

Preparation and Characterization of Polyoxetanes Anchoring the Pendant Spacer-Separated Phenolic Residues and Their Derivatives

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ABSTRACT: Uncross- and cross-linked polyoxetanes bearing *o*-, *m*-, and *p*-phenolic residual groups at the terminals of moderately long pendant spacers $-\text{CH}_2\text{O}(\text{CH}_2)_n-$, where $n=4$ and 6 , were prepared. The prepolymers having the pendant *O*-acetylated phenols were made by the BF_3 -initiated cationic ring-opening polymerization and then the pendant phenyl acetates were hydrolyzed with $2N$ aqueous NaOH in methanol to give the desired phenolic polyoxetanes. The pendant phenols were subjected to the diazocoupling reaction with 3 equiv of benzenediazonium chloride to examine their reactivities in aqueous media. Model polyoxetanes with the pendant phenyl benzoates containing the azo group were also prepared to confirm the structures of the diazocoupling product polymers.

KEY WORDS Oxetanes / Polyoxetanes / Cationic Ring-Opening / Polymerization / Pendant Phenols / Polymer Reaction /

So far, a variety of functional polymers were synthesized and their functioning abilities were examined. In the synthesis of functional polymers, pendant phenolic groups immobilized on polymer matrices are also recognized as one of typical, useful functional groups, since the physical and chemical properties of phenols were investigated in detail in organic chemistry and the phenols are applied to materials synthesis in a wide area. In addition, the functioning abilities of the pendant groups immobilized on polymer matrices are influenced by the physical properties of the matrices and enhanced by the placement of adequately long spacers between the pendant groups and the matrices. Therefore, selecting the types of matrices and spacers is also important to obtain functional polymers proper to the uses. In the course of our study of using a polyoxetane network as the polymer matrices of functional polymers, we consider that a polyoxetane network is promising as

polymer matrices due to the qualities of ether linkages in polyoxetane chain, *e.g.*, softness or flexibility, moderate polarity, more or less hydrophilicity, thermal stability up to about 300°C , and chemical stability, especially such as alkali-resistance.¹⁻⁴⁾

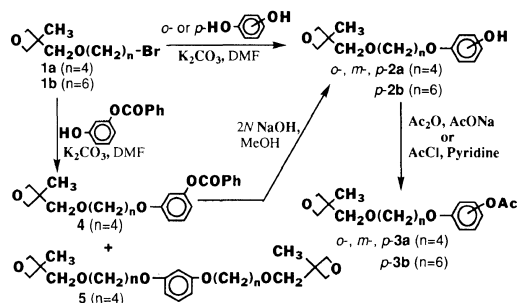
At the present day *p*-acetoxystyrene is available as a commercial reagent and poly(*p*-hydroxystyrene)s are prepared by the hydrolysis of the homo- and copolymers of *p*-acetoxystyrene. Divinylbenzene-cross-linked poly(*p*-hydroxystyrene)s were used as a chelate resin or the solid phase of *o*-nitrophenol type in peptide synthesis.^{5,6} However, there are few reports describing the preparation of functional polymers using pendant phenolic residues, especially, linked to adequately long spacers. Here, we are interested in obtaining uncross- and cross-linked polyoxetanes having pendant spacer-separated phenolic residues, because we expect that such polymers, which are not obtained yet, serve for key substrates in the

functional polymers synthesis. Thus, this report describes the preparation and characterization of polyoxetanes having *o*-, *m*-, and *p*-isomeric phenol residues at the side chain-end through moderately long spacers. The diazocoupling reaction of these pendant phenols was also examined with benzenediazonium chloride (BDC) in order to know their reactivities in polymer matrices in aqueous media.

RESULTS AND DISCUSSION

Polyoxetanes with Pendant Phenolic Residues and Their O-Acetylated Prepolymers

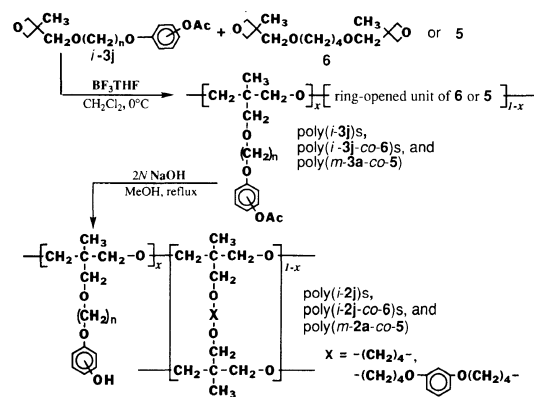
Scheme 1 shows the synthetic routes of oxetanes with the *o*-, *m*-, and *p*-phenolic residual groups at the terminal of the side chain. Bromides **1a** and **1b** gave their phenol-containing products *o*-**2a**, *p*-**2a**, and *p*-**2b** in yields of 64, 61, and 57%, respectively, by a reaction with one mole of catechol or 3 mol of hydroquinone to one mole of the bromide in *N,N*-dimethylformamide (DMF) at 80°C in the presence of potassium carbonate (K₂CO₃). The product *m*-**2a** was obtained in 63% yield based on **1a** via the alkaline hydrolysis of the corresponding benzoate **4** with 2*N* sodium hydroxide (NaOH) in methanol. The by-product **5** was also formed in about 6% yield in the preparation of the desired product **4** by the substitution reaction of **1a** with one mole of resorcinol monobenzoate available as a commercial reagent. The formation of **5** is ascribed to the substitution of the bromide **1a**



Scheme 1. Synthetic routes of oxetanes with pendant phenols and their acetic esters.

with the phenoxide of *m*-**2a**, as generated by an ester-exchange reaction on the ester carbonyl of **4** with the phenoxide of resorcinol monobenzoate.

The pendant phenols of these oxetanes were protected by *O*-acetylation with acetyl chloride and pyridine in dichloromethane (DCM) at 0°C or with acetic anhydride and sodium acetate in DCM at 40°C to be subjected to the cationic ring-opening polymerization initiated with a tetrahydrofuran (THF)-boron trifluoride (1:1) complex (BF₃·THF). In these polymerizations bisoxetanes **6** and **5** were also used as a cross-linking agent. The pendant phenols of these oxetanes were readily and completely hydrolyzed with 2*N* NaOH in methanol at refluxing temperature, as confirmed from the disappearance of the ester moiety by the IR and/or ¹H NMR spectra of the product polymers. The synthetic routes of the polymers are shown in Scheme 2 and the results of the polymer synthesis is summarized in Table I. The uncross-linked polymers were reprecipitated by using an appropriate solvent system, DCM-methanol or methanol-hexane, to give the viscous, oily product polymers. The cross-linked polymers were collected as the elastic gel products with easy handling by filtration. Gel permeation chromatography (GPC)-average molecular weights (*M*_{gpc}) lay in the region



Scheme 2. Synthetic routes of polyoxetanes with the pendant phenols: *i* = *o*-, *m*-, or *p*-; *j* = **a** or **b**.

