

Preparation and Characterization of Polyoxetane Resins Having a Primary Amino Group at the Side Chain-End through Moderately Long Spacer Arms

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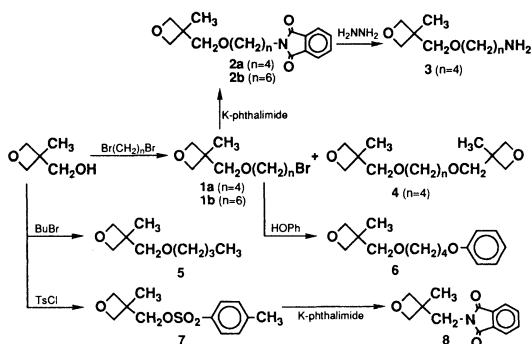
ABSTRACT: Uncross- and cross-linked polyoxetanes having a pendant hydrophilic primary amino group at the terminal of the $-\text{CH}_2\text{O}(\text{CH}_2)_n-$ spacers, where $n=4$ and 6 , were prepared. Their prepolymers were obtained by the BF_3 -initiated cationic ring-opening polymerization of oxetanes having the corresponding pendant phthalimido group at the C-3 position of the oxetane ring. In this polymerization a bisoxetane or an oxetane having the hydrophobic pendant was used as a cross-linking agent or a comonomer modifying the degree of hydrophilicity. The pendant phthalimide of the prepolymers was reduced with hydrazine in ethanol at 40°C to give the pendant amine of the product polymers. The characterization of the phthalimide- and amine-containing polyoxetanes was also performed to know their structures and qualities. The analogous oxetane with the phthalimidomethyl pendant at the C-3 position gave a tricyclic product via an intramolecular nucleophilic attack of the phthalimido oxygen atom on the methylene carbon atom of the oxetane ring.

KEY WORDS Cationic Ring-Opening Polymerization / Polyoxetanes /
Pendant Amine / Pendant Phthalimide /

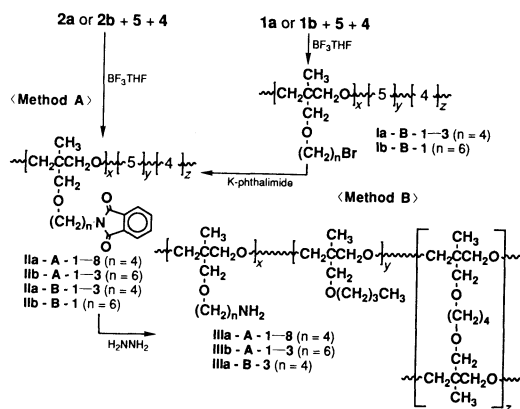
In a series of investigations of using polyethers as polymeric supports in organic synthesis, we synthesized polyethers carrying typical functional groups, such as halide, alcohol, phenol, amine, and carbonyl moieties, in the pendant side chain. The ordinary organic reactions of these functional groups are well-known, so various synthetic routes of functional polymers are expected to be found by chemical modification using the pendant functional groups as starting materials. Furthermore, we consider that polyether networks are promising as polymeric supports due to the desirable properties of ether linkages and that the existence of a spacer between the polymeric support and the functional group is also important in designing functional polymers.^{1,2} Polyethers with such functional groups, how-

ever, are so far scarcely prepared, especially those having functional groups at the terminal of moderately long spacer arms, although methylene spacer-separated pendant functional groups were obtained by a substitution reaction of poly[3,3-bis(chloromethyl)oxetane] with several nucleophiles under considerable hard conditions.³

Thus, since the primary amine is accepted as one of the key functional groups in the functional polymers synthesis, we have a great interest in the chemical reactivity and properties of the spacer-separated primary amine based on polyoxetanes. In our investigation, we found the cationic ring-opening polymerization of the oxetane rings of *N*-[6-(3-methyl-3-oxetanyl)-5-oxa-hexyl]- and *N*-[8-(3-methyl-3-oxetanyl)-7-oxa-octyl]phthalimides (**2a** and **2b**)



Scheme 1. Synthetic routes of oxetane monomers.

Scheme 2. Synthetic routes of polyoxetanes having a primary amino group at the side chain-end. $\text{---}[\text{---}4\text{---}]$ and $\text{---}[\text{---}5\text{---}]$ represent the monomeric units of **4** and **5** in polymers, respectively.

in the presence of a trifluoroboran (BF_3) initiator. These phthalimido groups, moreover, were readily reduced with hydrazine to yield the primary amino group at the side chain-end. In this report, therefore, we describe the preparation and characterization of the uncross- and cross-linked polyoxetanes having the pendant phthalimido and primary amino groups at the side chain-end through moderately long spacers. The synthetic routes of oxetane monomers used in the preparation of various polyoxetanes with a primary amino group are shown in Scheme 1 and the preparation methods of these amine polymers are shown in Scheme 2.

EXPERIMENTAL

Materials

Oxetanes **1a**, **1b**, **4**, **5**, **6**, and **7** and polymers **1a-B-1—3** and **1b-B-1** were prepared according to the methods of literature.^{4–6}

