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Radical Ring-Opening Polyaddition of Bis(vinyloxirane) Derivatives and Dithiols

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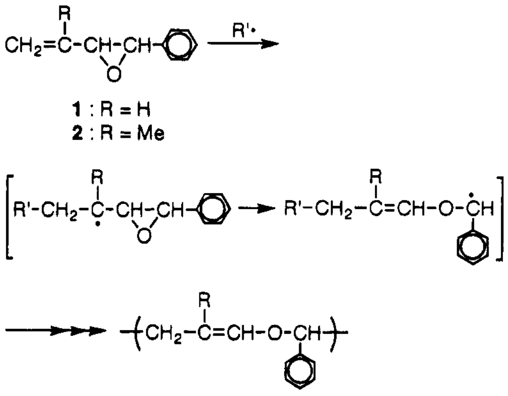
ABSTRACT: Radical polyadditions of bifunctional vinyloxiranes [1,4-bis(2-vinylepoxyethyl)benzene (**3**) and 1,4-bis(2-isopropenylepoxyethyl)benzene (**4**)] and dithiols are described. **3** and **4** were prepared by the phase transfer reaction of terephthaladehyde and the corresponding sulfonium salts. The radical polyaddition of **4** and aromatic dithiols [1,4-benzenedithiol (**5a**), 4,4′-isopropylidenebis(thiophenol) (**5b**), and bis(4-mercaptophenyl) sulfide (**5c**)] was carried out at 60 °C in PhCl in the presence of azobis(isobutyronitrile) (AIBN) as an initiator to obtain the corresponding polymers with high molecular weights in excellent yields. The same polyaddition also proceeded at 20 °C under photoirradiation to give polymers of molecular weights lower than those obtained using AIBN. On the other hand, only a gelled polymer was obtained by the polymerization of **4** and **5a** using di-*tert*-butyl peroxide (DTBP) at a higher temperature (120 °C) in PhCl. When **3** was used instead of **4** in the polyaddition with **5a** at 60 °C, a gelled polymer was also obtained, probably due to cross-linking of the formed polymer by the attack of a propagating thiyl radical on the resulting vinylene group in the main chain. The polyadditions of **4** and aliphatic dithiols gave the corresponding polymers with molecular weights lower than those from **4** and aromatic dithiols. The results of the model reactions of vinyloxiranes [2-phenyl-3-vinyloxirane (**1**) and 2-isopropenyl-3-phenyloxirane (**3**)] and thiols (benzenethiol and benzyl mercaptan) were consistent with those of the radical polyadditions of dithiols to bifunctional vinyloxiranes. The structure of the obtained polymers was confirmed by comparison with IR and NMR spectra of the model compounds obtained from **2** and benzenethiol in the presence of AIBN. These results indicate that the radical polyaddition proceeded mainly through the carbon–carbon bond cleavage of the oxirane ring of **4**, accompanied by a small amount of carbon–oxygen bond fission, and led to the formation of the polymers with a main unit having vinyl ether and sulfide groups and a minor unit having hydroxy groups.

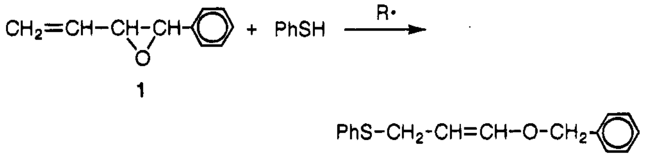
Introduction

Cyclic compounds that undergo radical ring-opening polymerization are important for the synthesis of polymers having functional groups such as ether, ester, ketone, and carbonate in the main chain.[1] Recently, we have reported that *para*-substituted 2-phenyl-3-vinyloxirane derivatives bearing an aryl group as a radical stabilizing group can undergo complete ring-opening polymerization *via* selective cleavage of the carbon–carbon bond of the oxirane ring to obtain the polymers bearing a vinyl ether moiety in the backbone.[2,3] Cho *et al.* have reported that the radical polymerization of 2-phenyl-3-vinyloxirane (**1**) can be carried out at 65 °C in benzene to obtain the corresponding polymer, whereas the polymerization at 120 °C in bulk gives a gelled polymer probably due to cross-linking by further reaction of the vinyl ether moiety of the formed polymer.[4] On the other hand, we have found that 2-isopropenyl-3-phenyloxirane (**2**), which has a methyl group at the α-position of the vinyl group of **1**, can give the corresponding soluble polymer even by radical polymerization at 120 °C in bulk (Scheme 1).[5]

Scheme 1



Scheme 2



In order to clarify the structure of the polymer obtained from **1**, the radical addition of **1** with benzenethiol as a model reaction was carried out in the presence of radical initiator to obtain the corresponding 1:1 adduct having vinyl ether and sulfide groups *via* carbon–carbon bond cleavage of the oxirane ring (Scheme 2).[4] These results prompted us to develop a new type of radical polyaddition of bifunctional vinyloxiranes and dithiols accompanying the ring-opening reaction of the oxirane ring. This radical polyaddition may be regarded as "radical ring-opening polyaddition". Although there are a lot of reports on ionic and radical polyadditions, the radical ring-opening polyaddition has not been reported so far.