Table I. Cationic ring-opening polymerization of oxetanes with the pendant phenyl acetates and their hydrolysis products^a

Monomer charged (Mole ratio)	Polymer ^b			Hydrolyzed polymer yield/%
	Yield %	$10^{-4} \times$ M_{GPC}^c	M_w/M_n	
<i>o</i> -3a	91	4.56	2.1	68 ^e
<i>o</i> -3a+6 (85/15)	86	—	—	95
<i>m</i> -3a	97	6.35	2.0	99
<i>m</i> -3a+6 (87/13)	81	—	—	97
<i>m</i> -3a+6 (77/23)	90	—	—	— ^f
<i>m</i> -3a+5 (87/13)	70	—	—	— ^f
<i>p</i> -3a	24	1.65 ^d	1.8	82
<i>p</i> -3a+6 (85/15)	55	—	—	81
<i>p</i> -3b	80	2.23	2.2	82
<i>p</i> -3b+6 (85/15)	82	—	—	80

^a Polymerization was carried out with 1 mol% of BF₃ to the oxetane ring in DCM at 0°C for 20 h at initial monomer concentrations of 1.8–2.2 mol dm⁻³.

^b For methanol-insoluble fractions.

^c Estimated by GPC relative to the polystyrene standards.

^d This chromatogram had a shoulder peak at M_{GPC} 25600.

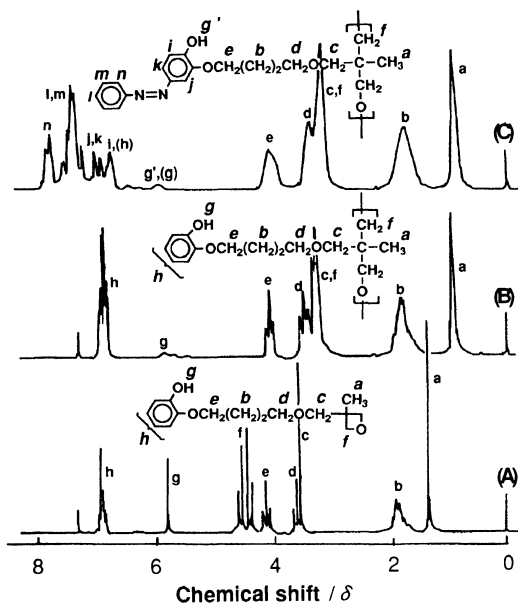
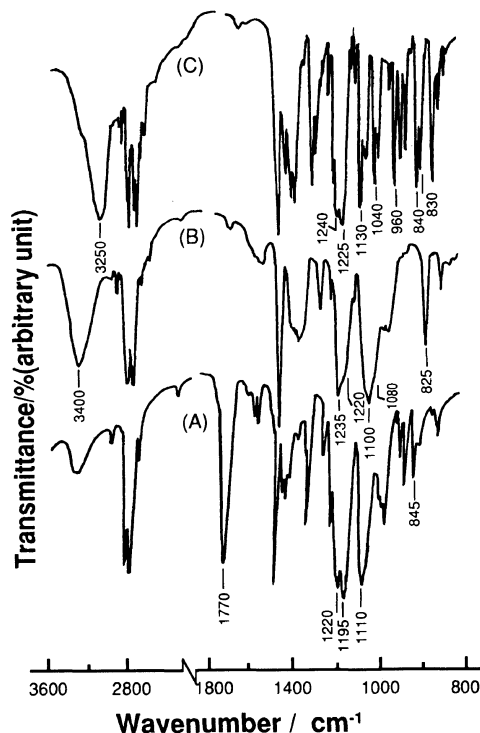
^e M_{GPC} 46700, M_w/M_n 2.3.

^f Not carried out.

around 16000 to 64000 for the uncross-linked, *O*-acetyl-protected prepolymers and the *o*-phenolic hydrolysis product, although the M_{GPC} s of the *m*- and *p*-phenolic analogs were not determined because of their insolubility in THF as a GPC solvent.

The structures of the uncross-linked prepolymers were readily confirmed from their ¹H NMR spectra in CDCl₃. The singlet due to the acetyl protons was observed around δ 2.3 and the AB-quartet due to the methylene protons of the oxetane ring was not observed at δ 4.2–4.6. The structures of the cross-linked prepolymers were confirmed by IR spectroscopy.

The ¹H NMR spectrum of poly(*o*-2a) is exemplified along with that of *o*-2a in parts B and A of Figure 1, respectively. These signals were assigned to the corresponding protons as shown in Figure 1. The spectrum of poly(*o*-2a)

**Figure 1.** ¹H NMR spectra of (A) *o*-2a, (B) poly(*o*-2a), and (C) its diazocoupling product I.**Figure 2.** IR spectra of (A) poly(*p*-3b-co-6), (B) its hydrolysis polymer poly(*p*-2b-co-6), and (C) *p*-2b.

resembles that of *o*-**2a**, which is presented as a model for the monomeric unit of the hydrolysis polymer, although as usual the cyclic or neighboring methylene and methyl protons (H^a , H^c , and H^f) of the oxetane ring resonate at higher chemical shifts than the corresponding protons of the polymer. The resin, poly(*p*-**3b-co-6**), cross-linked with 15 mol% of **6** shows its IR spectrum in Figure 2A. This IR bands due to the ester at 1770 and 1195 cm^{-1} disappear in the spectrum of the hydrolysis product poly(*p*-**2b-co-6**), which shows the strong IR band due to the hydroxyl group around 3600–3200 cm^{-1} (Figure 2B). The aromatic and acyclic ether linkages of poly(*p*-**3b-co-6**) indicate their IR bands at 1220 and 1110 cm^{-1} , respectively, and the corresponding bands of poly(*p*-**2b-co-6**) also appear at 1220 and 1100 cm^{-1} . The IR spectrum of poly(*p*-**2b-co-6**) is confirmed by comparing it with that of *p*-**2b** (Figure 2C), although the IR bands due to the cyclic ether at 960 and 830 cm^{-1} lack in the spectrum of poly(*p*-**2b-co-6**).