N-[6-(3-Methyl-3-oxetanyl)-5-oxahexyl]-phthalimide (**2a**); *Typical Procedure*. Bromide **1a** (12.7 mmol) and potassium phthalimide (PPI) (13.0 mmol) were stirred in *N,N*-dimethylformamide (DMF) (20 cm³) at 80°C for 3.5 h. DMF was evaporated and the residue was dissolved in ether (30 cm³). The ether solution was washed with a 5% sodium hydroxide (NaOH) solution (10 cm³) and water (2 × 10 cm³) successively, and dried over anhydrous sodium sulfate (Na_2SO_4). After removing the ether, the residue was dissolved in benzene and placed in a pot connected to a Dean–Stark apparatus containing calcium hydride (1 g) in the solvent trap. The benzene solution was refluxed for 30 h and then the solvent was distilled off under reduced pressure. The residue was dried in vacuum to give the oily product **2a** (95% yield), which was directly used as the monomer of cationic ring-opening polymerization: IR (neat) 3100, 3060, 3030, 1615, and 720 (1,2-disubstituted benzene), 1775 and 1710 (phthalimido C=O), 1115 (acyclic ether), and 980 and 835 cm⁻¹ (cyclic ether); ¹H NMR (CDCl_3) δ 1.30 (s, 3H, CH_3), 1.5–2.0 [m, 4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{N}$], 3.4–3.6 [total 4H: δ 3.47, s, CH_2 adjacent to the oxetane ring; δ 3.50, t, $J=6.8$ Hz, $\text{OCH}_2(\text{CH}_2)_3\text{N}$], 3.72 (t, 2H, $J=6.8$ Hz, CH_2 adjacent to the phthalimido), 4.32 and 4.88 (AB-q, each 2H, $J=5.6$ Hz, CH_2 of the oxetane ring), and 7.6–8.00 ppm (m, 4H, ArH).

Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4$: C, 67.27%; H, 6.92%; N, 4.62%. Found: C, 67.06%; H, 6.90%; N, 4.59%.

N-[8-(3-Methyl-3-oxetanyl)-7-oxaoctyl]-phthalimide (**2b**). Obtained from the bromide **1b** (29.0 mmol) in a 98% yield by the same procedure as described for preparing **2a**: IR (neat) 3100, 3060, 3030, 1615, and 720

(1,2-disubstituted benzene), 1775 and 1710 (phthalimido C=O), 1115 (acyclic ether), and 920 and 835 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.2–1.8 [total 11H: δ 1.30, s, CH_3 ; δ 1.2–1.8, m, $\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{N}$], 3.35–3.55 [total 4H: δ 3.45, t, $J=6.2$ Hz, $\text{OCH}_2(\text{CH}_2)_5\text{N}$; δ 3.46, s, CH_2 adjacent to the oxetane ring], 3.68 (t, 2H, $J=6.8$ Hz, CH_2 adjacent to the phthalimide), 3.42 and 4.47 (AB-q, each 2H, $J=5.7$ Hz, CH_2 of the oxetane ring), and 7.6–8.0 ppm (m, 4H, ArH).

Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_4$: C, 68.83%; H, 7.55%; N, 4.23%. Found: C, 68.28%; H, 7.71%; N, 4.19%.

N-[(3-Methyl-3-oxetanyl)methyl]phthalimide (**8**). Obtained by the reaction between *p*-toluenesulfonate **7** (19.5 mmol) and PPI (20.0 mmol) in DMF (30 cm^3) at 80°C for 6 h. The product **8** was purified by recrystallization from ether: yield 80%; mp 105–106°C; IR (KBr) 3100, 3060, 3030, 1615, 1495, 1460, and 730 (1,2-disubstituted benzene), 1760 and 1710 (phthalimido C=O), and 975 and 830 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.36 (s, 3H, CH_3), 3.87 (s, 2H, CH_2 adjacent to the oxetane ring), 4.34 and 4.70 (AB-q, each 2H, $J=6.4$ Hz, CH_2 of the oxetane ring), and 7.7–8.0 ppm (m, 4H, ArH).

Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$: C, 67.52%; H, 5.62%; N, 6.06%. Found: C, 67.60%; H, 5.59%; N, 5.87%.

3-(6-Amino-2-oxahexyl)-3-methyloxetane (**3**). To the phthalimide **2a** (9.4 mmol) in ethanol (5 cm^3) a solution of hydrazine monohydrate (41 mmol) dissolved in ethanol (5 cm^3) was added dropwise at 25°C. After the complete addition of the hydrazine to **2a**, the contents were stirred at 40°C for 5.5 h to form cream-like materials. The solvent was removed by an evaporator and the residue was mixed thoroughly with 30 cm^3 of 2*N* HCl and then filtered to remove phthalic hydrazide. The filtrate was made basic at pH 9 with NaOH, concentrated, and extracted with benzene (2 \times 15 cm^3). The combined organic layers were distilled to give the product **3** in a 23% yield:

bp 59–64°C (16 Pa); IR (neat) 3200–2600 (NH_2), 1115 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.31 (s, 3H, CH_3), 1.7–1.9 [m, 4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{NH}_2$], 1.93 (s, 2H, NH_2 , this signal disappeared by adding D_2O to the sample solution), 2.73 (t, 2H, $J=6.6$ Hz, CH_2NH_2), 3.4–3.6 [total 4H: δ 3.49, s, CH_2 adjacent to the oxetane ring; δ 3.25, t, $J=5.0$ Hz, $\text{OCH}_2(\text{CH}_2)_3\text{NH}_2$], and 4.34 and 4.49 ppm (AB-q, each 2H, $J=5.6$ Hz, CH_2 of the oxetane ring).