Recently, we have reported as a preliminary communication[6] that the radical polyaddition of aromatic dithiols to bifunctional vinyloxirane, bis(2-isopropenyl-

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epoxyethyl)benzene (**4**), can lead to the formation of polymers having vinyl ether and sulfide groups accompanying carbon–carbon bond cleavage of the oxirane ring.[6] This is the first example of radical ring-opening polyaddition involving bifunctional vinyloxiranes and dithiols.

In this paper, we wish to report in detail the radical ring-opening polyaddition of aromatic and aliphatic dithiols to bifunctional vinyloxiranes [1,4-bis(2-vinylepoxyethyl)benzene (**3**) and 1,4-bis(2-isopropenylepoxyethyl)benzene (**4**)] under various conditions.

Experimental Section

Materials. Extra-pure grade reagents were used for syntheses of **1**–**4** without further purification, unless otherwise stated. Benzene and chlorobenzene used as solvents were purified by distillation over calcium hydride after washing successively with concentrated sulfuric acid, aqueous sodium carbonate, and water.

Measurement. IR spectra were obtained with a JASCO FT/IR-3 or a JASCO A-3 IR spectrometer. ^{1}H NMR spectra were recorded with a JEOL JNX-EX-90 or a JEOL FX90Q NMR spectrometer with $CDCl_3$ as a solvent and Me_4Si as an internal standard. Gel permeation chromatograms were taken with a Shimadzu HPLC LC-6A system equipped with two columns (Shim-pack GPC-802 and GPC-804), and tetrahydrofuran (THF) was used as an eluent at 40 °C. Conversions of monomers were determined by gas liquid chromatography (GLC) on a Shimadzu GC-6AM (Silicon-GE SE-30 2m, 160–240 °C).

Preparation of 1,4-Bis(2-isopropenylepoxyethyl)benzene (4). A mixture of 3-bromo-2-methyl-1-propene (48.0 g, 0.355 mol) and dimethyl sulfide (28.8 g, 0.463 mol) in water (25 mL) was stirred at room temperature overnight. Unreacted dimethyl sulfide was removed at reduced pressure. Isopropyl alcohol (80 mL) and terephthaladehyde (19.1 g, 0.143 mol) were added to the reaction mixture at room temperature, and subsequently, sodium hydroxide (16.9 g, 0.423 mol) in water (30 mL) was added dropwise at room temperature with vigorous stirring. After stirring for 6 h, the resulting dimethyl sulfide was removed under reduced pressure and the solution was extracted with ether three times. The organic layer was washed with water and saturated sodium chloride successively and dried over anhydrous magnesium sulfate. The ether solution was distilled *in vacuo* to obtain **4** (14.2 g, 41%): bp 120–123 °C/0.08 mmHg; IR (neat) 1653, 1236, 902, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.40–1.86 (6H, m), 3.30–4.30 (4H, m), 4.76–5.23 (4H, m), 7.10–7.40 (4H, m) ppm. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.63; H, 7.81.

Preparation of 1,4-Bis(2-vinylepoxyethyl)benzene (3). **3** was synthesized similarly to **4** as mentioned above. Allyl bromide (38.8 g, 0.32 mol), dimethyl sulfide (22.1 g, 0.35 mol), and terephthaladehyde (13.4 g, 0.10 mol) were used to obtain 13.3 g (62%) of **3**: bp 140 °C/0.1 mmHg (lit.[2] 135 °C/0.05 mmHg); IR (neat) 1640, 1240, 920, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.20–4.26 (4H, m), 5.10–6.00 (6H, m), 7.10–7.43 (4H, m) ppm.

Preparation of 2-Phenyl-3-vinyloxirane (1). **1** was prepared by the method reported in our previous paper:[2] yield 75%; bp 67–69 °C/3.5 mmHg (lit.[2] 99–101 °C/16 mmHg); IR (neat) 1640, 1250, 930, 870 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 3.25–4.30 (2H, m), 5.10–5.80 (3H, m), 7.10–7.45 (5H, m) ppm.

