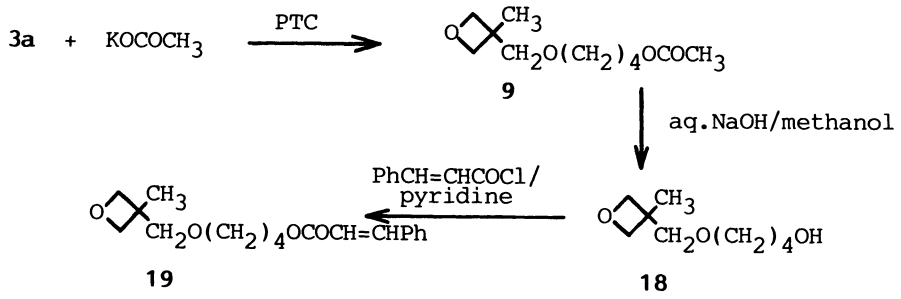
As reported by Shih and Tirrell, polyoxiranes carrying ω-hydroxyalkyl pendant chains were prepared by methanolysis of the corresponding ω-acetoxyl and -benzoyloxyl groups of the pendants. The benzoate was derived from the chloride of a 3-chloropropyl pendant group by a phase-transfer catalytic reaction using tetrabutylammonium benzoate as a PTC in DMF.[13] These resulting polyoxiranes are considered to be new hydrophilic polyether elastomers. Concerning this preparation method for elastic polyhydroxyl polyethers, we have also found a facile method for preparing the elastic polyoxetane networks carrying a terminal hydroxyl group in the side chain; a bromine atom of **3a** was converted into a hydroxyl group of **18** by a phase-transfer catalytic reaction using potassium acetate in refluxing benzene in the presence of TBAB and by subsequent hydrolysis of the resultant acetate **9** with a 2.5 mol dm^{-3} aqueous NaOH solution in methanol under reflux. Alcohol **18** was soluble in water, although both the bromide **3a** and the acetate **9** were insoluble in water. The hydroxyl group of **18** can be further changed to esters of other carboxylic acids by reactions of **18** with acid chlorides in the presence of pyridine; thus, the cinnamate **19** was obtained in a 77% yield when using cinnamoyl chloride as an acid chloride. Additionally, acetates with aromatic residues **20a** and **20b** were readily obtained by reduction of the corresponding acetophenone derivatives **14a** and **14b**



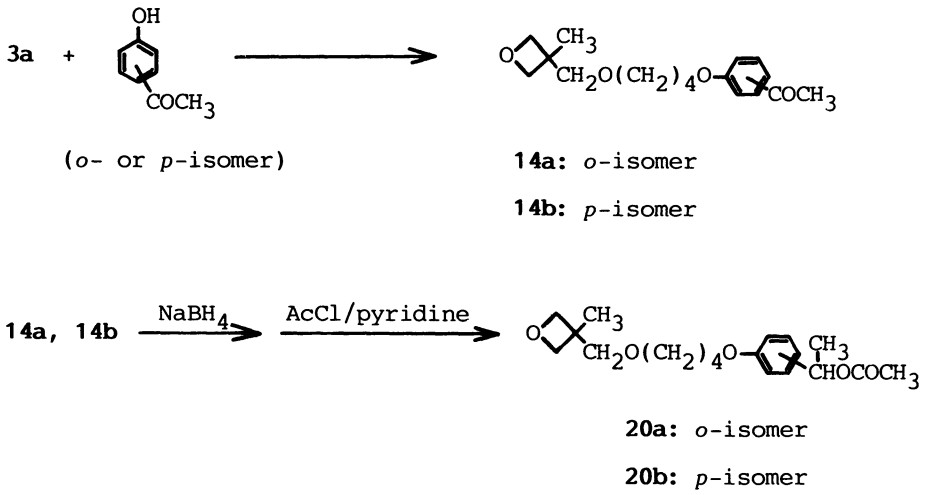
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

with $NaBH_4$ in ethanol, followed by *O*-acylation of the resultant secondary alcohols with acetyl chloride. In the preparation of such esters as **19**, **20a**, and **20b** via the *O*-acylation of the pendant alcohol moiety with acyl chlorides, pyridine should be employed as a base in order to avoid a ring-opening reaction of the oxetane ring by the used acyl chloride. When pyridine was not added to the above reaction mixture, the required ester was not obtained, since none of the IR bands (980 and 830 cm^{-1}) and of ^1H NMR signals (δ 4.3—4.7) assignable to the oxetane ring were indicated in the spectra of the product.

Phase-transfer catalysis of **3a** with hydroxyl compounds having such functional groups as cyclic acetal, ketone, and azo also afforded desirable products in the presence of TBAB in 50% NaOH and either of hexane or benzene. In the preparation of these products, use of an equimolar amount of the hydroxyl compound to **3a** was enough to realize fairly good yields of products. By the Williamson synthesis, sodium salts of alkoxides and phenoxides have been prepared using sodium metal, sodium hydride, or potassium carbonate as a base in dry alcoholic (which give their alkoxide anions with the base too) or aprotic polar solvents such as DMF, in order to obtain ether products by a reaction of the sodium salts with halides. The present method using a small amount of TBAB in 50% NaOH as a base and commercially available hexane or benzene as the solvent is more facile and less expensive. In particular it can be applied conveniently when the sodium salts are insoluble or hardly soluble in the reaction medium used in the Williamson synthesis. An example is described for the synthesis of **3a** and **4a** by a phase-transfer catalytic reaction between **1** and **2a**.[4]

Preparation of Polyoxetanes. Those oxetanes carrying a functional group at the C-3 position of an oxetane ring can be used as a monomer of the cationic ring-opening polymerization in dichloromethane (DCM) at 0 °C with a boron trifluoride (BF_3)–THF (tetrahydrofuran) complex as an initiator. A 20-h polymerization of those oxetanes gave viscous liquid polymers, which were soluble in such common organic solvents as DCM, chloroform, benzene, acetone, ether, DMF, and THF. Uncross-linked polymers with the comb-like oligo(oxyethylene) side chains were soluble in methanol but not in water, although all the corresponding monomers were appreciably soluble in water because of the hydrophilicity of their oligo(oxyethylene) groups. When the bisoxetane **4a** was used as a comonomer in the above polymerizations of the oxetane derivatives, elastic gel polymers insoluble in the ordinary solvents were produced.