5,6-Benzo-1-methyl-8,11,3-dioxazatricyclo-[5.2.2.0^{3,7}]undec-5-en-4-one (**10**). To the phthalimide **8** (0.2 g, 0.865 mmol) in a test tube, dry dichloromethane (DCM) (2 cm^3) and a diethyl ether– or tetrahydrofuran (THF)– BF_3 (1:1) complex (5 mol%) were added successively through a hypodermic or micro syringe under an atmosphere of nitrogen and the contents were stirred at 28°C for 30 h. After adding dry triethylamine (0.12 cm^3) to the contents, the mixture was stirred at this temperature for additional 2 h. The solvent was evaporated and the oily residue was subjected to column chromatography using Al_2O_3 as a stationary phase and CHCl_3 as an eluent, followed by recrystallization of the crude product from hexane containing a small portion of DCM to give **10** as needle crystals in a 42% yield; mp, 168–169°C; IR (KBr) 3060, 1620, 1470, and 800 (1,2-disubstituted benzene), 1720 (cyclic amide C=O), 1260 (C–N), 1100–1000 cm^{-1} (ether C–O); $^1\text{H NMR}$ (CDCl_3) δ 1.05 (s, 3H, CH_3), 3.75 (s, 2H, $\text{CH}_2\text{–N}$), 4.02 and 4.15 (AB-q, total 4H, $J=8.1$ Hz, CH_2O), 7.5–7.7 (m, 3H, ArH located at the *m*- and *p*-positions to the acyl group), and 7.7–7.9 ppm (m, 1H, ArH located at the *o*-position to the acyl group).

Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$: C, 67.52%; H, 5.67%; N, 6.06%. Found: C, 67.29%; H, 5.73%; N, 5.98%.

N-[2,2-Bis(hydroxymethyl)propyl]phthalimide (**11**). The tricyclic product **10** (30 mg, 0.13 mmol) was stirred in THF (2 cm^3)

containing 0.05 cm³ of 0.5*N* HCl at 20–25°C for 2 h. The mixture was extracted with ether and the organic layer was dried over Na₂SO₄. The solvent was evaporated and the residue was recrystallized from carbon tetrachloride containing a small portion of DCM to give 11 mg (34% yield) of **11**: mp 117–118°C; IR (KBr) 3400 and 1035 (alcohol), 3120, 3060, 3030, 1620, 1470, and 730 (1, 2-disubstituted benzene), 1770 and 1700 (phthalimido C=O), 1355 cm⁻¹ (C–N); ¹H NMR (CDCl₃) δ 0.88 (s, 3H, CH₃), 2.5–3.2 (b, 2H, OH), 3.38 and 3.50 (AB-q, each 2H, *J* = 12.0 Hz, CH₂OH), 3.83 (s, 2H, CH₂–N), and 7.7–8.0 ppm (m, 4H, ArH).

Anal. Calcd for C₁₃H₁₅NO₄: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.67%; H, 6.22%; N, 5.44%.

Polymerization

Cationic Ring-Opening Polymerization of Oxetanes with BF₃THF; Typical Procedure. In a test tube (20φ × 180), 3.5 m³ of a 1.80 mol dm⁻³ solution of **2a** in toluene was placed by a hypodermic syringe under nitrogen, and then 2.1 cm³ of a 3.05 mol dm⁻³ solution of **5** in toluene was added similarly. The contents were mixed at 20–25°C with 0.75 cm³ of a 0.5 mol dm⁻³ solution of a THF–BF₃ (1:1) complex (BF₃THF) in DCM. The test tube was closed by a ground-glass stopper and kept at 20–25°C for 20 h. The contents were poured into methanol (400 cm³) and the precipitate was purified by reprecipitation from toluene to methanol. The final precipitate was collected by decantation and dried in vacuum to give 2.61 g of the methanol-insoluble fraction of **IIa-A-3**. Cross-linked polymers were obtained by washing the polymerization product with 20% aqueous methanol, methanol, and ether successively and then by drying the product in vacuum.

Cationic Ring-Opening Isomerization Polymerization of 10. A test tube containing **10** (0.2 g, 0.78 mmol) and 1-benzylthiolanium hexafluoroantimonate⁷ was degassed in vac-

cum and then charged with dry nitrogen gas. Dry chlorobenzene (0.3 cm³) was placed into the test tube by a hypodermic syringe under nitrogen and the mixture was left standing in an oil bath at 120°C for 10 h. The contents were dissolved in a small portion of THF and poured into a large volume of hexane to precipitate the product polymer. The polymer was dried in vacuum to give 0.21 g of poly(**8**): IR (KBr) 1780 and 1710 (phthalimido C=O), 1110 (ether C–O), and 730 and 720 cm⁻¹ (1,2-disubstituted benzene); ¹H NMR (CDCl₃) δ 0.80 (s, 3H, CH₃), 3.17 (s, 4H, OCH₂), 3.61 (s, 2H, NCH₂), and 8.2–7.2 (m, 4H, ArH).

Polymer Reaction

Displacement of the Pendant Bromide with PPI; Typical Procedure. Cross-linked polymer **Ia-B-3** (1.98 g, about 6.3 mmol of the pendant bromide) was swollen in DMF (15 cm³) and stirred with PPI (7.2 mmol) at 80°C for 10 h. After a large portion of DMF was evaporated, the residue was washed with water and methanol successively and dried in vacuum to give the product polymer **IIa-B-3** in a 92% yield. Uncross-linked polymers were obtained by removing DMF from the reaction mixture and then by reprecipitating the residue from DCM to methanol.

Hydrazinolysis of the Pendant Phthalimide; Typical Procedure. Cross-linked polymer **IIa-B-3** (2.21 g, about 5.9 mmol of the phthalimide) was stirred with hydrazine monohydrate (41 mmol) in ethanol (16 cm³) at 40°C for 6 h. The ethanol was evaporated and the residue was made basic at pH 9 with NaOH. The product polymer was collected by filtration, washed with water and methanol successively, and dried in vacuum to give 1.45 g of **IIIa-B-3**. In the case of homopolymers, **IIIa-A-1** and **IIIb-A-1**, the reaction mixture was acidified at pH 3 with 3*N* HCl and filtered. The filtrate was made basic at pH 9 with NaOH and concentrated to an adequate volume. The concentrated aqueous solution was placed in a

bag made of a membrane sheet (102 × 152 mm, pore size 2.4 nm), and inorganic impurities were removed from the solution by dialysis at 25°C for 30 h against distilled water (3 × 200 cm³). The resultant aqueous solution was freeze-dried to give the amine polymer.

