Radical Polyaddition of Dithiols to Bis(alkoxyallene)s

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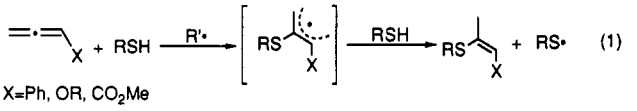
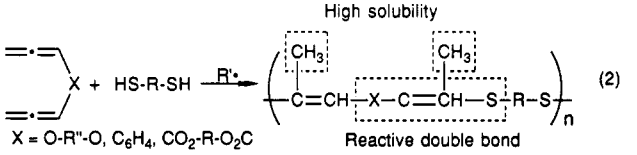
ABSTRACT: Radical polyadditions of 1,4-benzenedithiol or bis(4-mercaptophenyl) sulfide to bis(alkoxyallene) such as 1,4-bis(allenyloxy)xylene and bis(allenyloxy)ethane are described. Thiol groups were added to the terminal double bonds of allenyloxy groups selectively to afford polymers containing reactive carbon–carbon double bonds in the main chain. The geometrical structure of carbon–carbon double bonds in the polymer was isomerized from *E* to *Z* forms with reaction time. Furthermore, the polymers easily underwent cross-linking by the reaction of carbon–carbon double bonds in the backbone with Lewis acids.

Introduction

Although allene derivatives have been widely investigated in organic chemistry,[1] it has not been until recently that functional-group-substituted allenes have been regarded as polymerizable monomers in polymerization chemistry. We have recently reported that alkoxyallenes[2,3] and phenylallenes[4,5] undergo both radical and cationic polymerization to afford polymers having carbon–carbon double bonds *in the side chain* and alkoxyallene and cyanoallene undergo spontaneous zwitterionic copolymerization to give a polymer having diene structure *in the side chain*.[6] These polymers containing many carbon–carbon double bonds would be expected to be functional polymers for cross-linking or addition of other functional groups.

In our study of radical polymerization of allene derivatives, we have also found that thiols selectively add the terminal double bond of alkoxyallenes,[2] phenylallene,[4] and carbomethoxyallene[7] in the presence of radical initiator (eq 1),[8] despite nonselective radical additions of thiols to unsubstituted allene[9] and alkylallenes.[10] It stimulated us that new allene functional polymers containing carbon–carbon double bonds in the backbone could be synthesized if both the allenes and thiols in eq 1 had dual functionality as shown in eq 2. Further, the double bonds in the backbone would have various kinds of reactivity by changing diallene functional groups X in eq 2.



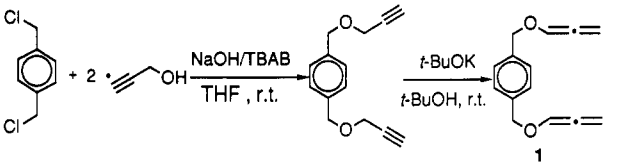


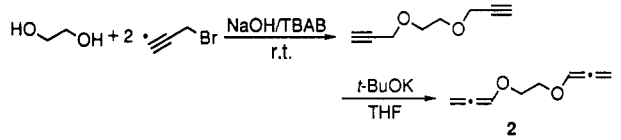
Radical polyaddition of thiols to diynes has been reported to give similar polysulfides containing carbon–carbon double bonds in the backbone, which are insoluble in any organic solvents.[11] However, the polymers resulting from the polyaddition of thiols to diallenes are anticipated to have high solubility in organic solvents by virtue of the methyl group in the side chain (eq 2).

In the present article, we described radical polyaddition of dithiols to bis(alkoxyallene)s such as 1,4-bis(allenyloxy)-xylene (**1**)[12] and bis(allenyloxy)ethane (**2**). Through the model reaction of monofunctional alkoxyallene (**3**) with thiols or dithiols, appropriate dithiols for this polyaddition were first revealed. Furthermore, the obtained polymers in the polyaddition were shown to undergo cross-linking easily by the reaction of double bonds in the backbone with Lewis acid.

Syntheses of Diallenes

The requisite diallene **1** was prepared by isomerization of 1,4-bis(propargyloxy)xylene, which was prepared by etherification of propargyl alcohol with xylylene dichloride in the presence of NaOH and a catalytic amount of tetrabutylammonium bromide (TBAB) in 88% yield, in the presence of a catalytic amount of *t*-BuOK and was purified by column chromatography on activated alumina gel (hexane) in 75% yield. The diallene **2** was also prepared similarly from ethanediol and propargyl bromide in 70% yield.