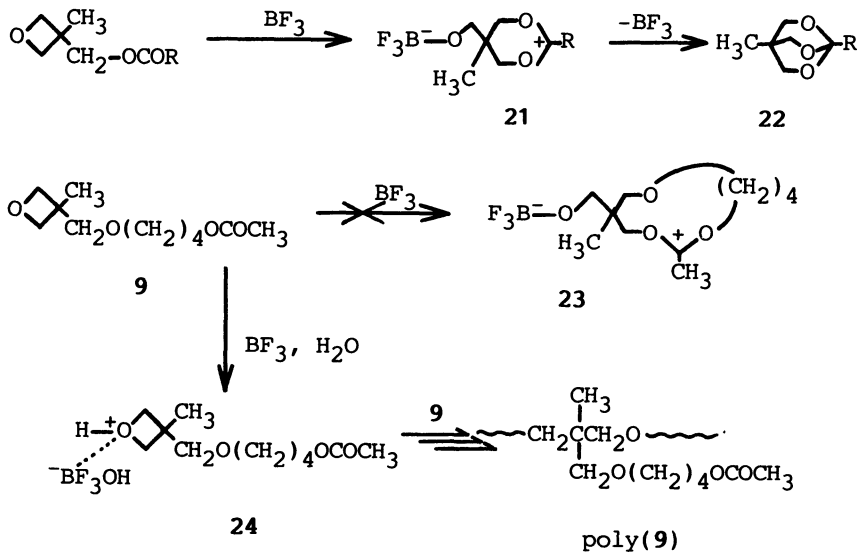
Table 2. Cationic Ring-Opening Polymerization of Oxetane Derivatives in CH_2Cl_2 at 0 °C for 20 h[a]

Monomer (Mole ratio)	Polymer[b]			
	Name	Yield/%	$10^{-3}\overline{M}_n$	Wavenumber[c]/cm^{-1}
5a	Poly (**5a**)	92	12.0	1750, 1250, 1030 (ester); 1100 (acyclic ether)
5a+**4a** (85/15)	**R-1**	89	Gel	
5b+**4a** (70/30)	**R-2**	89	Gel	
6	Poly (**6**)	91	5.9	1760, 1740, 1260, 1040 (ester) 1100 (acyclic ether)
7	Poly (**7**)	85	1.1	1740, 1250, 1070 (ester); 1720 (C=O); 1620 (C=C); 1100
8	—	0	—	—
9	Poly (**9**)	52[d]	16.4	1740, 1250, 1040 (ester); 1100
9+**4a** (91/9)	**R-3**	89	Gel	
19	Poly (**19**)	100	12.0	1715, 1170 (ester); 1640 (C=C) 765 (phenyl)
20a	Poly (**20a**)	66	n.d[e]	1740, 1240, 1060 (ester); 1100; 755 (ortho)
20b	Poly (**20b**)	96	n.d.	1740, 1240, 1060; 1100; 830 (para)
17	Poly (**17**)	53[f]	1.0	1720 (C=O); 1100 (acyclic ether)
17+**4a** (76/24)	**R-4**	57	Gel	
14a	Poly (**14a**)	90	1.3	1675 (C=O); 1240 (aromatic ether); 1120; 760 (ortho)
14a+**4a** (59/41)	**R-5**	75	Gel	
14b	Poly (**14b**)	90	1.5	1680; 1255; 1110; 835 (para)
14b+**4a** (90/10)	**R-6**	78	Gel	
10a	Poly (**10a**)	87	n.d	1110 (acyclic ether)
10b	Poly (**10b**)	78	n.d	
10c	Poly (**10c**)	83	n.d	
10d	Poly (**10d**)	72	n.d	
11+**4a** (72/28)	**R-7**	87	Gel	1110; 985, 830 (acetal)
12	Poly (**12**)	94	2.2	1100; 735, 700 (phenyl)
15	Poly (**15**)	33[g]	3.7	1255; 1110; 840 (para); 690 (phenyl)

a) Initiator, BF_3·THF (0.5 mol% to monomer); initial monomer concentration, 1.0—3.5 mol dm^{-3}. b) For a methanol-insoluble fraction. c) IR bands characteristic of functional groups are presented. d) For the rest, 39% yield of polymer with $\overline{M}_n$ of 2000 was obtained as a methanol-soluble fraction. e) Not determined. f) 37% of lower-molecular-weight polymer was obtained as a methanol-soluble fraction. g) In a methanol-soluble fraction, a considerable amount of unreacted monomer was present.

