Side Chain Liquid Crystalline Polyoxetanes with a Spacer-Separated Azobenzene Moiety. I. Preparation and Characterization

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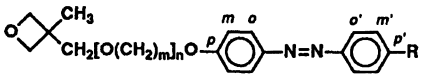
(Received January 21, 1993)

Several oxetane derivatives carrying the azobenzene moiety at the C-3 position of the oxetane ring through the spacer arms of differing lengths were prepared by a substitution reaction of the corresponding bromide or *p*-toluenesulfonate residue of the oxetane with 4-hydroxyazobenzenes. The polymers of these oxetane derivatives were readily obtained by cationic ring-opening polymerization using the adequately increased amount of a THF·BF_3 complex as an initiator at 20—30 °C. The liquid crystalline property of the polymers thus obtained were examined by differential scanning calorimetry and by optical polarized microscopy. From these measurements the influences of the *p'*-substituted azobenzene and of the spacer arm on the liquid crystalline property were found.

In a series of our investigation of using polyethers as the polymeric support or matrix of functional polymers,[1—7] we are interested in the synthesis of polyoxetanes with a pendant azobenzene moiety at the side chain-end, since we hope to obtain photosensitive, thermotropic liquid crystalline materials based on the side chains of the polyoxetane main chain; azobenzenes are known to be a mesogen susceptitble to the photochromic cis–trans isomerization. The flexibility of polymeric supports or matrices is required for the quick occurence of liquid crystalline phase transition of these materials and for lowering the mesomorphic temperature. The pendant mesogenic groups anchored to a flexible main chain can move more smoothly (or in lower heat energy) in the polymer matrices to create a liquid crystalline system than the mesogenic groups anchored to a rigid main chain. In general, the lowered mesomorphic temperature is observed for liquid crystalline polymers immobilizing a mesogenic group at the spacer chain-end of a flexible polymer main chain such as polysiloxane, compared with more rigid polymer main chains such as polyacrylate and polymethacrylate. Hence, a polyoxetane chain must also be examined as the polymeric support of thermotropic liquid crystalline polymers of the side chain type, since the polyoxetane chain is thought to be flexible or expandable due to the quality of ethereal carbon–oxygen bonds.

This paper, the first report of our studies concerning liquid crystalline polyethers, describes the preparation of polyoxetanes, which have pendant azobenzenes through spacer arms of differing lengths, by the cationic ring-opening polymerization of the corresponding oxetane derivatives **1**—**5** and the thermal behavior of the resulting polymers in order to prove their liquid crystalline property by differential scanning calorimetry (DSC) and by optical polarized microscopy (OPM) (Scheme 1).



1 - 5

Spacer n, m	Substituent R: H	CH_3O	*n*-C_4H_9O	*n*-C_4H_9	*n*-$C_8H_{17}O$
0, –		**1**			
1, 4	**2a**	**2b**	**2c**	**2d**	**2e**
1, 5	**3a**	**3b**			
1, 6	**4a**	**4b**			
2, 4		**5**			

Scheme 1. Oxetane derivatives with a pendant azobenzene moiety.

To our knowledge, there are few examples for the boron trifluoride (BF_3)-initiated cationic ring-opening polymerization of oxetanes carrying an aromatic azo group in the side chain, although our previous example was reported briefly for the oxetane **2a** with an azobenzene moiety.[3] For an example of the preparation of polyoxetanes containing nitrogen atoms in the pendant substituent, the cationic ring-opening polymerization of 3,3-bis(azidomethyl)oxetane has been reported using diethyl ether–BF_3 (1/1) as an initiator.[8] Recently, several polyoxetanes with *p'*-substituted biphenyl moieties at the spacer chain-end were synthesized. Among them, analogues having a cyano or fluoro group as the substituent were found to behave as liquid crystalline polymers.[9]

Results and Discussion

Oxetane Monomers. In our previous report, it was briefly described that the bromine atom of oxetane **7a** was displaced by the nucleophilic phenoxide anion generated from 4-hydroxyazobenzene **9a** with K_2CO_3 in *N,N*-dimethylformamide (DMF) to give an azobenzene-containing oxetane **2a**, which was further

converted to its polymer by cationic ring-opening polymerization with a tetrahydrofuran (THF)–BF_3 (1/1) complex in dichloromethane (DCM) at 0 °C.[3] According to this method, several azobenzene-containing oxetane monomers **1**—**5** were derived from the bromide or *p*-toluenesulfonate of **6**, **7a**, **7b**, **7c**, and **8** by a displacement reaction using K_2CO_3 in DMF, and subjected to the polymerization in DCM at 0 °C or in toluene at room temperature around 20 to 30 °C with a THF·BF_3 initiator (Scheme 2).

These oxetanes were assigned to the desired structures by IR and ^{1}H NMR spectroscopy. In general, the IR spectra of these oxetane derivatives showed absorption bands around 1250, 1110, and 980 and 845 cm^{-1} assignable to stretching vibration due to the aromatic, acyclic, and cyclic ethers, respectively, similarly as reported for other oxetane derivatives in our previous paper.[3] The ^{1}H NMR spectra are exemplified for **2a**, **2b**, and **2d** having an azobenzene moiety at the spacer chan-end. These protons were assigned to the corresponding signals in the spectra, as shown in Fig. 1. In this text, henceforth, italic letters *o*, *m*, and *p* are also taken for conveience in place of the corresponding Arabic figures (which are taken under the IUPAC rule) to represent the position names for the ten carbon atoms of the azobenzene ring of oxetane monomers and their polymers, as shown in Scheme 1; "prime" is marked for the position names of the five carbon atoms of the benzene ring linking the substituent R in the azobenzene structure.

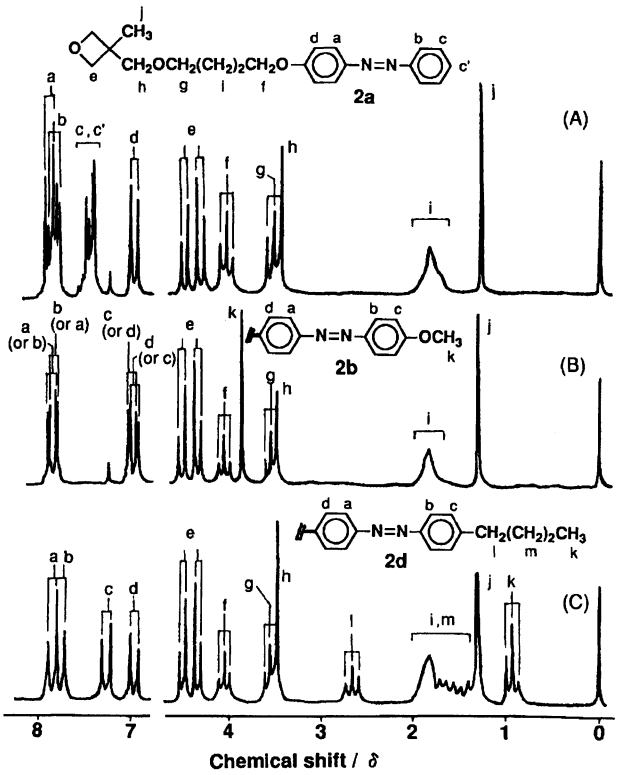
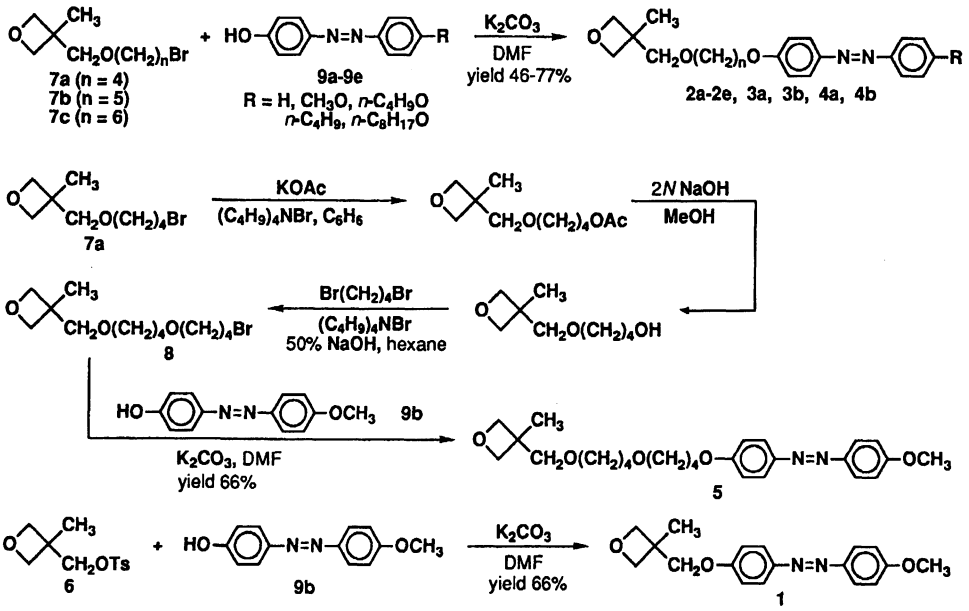