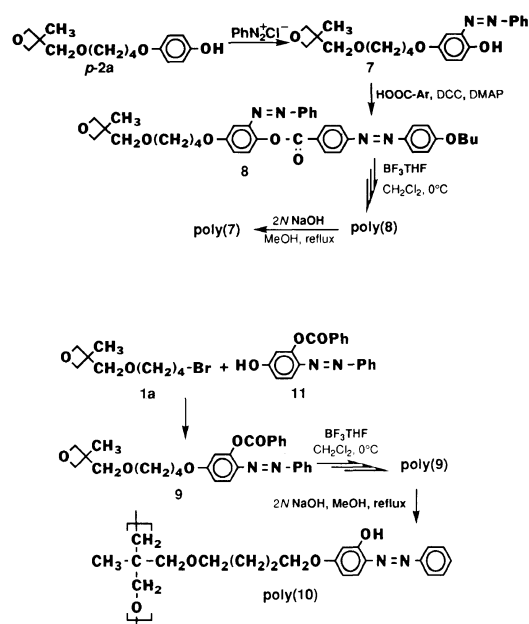
The dissolving behavior of the uncross-linked phenolic polymers in solvents is noticeable. The *m*- and *p*-phenolic polymers were soluble in methanol, but not in chloroform and DCM. On the other hand, the *o*-phenolic polymer was readily dissolved in chloroform and DCM, but not in methanol. The *o*-phenolic hydroxyl group can form an intramolecular hydrogen-bond with the phenoxyl oxygen atom located at the *ortho* position and the hydrogen-bond may be so rigid that the *o*-phenolic group is not solvated satisfactorily with methanol. The *m*- and *p*-phenols form intermolecular hydrogen-bonds, resulting in the formation of temporary cross-linkages between the polyether main chains, although such cross-linkages are released by the methanol solvent. Furthermore, the uncross-linked *m*- and *p*-phenolic polymers dissolved in an alkaline aqueous solution, although the *o*-phenolic polymer was difficult to dissolve smoothly in the alkaline solution.

This fact suggests that the polyoxetane chain is more or less hydrophilic, since it does not hinder the formation of the pendant sodium phenoxide moieties solvated adequately by water molecules. The cross-linked phenolic polyoxetanes also swelled well in an alkaline aqueous solution.

Diazocoupling Reaction of the Pendant Phenols Based on Polyoxetanes

The reactivities of the pendant phenols of uncross-linked polyoxetanes were examined by a diazocoupling reaction, which is one of the typical reactions of phenols, using BDC in aqueous media at 0–3°C. The azobenzene-containing product polymers were subjected to ^1H NMR spectroscopy and elemental analysis to know the substitution mode on the aromatic ring and the degree of functionalization (DF).

Poly(*p*-**2a**) was dissolved in aqueous 2*N* NaOH and allowed to react with the three-fold equiv of BDC to give the product polymer III (this structure is presented in Figure 3B).



Scheme 3. Synthetic routes of polyoxetanes with the pendant spacer-separated *o*-hydroxyazobenzenes poly(**7**) and poly(**10**).

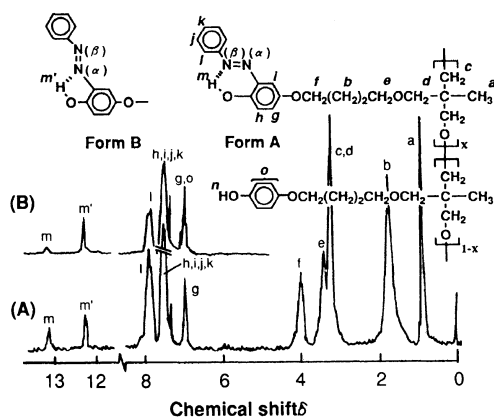


Figure 3. ^1H NMR spectra of (A) a model polymer poly(7) and (B) the diazocoupling product **III**.

Poly(7), *i.e.*, polymer **III** when $x = 1.0$, was also prepared as the authentic polymer for the sequence of the azobenzene-containing monomeric units in **III**, as shown in Scheme 3. The ^1H NMR spectra are shown in Figure 3 for the product polymer **III** and poly(7). In the spectrum of poly(7) (Figure 3A), signals (a) to (m') were assigned to the corresponding protons H^a to $\text{H}^{m'}$, as presented together with the assignment of **III** in Figure 3B. This assignment is supported from the findings of the ^1H NMR spectra of the derivatives of *o*- and *p*-hydroxyazobenzenes (*vide infra*). The spectrum of the product polymer **III** resembles that of poly(7), although **III** has the somewhat higher integral intensity ratio of the signals around δ 6.8–7.0 to those around δ 7.2–8.0 than poly(7). This higher intensity ratio is ascribable to overlapping the signal of the aromatic proton H^e of the produced pendant upon those of the aromatic protons H^o of the unchanged pendant. The signals of H^o , in fact, were observed at δ 6.75 in the spectrum of poly(*p*-2a). In each spectrum of **III** and poly(7), two signals at δ 13.3 and 12.4 were assigned to the phenolic proton of the pendant *o*-hydroxyazobenzene moiety, since these signals disappeared by treating the ^1H NMR sample with D_2O . It is known that *o*-hydroxyazobenzene forms the six-membered

chelate ring through the phenolic hydrogen atom, such as that in Form A.⁷ One signal, therefore, is ascribed to the phenolic proton of the six-membered chelate ring in Form A. Here the formation of the five-membered chelate ring of Form B is also considered for the assignment of the other signal. The phenolic proton H^m of Form A may be more stabilized by electron-delocalization due to a longer conjugate π -electron bonding system relative to that of Form B, and so, presumably, the proton H^m resonates at higher chemical shift than the proton $\text{H}^{m'}$. These structures are discussed in the latter section, too.

Polymer **I** was also obtained by a diazocoupling reaction using 3 mol of BDC to one mole of the pendant phenol of poly(*o*-2a). The ^1H NMR spectrum of **I** is shown in Figure 1C. The signals (a) to (n) were assignable to the protons H^a to H^n in **I**. The phenolic hydroxyl group of the pendant hydroxyazobenzene moiety is located at the *para* position to the azo group, since the phenolic proton H^e does not show its signal at chemical shift higher than δ 12; if the diazocoupling took place at the *ortho* position of the hydroxyl, the phenolic proton of the product should resonate at chemical shift higher than δ 12.