Preparation of 2-Isopropenyl-3-phenyloxirane (2). The same procedure as that for monomer **1** was employed. Methallyl iodide (25.5 g, 0.14 mol), dimethyl sulfide (10.9 g, 0.18 mol), and benzaldehyde (10.6 g, 0.10 mol) were used. A 6.6 g quantity (yield 41%) of 2-isopropenyl-3-phenyloxirane was obtained by distillation: bp 71–75 °C/3.0 mmHg (lit.[5] 95 °C/1.1 mmHg); IR (neat) 1655, 1235, 905, 880 cm^{-1}; ^{1}H NMR (CCl_4) 1.40–1.80 (3H, m), 3.10–4.10 (2H, m), 4.70–5.15 (2H, m), 7.05–7.25 (5H, m) ppm.

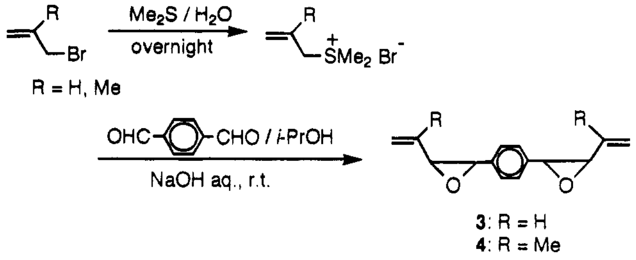
Radical Ring-Opening Polyaddition of Dithiols to 3 or 4: General Procedure. **3** or **4** (1.5 mmol), dithiol (1.5 mmol), initiator (6 mol % for dithiol), and chlorobenzene (1.2 mL) were placed in an ampule tube. The tube was degassed and sealed under reduced pressure. The reaction was carried out for 24 or 72 h. The reaction mixture was poured into *n*-hexane to precipitate polymer. After the hexane was removed by decantation, residual viscous polymer was collected and dried under vacuum. (The detailed reaction conditions are shown in Table 1.)

Table 1. Radical Ring-Opening Polyaddition of Aromatic Dithiols to 4

run	initiator[a]	dithiol	solvent	temp (°C)	yield (%)[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	AIBN	**5a**	PhCl	60	99	5980	2.95
2	DTBP	**5a**	PhCl	120	95[e]		
3	UV[b]	**5a**	$PhCH_3$	20	85	3720	2.01
4	AIBN	**5b**	PhCl	60	100	8590	3.53
5	UV[b]	**5b**	$PhCH_3$	20	87	7690	3.69
6	AIBN	**5c**	PhCl	60	100	7430	2.33

[a] Initiator (mol)/**4** and **5** (mol) = 0.03. [b] High-pressure Hg lamp. [c] Insoluble in hexane. [d] Estimated by GPC (based on PSt). [e] Only gelled polymer was obtained.

Scheme 3



Radical Addition of Benzenethiol to 2-Isopropenyl-3-phenyloxirane (2). **2** (3 mmol), benzenethiol (3 mmol), AIBN (1 mol % for **2**), and benzene (12 mmol) were placed in an ampule tube. The mixture was degassed, and the tube was sealed *in vacuo*. After the reaction at 60 °C for 24 h, the solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel, *n*-hexane/chloroform = 1/1) to give **7** (78%) and **8** (20%).

7: IR (neat) 3060, 3030, 2960, 2870, 1680, 1580, 1480, 1450, 1440, 1240, 1170, 1130, 1025, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.70 (3H, d), 3.55 (2H, d), 4.65 (2H, s), 5.85–5.95 (1H, m), and 7.05–7.45 (10H, m) ppm. Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71. Found: C, 75.24; H, 6.83.

8: IR (neat) 3410, 3060, 2930, 2910, 1580, 1480, 1450, 1440, 1380, 1090, 1050, 1020, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.90 (3H, s), 2.06 (1H, s), 2.60 (2H, d), 4.66–5.00 (1H, t), 5.90–6.10 (1H, m), 7.10–7.50 (10H, m) ppm; ^{13}C NMR ($CDCl_3$) 18.4 ($-CH_3$), 49.4 ($-SCH_2-$), 72.2 ($HOCH-$), 120.3 ($-CH=$), 125.9–132.2 (Ar–C), 143.9 ($=C-CH_3$) ppm. Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; S, 11.86. Found: C, 75.82; H, 7.05; S, 11.62.