Fig. 1. ^{1}H NMR spectra of oxetane monomers **2a** (A), **2b** (B), and **2d** (C).

The methylene protons of the oxetane ring indicate an AB-quartet around $\delta=4.2$—4.6 as usual. Among the nine aromatic protons of **2a** in the part A of Fig. 1, the five protons H^b and H^c and $H^{c'}$ on the phenyl ring were assignable to multiplet signals at $\delta=7.8$—8.0 and 7.3—7.6, respectively, since the protons at the four *o*-positions of unsubstituted azobenzene are known to resonate at $\delta=7.86$ and the remainder at the somewhat lower chemical shift of $\delta=7.40$. The four protons H^a and H^d on the other phenyl ring show an apparent AB-quartet spin-coupling pattern. The doublet assigned to two protons H^d located at the *m*-position to the azo group resonates at lower chemical shift than that of the two protons H^a located at the *o*-position. When the proton $H^{c'}$ of **2a** was replaced at the *p'*-position by the methoxyl group, i.e., in **2b**, the chemical shift of a doublet due to the proton H^c lies around $\delta=7.0$ at which the proton H^d also shows the same doublet (part B in Fig. 1). In the *p'*-octyloxy-substituted oxetane **2e**, furthermore, two doublets assigned to the protons H^c and H^d appear at the same chemical shift of $\delta=6.98$ and two doublets assigned to H^a and H^b appear at $\delta=7.86$; the two AB-quartets due to these aromatic protons are superimposed on each other (part A in Fig. 2). Similarly the aromatic protons of *p'*-butoxy-substituted oxetane **2c** also showed two AB-quartets superimposed on each other (see Experimetal). In *p'*-butyl-substituted oxetane **2d** (part C in Fig. 1), however, the protons H^c located at the *m'*-position resonate at higher chemical shift of $\delta=7.29$ relative to those of the *p'*-alkoxy-substituted oxetanes **2b**, **2c**, and **2e**, while the protons H^d at the *m*-position resonate at the approximately same chemical shift of $\delta=7.00$ as those of **2b**, **2c**, and **2e**. These findings show that the alkoxyl groups of the azobenzene moiety exert the influence of magnetic shielding on the aromatic protons located at the ortho position toward the alkoxyl groups, probably due to their mesomeric effect. In fact, the aromatic protons located at the *o*- and *p*-positions of anisol resonate at somewhat lower chemical shifts by about 0.3—0.4 ppm than those at the *m*-position.

Polyoxetanes. These azobenzene-containing oxetane monomers were used in the cationic ring-opening polymerization in DCM at 0 °C or in toluene at 20—30 °C with THF·BF_3 in 1—8 mol% respect to the monomer. The resultant polyoxetanes were soluble in the ordinary solvents such as DCM, chloroform, and THF, and reprecipitated with methanol from the polymer solution in DCM. The methanol-insoluble fraction was subjected to the characterization of the product polymer. The results for the polymerization of oxetanes are summarized in Table 1. These products were indentified to the desired polymers by IR and ^{1}H NMR spectroscopy and also confirmed by elemental analysis (Table 2). The ^{1}H NMR spectra of **2e** and its polymer, **IIe**-2, are shown as an example in Fig. 2.



Scheme 2. Preparation of oxetane derivatives.

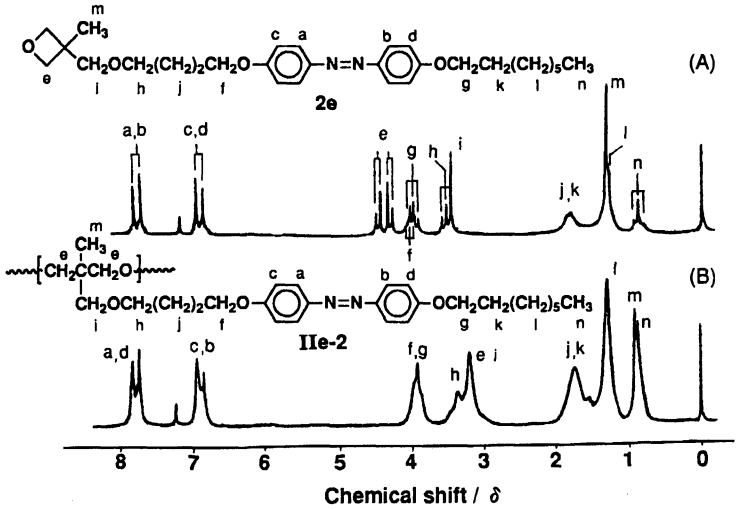


Fig. 2. ^{1}H NMR spectra of oxetane monomer **2e** (A) and its polymer **IIe**-2 (B).

These protons were assigned to the corresponding signals according to the above-mentioned assignment. Although the methylene (H^e and H^i) and methyl protons (H^m) of the **IIe**-2 appeared at lower chemical shifts compared with those of the corresponding protons H^e, H^i, and H^m of the monomer **2e**, respectively, the chemical shifts and patterns of the other signals of the polymer resembled those of the monomer. The IR spectrum of **IIe**-2 also showed the disappearance of the absorption bands due to the cyclic ether at 980 and 845 cm^{-1}, which appeared in the IR spectrum of **2e**.

When **2a** was polymerized in DCM at 0 °C with 1 mol% of THF·BF_3, the yield of **IIa** was achieved 93%. Monomer **2b** also gave an 80% yield of the product polymer **IIb**-1 using 1 mol% of THF·BF_3 in DCM at 0 °C for 4 h and then at 20—25 °C for 16 h; the **IIb**-1 was deposited on standing at 0 °C (Entries 1 and 7). However, the DCM solvent is not necessarily suitable for the polymerization of azobenzene-containing oxetanes in comparison with the polymerization in a toluene solvent under the comparable conditions; with the toluene 32 and 40% yields of the product polymer were obtained, respectively, from **4a** and **2c** (Entries 4 and 14) and, on the contrary, with the DCM 17 and 8% yields of the product polymer from **4a** and **2c**, respectively (Entries 3 and 13). Such low polymer yields are ascribed to the low solubility of the used monomer in DCM, which was employed ordinarily as the solvent suitable for the cationic ring-opening polymerization of oxetane derivatives in our previous investigations. In the usual cases of the present polymerizations, therefore, toluene was used as a solvent, since the azobenzene-containing monomers showed a tendency to have more sufficient solubilities in toluene than in DCM. Polymerization temperature was

Table 1. Cationic Ring-Opening Polymerization of Oxetanes Having an Azobenzene Moiety at the Side Chain-End[a)]