Existence of an ester group at the end of a 2-oxapolymethylene spacer did not prevent the oxetane monomer from expanding into its polymer with a considerably high molecular weight. It has been found by Corey and Raju that some esters of **1** are converted into the 2,6,7-trioxabicyclo[2.2.2]octane structure, but not the polyoxetane structure, via the zwitterion intermediate **21** which was derived from the (3-methyl-3-oxetanyl)methyl ester of a carboxylic acid in the presence of a 25 mol% of BF_3 etherate.[14] We also confirmed that (3-methyl-3-oxetanyl)methyl acetate could not give its polymer in the presence of a 0.5 mol% of BF_3·THF. However, **9** can be converted into its polymer, poly(**9**), but not an 11-membered heterocyclic intermediate **23**, via formation of a cyclic oxonium ion **24**, which is highly susceptible to a nucleophilic attack of **9**, by BF_3 besides a trace of moisture present in a reaction mixture.[15] Difficulty in forming the intermediate **23** may be ascribed to requiring a higher ring-strain energy for the formation of **23** than that of a stable six-membered ring in **21**, following the theory of ring-strain energies of cycloalkanes.[16]

Ester groups of poly(**9**), poly(**19**), and their **4a**-cross-linked analogues were hydrolyzed with 1.0 mol dm^{-3} NaOH in methanol at reflux temperature within reaction periods of 1 to 5 h, depending on the structure of the polymer used. The resultant uncross-linked polyols were soluble in methanol, but not in water. A **4a**-cross-linked polymer of **11** was also used to obtain a polyoxetane resin carrying a 1,3-glycol moiety at the spacer end; a cyclic acetal of **11** was refluxed in acetone containing 3.0 mol dm^{-3} aqueous HCl to give the 1,3-glycol moiety. The presence of this 1,3-glycol in the product is confirmed by its IR spectrum indicating absorption bands of the primary alcohol at 3400 and 1040 cm^{-1} as well as disappearance of bands due to the cyclic acetal at 1085 and 830 cm^{-1} (Fig. 2C). On the other hand, these acetal ring bands appear in the IR spectra of the copolymer **R-7** and monomer **11**, although IR bands due to the acetal and oxetane rings in **11** overlap each other at 830 cm^{-1} (Figs. 2A and 2B).



Scheme 7.

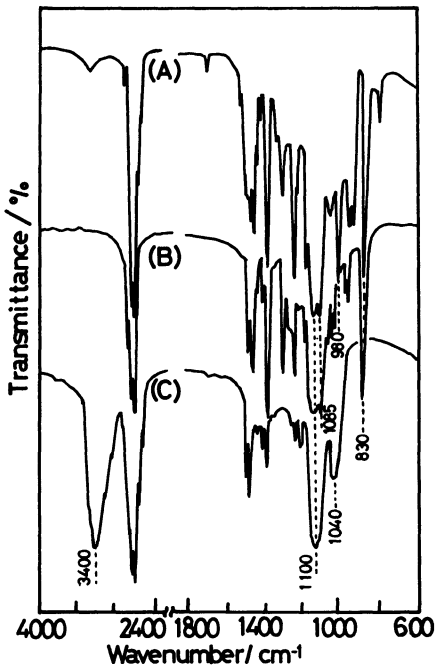


Fig. 2. IR spectra of (A) monomer **11**, (B) **4a**-cross-linked polymer of **11**, and (C) product polymer obtained by hydrolysis of the pendant cyclic acetal.

Polyoxetanes with terminal aliphatic and aromatic ketones in the side chain were prepared by cationic ring-opening polymerizations of **7**, **17**, **14a**, and **14b**, although they had low molecular weights of about 1000. In each of these polymerizations, the polymerization solution changed from colorless to orange or wine red during polymerization. This color disappeared on adding methanol to the solution after a reaction time of 20 h. Residual monomer was not detected by gas chromatography (GC) analysis of the polymerization mixture. These facts suggest that some other undesired side reaction than a termination reaction produced such low-molecular-weight polymers. On the other hand, **20a** and **20b** having an acetoxyl group in their side chains were polymerized under the same polymerization conditions as those applied for the polymerization of **14a** and **14b**, and gave colorless gel polymers, which were insoluble in the usual solvents, in spite of using no cross-linking agents such as **4a** and **4b** in this polymerization. The insolubility of those polymers may be interpreted as due to a high molecular weight, highly crystallized structure, or a cross-linked structure formed by an unexpected side reaction. The acetyl group of poly(**14a**) and poly(**14b**), which showed a strong IR band at 1680 cm^{-1}, were completely reduced with $NaBH_4$ to the corresponding secondary alcohol, a broad band of which appeared around 3400 cm^{-1}. IR spectra of the $NaBH_4$-reduced polymers were identified, respectively, with IR spectra of the polymers obtained by hydrolysis of poly(**20a**) and poly(**20b**) with 2.0 mol dm^{-3} NaOH in methanol. Presumably, the acetyl carbonyl group seems to be involved in the occurrence of a side reaction during the polymerization. A mechanism for this side reaction has not yet been clarified. The investigation of cationic ring-opening polymerization of **14a**, **14b**, **20a**, and **20b** is in progress in our laboratory. Oxetane **8** with a pendant cyano group did not give the corresponding polymer, presumably due to the existence of the cyano group which is considered to be a Lewis base capable of coordinating with a BF_3 initiator, resulting in lack of a reaction step initiated by BF_3.

Concerning the hydrolysis of the malonic ester group of **5**, a hydrolysis of the corresponding diester of a cross-linked polymer was also examined by warming

it in 1.0 mol dm^{-3} aqueous NaOH and methanol. One gram of the resultant polymer, which showed no IR bands due to the ester group, was neutralized with 7.3 mmol of NaOH, indicating that the hydrolyzed polymer had a pendant dibasic acid group. The calculated amount of the carboxyl group is 6.5 mmol per 1.0 g of the dry polymer containing a 15 mol% of **4a** as a cross-linking agent. If the polymer has a monobasic acid pendant group by decarboxylation of the dibasic acid formed intermediately upon the hydrolysis, the amount of carboxyl group is calculated to be 3.7 mmol per 1.0 g of the resultant polymer. Therefore, it is also confirmed that the decarboxylation reaction does not take place under reaction conditions applied for the hydrolysis of the malonic ester at the spacer end of the polyoxetane resin. Oxetane **16b** with a pendant carboxyl group polymerized on leaving **16b** in a test tube at room temperature for at least 3 months, as confirmed by the IR spectrum lacking absorption bands due to an oxetane ring.