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 CDCl₃ as a solvent and TMS as an internal standard at 25°C. Molecular-weight measurements were made by gel-permeation chromatography (GPC) using columns G4000H8 and G2500HXL (each 7.8φ × 300, TOSOH) arranged in a series and THF as the solvent (0.8 cm³ min⁻¹). The content of the pendant amino group was determined as usual by non-aqueous titration using hydroperchloric acid in methanol with an Eosine Y indicator.

RESULTS AND DISCUSSION

Preparation of Polyoxetanes Having a Primary Amino Group at the Side Chain-End

Oxethanes with the pendant amino group, such as **3**, are not allowed to polymerize with a BF₃·THF initiator. Therefore, the preparation of polyoxetanes, **IIa-As** and **IIb-As**, with the pendant phthalimido group is the main step for obtaining the amine polymers, **IIIa-As** and **IIIb-As**, by the Gabriel synthesis method. The preparation of phthalimide-containing polyoxetanes was carried out by the two procedures of Methods A and B, as shown in Scheme 2.

Cationic Ring-Opening Polymerization of Oxetanes by Method A. In the Method A, polyoxetanes, **IIa-As** and **IIb-As**, were obtained by the cationic ring-opening polymerization of oxetanes **2a** and **2b** in toluene at 20–30°C with BF₃·THF. The high purity of the viscous oily products **2a** and **2b**, obtained after modified post-treatment without purification by recrystallization or distillation, was confirmed

from their ¹H NMR spectra and elemental analysis data. In the polymerization of **2a** and **2b**, oxetanes **4** and **5** were also used, respectively, as a cross-linking agent and hydrophobic monomer unit. The results are summarized in Table I for the preparation of the pendant-phthalimide-containing polyoxetanes by Method A. The contents of monomeric unit of the product polymers were estimated by ¹H NMR spectroscopy for the uncross-linked polymers and by elemental analysis for the cross-linked polymers.

For the typical spectra of the product polymers, the ¹H NMR spectrum of **IIa-A-1** is shown in Figure 1 together with that of the corresponding monomer, **2a**, and the IR spectrum of cross-linked polymer **IIa-A-4** is shown in Figure 2 along with those of **3** and the corresponding polymer **IIIa-A-4**, obtained by hydrazinolysis of the **IIa-A-4**. The signals in Figures 1A and 1B are assigned to the corresponding protons of **IIa-A-1** and **2a**, respectively. In a comparison between the ¹H NMR spectra 1A and 1B, the AB-quartet due to the cyclic methylene protons (H^c) and singlets due to the neighboring methylene (H^f) and methyl protons (H^h) for the oxetane ring of **2a** appear as the signals H^c, H^f, and H^h of **IIa-A-1** at the higher magnetic field site after the ring-opening polymerization of **2a**. Such findings were also generally observed for other analogues oxetane derivatives prepared previously by us.⁵ Chemical shift values and patterns of the signals for the other protons in **2a** resemble those of the corresponding protons in **IIa-A-1**. In the IR spectrum of **IIa-A-4** (Figure 2A), the IR bands at 980 and 835 cm⁻¹ assignable to the cyclic ether of the corresponding monomer **2a** disappeared completely, but the strong bands appeared at 1772 and 1715 cm⁻¹ due to the phthalimido group and at 1110 cm⁻¹ due to the ether linkage of the polymer network.

In the polymerization of **2a** or **2b** with **4**, cross-linked polymers were obtained with easy handling by filtration and unchanged monomer

Table I. Preparation of phthalimide-containing polyoxetanes^a

Entry	Monomer (Mole ratio)	[OR] ₀ ^c mol dm ⁻³	Polymer		
			Name	Yield wt%	4 ^d mol%
1	2a ^b	1.8	IIa-A-1	85 ^f	0
2	2a + 5 (67/33)	2.1	IIa-A-2	61 ^g	33 ^e
3	2a + 5 (50/50)	2.3	IIa-A-3	89 ^h	50 ^e
4	2a + 4 (84/16)	2.6	IIa-A-4	90	21
5	2a + 4 (75/25)	3.5	IIa-A-5	99	23
6	2a + 4 (74/26)	0.9	IIa-A-6	42	31 ^e
7	2a + 4 (70/30)	2.5	IIa-A-7	93	33
8	2a + 4 (55/45)	2.5	IIa-A-8	89	43
9	2b	1.2	IIb-A-1	43 ⁱ	0
10	2b + 4 (85/15)	2.5	IIb-A-2	92	22
11	2b + 4 (75/25)	2.7	IIb-A-3	92	29

^a In toluene at 20–25°C for 20 h with 2–3 mol% of BF₃·THF to the total of oxetane ring.

^b With 8 mol% of BF₃·THF.

^c Initial concentration for the total of oxetane ring.

^d Monomeric unit fraction of 4 was estimated from elemental analysis data for the C and N atoms of the product polymer.

^e The monomeric unit content of 5 estimated from integral intensity by ¹H NMR spectroscopy.

^{f–i} Molecular weights (*M*_{GPC}) were as follows: f, 24500; g, 41600; h, 30700; and i, 5700.