Entry	Monomer	Conditions				Product polymer [c)]				
		$[M]_0$ [b)]	BF_3	Solvent	Time			Spacer		Yield
		mol dm^{-3}	mol%		h		R	n	m	%
1	**2a**	0.4	1	DCM	20 [d)]	**IIa**	H	1	4	93
2	**3a**	0.7	8	T	50	**IIIa**	H	1	5	77
3	**4a**	0.9	1	DCM	20 [d)]	**IVa**-1	H	1	6	17
4	**4a**	0.9	1	T	50	**IVa**-2	H	1	6	32
5	**4a**	0.7	8	T	50	**IVa**-3	H	1	6	84
6	**1**	0.4	8	T	50	**I**	CH_3O	0	—	81
7	**2b**	1.3	1	DCM	4+16 [e)]	**IIb**-1	CH3O	1	4	80
8	**2b**	0.6	8	T	50	**IIb**-2	CH_3O	1	4	98
9	**3b**	0.7	8	T	50	**IIIb**	CH_3O	1	5	85
10	**4b**	0.6	1	T	132	**IVb**-1	CH_3O	1	6	32
11	**4b**	0.3	8	T	50	**IVb**-2	CH_3O	1	6	87
12	**5**	0.6	8	T	50	**V**	CH_3O	2	4	87
13	**2c**	1.1	1	DCM	50 [d)]	**IIc**-1	C_4H_9O	1	4	8
14	**2c**	0.8	1	T	50	**IIc**-2	C_4H_9O	1	4	40
15	**2e**	0.5	1	T	132	**IIe**-1	$C_8H_{17}O$	1	4	Trace
16	**2e**	0.5	8	T	24	**IIe**-2	$C_8H_{17}O$	1	4	86

a) Carried out in a solvent of dichloromethane (DCM) or toluene (T) at 20—30 °C. b) Initial concentration of charged monomer. c) For a methanol-insoluble fraction. d) Polymerized at 0 °C. e) Polymerized at 0 °C for 4 h and then at 20—30 °C for 16 h.

Table 2. Elemental Analysis Data of Azobenzene-Containing Polyoxetanes **I**—**V**

Polymer	Anal (%)					
	Calcd			Found		
	C	H	N	C	H	N
I	69.20	6.47	8.97	68.96	6.56	8.83
IIa	71.15	7.41	7.90	70.67	7.43	7.92
IIIa	71.70	7.67	7.60	71.58	7.83	7.55
IVa-1	72.21	7.92	7.33	71.45	8.00	7.30
IIb-2	68.71	7.36	7.29	68.48	7.42	7.17
IIIb	69.31	7.60	7.03	69.12	7.71	6.94
IVb-2	69.86	7.83	6.79	69.22	7.90	6.65
IIc-2	70.38	8.05	6.57	70.14	8.11	6.57
IIe-2	72.15	8.79	5.80	71.43	8.98	5.71
V	68.38	7.96	6.14	68.12	8.15	6.16

also set at 20—30 °C rather than 0 °C to increase the solubility of the monomer in the solvent. When the BF_3 initiator was used in 8 mol% respect to the monomer, the product polymer showed a tendency to be obtained in higher yield, compared with those of the polymers obtained with 1 mol% of THF·BF_3 (Entries 4 and 5, 10 and 11, and 15 and 16).

The molecular weights of polyoxetanes were estimated from the calibration curve based on polystyrene standards by gel permeation chromatography (GPC), as shown in Table 3.

In the GPC chromatograms of **IIb**-1 and **IIb**-2 obtained with 1 and 8 mol% of THF·BF_3, respectively, the GPC-average molecular weight (M_{GPC}) of **IIb**-1 was found to be 68300 and its distribution of molecuar weight (DMW) seemed approximately monodispersed. The **IIb**-2 also showed the considerably high M_{GPC} around 28900 in spite of using 8 mol% of the initiator, although the polymer did not show a monodispersed DMW, i.e., its DMW had a shoulder peak around M_{GPC} 11500. Some of the other product polymers also did not show monodispersed DMW by GPC. Moreover, minor GPC peaks below M_{GPC} 2000 may be due to oligomers which were not removed by the twice-repeated reprecipitation of the raw product polymer. It is known that the cationic ring-opening polymerization of oxetanes had a tendency to produce the corresponding cyclic oligomers. The GPC chromatograms of **IIc**-1 and **IIc**-2 are shown in Fig. 3 for the representatives of the product polymers shown in Table 3.

Thus, the polymerization conditions using the THF·BF_3 initiator in about 8 mol% respect to the oxetane monomer in toluene at room temperature were taken mainly for obtaining the desired azobenzene-containing polyoxetanes with considerably high molecular weight in fairly good yield.

A yellowish brown monomer solution in toluene or DCM was turned to a dark red color immediately by adding the THF·BF_3 initiator to the solution, suggesting a Lewis acid-base interaction between the BF_3 and the azo moiety of the monomer. The increased amount, such as 8 mol%, of the initiator may be required for the smooth initiation of the cationic ring-opening polymerization of the azobenzene-containing oxetane, since the BF_3 (as a Lewis acid) trapped by the azo moiety (as a Lewis base) probably cannot act as an initiator. The tertiary oxonium mechanism for the cationic ring-opening polymerization of oxetane in the presence of

Table 3. GPC - Average Molecular Weights (M_{GPC}) and Polydispersities (M_w/M_n) of Azobenzene-Containing Polyoxetanes

Polymer				$10^{-4}M_{GPC}$ (M_w/M_n) [a]	
	R	n	m	Main peak	Minor peak[c]
IIa	H	1	4	0.99(1.70)	0.09(5.8)
IIIa	H	1	5	2.57(1.13), 1.68(1.56), 0.90[b]	0.08(7.9)
IVa-1	H	1	6	1.00(1.63)	0.09(6.4)
IVa-2	H	1	6	0.93(1.69)	0.09(9.7)
IVa-3	H	1	6	0.94(1.75), 0.15[b]	0.09(22.3)
I	CH_3O	0	—	4.09(3.09), 1.07[b], 0.17[b]	
IIb-1	CH_3O	1	4	6.83(2.21)	
IIb-2	CH_3O	1	4	2.89(2.40), 1.15[b], 0.13[b]	0.09(6.6)
IIIb	CH_3O	1	5	1.20(1.76), 1.32[b]	0.11(11.3)
IVb-1	CH_3O	1	6	0.60(1.39)	0.11(24.1)
IVb-2	CH_3O	1	6	0.99(1.60), 0.17[b]	0.12(25.8)
V	CH_3O	2	4	2.29(1.07), 1.50(1.38), 1.14[b]	0.16(8.0)
IIc-1	C_4H_9O	1	4	1.25(1.58), 1.48[b]	
IIc-2	C_4H_9O	1	4	2.64(1.11), 1.61(1.31)	0.16(3.9)
IIe-2	$C_8H_{17}O$	1	4	2.82(1.14), 1.30(1.20)	0.24(8.7)

a) Molecular weights were estimated by GPC relative to polystyrene standards. b) These peaks were observed to be the shoulder of the main peak. c) Values in parentheses indicate percentage for the area of the minor peak to the total area of GPC chromatogram.