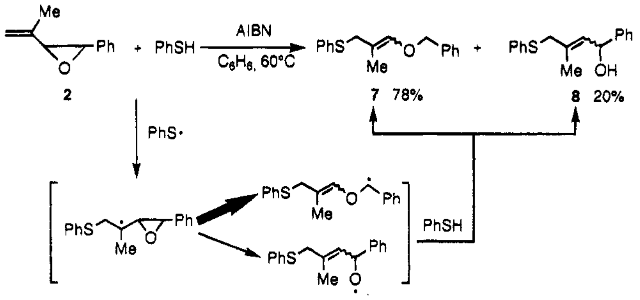
Results and Discussion

1. Radical Polyaddition of Aromatic Dithiols to 3 or 4.

1,4-Bis(2-vinylepoxyethyl)benzene (**3**) and 1,4-bis(2-isopropenylepoxyethyl)benzene (**4**) were synthesized by the phase-transfer reaction of allyldimethylsulfonium salt and methallyldimethylsulfonium salt with terephthalaldehyde, respectively, according to the method reported previously[2,4] (Scheme 3).

In the radical ring-opening polymerization of **2**, the resulting polymer cannot undergo cross-linking as a radical side reaction because of steric hindrance of the olefin due to the methyl group in the main chain.[5] Therefore, **4** was first used as a bifunctional vinyloxirane in this work. The radical polyadditions of aromatic dithiols [1,4-benzenedithiol (**5a**), 4,4′-isopropylidenebis(thiophenol) (**5b**), and bis(4-mercaptophenyl) sulfide (**5c**)] to **4** were carried out in sealed tubes under various conditions, and their results are summarized in Table 1.

Scheme 4



Although the polyaddition of **4** and **5a** in the presence of di-*tert*-butyl peroxide (DTBP) at 120 °C resulted in the formation of a gelled polymer (run 2), the solvent-soluble polymers (**6a**–**c**) could be obtained quantitatively when the polyadditions were conducted at 60 °C for 24 h in the presence of azobis(isobutyronitrile) (AIBN) in PhCl (runs 1, 4, and 6). The structure of the polymers was confirmed by comparison with the IR and ^{1}H NMR spectra of the products obtained by the radical addition of **2** and benzenethiol as a model reaction. **2** reacted with benzenethiol at 60 °C for 24 h in the presence of AIBN in benzene to give two kinds of adducts (**7** and **8**) (Scheme 4). It is obvious that the main product **7** bearing vinyl ether and sulfide moieties can be formed in the same manner as the adduct obtained from **1** and benzenethiol (Scheme 2). The minor adduct **8** seems to be obtained *via* carbon–oxygen bond cleavage of the radical intermediate generated by the attack of the thiophenol radical on **2**. The ^{1}H NMR and IR spectra of **7** are shown in Figures 1a and 2a. The ^{1}H NMR spectra of all the obtained polymers were very similar to that of **7**. Figure 1b shows polymer **6a**, and the signals due to vinyl and benzyl protons were observed around 5.9 and 4.6 ppm, respectively. The observation of the vinyl and benzyl protons indicates the occurrence of carbon–carbon bond cleavage of the oxirane ring. The E/Z ratio for **7** was almost identical with that for **6a**, estimated from the ^{1}H NMR spectra: 63/37 for **7** and 64/36 for **6a**, respectively. In both the IR spectra of the obtained polymers and model compound **7**, a strong absorption could be observed around 1680 cm^{-1} based on the vinyl ether group. However, a weak absorption based on the hydroxy group was also observed around 3480 cm^{-1} in all the polymers. The IR spectrum of **6a** is shown in Figure 2b. These spectral data suggest that the radical polyadditions proceed mainly through the carbon–carbon bond cleavage of the oxirane ring of **4** somewhat accompanying the carbon–oxygen bond cleavage to give the polymers having two units, as shown in Scheme 5. From the ^{1}H NMR spectrum (Experimental Section) of model compound **8**, it is presumed that a small signal at 1.90 ppm in Figure 1b is based on the methyl protons of y unit in **6a**. Consequently, x unit (with vinyl ether and sulfide groups):y unit (with hydroxy groups) was estimated at about 8:2. These results described above indicate that the model reaction reflects the polyaddition very well.

The polyadditions of aromatic dithiols (**5a** and **5b**) to **4** also proceeded under photoirradiation at 20 °C in toluene to afford the corresponding polymers of which the structure was the same as that of the polymers obtained by the radical polyaddition. The molecular weight of the polymers, however, was lower than that of the polymers obtained with AIBN (runs 3 and 5).