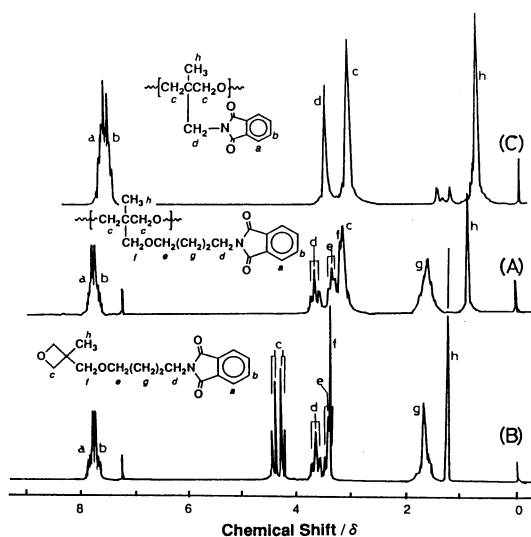


Figure 1. ¹H NMR spectra of (A) IIa-A-1, (B) 2a, and (C) poly(8).

2a or 2b was recovered from the filtrate, while 4 was hardly detected in the filtrate. Therefore, the degree of cross-linking must be reestimated

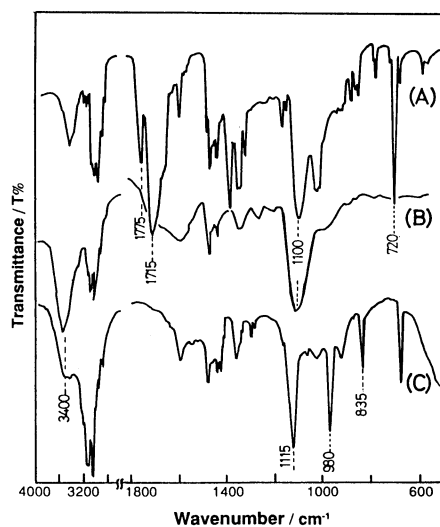


Figure 2. IR spectra of (A) IIa-A-4, (b) IIIa-A-4, and (C) 3.

for the product polymers. The monomeric unit content for 4 in the product polymer is estimated to be higher than that in feed. The cross-linked polymers did not seem to contain

such organic compounds as toluene and methanol used as a polymerization solvent or a washing solvent, as suggested from the ^1H NMR spectra, *e.g.*, Figure 1A, of the uncross-linked polymers dried thoroughly in vacuum. The degrees of cross-linking of the product polymers, **IIa-As** and **IIb-As**, were reestimated from elemental analysis data for the carbon and nitrogen atoms, and then the theoretical values of the elemental content were calculated for the product polymers, which were assumed to be composed of **2a** or **2b** and **4** in these reestimated degrees of cross-linking. These values are fairly close to the observed ones (Table III), indicating that the product polymers scarcely contained any organic impurities due to the solvents used. However, the observed elemental contents for **IIIa-As** and **IIIb-As**, obtained by hydrazinolysis of the corresponding phthalimide polymers, are somewhat different from the theoretical contents (*vide infra*). These results for the reestimated monomeric unit contents of **4** are shown in Figure 3 together with results not listed in Table I. In each product polymer, the mole fraction of monomeric unit for **4** shows a tendency to be appreciably higher relative to that of the charged **4**.

The initial total concentration $[\text{OR}]_0$ for the oxetane ring of the charged monomers must be set about 2.0 mol dm^{-3} . When the $[\text{OR}]_0$ was set at 0.9 to 1.2 mol dm^{-3} , the product polymers **IIa-A-6** and **IIb-A-1**, which were collected as a methanol-insoluble fraction, were obtained in low yields up to 43% (Entries 6 and 9), and the main component of these methanol-soluble fractions was the unchanged monomer **2a** or **2b**. Additionally, the GPC-average molecular weight (M_{GPC}) of **IIb-A-1** was considerably lower than that of **IIa-A-1**, obtained in a 85% yield using an increased amount of $\text{BF}_3\cdot\text{THF}$ such as 8 mol%. The results may be ascribed to the low propagation rate constants for the phthalimide-containing monomers. Furthermore, the product polymer **IIa-A-6** was soluble in such solvents as DCM,

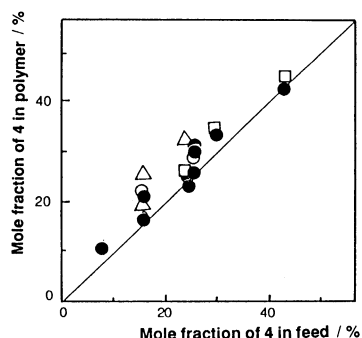


Figure 3. Relationship between the mole fraction of **4** in polymer and that of **4** in feed: (●) poly(**2a-co-4**)s and (□) their hydrazinolysis products; (○) poly(**2b-co-4**)s and (△) their hydrazinolysis products.

chloroform, and benzene, in spite of containing 31 mol% the cross-linking agent in the polymer network. This polymer, which was purified by reprecipitating it from DCM to methanol, contained no unchanged oxetane ring, and monomeric unit fractions were estimated by ^1H NMR using CDCl_3 as a solvent. As to the preparation of divinylbenzene-cross-linked polystyrene resins, it is known that a macroporous network is formed with the generation of considerable porosity under the preparation conditions using large quantities of cross-linking agent up to about 20 mol% in the solvent which solvates both monomer and polymer.⁸ Probably, our polyether network was also formed with the generation of wide meshes when a large amount of the solvent was used relative to the amount of the oxetane monomers, *i.e.*, at the low $[\text{OR}]_0$. Such a network could contain the solvent abundantly so as to be dissolved in it, although the cross-linking agent **4** was incorporated in the network in the considerable amount of 31 mol%, indicating that the cross-linked polymers obtained in this study have a fully expandable, soft polyether network and so are swellable with the organic solvents used.