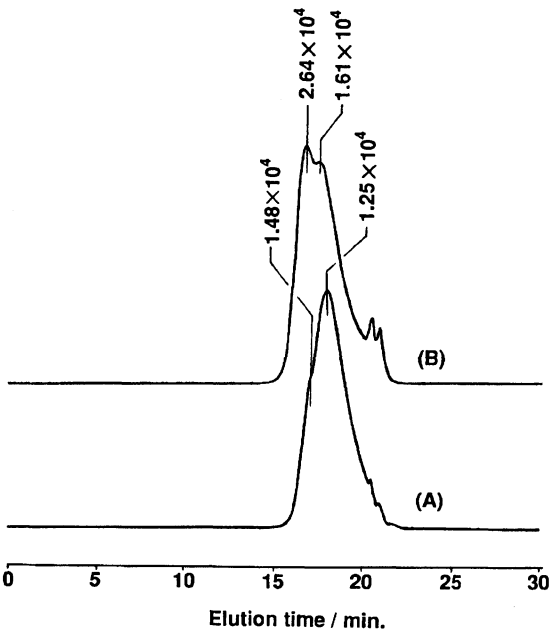
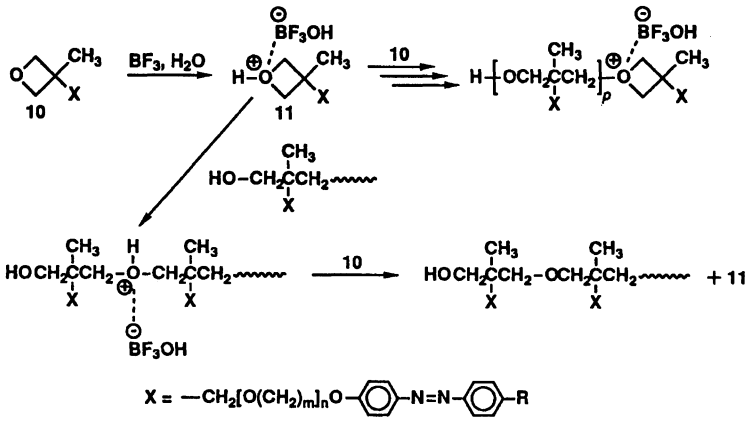


Fig. 3. GPC chromatograms of polymers **IIc**-1 (A) and **IIc**-2 (B).

BF_3 was probed in 1956 by Rose. In this mechanism it is demonstrated that a protonic acid H[BF_3OH] generated from the BF_3 with a trace of moisture present in the polymerization system can initiate the oxetane polymerization.[10] On the other hand, the activated-monomer mechanism was proposed in 1986 by Penczek et al. on the basis of the results of the oxirane polymerization, in which the α carbon of a protonated oxirane monomer is attacked by the nucleophilic oxygen atom of the terminal hydroxyl group of a polyoxirane.[11] In both mechanisms the proton plays an important role to form the polyethers from the cyclic ethers. According to these mechanisms, the polymerization steps of our monomers are also presumed as follows (Scheme 3).

Although it is not cleared at this time which mechanism the present polymerization is operated over, the azo moiety of the oxetane may trap not only the BF_3 but also the proton generated in the polymerization solution. Recently, it was suggested that the cationic ring-opening polymerization of 3,3-bis(azidomethyl)oxetane was operated over the activated-monomer mechanism. This monomer also required the high concentrations of diethyl ether–BF_3 (1/1) to give appreciable polymerization yields, since the azido groups, which could be assumed to be a base capable of trapping the protons, decreased the concentration of the activated-monomer and, consequently, the overall propagation rate.[8] Furthermore, some of our polyoxetanes did not show monodispersed DMWs on the present GPC measurements, suggesting that at least more than two types of active species existed in the propagation step yielding polyoxetane chains. Presumably, the pendant azo groups may influence the characters of the oxonium ions and/or the counter anion, resulting in the formation of plural active propagating species, e.g., tertiary oxonium, secondary oxonium (protonated oxetane), and loose and tight ion pairs.

DSC of Polyoxetanes with a Pendant Azobenzene Moiety. The DSC of oxetanes and their polymers was performed in order to show the influences of the substituent tail and of the spacer arm, which were attached, respectively, at the p'- and p-positions of the



Scheme 3. Propagation mechanism presumed for cationic ring-opening polymerization of oxetane derivatives.

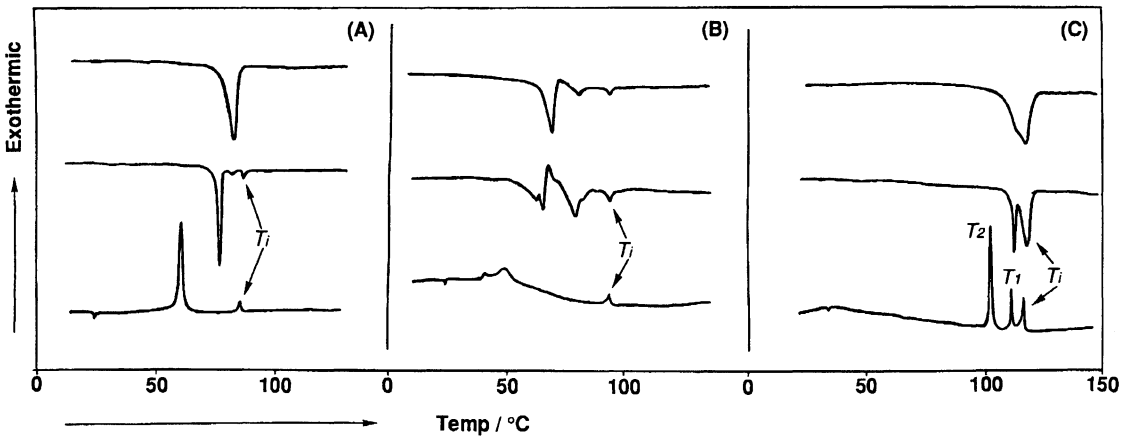


Fig. 4. DSC traces of polymers **IIb**-2 (A), **IVb**-2 (B), and **IIe**-2 (C). In each of parts A, B, and C, the DSC traces were taken on the 1st heating (top), the 2nd heating (middle), and the 1st cooling (bottom).

azobenzene moiety of the oxetanes and their polymers, on their thermal behavior. Typical DSC traces are shown in Fig. 4 for **IIb**-2, **IVb**-2, and **IIe**-2 and in Fig. 6 for **V**.

On the 2nd heating and 1st cooling of the DSC measurements for **IIb**-2, thermal peaks at temperature T_i are due to isotropic phase transition as confirmed by OPM and the other thermal peaks at lower temperatures than the T_i are thought to be ascribed to other phase transitions, while on the 1st heating only an endothermic peak appears at T_i. Between the T_i and the lower temperatures on each process, schlieren and/or spherulite textures were observed by OPM, as exemplified for **IIb**-2 and **V** in Figs. 5 and 6, respectively. Hence, the T_i and the other thermal transitions are summarized in Table 4 together with representative textures observed by OPM.

Polymers **IIb**-1 and **IIb**-2 had their T_is around 87—89 °C both on heating processes and on cooling ones in spite of differing from each other in M_{GPC} and in DMW (Entries 18 and 19). Other polymers also had the tendency similar to the above observation with respect to T_i (Entries 20, 21, and 23), or showed lower T_i on cooling than that on heating (Entries 17, 22, and 24). The **IIb**-2 having the M_{GPC} lower than **IIb**-1 and bidispersed DMW showed the development of mesophase domains within a shorter annealing period than **IIb**-1 (Fig. 5). This is interpreted from the influence of the molecular weight and DMW of the used polymer on its melt viscosity.