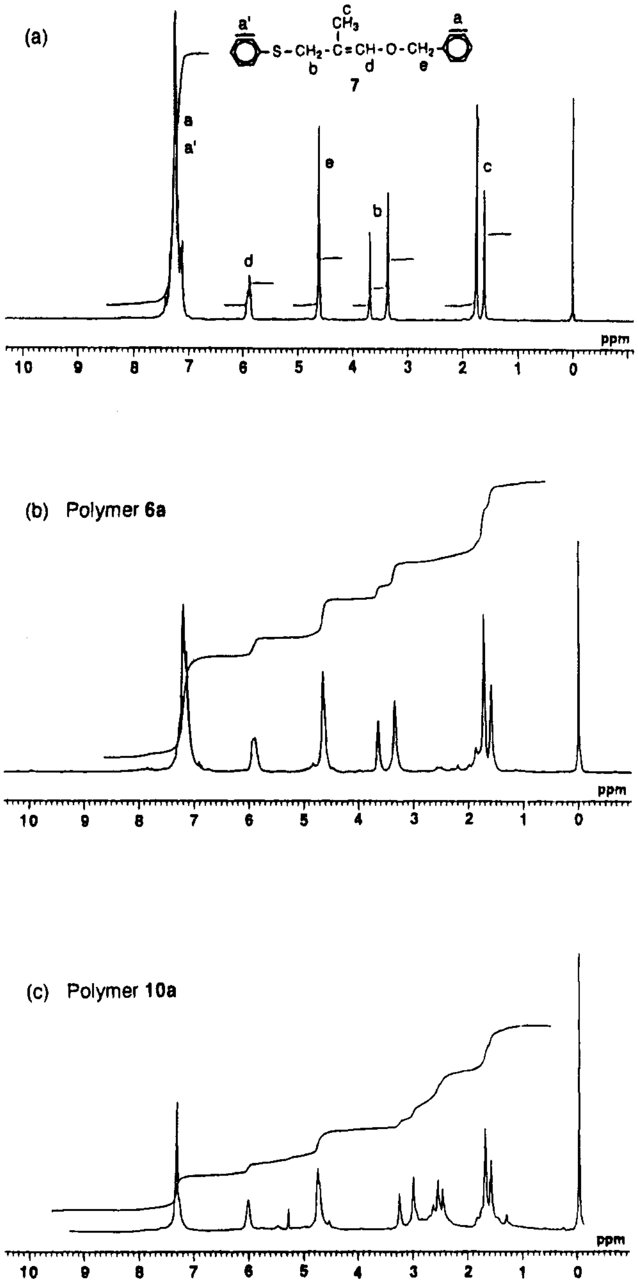
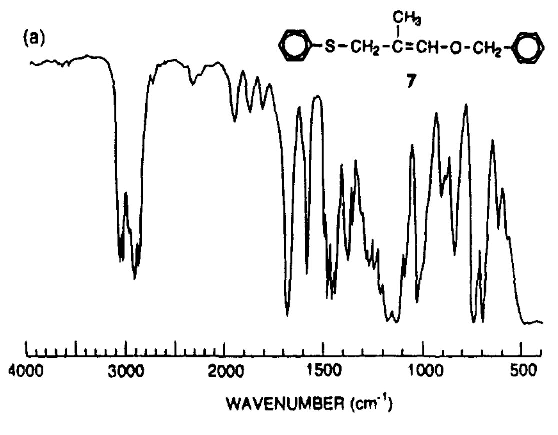


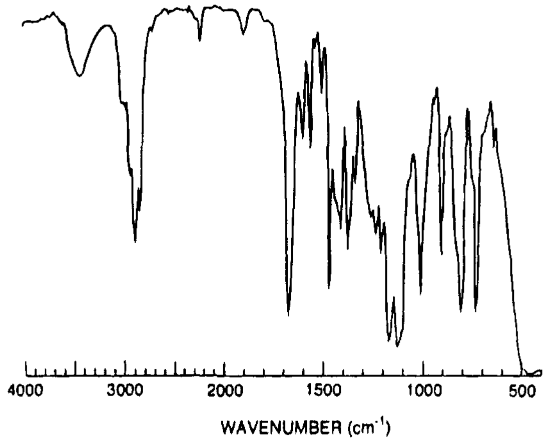
Figure 1. ^{1}H NMR spectra of (a) **7**, (b) polymer **6a** obtained using AIBN at 60 °C, and (c) polymer **10a** obtained using DTBP at 120 °C.