The preceding information about the chemical reactions of the oxetane derivatives and their polymers will be of assistance in guiding work on the design of functional polymers that are composed of a soft, somewhat polar polyether network with qualities different from those of a hard, less polar polystyrene support widely used in functional polymer synthesis.

Experimental

Materials. Oxetanes **3a** and **3b**, and bisoxetanes **4a** and **4b** were obtained according to the method described by us previously.[4]

Diethyl 7-(3-Methyl-3-oxetanyl)-6-oxaheptane-1,1-dicarboxylate (5a) and Diethyl 9-(3-Methyl-3-oxetanyl)-8-oxanonane-1,1-dicarboxylate (5b): Diethyl sodiomalonate was formed from diethyl malonate (26 mmol) and sodium metal (21 mmol) in dry ethanol (200 ml) and, subsequently, allowed to react with **3a** or **3b** (17 mmol) under reflux for 2 h. After removing ethanol from the reaction mixture by evaporation, the residue was neutralized with acetic acid and shaken both with ether and water. The organic layer was separated from the aqueous layer, dried over Na_2SO_4, and distilled to give **5a** (88%) or **5b** (75%).

5a: bp 140—142 °C (79 Pa); IR (neat) 1750, 1735, 1240, 1155, and 1025 (ester), 1115 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.25 (6H, t, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.28 (3H, s, CH_3 on the oxetane ring), 1.6—2.2 [6H, m, $CH_2OCH_2(C\underline{H}_2)_3CH$], 3.28—3.70 [total 5H: s (δ=3.46), CH_2 adjacent to the oxetane ring; m, $CH_2OC\underline{H}_2(CH_2)_3C\underline{H}$], 4.18 (4H, q, J=7.0 Hz, $C\underline{H}_2CH_3$), and 4.31 and 4.47 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring].

Found: C, 60.65; H, 9.03%. Calcd for $C_{16}H_{28}O_6$: C, 60.73; H, 8.94%.

5b: bp 173—175 °C (53 Pa); IR (neat) 1755, 1735, 1240, and 1025 (ester), 1115 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.00—2.13 [total 19H: t (δ=1.26), J=7.0 Hz, $CH_2C\underline{H}_3$; s (δ=1.31), CH_3 on the oxetane ring; m, $CH_2OCH_2(C\underline{H}_2)_5CH$], 3.25—3.65 [total 5H: s (δ=3.48), CH_2 adjacent to the oxetane ring; m, $CH_2OC\underline{H}_2(CH_2)_5C\underline{H}$], 4.23 (4H, q, J=7.0 Hz, $C\underline{H}_2CH_3$), and 4.35 and 4.49 (each 2H, AB quartet, J=5.0 Hz, CH_2 of the oxetane ring).

Found: C, 62.48; H, 9.57%. Calcd for $C_{18}H_{32}O_6$: C, 62.75; H, 9.38%.

9-(3-Methyl-3-oxetanyl)-8-oxanonane-1,1-dicarboxylic Acid (16b): **5b** was allowed to react with 1.0 mol dm^{-3} NaOH (twofold equivalence to the ester) in 50% aqueous methanol at reflux temperature for 5 h. After the reaction mixture has been concentrated by means of an evaporator, the residue was acidified to pH 5 with aqueous HCl, saturated with Na_2SO_4, and extracted three times with ether. The combined extracts were evaporated to obtain an oily hydrolysis product **16b** in a 72% yield: IR (neat) 3400 and 1720 (COOH), 1110 (acyclic ether), and 980 and 830 (cyclic ether) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10—1.74 [total 11H: s (δ=1.31), CH_3; m, $CH_2OCH_2(C\underline{H}_2)_4CH_2CH$], 1.74—2.10 [2H, m, $C\underline{H}_2CH(COOH)_2$], 3.20—3.60 [total 5H: s (δ=3.46), CH_2 adjacent to the oxetane ring; m, $CH_2OC\underline{H}_2(CH_2)_4CH_2C\underline{H}$], 4.41 and 4.59 (each 2H, AB quartet, J=5.9 Hz, CH_2 of the oxetane ring), and 8.58 (2H, bs, COOH).

Triethyl 7-(3-Methyl-3-oxetanyl)-6-oxaheptane-1,1,1-tricarboxylate (6): Prepared in a 74% yield by a phase-transfer catalytic reaction between triethyl sodiomethane-1,1,1-tricarboxylate[17] (21 mmol) and **3a** (21 mmol) in the presence of TBAB (1.1 mmol) in toluene (50 ml) at 100 °C for 7 h: bp 156 °C (10 Pa); IR (neat) 1760, 1749, 1260, and 1040 (ester), 1110 (acyclic ether), and 980 and 830 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.29 (9H, t, J=6.6 Hz, $CH_2C\underline{H}_3$), 1.31 (3H, s, CH_3 on the oxetane ring), 1.46—1.95 [4H, m, $CH_2OCH_2(C\underline{H}_2)_2CH_2C$], 1.95—2.39 [2H, m, $CH_2OCH_2(CH_2)_2C\underline{H}_2C$], 3.37—3.70 [total 4H: m, $CH_2OC\underline{H}_2(CH_2)_2CH_2C$; s ($\delta$=3.50), CH_2 adjacent to the oxetane ring], 4.29 (6H, q, J=6.6 Hz, $C\underline{H}_2CH_3$), and 4.35 and 4.53 (each 2H, AB quartet, J=5.8 Hz, CH_2 of the oxetane ring).

Found: C, 58.57; H, 8.34%. Calcd for $C_{19}H_{32}O_8$: C, 58.74; H, 8.32%.