In addition, an interesting exothermic peaks were observed on each heating process of the DSC measurements of the **IVb**-2 and **V** which have considerably long spacer arms among the present polyoxetanes, presumably suggesting a more highly ordered assembly of the mesogenic groups (Entries 21 and 24, and Fig. 6). It is known that mesogenic groups are packed more densely in polymer matrices by introducing a long spacer between the mesogenic group and the polymer main chain.[12] In the OPM of **V** of Fig. 6, a schlieren texture first appeared at 63 °C by cooling the isotropic fluid of the polymer sample (part C), and then spherulitic domains began to appear in the schlieren texture within about 1 min by leaving the polymer sample standing at temperature around 63—62 °C (part D). These spherulitic domains developed to give the

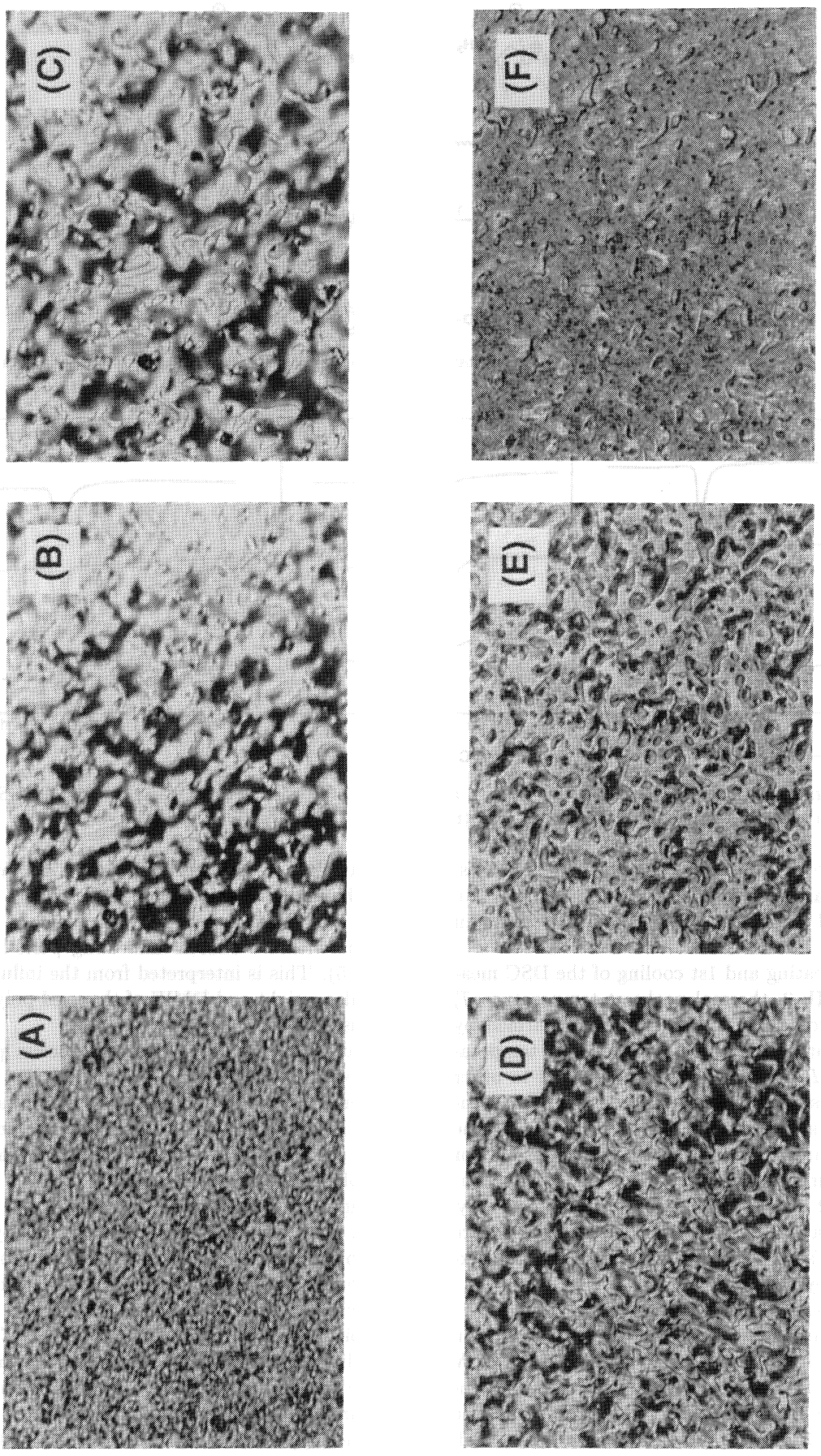


Fig. 5. Optical polarized photomicrographs (magnification × 200) taken on the 1st cooling for **IIb-1** annealed at 79 °C for (A) 3, (B) 10, and (C) 15 min, and for **IIb-2** annealed at 75 °C for (D) 2, (E) 3, and (F) 5 min.

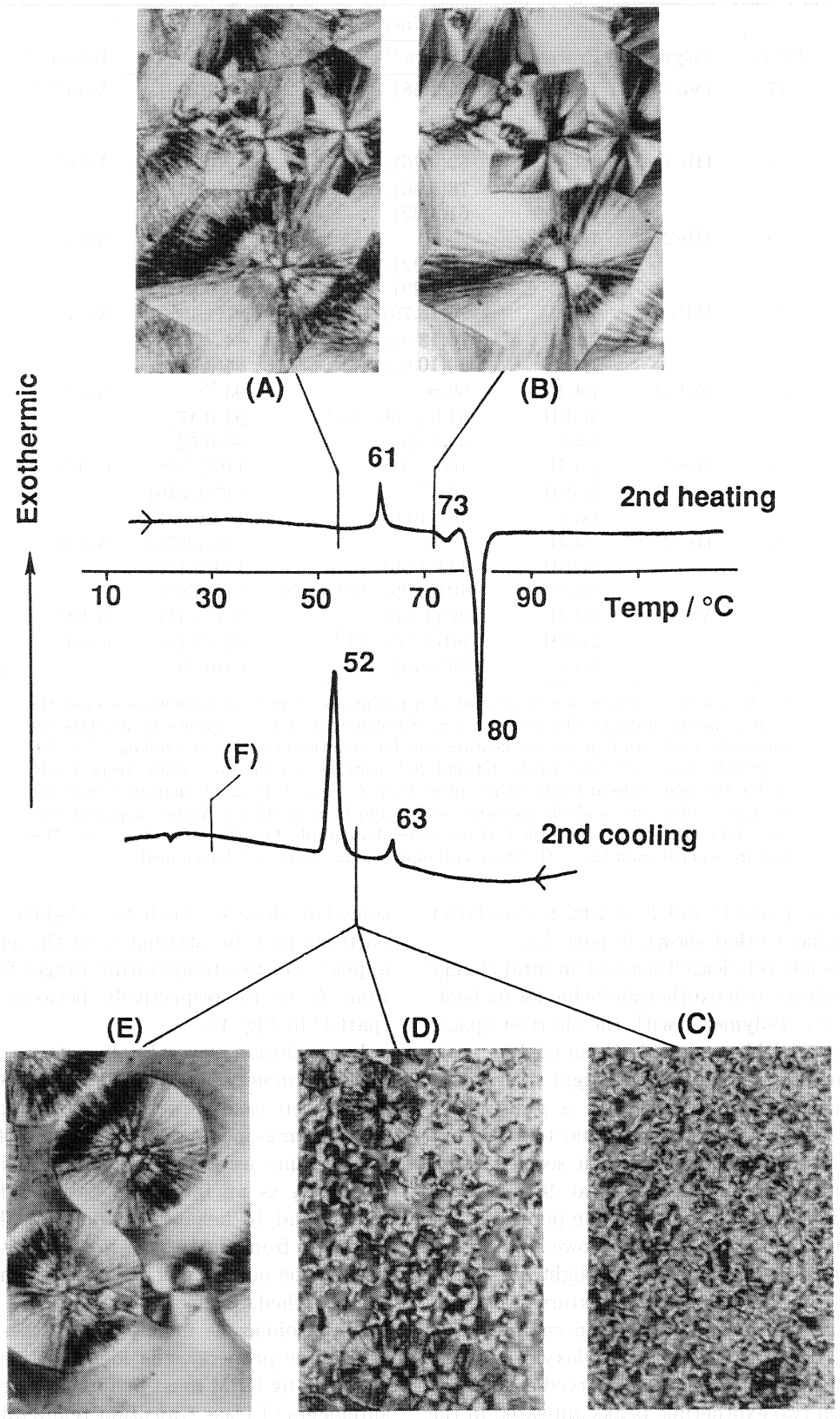


Fig. 6. DSC traces and optical polarized photomicrographs (magnification × 200) for **V**. The temperature (°C) and time (min) of annealing: (A) 54, 0.5; (B) 72, 0.5; (C) 57, 0.5; (D) 57, 2; and (E) 57, 3.