Hydrazinolysis of the Pendant Phthalimido Group. The pendant phthalimido groups of the **IIa-As** and **IIb-As** were warmed with an excess of hydrazine monohydrate in ethanol at 40°C

Table II. Preparation of polyoxetanes having the pendant primary amino group by hydrazinolysis of the corresponding phthalimide^a

Entry	Starting polymer ^b wt/g		Product polymer					
			Name	Yield ^c	4 ^d	H ₂ O ^e	NH ₂ ^g /mmol g ⁻¹	
				g/%	mol%	wt%	HClO ₄	Anal.
12	IIa-A-1	1.30	IIIa-A-1	0.41 (55)	0			
13	IIa-A-3	1.80	IIIa-A-3	1.35 (100)	50 ^f			
14	IIa-A-4	1.03	IIIa-A-4	0.66 (97)	20 (21)	1.5	4.39	4.10
15	IIa-A-5	1.22	IIIa-A-5	0.71 (85)	24 (24)	3.7	3.87	3.75
16	IIa-A-7	1.35	IIIa-A-7	0.85 (88)	32 (33)	2.4	3.86	3.28
17	IIa-A-8	1.33	IIIa-A-8	0.95 (94)	46 (45)	1.5	2.67	2.51
18	IIb-A-1	0.59	IIIb-A-1	0.29 (81)	0			
19	IIb-A-2	4.26	IIIb-A-2	2.57 (87)	25 (24)	1.7		
20	IIb-A-3	2.50	IIIb-A-3	3.13 (88)	32 (31)	1.3		

^a Hydrazinolysis was carried out using 7–10 mmol of NH₂NH₂·H₂O per 1.0 mmol of the phthalimido group in ethanol (3–5 cm³) at 40°C for 6 h.

^b These are shown in Table I.

^c Theoretical yield of the product polymer containing the adsorbed water was calculated using the average degree of cross-linking (also see the footnotes d and e).

^d Monomeric unit content of **4** was estimated from the elemental analysis data of the product polymer. Values in parentheses show the average between the degree of cross-linking of the starting polymer and that of the product polymer.

^e Content of the water adsorbed in the product polymer was estimated from elemental analysis data.

^f Monomeric unit content of **5** determined by ¹H NMR spectroscopy.

^g Determined by non-aqueous titration with HClO₄ and by elemental analysis for the nitrogen atom.

to be converted to the corresponding primary amino groups of **IIIa-As** and **IIIb-As**. The results of the hydrazinolysis are summarized in Table II. Cross-linked polymers were obtained in good yields with easy handling such as filtration, and uncross-linked copolymers, *e.g.*, **IIIa-A-3**, were purified by reprecipitating the raw product polymers from DCM to methanol. However, homopolymers, **IIIa-A-1** and **IIIb-A-1**, were soluble in water and methanol and so must be separated from inorganic impurities by dialysis at room temperature against distilled water. The monomeric unit content for **4** or **5** of the product polymer was also reestimated in the same manner as described in Table I. In each Entry of Table I, the degree of cross-linking of the monomeric unit **4** in the amine polymer seems fairly close to that of the corresponding phthalimide polymer. The theoretical elemental contents required for the

amine polymers were calculated using the reestimated degrees of cross-linking for **4**, assuming that the amine polymers contained no organic impurities such as the polymerization- and washing-solvents as suggested from the results of the ¹H NMR spectra of the amine polymers dried thoroughly in vacuum (Table III). However, the calculated contents did not agree with the corresponding observed ones, especially for carbon content. The deviation between the calculated and observed contents is considered to be ascribable to the slight amounts of the moisture adsorbed on the amine polymers. The corresponding amine-containing homopolymers were readily soluble in water due to the hydrophilicity of the pendant amino group, which can make hydrogen bonds with water molecules and generate ammonium cations in water for a part of the amino groups. In fact, homopolymers, **IIIa-A-1** and **IIIb-A-1**,

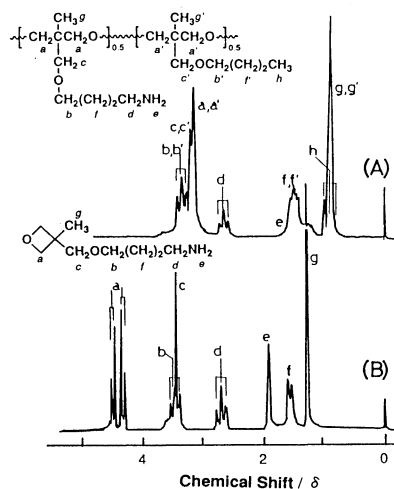
Table III. Elemental analysis data of phthalimide- and amino-containing cross-linked polyoxetanes obtained by Method A

Polymer name	Anal/%					
	Found			Calcd ^a		
	C	H	N	C	H	N
IIa-A-4	66.55	7.48	3.73	66.89	7.58	3.79
IIa-A-5	66.45	7.52	3.69	66.87	7.63	3.68
IIa-A-7	66.51	7.72	3.25	66.64	7.93	3.25
IIa-A-8	66.03	8.31	2.79	66.43	8.23	2.73
IIb-A-2	67.96	7.99	3.47	68.17	8.08	3.46
IIb-A-3	67.27	8.30	3.18	67.93	8.23	3.21
IIIa-A-4	62.15	10.63	5.75	63.11	10.82	5.89
IIIa-A-5	60.93	10.70	5.26	63.24	10.78	5.50
IIIa-A-7	61.97	10.41	4.60	63.49	10.70	4.75
IIIa-A-8	62.92	10.19	3.52	63.88	10.56	3.56
IIIb-A-2	64.34	11.52	4.79	65.45	11.13	4.87
IIIb-A-3	64.58	11.11	4.26	65.41	11.02	4.34

^a For the phthalimide polymers, composed of **2a** (or **2b**) and **4** with the degrees of cross-linking reestimated from the contents of C and N atoms. Obtained similarly for the amine polymers. Also see the text.

dissolved in water indicated basicity of pH 7.5 to 8.5, and their pK_a were estimated to be 1.9 and 3.4, respectively, by titration with aqueous NaOH, although, in general, methyl- and ethylamines and monoalkylamines with longer alkyl chains have their pK_a around 10.5. The lowered basicity of the amine polymer in water may be ascribed to preventing the generation of the ammonium cations in a high density in the polymer matrices, since the cations immobilized densely in the matrices repulse each other more strongly compared with those of ordinary organic amines capable of moving freely in aqueous solution.