The diazocoupling of poly(*m*-2a) was also carried out under the same reaction conditions as mentioned for poly(*o*-2a) and poly(*p*-2a). The ^1H NMR spectrum of the product polymer **II** is presented in Figure 4 along with that of poly(10), prepared in the pathway outlined in Scheme 3. In the ^1H NMR spectrum of **II**, obviously, the appearance of a signal (s) at δ 13.9 indicates the placement of an azo group at the *ortho* position of the pendant phenol of poly(*m*-2a). The ^1H NMR spectra of poly(10) and 6-butoxy-2-hydroxyazobenzene (14), which have an *o*-hydroxyazobenzene moiety, however, are different from that of polymer **II** (Figures 4A, 4B, and 5D). The nitrogen content (9.65%) of **II**, moreover, is higher than that (7.56%) required theoretically for the structure of poly(10). It is estimated from the carbon and

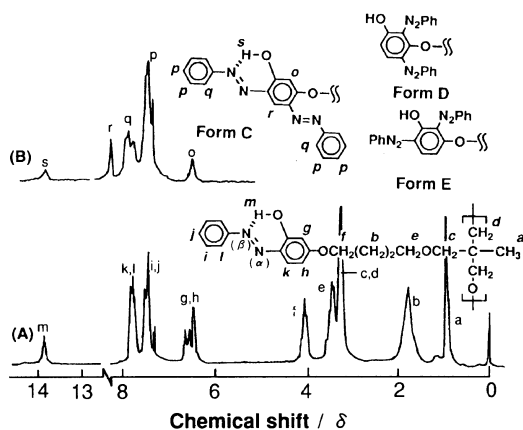


Figure 4. ^1H NMR spectra of (A) a model polymer poly(**10**) and (B) the diazocoupling product **II**.

nitrogen contents of **II** that the majority of the pendant phenol rings were substituted by at least two phenylazo groups. Thus, we think that the main structure of **II** has the moiety of Form C, as shown in Figure 4B, although we failed to isolate a model compound for Form C, 5-butoxy-2,4-bis(phenylazo)phenol, from a reaction mixture of 3-butoxyphenol with BDC (*vide infra*). In Form C the signal (*r*) at δ 8.2 is assigned to the proton H^r which is located at the common *ortho* position of the two phenylazo groups acting as an electron-attracting group. In fact the *ortho* aromatic protons of azobenzene resonate at somewhat higher chemical shift than the rest of the aromatic protons. The aromatic protons of Forms D and E are not expected to show their signals at higher chemical shifts beyond δ 8.0, since neither of these aromatic protons has two *ortho* phenylazo groups. The results of these diazocoupling reactions are summarized in Table II.

o- and *p*-Hydroxyazobenzenes **11**–**14** were prepared to confirm the structures of the diazocoupling products **I**, **II**, and **III** and their model polymers. The synthetic routes of **11**–**14** are shown in Scheme 4. The ^1H NMR spectra of **11**–**14** are presented in the region of δ 4–15 in Figure 5. The *o*-hydroxyazobenzenes **12**, **13**, and **14** indicate the signals due to the phenolic proton H^d around

Table II. Diazocoupling reactions of pendant phenols with BDC^a

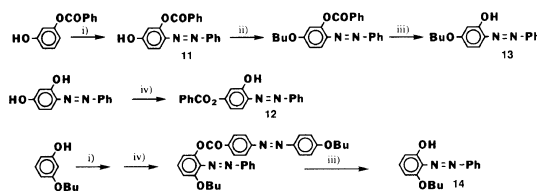
Polymer name	Yield ^c g	Anal. (Found)/%			DF ^d X
		C	H	N	
I	1.34	67.91	7.28	6.13	0.76
II	1.39	66.39	6.42	9.65	0.75
III	1.39	63.70	6.51	7.20	1.02

^a Carried out with 3 mol of benzenediazonium chloride (BDC) at 0–3°C to 1 mol of the pendant phenol dissolved in 10% NaOH.

^b These structures are presented in Figures 1, 3, and 4.

^c Based on 1 g of phenolic polymers.

^d Degrees of functionalization (DF) were estimated from elemental analysis data.



Scheme 4. Synthetic routes of hydroxyazobenzenes **11**–**14**. Conditions: i) 1 or 3 equiv of PhN_2Cl , aq NaOH; ii) *n*-BuBr, K_2CO_3 , DMF, 80°C; iii) 2N NaOH, MeOH, reflux; iv) ArCO_2H , DCC, DMPA, DCM, or THF, 0°C.

δ 12–14, but *p*-hydroxyazobenzene **11** shows the phenolic proton H^d at δ 5.9. As confirmed in our previous report also, *p*-hydroxyazobenzenes mostly showed the signal of the phenolic proton around δ 5–6.⁴ The product **14** of a diazocoupling reaction at the C-2 position of 3-butoxyphenol was isolated from the reaction mixture with BDC, although the diazocoupling reactions at the C-4 and -6 positions were not clarified, indicating that the diazocoupling reaction could take place at least at the C-2 position of the phenolic ring. The isomeric product **13**, which corresponds to the product of a diazocoupling reaction at the C-6 position of 3-butoxyphenol, however, was prepared from **11** through another synthetic route. The isomer **13** was different from **14** in their melting points and ^1H NMR spectra (Figures 5C and 5D). In Figure 5D, further-

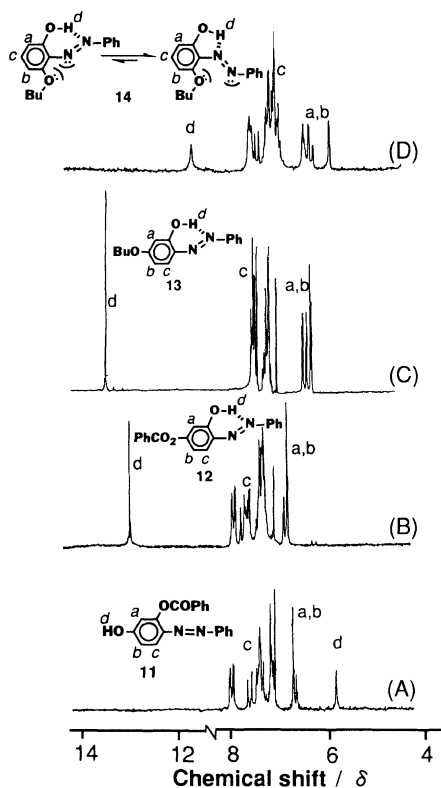


Figure 5. ^1H NMR spectra of model compounds 11–14.