Ethyl 8-(3-Methyl-3-oxetanyl)-2-acetyl-7-oxaoctanoate (7) and 9-(3-Methyl-3-oxetanyl)-8-oxa-2-nonanone (17): **7** was prepared from ethyl acetoacetate (50 mmol), bromide **3a** (42 mmol), and sodium metal (50 mmol) in dry ethanol. Working up the reaction mxture and distilling the resultant organic layer gave **7** with a purity of 98% by GC analysis: bp 116—124 °C (57 Pa); IR (neat) 1740, 1240—1150, and 1060—1020 (ester), 1710 (C=O), 1620 (C=C of an enol form), 1120 (acyclic ether), and 980 and 830 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.0—2.0 [total 12H: t (δ=1.27), J=7.0 Hz, $CH_2C\underline{H}_3$; s (δ=1.30), CH_3 on the oxetane ring; m, $CH_2OCH_2(C\underline{H}_2)_3CH$], 2.21 (3H, s, $COCH_3$), 3.28—3.70 [total 5H: s (δ=3.47), CH_2 adjacent to the oxetane ring; m, $CH_2OC\underline{H}_2(CH_2)_3C\underline{H}$], 4.21 (2H, q, J=7.0 Hz, $C\underline{H}_2CH_3$), and 4.31 and 4.39 (each 2H, AB quartet, J=5.0 Hz, CH_2 of the oxetane ring).

Oxo ester **7** (42 mmol) was stirred in 1.0 mol dm^{-3} NaOH (84 mmol) at 50 °C for 3 h until an oily layer of **7** disappeared completely. The alkaline solution was heated at 90 °C for 4 h. The resulting organic layer was extracted with ether, separated from the aqueous layer, dried over Na_2SO_4, and distilled to give pure **17** in a 53% yield based on **3a:** bp 110—115 °C (107 Pa); IR (neat) 1710 (C=O), 1120 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$)

δ=1.21—1.96 [total 9H: s (δ=1.29), CH_3 on the oxetane ring; m, $CH_2OCH_2(CH_2)_3CH_2$], 2.12 (3H, s, $COCH_3$), 2.24—2.63 (2H, m, CH_2Ac), 3.31—3.64 [total 4H: s (δ=3.46), CH_2 adjacent to the oxetane ring; m, $CH_2OCH_2(CH_2)_3CH_2$], and 4.32 and 4.47 (each 2H, AB quartet, J=5.6 Hz, CH_2 of the oxetane ring).

6-(3-Methyl-3-oxetanyl)-5-oxahexyl Acetate (9) and 3-(6-Hydroxy-2-oxahexyl)-3-methyloxetane (18): **3a** (84.3 mmol) was heated with powdered potassium acetate (0.28 mol) in benzene (50 ml) in the presence of TBAB (4.3 mmol) under reflux for 6 h with efficiently stirring. The organic layer was washed with water and dried over Na_2SO_4. After removing the solvent from the reaction mixture, fractional distillation of the residue gave slightly impure **9** in about 84% yield: bp 107 °C (116 Pa); IR (neat) 1745, 1245, and 1040 (ester), 1110 (acyclic ether), and 980 and 830 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.33 (3H, s, CH_3), 1.48—1.90 [4H, m, $OCH_2(CH_2)_2CH_2OAc$], 2.05 (3H, s, $COCH_3$), 3.35—3.78 [total 6H: m, $CH_2OCH_2(CH_2)_2CH_2OAc$; s (δ=3.49), CH_2 adjacent to the oxetane ring], 4.13 (2H, t, J=5.6 Hz, CH_2OAc), and 4.37 and 4.53 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring).

The acetate **9** was refluxed with 2.5 mol dm^{-3} NaOH in methanol for 2 h. The methanol was evaporated and the residue shaken with hexane. The alkaline aqueous layer was separated from the organic layer, saturated with sodium chloride, and shaken with ether to extract an alcoholic product. The ethereal layer was concentrated and distilled to give **18** in a 73% yield based on **3a:** bp 98—99 °C (93 Pa); IR (neat) 3400 and 1065 (alcohol), 1120 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3), 1.43—1.90 [4H, m, $OCH_2(CH_2)_2CH_2OH$], 3.12—3.86 [total 7H: m, $CH_2OCH_2(CH_2)_2CH_2OH$; s (δ=3.50), CH_2 adjacent to the oxetane ring], and 4.35 and 4.51 (each 2H, AB quartet, CH_2 of the oxetane ring).

Found: C, 61.89; H, 10.64%. Calcd for $C_9H_{18}O_2$: C, 62.02; H, 10.43%.

6-(3-Methyl-3-oxetanyl)-5-oxahexyl Cinnamate (19): The alcohol **18** (32 mmol) was esterified with cinnamoyl chloride (33 mmol) and pyridine (3 ml) in DCM (30 ml) at −10 to 0 °C for 5 h. The desired product **19** was isolated in a 77% yield by distillation: bp 172—174 °C (12 Pa); IR (neat) 1580, 1500, 1450, and 770 (phenyl), 1715, 1315, and 1175 (ester), 1640 (C=C), 1120 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.34 (3H, s, CH_3), 1.57—2.07 [4H, m, $CH_2OCH_2(CH_2)_2$], 3.36—3.73 [total 4H: s (δ=3.50), CH_2 adjacent to the oxetane ring; m, $CH_2OCH_2(CH_2)_2$], 4.41—4.69 [total 6H: m, CH_2OCO; AB quartet (δ=4.39 and 4.55), J=6.9 Hz, CH_2 of the oxetane ring], 6.49 (1H, d, J=16.0 Hz, CH=CHPh), and 7.34—7.69 [total 6H: m, ArH; d (δ=7.27), J=16.0 Hz, CH=CHPh].