The ¹H NMR spectrum of amine polymer **IIIa-A-3** is shown in Figure 4 to represent amine polymers besides that of **3**. In Figure 4A, compared with Figure 1A, the aromatic protons of the phthalimido group are not observed and the methylene protons (H^d) adjacent to the amino group resonate at lower chemical shift than that of the corresponding methylene protons adjacent to the phthalimido group. The spectrum of Figure 4A is similar to that of Figure 4B, which is shown for a

**Figure 4.** ¹H NMR spectra of (A) **IIIa-A-3** and (B) **3**.

model compound of the monomeric unit of the pendant-amine-containing polymers, although the signals of the methylene and methyl groups of the oxetane ring are different from those of the polymer main chain.

To examine the cleavage of ether linkages of the polymer and side chains during hydrazino-

Table IV. Preparation of polyoxetanes by Method B^a

Entry	Starting polymer ^b	Product polymer			
		No.	Yield %	4 mol%	$10^{-4} M_{\text{GPC}}$
21	Ia-B-1 (1a)	IIa-B-1	74	0	4.16
22	Ia-B-2 (1a + 5, 46/54)	IIa-B-2	74	54 ^d	3.57
23	Ia-B-3 (1a + 4, 75/25)	IIa-B-3	92 ^e	20 ^e	—
24	IIa-B-3 (2a + 4, 80/20)^c	IIa-B-3	95 ^e	24 ^f (3.7)	—
25	Ib-B-1 (1b)	IIb-B-1	92	0	7.08

^a 1.2 mmol of PPI per 1.0 mmol of the pendant bromine atom was used in 8–10 cm³ of DMF per 1.0 g of the starting polymer at 80°C for 8–10 h.

^b Monomers and charge ratios used for preparing polymers, **Ia-B-1**–**3** and **Ib-B-1**, with the pendant bromine atom are given in parentheses.

^c Polymer with the pendant phthalimido group, obtained in Entry 23, was used. Reaction conditions were presented in Table II.

^d Monomeric unit fraction of **5** determined by ¹H NMR spectroscopy.

^e Determined from analytical data; C, 66.25%; H, 7.46%; Br, 0.00%; N, 3.75%.

^f Determined from analytical data: C, 60.78%; H, 10.18%; N, 5.30%. Figures in parenthesis show the content of moisture (wt%) in the product polymer.

^g Theoretical yield was calculated based on the estimated contents of the monomeric unit **4** and of the moisture for the product polymer.

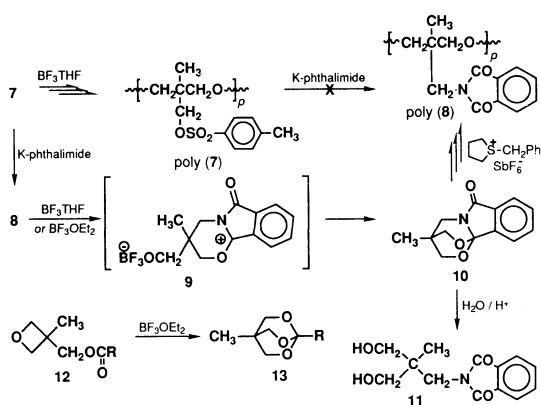
lysis, poly(**6**) (the structure of **6** is shown in Scheme 1) was treated with hydrazine monohydrate under reaction conditions comparable to the hydrazinolysis conditions for the phthalimide-containing polymers. The GPC chromatogram of the examined poly(**6**) was close to that of the polymer recovered almost quantitatively after treatment with hydrazine, *i.e.*, the original poly(**6**) had $M_{\text{GPC}} 1.11 \times 10^4$ ($M_w/M_n 2.65$) and the recovered polymer $M_{\text{GPC}} 1.22 \times 10^4$ ($M_w/M_n 1.99$). The spectra of these polymers also coincided with each other.

Displacement of the Pendant Bromide Group with PPI by Method B. Polymers, **IIa-Bs** and **IIb-Bs**, having the pendant phthalimido group through long spacers such as 2-oxahexa- and 2-oxaoctamethylenes were smoothly obtained by the displacement of the pendant bromine atoms of **Ia-B-1**–**3** and **Ib-B-1** with the phthalimido group of PPI in DMF at 80°C. The IR and ¹H NMR spectra of the product polymers coincided, respectively, with those of the product polymers obtained by Method A. The results of these displacement reactions are

shown in Table IV. The phthalimido groups were smoothly and completely reduced by hydrazinolysis to give the corresponding primary amino groups in fairly good yield, as exemplified for the hydrazinolysis of **IIa-B-3**.