more, this ^1H NMR spectrum is not ascribable to that of the product diazocoupled at the C-4 position of 3-butoxyphenol, since no *p*-phenolic proton was proved in the spectrum; when the ^1H NMR sample was treated with D_2O , the signal pattern did not change except the disappearance of the signal due to the *o*-phenolic proton around δ 12. In addition to these findings, the phenolic proton H^d of **14** resonated at the lower chemical shift of δ 11.8 relative to the chemical shift of δ 12.5 observed for 2-hydroxyazobenzene which forms the usual six-membered chelate ring, while the phenolic proton of **13** resonated at the higher chemical shift of δ 13.9. When **14** forms the six-membered chelate ring, the non-covalent electron pairs repel each other between the nitrogen and oxygen atoms of the azo and ether groups, respectively, favoring the formation of the five-membered chelate ring, as illustrated

in Figure 5D. The *o*-hydroxyazobenzene moieties of **III** and poly(**7**) form not only the six-membered chelate ring of Form A but also the five-membered chelate ring of Form B. However, the *o*-hydroxyazobenzene moiety of **II** forms only the six-membered chelate ring, since **II** indicated the signal (s) due to the phenolic proton only at δ 13.9. The β -nitrogen atom of the *o*-hydroxyazobenzene of **II** may have higher electron density than that of **III**, since, in **II**, the ether oxygen atom of the spacer which is located at the *para* position of the azo group acts as an electron-releasing group in a resonance structure. In the azo groups of **III** and poly(**7**), however, neither of the α - and β -nitrogen atoms are favored to enhance their electron density by such positive mesomeric effect. In this text, the β -position is given for the nitrogen atom adjacent to the unsubstituted phenyl ring of the azobenzene.

When 3-butoxyphenol was treated with 1 or 2 equiv of BDC, considerable amounts of the unreacted phenol were recovered by steam-distillation. Therefore, the pendant phenols were subjected to the diazocoupling with 3 equiv of BDC. The substitution mode of diazocoupling reaction, furthermore, does not seem simple for the *m*-phenolic ring such as those of poly(*m*-**2a**) and 3-butoxyphenol. In the diazocoupling of 3-butoxyphenol with BDC, the final product **14** was obtained in a low yield below 10% through a troublesome purification process. Although the diazocoupling of guaiacol was also attempted, the desired product was not isolated and a mixture of guaiacol and some products was confirmed by thin layer chromatography (TLC) and by ^1H NMR spectroscopy.

Several polyoxetanes with both of the pendant aryl benzoate and azobenzene moieties were also prepared by the BF_3 -initiated cationic ring-opening polymerization of the oxetanes **8**, **9**, **15a**, and **15b**. These polymerizations were carried out with 8 mol% of BF_3 THF due to the presence of the azo group capable of acting as a Lewis Base.⁴ Poly(**8**) and poly(**9**)

Table III. Polyoxetanes with the pendant azobenzene moiety

Polymer name	Yield %	$10^{-3} \times$ $M_{\text{GPC}}^{\text{a}}$	Anal./%					
			Calcd			Found		
			C	H	N	C	H	N
poly(8)	63	8.4	70.12	6.52	8.61	69.63	6.24	9.53
poly(7) ^b	42 ^d	nd ^e	68.08	7.09	7.56	68.69	7.27	8.34
poly(10) ^c	92 ^d	nd ^e	68.08	7.09	7.56	68.09	7.09	7.38
poly(15a)	67	7.4	70.30	7.02	5.13	70.17	6.94	5.01
poly(15b)	93	8.7	71.04	7.38	4.88	70.28	7.45	4.88

^a Estimated by GPC relative to the polystyrene standards.

^b Obtained by the alkaline hydrolysis of poly(**8**).

^c Obtained by the alkaline hydrolysis of poly(**9**) (M_{GPC} 3500).

^d Yields of these alkaline hydrolyses.

^e Not determined.

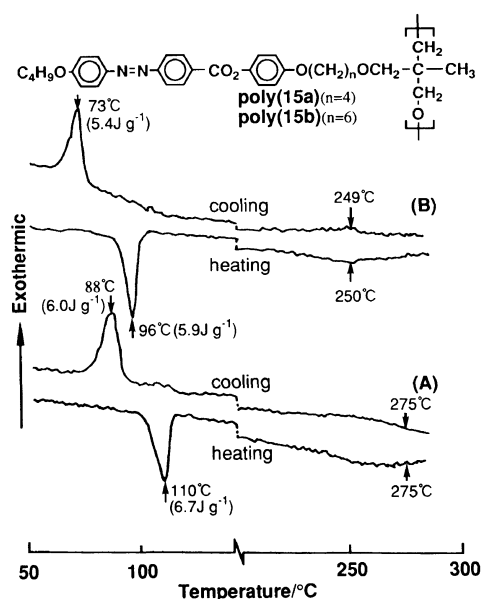


Figure 6. DSC curves of (A) poly(**15a**) and (B) poly(**15b**) at a scanning rate of $5^{\circ}\text{C min}^{-1}$. Figures in parentheses indicate enthalpy per g of polymer.

were hydrolyzed with 2N NaOH in methanol to give poly(**7**) and poly(**10**), respectively. The results are summarized in Table III. The hydrolysis products, poly(**7**) and poly(**10**), were used as model polymers to confirm the structures of the diazocoupling product polymers **III** and **II**, as mentioned above. Poly(**15a**)

and poly(**15b**) showed the DSC profiles given in Figures 6A and 6B, respectively, obviously indicating that these polymers were thermally stable up to about 300°C . Furthermore, poly(**15a**) and poly(**15b**) were found to be liquid crystalline polymers which indicated fan-shaped textures, respectively, between 275°C and 80°C and between 249°C and 73°C on cooling.⁸

In conclusion, several types of polyoxetanes anchoring the pendant isomeric phenols were readily obtained by alkaline hydrolysis of the corresponding phenyl acetates of prepolymers. Probably, the pendant phenols of oxetane monomers must be protected by appropriate groups such as the acetyl and benzoyl groups examined in this study, since the phenol moiety interferes with the propagation of cationic ring-opening polymerization. Uncross-linked, phenol-containing polyoxetanes were soluble in aqueous NaOH. The diazocoupling reactions of the pendant phenols in polyoxetane networks also proceeded in fairly high DF in spite of using an aqueous solvent. These results suggest that the polyoxetane networks are considerably hydrophilic compared with polystyrene networks. The polyoxetane network, therefore, may be useful as the polymeric support of the pendant groups capable of

functioning smoothly in aqueous media.