3-(2,7,10,13-Tetraoxatetradecyl)- (10a), 3-(2,7,10,13,16-Pentaoxaheptadecyl)- (10b), 3-(2,7,10,13-Tetraoxaheptadecyl)- (10c), and 3-(2,7,10,13,16-Pentaoxaicosyl)-3-methyloxetanes (10d): Each of these compounds was prepared by the phase-transfer catalytic reaction of **3a** (41 mmol) with an appropriate di- or triethylene glycol monoalkyl ether (21 mmol) in hexane (20 ml) and 50% NaOH (28 g) for 5 h under reflux in the presence of TBAB (1.1 mmol). The reaction mixture was diluted with water (70 ml), saturated with Na_2SO_4, and extracted continuously with ether for 30 h. The ether extract was distilled to give **10a** (69%), **10b** (59%), **10c** (68%), or **10d** (67%). These compounds had characteristic IR bands at 1110 (acyclic ether) and 980 and 835 cm^{-1} (cyclic ether).

10a: bp 116—119 °C (20 Pa); ^1H NMR ($CDCl_3$) δ=1.30 (3H, s, CH_3 on oxetane ring), 1.50—1.85 [4H, m, $CH_2OCH_2(CH_2)_2CH_2$], 3.31—3.89 [total 17H: s (δ=3.38), OCH_3; s (δ=3.48), CH_2 adjacent to the oxetane ring; s (δ=3.62), $(CH_2CH_2O)_2$; m, $CH_2OCH_2(CH_2)_2CH_2$], and 4.32 and 4.50 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring).

10b: bp 144—145 °C (49 Pa); ^1H NMR ($CDCl_3$) δ=1.30 (3H, s, CH_3 on the oxetane ring), 1.40—1.84 [4H, m, $CH_2OCH_2(CH_2)_2CH_2O$], 3.30—3.80 [total 21H: s, (δ=3.37), OCH_3; s (δ=3.47), CH_2 adjacent to the oxetane ring; s (δ=3.60), $OCH_2CH_2OCH_2CH_2OCH_2CH_2O$; s ($\delta$=3.66), $OCH_2CH_2OCH_2CH_2OCH_2CH_2O$; m, $CH_2OCH_2(CH_2)_2CH_2O$], and 4.32 and 4.48 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring).

Found: C, 60.02; H, 10.27%. Calcd for $C_{16}H_{32}O_6$: C, 59.96; H, 10.09%.

10c: bp 120—132 °C (45 Pa); ^1H NMR ($CDCl_3$) δ=0.71—1.06 (3H, m, CH_3 of butyl), 1.22—1.81 [total 11H: s (δ=1.24), CH_3 on the oxetane ring; m, $CH_2OCH_2(CH_2)_2CH_2O$ and $OCH_2(CH_2)_2CH_3$], 3.29—3.78 [total 16H: s (δ=3.46), CH_2 adjacent to the oxetane ring; s (δ=3.60), $O(CH_2CH_2O)_2$; m, $CH_2OCH_2(CH_2)_2CH_2O$ and $OCH_2(CH_2)_2CH_3$], and 4.31 and 4.49 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring).

10d: bp 142—157 °C (51 Pa); ^1H NMR ($CDCl_3$) δ=0.76—1.12 (3H, m, CH_3 of butyl), 1.24—1.94 [total 11H: s (δ=1.31), CH_3 on the oxetane ring; m, $CH_2OCH_2(CH_2)_2CH_2O$ and $OCH_2(CH_2)_2CH_3$], 3.32—3.48 [total 20H: s (δ=1.47), CH_2 adjacent to the oxetane ring; s (δ=1.61), $OCH_2CH_2OCH_2CH_2OCH_2CH_2O$; s ($\delta$=1.66), $OCH_2CH_2OCH_2CH_2OCH_2CH_2O$; m, $OCH_2(CH_2)_2CH_2O$ and $OCH_2(CH_2)_2CH_3$], and 4.33 and 4.49 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring).

3-[8-(2,2,5-Trimethyl-1,3-dioxan-5-yl)-2,7-dioxaoctyl]-3-methyloxetane (11): **11** was prepared by a phase-transfer catalytic reaction using **3a** (21 mmol) and 5-hydroxymethyl-2,2,5-trimethyl-1,3-dioxane (21 mmol) in hexane (30 ml) and 50% NaOH (28 g) in the presence of TBAB (1.1 mmol) at reflux temperature for 12 h. The ordinary work-up gave pure **11** in a 58% yield: bp 126.0—126.5 °C (69 Pa); IR (neat) 1110 (acyclic ether), 980 and 830 (cyclic ether), and 1085 and 830 cm^{-1} (cyclic acetal); ^1H NMR ($CDCl_3$) δ=0.87 (3H, s, nongeminal CH_3 on the acetal ring), 1.31 (3H, s, CH_3 on the oxetane ring), 1.39 and 1.42 (each 3H, each s, geminal CH_3), 1.50—1.74 [4H, m, $CH_2OCH_2(CH_2)_2CH_2OCH_2$], 3.32—3.80 [total 12H: s (δ=3.39), CH_2 adjacent to the acetal ring; s (δ=3.47), CH_2 adjacent to the oxetane ring; m (δ=3.32—3.52), $CH_2OCH_2(CH_2)_2CH_2OCH_2$; AB quartet ($\delta$=3.53 and 3.70), J=11.0 Hz, CH_2 of the acetal ring], and 4.43 and 4.50 (each 2H, AB quartet, J=5.6 Hz, CH_2 of the oxetane ring).