Table 4. Transition Temperatures of Azobenzene-Containing Polyoxetanes

Entry	Polymer	Process [b]	Thermal transition [a]/°C		Texture [d]
			Others [c]	T_i	
17	**IVa**-3	1st-H	55(1.58)	82(10.20)	A(45) [e]
		2nd-H		82(12.40)	
		1st-C		48(15.73)	
18	**IIb**-1	1st-H	62(0.76), 82(7.15)	89(0.39)	A(78)
		2nd-H	76(5.66), 84 [f]	89(0.91)	
		1st-C	61(4.22)	89(0.43)	
19	**IIb**-2	1st-H		85(16.10)	A(76)
		2nd-H	78(9.82), 83 [f]	88(0.33)	
		1st-C	62(7.29)	87(0.58)	
20	**IIIb**	1st-H	76(15.79)	97(1.13)	A(71)
		2nd-H	76(13.91)	84 [f]	
		1st-C	60(10.63)	84(0.41)	
21	**IVb**-2	1st-H	69,80 [f]	93 [f]	A(82)
		2nd-H	61,64, [66], 78 [f]	93(0.47)	
		1st-C	48(2.26)	93(0.52)	
22	**IIc**-2	1st-H	100(0.31)	116(13.38)	C(97)
		2nd-H	101 [f]	117(13.49)	
		1st-C	104(10.64)	109(0.31)	
23	**IIe-2**	1st-H		118(11.73)	A(112)
		2nd-H	114(4.36)	119(8.17)	
		1st-C	104(6.78), 112(1.67)	117(0.87)	
24	**V**	1st-H	[62(1.84)]	80(12.41)	A(63),
		2nd-H	[61(3.17)], 73 [f]	80(12.17)	C(53)
		1st-C	53(8.18)	63(0.50)	

a) Indicated as temperatures read at thermal peaks. Values in parentheses show the corresponding enthalpy changes per 1 g of polymer in J g^{-1}. Values in brackets are shown for exothermic peaks on heating and for endothermic ones on cooling. b) 1st-H, 2nd-H, and 1st-C refer to the 1st and 2nd heatings and the 1st cooling, respectively. c) For thermal peaks at temperatures other than T_i. d) A, B, and C indicate textures of schlieren, spherulite, and the coexistence of A and B, respectively. Values in parentheses show temperatures at which the textures were photographed on the 1st cooling. e) This texture seemed sand-like. f) These enthalpy changes were not determined.

textures shown in parts E and F of Fig. 6 (the latter texture was similar to that shown in part A).

However, it is not yet cleared what structural change (or phase transition) such exothermic behavior on heating is ascribed to. Polymer **I** with the shortest spacer arm did not show OPM textures both on cooling processes and on heating ones, once the virgin sample was melted. Polymers **IIa** and **IIIa** with a *p'*-unsubstituted azobenzene moiety also showed no textures but **IVa** showed a schlieren texture, which seemed sand-like, on cooling processes. Cooled at 97 °C from the isotropic fluid and kept at this temperature, **IIc** showed the schlieren texture which showed the development of spherulitic domains after a slight period, although the monomer **2c** showed the texture assignable to a schlieren pattern around 58 °C on cooling. The mesophase of **IIe** which has a *p'*-octyloxyazobenzene moiety at the spacer chain-end was observed over 117 to 104 °C, in which two exothermic peaks appeared in the DSC trace. The schlieren pattern appeared smoothly by leaving the polymer sample standing at 112 °C and after the annealing for a few minutes around this temperature the domains of the schlieren pattern became somwhat shrunk. Such two slightly different texture patterns may be attributed to the mesophases which appear over two temperature ranges from T_i to T_1 and from T_1 to T_2, respectively, between 117 and 104 °C (part C in Fig. 4).

In conclusion, several polyoxetanes carrying the azobenzene moiety at the side chain-end through the spacer were easily prepared in fairly good yields by the cationic ring-opening polymerization of the corresponding oxetanes using the adequately increased amount of $THF{\cdot}BF_3$ as an initiator. Several of these polymers were found to behave as side chain liquid crystalline polymers from the observation by DSC and OPM. Although the influence of the spacer arm and substituent tail attached, respectively, at the *p*- and *p'*-positions of the azobenzene moiety was discussed on the liquid crystalline property, the identification of the textures observed by OPM must be further investigated by measurements of glass transition temperature (T_g) and X-ray diffraction. T_g was difficult to be found for all the present polyoxetanes with a pendant azobenzene moiety by the DSC carried out above room temperature. These T_gs may be observed by the DSC per-

formed below the room temperature; in most cases, T_gs of poly(oxytrimethylene) and its 3-mono- and 3,3-dialkyl analogues were found below 0 °C.[13] The polyoxetane main chain is thought to be considerably soft or flexible and to play an important role to realize the thermotropic liquid crystalline properties in both the azobenzene-containing polyoxetanes and the bipheyl-containing ones, which were prepared by us and the other authors, respectively.[9] In comparison with the T_is observed at 80 to 119 °C on the 2nd heating for the azobenzne-containing polyoxetanes, however, somewhat higher T_is were observed at 115 to 154 °C for the polyoxetanes having 4′-methoxy- to 4′-butoxybiphenyl groups through the spacers of $-CH_2O-$ and $-CH_2O(CH_2)_nO-$, where $n=2$, 3, and 4. Furthermore, the 4′-alkoxybiphenyl-containing polyoxetanes showed spherulite- or star-like or sand-like textures on the OPM measurements after somewhat prolonged annealing time of 30 min, while some analogues with the pendant 4′-cyano- and 4′-fluorobiphenyl groups had a tendency to show fan-shaped textures at lowered temperatures around 84 to 103 °C although prolonged annealing time, such as 2 d, was required for the development of mesomorphic domains. On the other hand, the mesomorphic domains of the azobenzene-containing polyoxetanes developed smoothly over a short period of annealing, e.g., within 10 min for polymer **IIb**-2. These findings may be interpreted as follows: A highly ordered assembly of mesogenic groups is achieved more smoothly by the planar structure of an azobenzene compared with the more bulky biphenyl structure, in which the two benzene rings may lie in different planes at higher temperature; it is known that these planes of biphenyl make an angle of almost 45° in the state of solution.

Thus, polyoxetanes will also be chosen as one of matrices for preparing side chain liquid crystalline polymers.

Experimental

Materials. Oxetanes **7a**, **7b**, and **7c** were obtained according to our method described previously.[1] (3-Methyl-3-oxetanyl)methyl *p*-toluenesulfonate (**6**) was prepared by the method of literature.[9]

3-(11-Bromo-2,7-dioxaundecyl)-3-methyloxetane (8): 3-(6-Hydroxy-2-oxahexyl)-3-methyloxetane[3] (28.7 mmol) was stirred with 1,4-dibromobutane (86.2 mmol) in 50% aqueous NaOH (20 g) and hexane (30 cm^3) at 65 °C for 2.5 h in the presence of tetrabutylammonium bromide (1.4 mmol). The resultant mixture was diluted with water (30 cm^3) and extracted with ether (3×30 cm^3). After being dried over anhydrous Na_2SO_4, the organic layer was concentrated by evaporator and distilled to give **8** in a 77% yield: bp 98—112 °C (5.3 Pa); IR (neat) 1120 (acyclic ether) and 980 and 825 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.30 (3H, s, CH_3), 1.6—2.1 [8H, m, $[OCH_2(C\underline{H}_2)_2CH_2]_2Br$], 3.3—3.7 [total 10H: δ=3.47, s, CH_2 adjacent to the oxetane ring; δ=3.44, t, J=6.3 Hz, $OC\underline{H}_2(CH_2)_2C\underline{H}_2OC\underline{H}_2(CH_2)_2C\underline{H}_2Br$], and 4.35 and 4.51 (each 2H, AB-q, J=5.8 Hz, CH_2 of the oxetane ring).