EXPERIMENTAL

Materials

Oxetanes **1a** and **1b** and bisoxetane **6** were obtained by the method described in our report.⁹

4-[7-(3-Methyl-3-oxetanyl)-1,6-dioxaheptyl]phenol (*p*-**2a**). Bromide **1a** (21 mmol) was stirred with hydroquinone (62 mmol) in DMF (40 cm³) at 85°C for 4.5 h in the presence of K₂CO₃ (3 g). DMF was evaporated and the residue was shaken with DCM and 10% NaOH. The aqueous layer was acidified at pH 4 with aqueous HCl and extracted with ether. The raw product, obtained by evaporating the solvent, was washed several times with hot water till the product indicated one spot on TLC: yield 61%; mp 82–84°C; IR (KBr) 3400 and 1220 (phenolic OH), 3070, 3050, 1515, 1480, 1455, and 835 (1,4-disubstituted benzene), 1235 (aromatic ether), 1130 (acyclic ether), and 960 and 840 cm⁻¹ (cyclic ether); ¹H NMR (CDCl₃) δ 1.31 (s, 3H, CH₃), 1.6–2.0 [m, 4H, OCH₂(CH₂)CH₂O], 3.4–3.6 [total 4H: δ 3.48, s, CH₂ adjacent to the oxetane ring; δ 3.53, t, *J* = 5.7 Hz, OCH₂(CH₂)₃OAr], 3.92 (t, 2H, *J* = 5.7 Hz, CH₂OAr), 4.37 and 4.53 (AB-q, each 2H, *J* = 5.8 Hz, CH₂ of the oxetane ring), 5.08 (br s, 1H, OH), and 6.75 (s, 4H, ArH).

4-[9-(3-Methyl-3-oxetanyl)-1,8-dioxanonyl]phenol (*p*-**2b**). Obtained in a 57% yield in the same manner as the preparation of *p*-**2a**: mp 63–68°C; IR (KBr) 3240 and 1225 (phenolic OH), 3080, 3050, 1520, 1480, 1460, and 840 (1,4-disubstituted benzene), 1240 (aromatic ether), 1130 (acyclic ether), and 960 and 830 cm⁻¹ (cyclic ether); ¹H NMR (CDCl₃) δ 1.31 (s, 3H, CH₃), 1.2–2.0 [m, 8H, OCH₂(CH₂)₄CH₂O], 3.3–3.6 [total 4H: δ 3.47, s, CH₂ adjacent to the oxetane ring; δ 3.47, t, *J* = 6.7 Hz, OCH₂(CH₂)₅OAr], 3.83 (t, 2H, *J* = 6.4 Hz, CH₂OAr), 4.36 and 4.52 (AB-q, each 2H, *J* = 5.8 Hz, CH₂ of the oxetane ring),

4.8–5.3 (br s, 1H, OH), and 6.76 (s, 4H, ArH).

2-[7-(3-Methyl-3-oxetanyl)-1,6-dioxaheptyl]phenol (*o*-**2a**). Obtained in a 64% yield by a reaction using **1a** (42 mmol) and catechol (42 mmol) in DMF (25 cm³) at 85°C for 8.5 h in the presence of K₂CO₃ (2 g): IR (KBr) 3350 and 1220 (phenolic OH), 1610, 1595, 1505, 1465, and 740 (1,2-disubstituted benzene), 1260 (aromatic ether), 1110 (acyclic ether), and 980 and 835 cm⁻¹ (cyclic ether); ¹H NMR (CDCl₃) δ 1.31 (s, 3H, CH₃), 1.6–2.1 (m, 4H, OCH₂(CH₂)₂CH₂O), 3.4–3.7 [total 4H: δ 3.43, s, CH₂ adjacent to the oxetane ring; δ 3.55, t, *J* = 5.9 Hz, OCH₂(CH₂)₃OAr], 4.08 (t, 2H, *J* = 6.0 Hz, CH₂OAr), 4.36 and 4.51 (AB-q, each 2H, *J* = 5.6 Hz, CH₂ of the oxetane ring), and 6.8–7.0 (m, 4H, ArH).

3-[7-(3-Methyl-3-oxetanyl)-1,6-dioxaheptyl]phenol (*m*-**2a**). Five grams of **1a** (21 mmol) was stirred with resorcinol monobenzoate (22 mmol) in DMF (13 cm³) at 85°C for 11 h in the presence of K₂CO₃ (2.5 g). The residue, obtained after the ordinary post-treatment of the reaction mixture, was distilled to give 6.7 g of a fraction boiling at 145–185°C (12 Pa). The distillate (6.6 g) was stirred in 2*N* NaOH (20 cm³) in methanol (15 cm³) under reflux for 5 h. After evaporating methanol the alkaline solution was extracted with ether to separate *m*-**2a** from **5**. The aqueous layer was acidified and extracted with ether to give the oily product *m*-**2a** in a 63% yield based on **1a**: IR (KBr) 3300 and 1150 (phenolic OH), 1600, 1500, 1470, 770, and 690 (1,3-disubstituted benzene), 1290 (aromatic ether), 1120 (acyclic ether), and 975 and 840 cm⁻¹ (cyclic ether); ¹H NMR (CDCl₃) δ 1.31 (s, 3H, CH₃), 1.4–2.1 (m, 4H, OCH₂(CH₂)₂CH₂O), 3.4–3.7 [total 4H: δ 3.44, s, CH₂ adjacent to the oxetane ring; δ 3.55, t, *J* = 5.9 Hz, OCH₂(CH₂)₃OAr], 3.99 (t, 2H, *J* = 6.7 Hz, CH₂OAr), 4.39 and 4.62 (AB-q, each 2H, *J* = 5.7 Hz, CH₂ of the oxetane ring), 6.00 (s, 1H, OH), 6.3–6.5 (m, 3H, *o*- and *p*-ArHs), and 7.0–7.3 (m, 1H, *m*-ArH).

1,3-Bis[7-(3-methyl-3-oxetanyl)-1,6-dioxaheptyl]benzene (**5**). This was contained in the

ether extract of the alkaline hydrolysis product in the preparation of *m*-2a. Nearly pure 5 was obtained in a 6% yield based on 1a by evaporating the ether solvent: IR (neat) 1610, 1590, 1500, 1485, 835, and 765 (1,3-disubstituted benzene), 1290 (aromatic ether), 1160 and 1120 (acyclic ether), and 985 and 840 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.31 (s, 6H, CH_3), 1.4–2.0 [m, 8H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 3.4–3.6 [total 8H: δ 3.48, s, CH_2 adjacent to the oxetane ring; δ 3.53, t, $J=5.7$ Hz, $\text{OCH}_2(\text{CH}_2)_3\text{OAr}$], 3.96 (t, 4H, CH_2OAr), 4.35 and 4.51 (AB-q, each 4H, CH_2 of the oxetane ring), 6.4–6.6 (m, 3H, ArHs *ortho* or *para* to the alkoxy), and 7.0–7.2 (m, 1H, ArH *meta* to the alkoxy).