Influence of Spacers on Ring-Opening Polymerization and Polymer Reaction

Up to this time, we thought that the Methods A and B are general procedures for obtaining the phthalimide-containing polyoxetanes with spacers of differing length. As shown in Scheme 3, however, these methods were quite ineffective on the ring-opening polymerization of oxetane **8** with BF₃ and on the displacement of the pendant *p*-toluenesulfonate of poly(**7**) with PPI. This indicates the influence of the spacer on the reactivities of an oxetane ring and the pendant substrate of a polyoxetane. Therefore, the role of the spacer may be further clarified by showing these results about **8** and poly(**7**) in this section. Thus, the oxetane **8** was mixed with 1 mol% of BF₃·THF and left stand in the same manner as described above

Scheme 3. Reaction routes of **7** and **8**.

for the polymerization of oxetanes. After 24 h-standing at 0°C , an aliquot was withdrawn from the mixture by means of a hypodermic syringe under nitrogen to be subjected to ^1H NMR spectroscopic measurements (Figure 5). This spectrum is shown in Figure 5A which is much different from that of **8** as shown in Figure 5C. A few drops of D_2O were added to the aliquot at room temperature. The spectrum of the resultant solution is presented in Figure 5B. The signals of the spectra of Figures 5A and 5B were assigned to those of the products **10** and **11**, respectively, the structures of which were also confirmed by the authentic samples. Previously it was reported that oxetanes **12** with the acyloxymethyl pendant at the C-3 position gave 2,6,7-trioxabicyclo[2.2.2]octanes (**13**) in DCM at 0°C in the presence of BF_3 .⁹ According to this report, the reaction mechanism from **8** to **10** may be as follows: the methylene carbon atom of the oxetane ring of **8** is attacked intramolecularly in the presence of BF_3 by the carbonyl oxygen atom of the phthalimido group to form the bicyclic zwitterion intermediate **9**, but not intermolecularly by the cyclic ether oxygen atom of another **8**. The paired ions of the zwitterion **9** linked to each other intramolecularly to give the carbon-oxygen covalent bond of the tricyclic product **10**. This was readily hydrolyzed

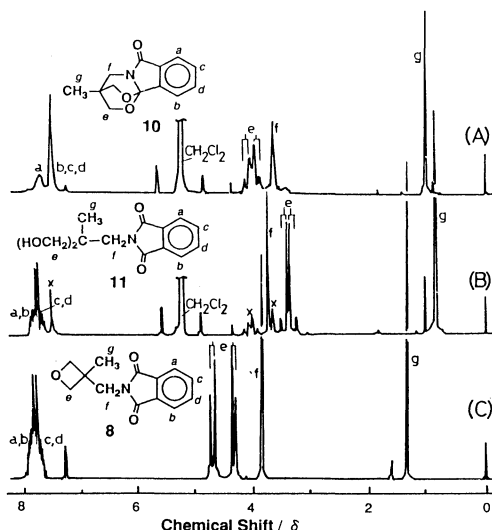


Figure 5. ^1H NMR spectra of (A) an aliquot taken from the resultant solution of **8** left standing in DCM at room temperature for 20 h, (B) the reaction mixture containing the main product **11** obtained by adding D_2O to the aliquot, and (C) the solution of **8** in CDCl_3 .

with the added water in the presence of a protonic acid, which was generated from BF_3 and the water. Therefore, the oxetane **8** could not be converted to the corresponding polymer by ring-opening polymerization with BF_3 . Compared with the reaction type of the carboxylic esters **12** in the presence of BF_3 , the *p*-toluenesulfonate **7** was polymerized with 1 mol% of $\text{BF}_3 \cdot \text{THF}$ to give the corresponding polymer in a 76% yield. This indicates that the sulfonyl oxygen atom of the tosyloxy group of **7** does not attack intramolecularly the methylene carbon of the oxetane ring, presumably due to avoiding the formation of an unstable zwitterion intermediate with a five-valent sulfur atom. Furthermore, the pendant *p*-toluenesulfonate group of poly(**7**) was not displaced by PPI to be converted to the phthalimido group of poly(**8**). The *p*-toluenesulfonate group of **7** was readily replaced by the corresponding phthalimido residue. The pendant methylene carbon atom of poly(**7**) resembles that of the neopentyl group which is remarkably unsusceptible to the

S_N2 reaction. These findings show that the degree of steric hindrance is more or less relaxed around the methylene carbon atom adjacent to the oxetane ring compared with that around the neopentyl-like methylene carbon atom adjacent to the quaternary carbon atom of the polymer main chain, *i.e.*, the quaternary carbon atom of the oxetane ring takes a molecular orbital that is somewhat different from the ordinary sp^3 hybrid orbital.

Thus, the desired polymer product, poly(**8**), was not obtained by the cationic ring-opening polymerization of **8** in the presence of BF_3 or by the polymer reaction of the *p*-toluenesulfonate of poly(**7**) with PPI. Fortunately, however, tricyclic product **10** was converted almost quantitatively to the poly(**8**) with M_{GPC} about 4000 by cationic ring-opening isomerization polymerization using 1-benzylthiolanium hexafluoroantimonate in chlorobenzene at 120°C for 10 h, according to the reported procedure.⁷ The structure of poly(**8**) was confirmed by its ¹H NMR (Figure 1C) and IR spectra.

In conclusion, desired polyoxetanes with a primary amino group through the moderately long spacers were prepared from the corresponding phthalimide-containing polymers by both of methods A and B. The degree of hydrophilicity of the amino polymer could be changed by varying the mole fraction of the hydrophobic monomer **5** in the copolymer. At this point we find it difficult to judge which is better Methods A or B, since the polymers obtained by Methods A and B seem similar to each other as to their IR and ¹H NMR spectra and elemental analysis data. For the merits and

demerits of Methods A and B, we mentioned that the polymerizations of **2a** and **2b** never contain the bromide group, which may be contained as an unchanged pendant substrate in the product polymer obtained by Method B depending on the reaction conditions, although the purification of the phthalimido monomers **2a** and **2b** is somewhat troublesome. In this study, other desired products, poly(**8**) and cross-linked analogues, could not be obtained by Method A or B. However, the primary amino group anchored to the soft, expandable polyoxetane network through the moderately long spacers will be examined for use as a key substrate for preparing functional polymers.

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