3-[8-Phenyl-2,7-dioxaoctyl]-3-methyloxetane (12): A phase-transfer catalytic reaction of **3a** (42 mmol) with benzyl alcohol (38 mmol) gave **12** in a 72% yield in the presence of TBAB (1.9 mmol) in hexane (40 ml) and 50% NaOH (50 g): bp 144.0—144.5 °C (67 Pa); IR (neat) 1605, 1590, 1500, 740, and 700 (monosubstituted benzene), 1110 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.28 (3H, s, CH_3), 1.47—1.97 [4H, m, $OCH_2CH_2(CH_2)_2CH_2O$], 3.29—3.71 [total 6H: m, $OCH_2(CH_2)_2CH_2O$; s (δ=3.43), CH_2 adjacent to the oxetane ring], 4.23—4.65 [total 6H: s

(δ=4.49), CH_2Ph; AB quartet (δ=4.31 and 4.49), J=5.5 Hz, CH_2 of the oxetane ring], and 7.3—7.5 (5H, m, ArH).

Found: C, 72.73; H, 9.39%. Calcd for $C_{16}H_{24}O_3$: C, 72.68; H, 9.17%.

3-[8-(3,4-Methylenedioxyphenyl)-2,7-dioxaoctyl]-3-methyloxetane (13): In the same way as above, **13** was prepared from **3a** and piperonyl alcohol in a 72% yield: bp 152—160 °C (7.3 Pa); IR (neat) 1110 (acyclic ether), 980 and 830 (cyclic ether), 1040 and 930 (cyclic acetal), and 1610, 1505, 1495, and 810 cm^{-1} (1,2,4-trisubstituted benzene); ^1H NMR ($CDCl_3$) δ=1.29 (3H, s, CH_3), 1.56—1.76 [4H, m, $CH_2OCH_2(CH_2)_2CH_2$], 3.36—3.56 [total 6H: s (δ=3.47), CH_2 adjacent to the oxetane ring; m, $CH_2OCH_2(CH_2)_2CH_2OCH_2Ar$], 4.39 (2H, s, CH_2Ar), 4.33 and 4.49 (each 2H, AB quartet, J=5.8 Hz, CH_2 of the oxetane ring), 5.93 (2H, s, CH_2 of acetal), and 6.72—6.87 (3H, m, ArH).

Found: C, 66.10; H, 8.08%. Calcd for $C_{17}H_{24}O_5$: C, 66.20; H, 7.86%.

3-[7-(2- and 4-Acetylphenyl)-2,7-dioxaheptyl]-3-methyloxetanes (14a and 14b): These products were prepared by the phase-transfer catalytic reaction of *o*- or *p*-hydroxyacetophenone (37 mmol) with **3a** (37 mmol) in benzene (50 ml) and 50% NaOH (49 g) at 80 °C for 6—8 h in the presence of TBAB (1.8 mmol). The ordinary work-up of the reaction mixture gave **14a** (81%) or **14b** (88%).

14a: bp 172 °C (19 Pa); IR (neat) 1600, 1580, 1490, and 760 (1,2-disubstituted benzene), 1675 (acetyl C=O), 1240 (aromatic ether), 1115 (acyclic ether), and 980 and 830 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.29 (3H, s, CH_3 on the oxetane ring), 1.52—2.20 [4H, m, $CH_2OCH_2(CH_2)_2CH_2O$], 2.62 (3H, s, $COCH_3$), 3.37—3.70 [total 4H: s (δ=3.47), CH_2 adjacent to the oxetane ring; m, $CH_2OCH_2(CH_2)_2CH_2OAr$], 4.08 (2H, bt, CH_2OAr), 4.32 and 4.50 (each 2H, AB quartet, CH_2 of the oxetane ring), and 6.8—7.9 (4H, m, ArH).

Found: C, 69.66; H, 8.29%. Calcd for $C_{17}H_{24}O_4$: C, 69.82; H, 8.29%.

14b: bp 154—156 °C (8Pa); IR (neat) 1600, 1575, 1515, and 835 (1,4-disubstituted benzene), 1680 (acetyl C=O), 1255 (aromatic ether), 1115 (acyclic ether), and 980 and 830 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.12 (3H, s, CH_3 on the oxetane ring), 1.40—1.97 [4H, m, $CH_2OCH_2(CH_2)_2CH_2O$], 2.34 (3H, s, $COCH_3$), 3.25—3.52 [total 4H: s (δ=3.30), CH_2 adjacent to the oxetane ring; m, $CH_2OCH_2(CH_2)_2CH_2OAr$], 3.88 (2H, bt, CH_2OAr), 4.15 and 4.33 (each 2H, AB quartet, CH_2 of the oxetane ring), and 6.6—7.9 (4H, AB quartet-like, ArH).

Found: C, 69.65; H, 8.46%. Calcd for $C_{17}H_{24}O_4$: C, 69.82; H, 8.29%.

3-[7-[2- and 4-(1-Acetoxyethyl)phenyl]-2,7-dioxaheptyl]-3-methyloxetanes (20a and 20b): **14a** or **14b** (17 mmol) was stirred with $NaBH_4$ (17 mmol) in ethanol (80 ml) at 60 °C for 2 h. The ethanol was evaporated, and the residue shaken with both water and ether. The organic layer was separated from the aqueous layer and dried over Na_2SO_4. The crude product, which was obtained by removing the solvent from the organic layer, was allowed to react with acetyl chloride (17 mmol) in DCM (50 ml) containing pyridine (3 ml) at 20—25 °C for 9 h. The reaction mixture was poured into ice and extracted with DCM. The organic layer was washed with water and dried over Na_2SO_4. Removal of the solvent followed by distillation of the residue gave **20a** (90%) or **20b** (83%).