When bifunctional vinyloxirane **3** was used instead of **4** in the radical polyaddition with benzenedithiol **5a**, the different reaction behavior was observed. The reaction was carried out using DTBP at 120 °C in PhCl to obtain only a gelled polymer quantitatively similar to the result with **4** under the same conditions. However, **3** gave the polymer with highly broad molecular weight distribution ($\bar{M}_w/\bar{M}_n > 100$) in the polymerization using AIBN at 60 °C in PhCl, and the obtained polymer gelled on standing for a few days (Scheme 6). These results suggest that the attack of a propagating thiyl radical on the polymer based on **3** occurs easier than that on **4** and are consistent with the results of the radical polymerizations of vinyloxirane **1** and **2**.[4,5]

2. Radical Polyaddition of Aliphatic Dithiols to 3 or 4. The radical polyadditions of aliphatic dithiols [1,2-ethanedithiol (**9a**) and 1,6-hexanedithiol (**9b**)] to **4** were carried out in sealed tubes under various conditions, as shown in Table 2. Although the polyaddition of **4** and aromatic dithiol **5a** in the presence of AIBN at 60 °C in PhCl afforded the corresponding polymer ($\bar{M}_n$



(b) Polymer **6a**



(c) Polymer **10a**

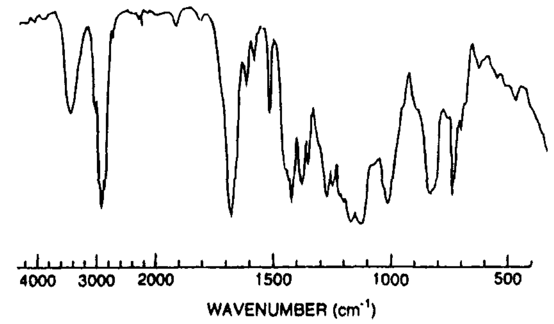
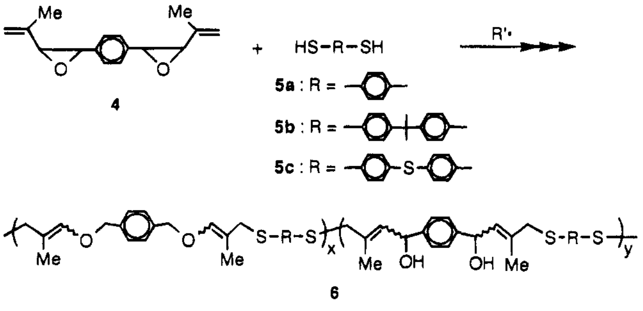


Figure 2. IR spectra of (a) **7**, (b) polymer **6a** obtained using AIBN at 60 °C, and (c) polymer **10a** obtained using DTBP at 120 °C.

Scheme 5



Scheme 6

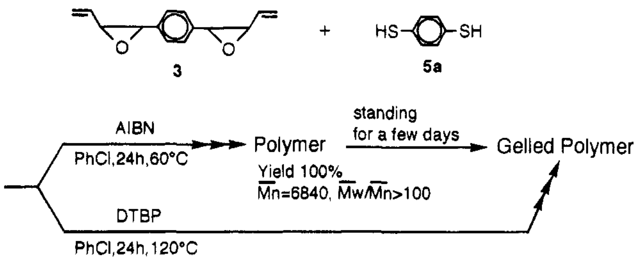
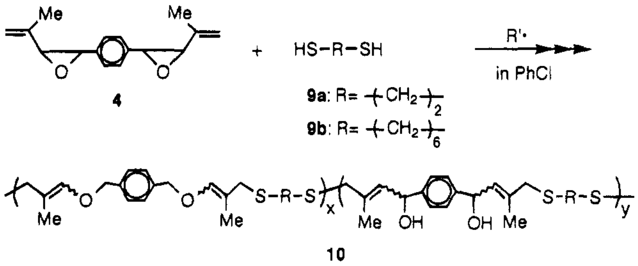


Table 2. Radical Ring-Opening Polyaddition of Dithiols (9a and 9b) to 4

run	initiator[a]	dithiol	temp (°C)	time (h)	conc (M)	yield (%)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	AIBN	**9a**	60	24	2.4	55	1570	1.82
2	DTBP	**9a**	120	24	2.4	91	2160	2.77
3	AIBN	**9a**	60	72	2.4	86	2640	2.29
4	AIBN	**9a**	60	24	4.8	79	2010	2.31
5	AIBN	**9b**	60	24	2.4	23	1910	2.30

[a] 6 mol % for **4**. [b] Insoluble in *n*-hexane. [c] Estimated by GPC (based on polystyrene).