4-Methoxy-4′-[7-(3-methyl-3-oxetanyl)-1,6-dioxaheptyl]azobenzene (2b); Typical Procedure: Oxetane **7a** (8.4 mmol) was stirred with 4-hydroxy-4′-methoxyazobenzene (**9b**) (8.3 mmol) in DMF (12 cm^3) at 80 °C for 10 h in the presence of powdered anhydrous K_2CO_3 (4.3 mmol). The reaction mixture was filtered and the DMF was removed from the filtrate under reduced pressure. The remaining oil was extracted with ether (3×20 cm^3) and washed successively with 10% NaOH and water. The organic layer was evaporated and the residue was twice recrystallized from ethanol to give a reddish yellow powder of **2b** in a 65% yield: mp 142.5—144.0 °C (ethanol); IR (KBr) 3080, 3020, 1600, 1585, and 855 (1,4-disubstituted benzene), 1260 (aromatic ether), 1110 (acyclic ether); ^1H NMR ($CDCl_3$) δ=1.32 (3H, s, CH_3), 1.7—2.0 [4H, m, $OCH_2(C\underline{H}_2)_2CH_2O$], 3.45—3.65 [total 4H: δ=3.50, s, CH_2 adjacent to the oxetane ring; δ=3.55, t, J=6.1 Hz, $OC\underline{H}_2(CH_2)_3OAr$], 3.88 (3H, s, OCH_3), 4.07 [2H, t, J=6.1 Hz, $O(CH_2)_3C\underline{H}_2OAr$], 4.36 and 4.52 (each 2H, AB-q, J=5.6 Hz, CH_2 of the oxetane ring), and 6.8—8.0 (total 8H for two AB-quartets overlapping each other: δ=6.98 and 7.86, J=9.2 Hz; δ=7.00 and 7.87, J=9.4 Hz; ArH).

4-Methoxy-4′-[(3-methyl-3-oxetanyl)methoxy]azobenzene (1): Obtained by the reaction between *p*-toluenesulfonate **6** (15.6 mmol) and azobenzene **9b** (15.6 mmol) in DMF (20 cm^3) at 60 °C for 10 h in the presence of powdered anhydrous K_2CO_3 (8.0 mmol) in the similar manner to that described for preparing **2b**: Yield 66%; mp 129—131 °C (ethanol); IR (KBr) 3080, 3060,1600, 1580, 1500, and 840 (1,4-disubstituted benzene), 1240 (aromatic ether), 1020 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.46 (3H, s, CH_3), 3.88 (3H, s, $ArOCH_3$), 4.10 (2H, s, CH_2 adjacent to the oxetane ring), 4.48 and 4.65 (each 2H, AB-q, J=5.9 Hz, CH_2 on the oxetane ring), and 6.9—8.0 (total 8H for two AB-quartets overlapping each other: δ=7.00 and 7.88, J=9.1 Hz; δ=7.03 and 7.88, J=9.2 Hz; ArH).

4-[7-(3-Methyl-3-oxetanyl)-1,6-dioxaheptyl]azobenzene (2a): Yield 68%; mp 56.5—59.0 °C (ethanol); IR (KBr) 3080, 1650, 1580, 1505, and 840 (1,4-disubstituted benzene), 770 and 690 (monosubstituted benzene), 1260 (aromatic ether), 1105 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3), 1.6—2.1 [4H, m, $OCH_2(C\underline{H}_2)_2CH_2O$], 3.4—3.6 [total 4H: δ=3.54, s, CH_2 adjacent to the oxetane ring; δ=3.54, t, J=6.1 Hz, $OC\underline{H}_2(CH_2)_3OAr$], 4.06 (2H, t, J=6.1 Hz, CH_2OAr), 4.36 and 4.52 (each 2H, AB-q, CH_2 on the oxetane ring), and 6.8—8.0 (total 9H: δ=6.99 and 7.91, AB-q, J=9.1 Hz, *m*- and *o*-ArH; δ=7.3—7.6, m, *m*′- and *p*′-ArH; δ=7.8—8.0, m, *o*′-ArH; respectively).

4-Butoxy-4′-[7-(3-methyl-3-oxetanyl)-1,6-dioxaheptyl]azobenzene (2c): Yield 64%; mp 67.0—71.5 °C (ethanol); IR (KBr) 3080, 1605, 1595, 1505, and 840 (1,4-disubstituted benzene), 1250 (aromatic ether), 1110 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=0.99 (3H, t, J=6.6 Hz, CH_3 of the butyl), 1.31 (3H, s, CH_3 on the oxetane ring), 1.4—2.1 [total 8H, m, $OCH_2(C\underline{H}_2)_2CH_2O$ and $OCH_2(C\underline{H}_2)_2CH_3$], 3.4—3.6 [total 4H: δ=3.50, s, CH_2 adjacent to the oxetane ring; δ=3.55, t, J=5.9 Hz, $OC\underline{H}_2(CH_2)_3OAr$], 3.9—4.2 [total 4H: δ=4.03,

t, J=6.4 Hz, $ArOC\underline{H}_2C_3H_7$; δ=4.06, t, J=6.0 Hz, $O(CH_2)_3C\underline{H}_2OAr$], 4.36 and 4.52 (each 2H, AB-q, CH_2 on the oxetane ring), and 6.98 and 7.86 (each 4H, two AB-quartets superimposed on each other, J=9.1 Hz, *m*- and *m'*-ArH and *o*- and *o'*-ArH, respectively).

4-Butyl-4'-[7-(3-methyl-3-oxetanyl)-1,6-dioxaheptyl]azobenzene (2d): Yield 46%; bp 162.5—172.0 °C (16—17 Pa); IR (neat) 3060, 3030, 1605, 1585, 1510, and 840 (1,4-disubstituted benzene), 1260 (aromatic ether), 1050 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=0.94 (3H, t, CH_3, 6.4 Hz, CH_3 of the butyl); 1.31 (3H, s, CH_3 on the oxetane ring), 1.4—2.0 (total 8H, m, $ArCH_2(C\underline{H}_2)_2CH_3$ and $OCH_2(C\underline{H}_2)_2CH_2O$], 2.68 (2H, t, J=7.4 Hz, CH_2Ar), 3.4—3.6 [total 4H: δ=3.49, s, CH_2 adjacent to the oxetane ring; δ=3.55, t, J=5.9 Hz, $OC\underline{H}_2(CH_2)_3OAr$], 4.07 (2H, t, J=5.9 Hz, CH_2OAr), 4.36 and 4.52 (each 2H, AB-q, J=5.7 Hz, CH_2 of the oxetane ring), and 6.9—8.0 (total 8H for two AB-quartets overlapping each other: δ=7.00 and 7.86, J=9.0 Hz, *m*- and *o*-ArH; δ=7.29 and 7.79, J=8.3 Hz, *m'*- and *o'*-ArH; respectively).

4-[7-(3-Methyl-3-oxetanyl)-1,6-dioxaheptyl]-4'-octylazobenzene (2e): Yield 52%; mp 55.0—65.0 °C (ethanol); IR (KBr) 3080, 3060, 1605, 1580, 1510, and 840 (1,4-disubstituted benzene), 1250 (aromatic ether), 1115 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=0.89 (3H, t-like, CH_3 of the octyl), 1.2—1.4 [total 13H: δ=1.32, s, CH_3 on the oxetane ring; m, $OCH_2CH_2(C\underline{H}_2)_5CH_3$], 1.7—2.0 [total 6H, m, $OCH_2(C\underline{H}_2)_2CH_2O$ and $OCH_2C\underline{H}_2C_6H_{13}$], 3.4—3.6 [total 4H: δ=3.50, s, CH_2 adjacent to the oxetane ring; δ=3.55, t, J=6.1 Hz, $OC\underline{H}_2(CH_2)_3OAr$], 4.36 and 4.52 (each 2H, AB-q, J=5.8 Hz, CH_2 of the oxetane ring), and 6.9—8.0 (total 8H for two AB-quartets superimposed on each other: δ=6.98 and 7.86, J=9.1 Hz, *m*- and *m'*-ArH and *o*- and *o'*-ArH, respectively).