2-, 3-, and 4-[7-(3-Methyl-3-oxetanyl)-1,6-dioxheptyl]phenyl Acetates (*o*-, *m*-, and *p*-3a) and 4-[9-(3-Methyl-3-oxetanyl)-1,8-dioxanonyl]phenyl Acetate (*p*-3b). The corresponding phenol (13 mmol) was stirred with acetic anhydride (53 mmol) and sodium acetate (26 mmol) in DCM (15 cm^3) for 7 h under reflux. After the ordinary post-treatment of the reaction mixture, the desired products were isolated by distillation. These products were also prepared by using acetyl chloride (41 mmol) and pyridine (81 mmol) to the phenol (27 mmol) in DCM at 0°C.

o-3a: Yield 81%; bp 170–197°C (40 Pa); IR (neat) 3080, 3050, 1610, 1510, and 750 (1,2-disubstituted benzene), 1770, 1215, and 1180 (ester), 1260 (aromatic ether), 1110 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.31 (s, 3H, CH_3 on the oxetane ring), 1.6–2.0 [m, 4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 2.30 (s, 3H, CH_3CO), 3.4–3.6 [total 4H, δ 3.48, s, CH_2 adjacent to the oxetane ring; δ 3.52, t, $J=5.7$ Hz, $\text{OCH}_2(\text{CH}_2)_3\text{OAr}$], 4.01 (t, 2H, $J=5.7$ Hz, CH_2OAr), 4.35 and 4.50 (AB-q, each 2H, $J=5.7$ Hz, CH_2 of the oxetane ring), and 6.8–7.3 (m, 4H, ArH).

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_5$: C, 66.20%; H, 7.86%. Found: C, 65.92%; H, 8.01%.

m-3a: yield 74%; bp 120–178°C (80 Pa); IR (neat) 3080, 3030, 1610, 1590, 1490, 785, and

690 (1,3-disubstituted benzene), 1770, 1210, and 1020 (ester), 1265 (aromatic ether), 1140 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.31 (s, 3H, CH_3 on the oxetane ring), 1.6–2.0 [m, 4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 3.4–3.6 [total 4H: δ 3.48, s, CH_2 adjacent to the oxetane ring; δ 3.54, t, $J=5.7$ Hz, $\text{OCH}_2(\text{CH}_2)_3\text{OAr}$], 3.97 (t, 2H, $J=5.4$ Hz, CH_2OAr), 4.35 and 4.51 (AB-q, each 2H, $J=5.7$ Hz, CH_2 of the oxetane ring), 6.6–6.9 (m, 3H, *o*- and *p*-ArH), and 7.1–7.4 (m, 1H, *m*-ArH).

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_5$: C, 66.20%; H, 7.86%. Found: C, 65.94%; H, 7.80%.

p-3a: Yield 76%; bp 125–145°C (80 Pa); IR (neat) 3050, 1610, 1600, 1510, 1475, and 840 (1,4-disubstituted benzene), 1765 and 1190 (ester), 1220 (aromatic ether); 1110 (acyclic ether), and 980 and 840 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.31 (s, 3H, CH_3 on the oxetane ring), 1.7–2.0 [m, 4H, $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$], 2.28 (s, 3H, CH_3CO), 3.4–3.7 [total 4H: δ 3.49, s, CH_2 adjacent to the oxetane ring; δ 3.54, t, $J=5.7$ Hz, $\text{OCH}_2(\text{CH}_2)_3\text{OAr}$], 3.97 (t, 2H, $J=6.0$ Hz, CH_2OAr), 4.36 and 4.51 (AB-q, each 2H, $J=5.7$ Hz, CH_2 of the oxetane ring), and 6.8–7.1 (m, 4H, ArH).

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_5$: C, 66.20%; H, 7.86%. Found: C, 66.25%; H, 8.04%.

p-3b: Yield 73%; bp 92–126°C (11 Pa); IR (neat) 3050, 1610, 1590, 1505, 1475, and 835 (1,4-disubstituted benzene), 1760 and 1190 (ester), 1220 (aromatic ether), 1110 (acyclic ether), and 980 and 835 cm^{-1} (cyclic ether); $^1\text{H NMR}$ (CDCl_3) δ 1.31 (s, 3H, CH_3 on the oxetane ring), 1.2–2.0 [m, 8H, $\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{O}$], 2.27 (s, 3H, CH_3CO), 3.4–3.6 [total 4H: δ 3.48, s and t ($J=6.9$ Hz), CH_2 adjacent to the oxetane ring and $\text{OCH}_2(\text{CH}_2)_5\text{OAr}$, respectively] 4.35 and 4.50 (AB-q, each 2H, $J=5.7$ Hz, CH_2 of the oxetane ring), and 6.8–7.2 (m, 4H, ArH).

Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_5$: C, 67.82%; H, 8.40%. Found: C, 67.59%; H, 8.55%.

Oxetane Monomers, 8, 9, 15a, and 15b, Having Azobenzene moieties in the Pendant.

Phenol **p-2a** dissolved in 10% NaOH was diazocoupled with 1 equiv of BDC at 0°C and the crude product **7** was esterified with 1 equiv of 4-(4-butoxyphenylazo)benzoic acid in THF at 0°C in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to give the ester **8** in a 42% yield by recrystallization from ethanol. The benzoate **9** was obtained in a 61% yield by the substitution reaction of **1a** with *p*-hydroxyazobenzene **11**, produced by the diazocoupling reaction of resorcinol monobenzoate with BDC. The oxetanes **15a** and **15b** were also prepared, respectively, in 68 and 50% yields by the esterification of the pendant phenol with the corresponding benzoic acid (each 3.8 mmol) in the presence of DCC (3.8 mmol) and DMAP (0.4 mmol) in THF at 0°C for 8 h and then at 25°C for 10 h.