Scheme 7

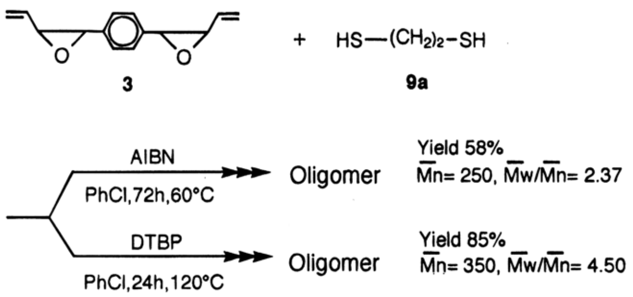


= 5980) quantitatively (run 1 in Table 1), in the polymerization of **4** and aliphatic dithiols **9a** or **9b** under the same conditions, polymers with lower molecular weights were obtained in moderate yields (runs 1 and 5). The polyaddition of **4** and **5a** using DTBP at 120 °C in PhCl afforded only a gelled polymer, as described previously (run 2 in Table 1). On the other hand, solvent-soluble polymer ($\bar{M}_n$ = 2160) was obtained in good yield by the polyaddition of **4** and **9a** under these conditions (run 2). In the polyaddition of **4** and **9a**, the molecular weight and yields of the obtained polymers increased with increasing temperature, time, and monomer concentration (runs 1–4).

The structure of the obtained polymers was confirmed by comparing their IR and ^{1}H NMR spectra with those of the model compounds **7** and **8**. All the IR and ^{1}H NMR spectra of the polymers obtained from **4** and **9** were very similar. Figures 1c and 2c show the ^{1}H NMR and IR spectra of the polymer **10a** obtained from **4** and **9a** (run 2 in Table 2). The ^{1}H NMR spectrum is analogous to that of **7**, and the signals based on vinyl and benzyl protons were observed around 5.9 and 4.7 ppm, respectively. Consequently, it is obvious that carbon–carbon bond fission takes place in the polyaddition. The IR spectrum of the polymer in which weak absorption based on hydroxy group was observed around 3450 cm^{-1} indicates that a small amount of carbon–oxygen bond cleavage of the oxirane ring of **4** occurs in the polyaddition. These spectral data were similar to those obtained from **4** and aromatic dithiols. Therefore, it is suggested that the obtained polymers as well as the polymers from **4** and aromatic dithiols have a main unit with vinyl ether and sulfide moieties and a minor unit with hydroxy groups (Scheme 7).

The radical polyaddition of **3** and **9a** using AIBN at 60 °C for 72 h in PhCl was also carried out to obtain an

Scheme 8



oligomer in moderate yield. Furthermore, the desired polymer could not be obtained by polyaddition at 120 °C in the presence of DTBP (Scheme 8).

3. Time–Conversion Curves: Radical Additions of Vinyloxiranes (1 and 2) and Thiols as Model Reactions. We found that the radical ring-opening polyaddition proceeded successfully when **4** and aromatic dithiols were used, and an oligomer was obtained using **3** and aliphatic dithiol **9a**. Thus, the polyaddition was dependent on the structure of the bifunctional vinyloxirane and the kind of dithiol. Therefore, we performed the radical additions of vinyloxiranes (**1** and **2**) and thiols as model reactions, and measured the conversions *vs* reaction time in order to study the polymerization behavior of bifunctional vinyloxiranes and dithiols.

The radical additions were carried out at 60 °C in the presence of AIBN in PhCl, and the conversions were monitored by gas chromatography. Benzenethiol and benzyl mercaptan were used as model compounds of aromatic and aliphatic dithiols, respectively. Figure 3a shows that the addition of **2** and benzenethiol proceeded rapidly and was almost complete in 12 h. The rate of reaction with **2** and benzyl mercaptan was slower than that of **2** and benzenethiol, and the reactants were consumed completely after 24 h (Figure 3c). It is known that thiyl radicals are electrophilic and easily attack electron-rich olefins rather than electron-deficient olefins.[7,8] Since **2** is a somewhat electron-rich olefin and the thiyl radical from benzenethiol is more electrophilic than that from benzyl mercaptan, it is speculated that the radical addition of **2** and benzenethiol was faster, compared with that of **2** and benzyl mercaptan. In the time–conversion curves of **1** and benzenethiol, the conversion of benzenethiol reached almost 100% after 12 h, but about 20% of **1** remained unreacted even after 24 h (Figure 3b). The reason may be due to further reaction of benzenethiol with product. The radical addition of **1** and benzyl mercaptan was found to be the slowest reaction among four model reactions with **1**, **2**, benzenethiol, and benzyl mercaptan (Figure 3d). The rate of the radical additions decreased in the following order: **2** + benzenethiol, **1** + benzenethiol > **2** + benzyl mercaptan > **1** + benzyl mercaptan. These results support the results of the radical polyaddition of bifunctional vinyloxiranes and dithiols: (a) **4** reacted with aromatic dithiols at 60 °C in PhCl to afford the polymers with high molecular weights in excellent yields. (b) When **3** was used instead of **4**, a gelled polymer was obtained, probably due to cross-linking of the resulting polymer by the attack of a propagating thiyl radical on the main chain as a side reaction. (c) The polyaddition of **4** and aliphatic dithiols gave the corresponding polymers with molecular weights lower than those from **4** and aromatic dithiols. (d) An oligomer was obtained by the polyaddition of **3** and aliphatic dithiol.