4-[8-(3-Methyl-3-oxetanyl)-1,7-dioxaoctyl]azobenzene (3a): Yield 56%; mp 49.0—51.0 °C (ethanol); IR (KBr) 3075, 3050, 1605, 1580, and 830 (1,4-disubstituted benzene), 1260 (aromatic ether), 1125 and 1110 (acyclic ether), and 975 and 830 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3), 1.4—2.0 [6H, m, $OCH_2(C\underline{H}_2)_3CH_2O$], 3.4—3.6 [total 4H: δ=3.48, s, CH_2 adjacent to the oxetane ring; δ=3.50, t, J=5.7 Hz, $OC\underline{H}_2(CH_2)_4OAr$], 4.05 (2H, t, J=6.2 Hz, CH_2OAr), 4.36 and 4.51 (each 2H, AB-q, J=5.7 Hz, CH_2 of the oxetane ring), and 6.9—8.0 (total 9H: δ=6.99 and 7.91, AB-q, J=8.8 Hz, *m*- and *o*-ArH, respectively; δ=7.4—7.6, m, *m'*- and *p'*-ArH; δ=7.8—8.0, m, *o'*-ArH).

4-Methoxy-4'-[8-(3-methyl-3-oxetanyl)-1,7-dioxaoctyl]azobenzene (3b): Yield 74%; mp 76.0—77.0 °C (ethanol); IR(KBr) 3080, 3050, 1595, 1580, 1500, and 845 (1,4-disubstituted benzene), 1255 (aromatic ether), 1145 and 1105 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3), 1.4—2.0 [6H, m, $OCH_2(C\underline{H}_2)_3CH_2O$], 3.4—3.6 [total 4H: δ=3.48, s, CH_2 adjacent to the oxetane ring; δ=3.50, t, J=6.0 Hz, $OC\underline{H}_2(CH_2)_4OAr$], 3.88 (3H, s, OCH_3), 4.03 (2H, t, J=6.1 Hz, CH_2OAr), 4.35 and 4.51 (each 2H, AB-q, J=5.8 Hz, CH_2 of the oxetane ring), and 6.8—8.0 (total 8H for two AB-quartets overlapping each other: δ=6.98 and 7.86, J=8.5 Hz; δ=6.99 and 7.86, J=8.6 Hz; ArH).

4-[9-(3-Methyl-3-oxetanyl)-1,8-dioxanonyl]azobenzene (4a): Yield 77%; mp 75.0—81.0 °C (ethanol); IR (KBr) 3050, 1605, 1585, 1505, and 840 (1,4-disubstituted benzene) 775 and 695 (monosubstituted benzene), 1255 (aromatic ether), 1105 (acyclic ether), and 980 and 845 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3), 1.4—2.0 [8H, m, $OCH_2(C\underline{H}_2)_4CH_2O$], 3.4—3.6 [total 4H: δ=3.47, s, CH_2 adjacent to the oxetane ring; δ=3.48, t, J=6.1 Hz, $OC\underline{H}_2(CH_2)_5OAr$], 4.04 (2H, t, J=6.3 Hz, CH_2OAr), 4.35 and 4.51 (each 2H, AB-q, CH_2 of the oxetane ring), and 6.8—8.0 (total 9H: δ=6.99 and 7.92, AB-q, J=10.5 Hz, *m*- and *o*-ArH, respectively; δ=7.4—7.6, m, *m'*- and *p'*-ArH; δ=7.8—8.0, m, *o'*-ArH).

4-Methoxy-4'-[9-(3-methyl-3-oxetanyl)-1,8-dioxanonyl]azobenzene (4b): Yield 67%; mp 75.5—82.0 °C (ethanol); IR (KBr) 3080, 3060, 1605, 1585, 1510, and 840 (1,4-disubstituted benzene), 1250 (aromatic ether), 1110 (acyclic ether), and 980 and 850 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.31 (3H, s, CH_3 on the oxetane ring), 1.4—2.0 [8H, m, $OCH_2(C\underline{H}_2)_4CH_2O$], 3.1—3.3 [total 4H: δ=3.45, s, CH_2 adjacent to the oxetane ring; δ=3.45, t, J=5.4 Hz, $OC\underline{H}_2(CH_2)_5OAr$], 3.88 (3H, s, OCH_3), 4.03 (2H, t, J=6.3 Hz, CH_2OAr), 4.35 and 4.51 (each 2H, AB-q, CH_2 of the oxetane ring), and 6.9—7.1 [total 8H for two AB-quartets overlapping each other: δ=6.98 and 7.87, J=8.6 Hz; δ=7.00 and 7.87, J=9.0 Hz; ArH).

4-Methoxy-4'-[12-(3-methyl-3-oxetanyl)-1,6,11-trioxadodecyl]azobenzene (5): Yield 66%; mp 42.0—43.0 °C (ethanol); IR (KBr) 3080, 3050, 1600, 1580, 1505, and 850 (1,4-disubstituted benzene), 1250 (aromatic ether), 1110 (acyclic ether), and 980 and 850 cm^{-1} (cyclic ether); ^1H NMR ($CDCl_3$) δ=1.30 (3H, s, CH_3 on the oxetane ring), 1.5—2.0 [8H, m, $[OCH_2(C\underline{H}_2)_2CH_2]_2OAr$], 3.3—3.9 [total 8H: δ=3.46, s, CH_2 adjacent to the oxetane ring; δ=3.49, t, J=5.9 Hz, $OC\underline{H}_2(CH_2)_2C\underline{H}_2OC\underline{H}_2(CH_2)_3OAr$], 3.88 (3H, s, OCH_3), 4.06 (2H, t, J=6.1 Hz, CH_2OAr), 4.34 and 4.50 (each 2H, AB-q, J=5.6 Hz, CH_2 of the oxetane ring), and 6.9—8.0 (total 8H for two AB-quartets overlapping each other: δ=6.98 and 7.86, J=8.5 Hz; δ=6.99 and 7.87, J=8.4 Hz; ArH).

4-(4-Substituted Phenylazo)phenols: These compounds were obtained by a coupling reaction between phenol and the corresponding benzenediazonium chloride, prepared by diazotizing the 4-substituted aniline with $NaNO_2$ in aqueous HCl at 0—3 °C. *p'*-Unsubstituted azobenzene **9a** was used without further purification of a commercial reagent.

9b: Yield 76%, mp 138.0—140.0 °C (benzene); **9c**: Yield 58%, mp 104.0—108.0 °C (10% hexane–benzene); **9d**: Yield 48%, mp 79.0—82.0 °C (10% hexane–benzene); **9e**: Yield 69%, mp 92.0—95.0 °C (10% hexane–benzene).

Preparation of Polymers. Polymers of oxetanes with a pendant aromatic azobenzene moiety were prepared by their cationic ring-opening polymerization in DCM or toluene with $THF{\cdot}BF_3$, as described in our previous reports.[1—7]

Measurements. IR spectra of the products were recorded on a JASCO A-202 spectrometer and ^1H NMR on a 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 GPC using G4000H8 and G2500HXL (each 7.8ϕ×300, TOSOH) arranged in a series and THF as the solvent (0.8 cm^3 min^{-1}). DSC measurements were carried out in a DSC-50 (Shimadzu) at a heating

or cooling rate of 5 °C min^{-1} for a sample in helium. Optical polarized micrographs were obtained by a BHS-751P apparatus (OLYMPUS).

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