20a: bp 151 °C (23 Pa); IR (neat) 1740, 1250, and 1060 (ester), 1605, 1590, 1500, 1475, 755 (1,2-disubstituted benzene), 1240 (aromatic ether), 1120 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.21 (3H, s, CH_3 on the oxetane ring), 1.50 [3H, s, J=6.6 Hz, $CH_3CH(OAc)Ar$], 1.64—2.05 [4H, m, $CH_2OCH_2(CH_2)_2CH_2O$], 2.07 (3H, s, $OCOCH_3$), 3.34—3.70 [total 4H: s (δ=3.49), CH_2 adjacent to the oxetane ring; t-like, $CH_2OCH_2(CH_2)_2CH_2OAr$], 3.87—4.19 (3H, t-like, CH_2OAr), 4.33 and 4.51 (each 2H, AB quartet, J=6.0 Hz, CH_2 of the oxetane ring), 6.30 (1H, q, J=6.6 Hz, CHAr), and 6.2—7.5 (4H, m, ArH).

20b: bp 174—175 °C (41 Pa); IR (neat) 1744, 1245, and 1060 (ester), 1620, 1590, 1520, and 835 (1,4-disubstituted benzene), 1240 (aromatic ether), 1120 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.29 (3H, s, CH_3 on the oxetane ring), 1.39 [3H, d, J=7.0 Hz, $CH_3CH(OAc)Ar$], 1.63—1.93 [4H, m, $CH_2OCH_2(CH_2)_2CH_2O$], 2.04 (3H, s, $OCOCH_3$), 3.41—3.69 [total 4H: s (δ=3.51), CH_2 adjacent to the oxetane ring; t-like, $CH_2OCH_2(CH_2)_2CH_2OAr$], 3.88—4.18 (2H, t-like, CH_2OAr), 4.35 and 4.53 (each 2H, AB quartet, J=5.0 Hz, CH_2 of the oxetane ring), 5.87 (1H, q, J=7.0 Hz, CHAr), and 6.8—7.5 (4H, AB quartet-like, ArH).

4-[[6-(3-Methyl-3-oxetanyl)-5-oxahexyl]oxy]azobenzene (15): **15** was prepared by a phase-transfer catalytic reaction using **3a** (21 mmol) and 4-hydroxyazobenzene (21 mmol) in toluene (30 ml) and 50% NaOH (30 g) in the presence of TBAB (1.1 mmol) at reflux temperature. After working up the reaction mixture in the ordinary way, recrystallization of the crude product from ethanol–DCM gave a yellow-colored **15** in a 41% yield: mp 57—59 °C; IR (KBr) 1615, 1580, 1475, 840, and 685 (mono- and disubstituted benzenes), 1260 (aromatic ether), 1110 (acyclic ether), and 980 and 840 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3), 1.36—2.00 [4H, m, $CH_2OCH_2(CH_2)_2CH_2$], 3.40—3.60 [total 4H: s (δ=3.48), CH_2 adjacent to the oxetane ring; t-like, $CH_2OCH_2(CH_2)_2CH_2OAr$], 3.92—4.14 (2H, t-like, CH_2OAr), 4.35 and 4.52 (each 2H, AB quartet, J=5.9 Hz, CH_2 of the oxetane ring), and 6.8—8.0 (9H, m, ArH).

Preparation of Polymers: Polymers of oxetane derivatives were prepared by their cationic ring-opening polymerization in DCM with BF_3·THF as an initiator, according to the method we previously reported.[4]

Polymer Reactions. Hydrolysis of Malonic Ester Groups of Cross-Linked Resins: The ester groups were hydrolyzed by warming the resins with an excess amount of 1.0 mol dm^{-3} NaOH in methanol under reflux. The reaction mixture was concentrated by means of an evaporator and acidified to pH 5 with aqueous HCl. The resinous product was filtered and washed with water and then with methanol. After drying the resin, its weight was measured (yield, 94%). After immersing the resin in 0.05 mol dm^{-3} NaOH for 24 h, an aliquot of the alkaline supernatant was withdrawn to determine acid equivalent of the carboxyl group of the resin by back titration with 0.05 mol dm^{-3} HCl; 1 g of the dry resin was neutralized with 7.28 mmol of NaOH.

Hydrolysis of Polymers Carrying Acetate and Cinnamate Groups in the Side Chain: These polymers were stirred with an excess amount of 2.5 mol dm^{-3} NaOH in methanol under reflux for 1—5 h. After removing the methanol by evaporation, the residue was extracted with ether or benzene in the case of the hydrolysis of uncross-linked polymers.

When using cross-linked polymers, the resultant polymers were filtered and washed successively with water and methanol. Hydrolyzed polymers were obtained in 85—95% yields. IR spectra of these product polymers indicated a strong band due to the hydroxyl group around 3400 cm^{-1}, but did not show bands due to ester and carboxylate groups.

Hydrolysis of a Cyclic Acetal of Resin R-7: A **4a**-cross-linked polymer, **R-7**, was stirred in acetone containing 10% of its volume of 3.0 mol dm^{-3} aqueous HCl for 8 h under reflux. The acetone was removed by evaporation. A polymerized product was collected by filtration and washed successively with water and methanol. After being dried at 70 °C for 7 h in vacuo, the polymer was weighed (yield, 95%).

Measurement. GC analysis of the products was performed in a Shimadzu GC-8A apparatus: glass column (3.2ϕ×1 m) packed with Silicone High Vacuum Grease (30%)/Celite (80—100 mesh); carrier gas, He (66 cm^3 min^{-1}); temp, 200 °C. The IR spectra were recorded on a JASCO A-202 spectrometer and ^1H NMR on a 60 (Hitach R-24B) or 100 MHz instrument (JEOL FX-100S) using $CDCl_3$ as a solvent and TMS as an internal standard at 25 °C. Molecular weight measurements were made by VPO in a Corona molecular weight apparatus (model 117).

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