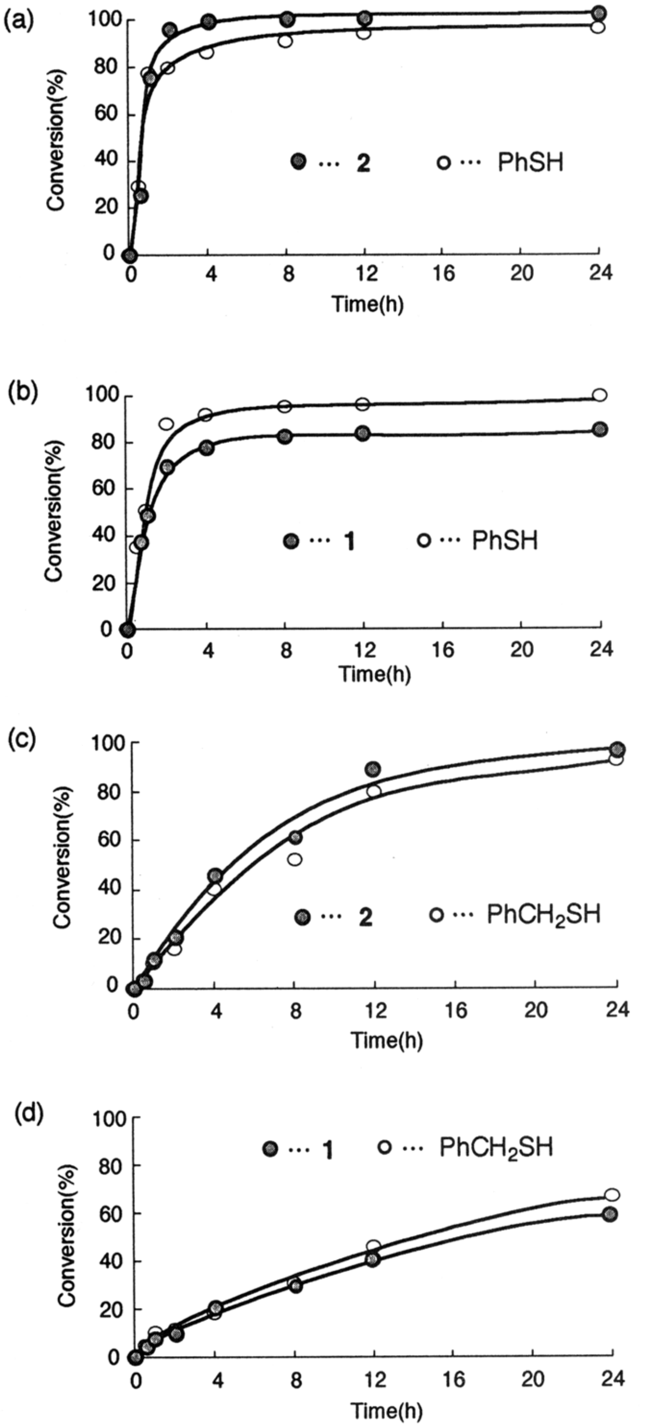


Figure 3. Time–conversion curves for the radical additions of benzenethiol or benzyl mercaptan to vinyloxiranes (**1** and **2**).

Conclusion

In this work, we found that the radical polyaddition of dithiols (**5a–c**, **9a**, and **9b**) to bifunctional vinyloxirane **4** could lead to the formation of the polymers with a main unit having vinyl ether and sulfide groups and could demonstrate the first example of radical ring-opening polyaddition as a novel polymerization method. The polyaddition proceeded mainly through the carbon–carbon bond cleavage of the oxirane ring of **4**, accompanied by a small amount of carbon–oxygen bond cleavage. Although **3** reacted with aliphatic dithiol **9a** at 60 °C in PhCl to give only an oligomer, the combination of **4** and aromatic dithiols was a better way to obtain polymers with higher molecular weights in excellent yields. The radical additions of vinyloxiranes **1** and **2** with thiols as model reactions were performed at 60 °C in PhCl in order to clarify the polymerization behavior of bifunctional vinyloxiranes and dithiols. The results of the model reactions were consistent with those of the polyadditions, indicating that the best choice of monomers was **4** and aromatic dithiols.

References and Notes

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