8: 113–133°C (ethanol); IR (KBr) 1740, 1260, and 1065 (ester), 1270 (aromatic ether), 1140 (acyclic ether), 980 and 840 (cyclic ether), and 865, 840, 770, and 690 cm⁻¹ (substituted benzenes); ¹H NMR (CDCl₃) δ 1.00 (t, 3H, *J*=6.9 Hz, CH₃ of the butyl), 1.33 (s, 3H, CH₃ on the oxetane ring), 1.4–2.1 [m, 8H, OCH₂(CH₂)₂CH₂O and OCH₂(CH₂)₂CH₃], 3.4–3.7 [total 4H: δ 3.51, s, CH₂ adjacent to the oxetane ring; δ 3.57, t, *J*=5.7 Hz, OCH₂(CH₂)₃OAr], 4.08 (two triplets superimposed on each other, 4H, *J*=6.1 Hz, each CH₂OAr), 4.37 and 4.53 (AB-q, each 2H, *J*=5.8 Hz, CH₂ of the oxetane ring), 6.9–7.1 (m, 3H, ArHs *ortho* to OC₄H₉ and OCOAr), 7.3–7.6 (m, 5H, *m*- and *p*-ArHs of N₂C₆H₅ and ArHs *ortho* and *para* to N₂C₆H₅), 7.7–8.1 (m, 6H, *o*-ArHs of C₆H₄N₂C₆H₄ and N₂C₆H₅), and 8.3–8.6 (m, 2H, ArHs *ortho* to the acyl group).

9: mp 93–95°C (ethanol); IR (KBr) 1745 and 1240 (ester), 1270 (aromatic ether), 1110 (acyclic ether), 980 and 835 (cyclic ether), and 775, 710, and 690 cm⁻¹ (substituted benzenes); ¹H NMR (CDCl₃) δ 1.32 (s, 3H, CH₃), 1.6–2.1 [m, 4H, OCH₂(CH₂)₂CH₂O], 3.4–3.7 (total 4H: δ 3.45, s, CH₂ adjacent to the oxetane ring;

δ 3.55, t, *J*=5.9 Hz, OCH₂(CH₂)₃OAr], 4.09 (t, 2H, CH₂OAr), 4.36 and 4.52 (AB-q, each 2H, *J*=5.8 Hz, CH₂ of the oxetane ring), 6.8–7.0 (m, 2H, ArH *ortho* to the spacer), 7.2–7.4 (m, 3H, *m*- and *p*-ArHs of N₂C₆H₅), 7.5–8.0 (m, 6H, *o*-ArHs of N₂C₆H₅, ArHs *meta* and *para* to the acyl group, and ArH *meta* to the spacer), and 8.2–8.4 (m, 2H, ArHs *ortho* to the acyl group).

15a: mp 99.9–101.0°C (ethanol); IR (KBr) 3030, 1595, 1510, 1475, and 840 (1,4-disubstituted benzene), 1730, 1200, and 1075 (ester), 1255 (aromatic ether), 1120 (acyclic ether), and 980 and 835 cm⁻¹ (cyclic ether); ¹H NMR (CDCl₃) δ 1.00 (t, 3H, *J*=6.2 Hz, CH₃ of the butyl), 1.32 (s, 3H, CH₃ of the oxetane ring), 1.3–2.0 [m, 4H, OCH₂(CH₂)₂CH₂O], 3.5–3.7 [total 4H: δ 3.50, s, CH₂ adjacent to the oxetane ring; δ 3.55, t, *J*=5.4 Hz, OCH₂(CH₂)₃OAr], 3.9–4.2 (total 4H: δ 4.01 and 4.07, two triplets overlapping each other, *J*=6.1 and 6.4 Hz, each CH₂OAr), 4.36 and 4.52 (AB-q, each 2H, *J*=5.6 Hz, CH₂ of the oxetane ring), and 6.8–8.4 (total 12H for three AB-quartets overlapping one another due to the aromatic protons: δ 6.93 and 7.95, *J*=8.8 Hz; δ 7.04 and 7.14, *J*=9.1 Hz; and δ 7.96 and 8.32, *J*=8.7 Hz).

15b: mp 82–90°C (ethanol); IR (KBr) 3080, 1600, 1515, and 840 (1,4-disubstituted benzene), 1735, 1205, and 1075 (ester), 1260 (aromatic ether), 1110 (acyclic ether), and 980 and 840 cm⁻¹ (cyclic ether); ¹H NMR (CDCl₃) δ 0.99 (t, 3H, *J*=6.2 Hz, CH₃ of the butyl), 1.34 (s, 3H, CH₃ on the oxetane ring), 1.3–2.0 [m, 8H, OCH₂(CH₂)₄CH₂O], 3.4–3.6 [total 4H: δ 3.48, s and t (*J*=6.8 Hz), CH₂OCH₂(CH₂)₅OAr], 3.8–4.2 (total 4H: δ 3.96 and 4.07, two triplets overlapping each other, *J*=6.7 and 5.7 Hz, each CH₂OAr), 4.36 and 4.51 (AB-q, each 2H, *J*=6.1 Hz, CH₂ of the oxetane ring), and 6.7–8.4 (total 12H for three AB-quartets overlapping one another due to the aromatic protons: δ 6.91 and 7.94, *J*=8.1 Hz; δ 7.03 and 7.11, *J*=9.9 Hz; and δ 7.95 and 8.31, *J*=9.3 Hz).

o- and *p*-Hydroxyazobenzenes **11**–**14**. These were obtained by the synthetic routes outlined in Scheme 5. The *O*-alkylation and -acylation reactions were carried out by the same procedures as described for preparing **8** and **9**: **11**, mp 169–172°C (benzene); **12**, mp 130–134°C (ethanol); **13**, mp 49–50°C (hexane); **14**, mp 83.5–84.0°C (50% hexane–DCM). The ¹H NMR spectra of the aromatic protons of **11**–**14** were shown in Figure 6.

Polymerization and Polymer Reactions

The polyoxetanes with the pendant phenyl esters were obtained by cationic ring-opening polymerization as described in our previous papers.^{1–6} One mmole of the pendant phenyl ester was hydrolyzed with 2*N* NaOH (1.7 cm³) in methanol (5 cm³) under reflux for 10 h. One mmole of the pendant phenols of uncross-linked polyoxetanes was dissolved in 10% NaOH (6.4 cm³) and then mixed at 0–3°C with a BDC solution, prepared from each 3 mmol of aniline and sodium nitrite in 6*N* HCl at 0°C. After being converted to the acid form with aqueous HCl, the product polymers were collected by decantation, washed with water and methanol successively, and dried in vacuum.

Measurement

IR and ¹H NMR spectroscopy and GPC and DSC measurements were performed as described in our previous paper.⁴

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