Addition Reaction of Thiols to (Benzyloxy)allene (3)

The additions of thiols such as benzenethiol or ethanethiol to (benzyloxy)allene (**3**) were carried out with AIBN at 60 °C in benzene in a sealed tube as one of model reaction of the polyaddition. The reaction was first carried out with an equimolar benzenethiol or ethanethiol to afford trisubstituted olefins **5** in 100% and 91% yields, respectively. Olefins **5** may be formed by attack of thiyl radical to the center carbon of the allenyl group of **3** to give trisubstituted allenyl radical **4**, followed by hydrogen

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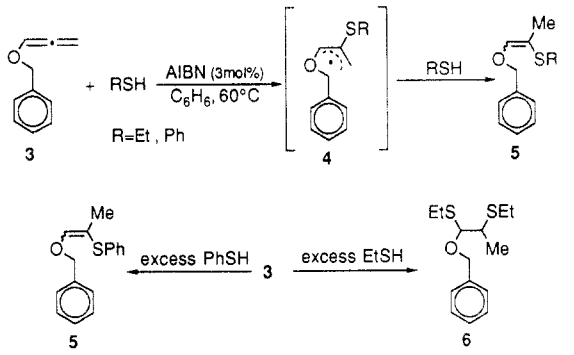
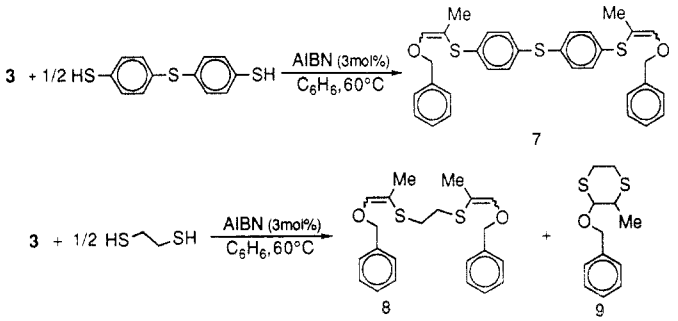
abstraction from thiol. The reaction was next carried out with an excess of benzenethiol or ethanethiol. The same trisubstituted olfein **5** was obtained even with excess benzenethiol, whereas saturated ether **6**, which was formed by addition of further thiol to **5**, was obtained with excess ethanethiol.



Addition Reaction of Dithiols to 3

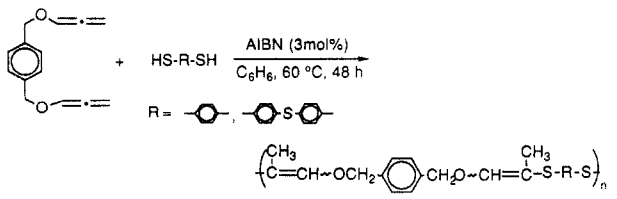
The additions of a half equivalent of dithiols such as ethanedithiol and bis(4-mercaptophenyl) sulfide (MPS) to **3** were carried out under the same conditions. The reaction of **3** with MPS produced quantitatively a 2:1 adduct **7**, whereas the reaction with ethanedithiol gave 2:1 adduct **8** and dithiane derivative **9** which would be produced by intramolecular addition of the second thiol group after the addition of one of the thiol groups of ethanedithiol. The formation of **9** can be also observed in the addition reaction of excess ethanethiol to **3**. From



the results of these model reactions, rigid aromatic dithiols would be suitable for the desired polyaddition to diallene.

Polyaddition

The polyadditions of 1,4-benzenedithiol (BDT) or MPS to **1** were carried out under conditions similar to the model reaction. The obtained polymers were purified by reprecipitation in hexane. The results are summarized in Table I. In both polyaddition of BDT or MPS to **1**, the yields of polymers are almost quantitative irrespective of reaction time, whereas their average molecular weights increase with time, indicating that the polymerization proceeds via polyaddition without serious side reactions.



All of the obtained polymers were soluble in common solvents such as benzene, chloroform, tetrahydrofuran,

Table I. Radical Polyaddition of Dithiols to Bisallene 1[a]

entry	R	time (h)	Y (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	E/Z[c]
1	BDT	3	95	2700	4.97	48/52
2	BDT	6	98	5500	3.53	27/73
3	BDT	12	90	6000	3.99	14/86
4	BDT	24	95	8000	2.85	12/88
5	BDT	48	96	9600	2.75	12/88
6	MPS	3	92	3800	4.27	47/53
7	MPS	6	98	4000	2.93	39/61
8	MPS	12	92	5900	3.41	35/65
9	MPS	24	88	9600	3.67	14/86
10	MPS	48	97	11500		12/88

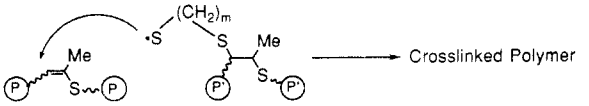
[a] The polyaddition was carried out at 60 °C in benzene (2.5 M) with AIBN (3 mol %). [b] Estimated by GPC based on PSt. [c] Estimated by ^{1}H NMR.

etc., as expected by us. The IR spectra of polymers showed the characteristic absorptions of trisubstituted C–C double bond at 1641–1640 and 814–811 cm^{-1}, and an absorption attributable to the vinyl ether group at 1263 cm^{-1}. The ^{1}H NMR spectra measured in C_6D_6 showed the signals corresponding to the olefinic protons at 6.60–6.58 and 6.13–6.12 ppm and the signals assignable to methyl protons attached to C–C double bound at 2.05–2.01 and 1.72–1.71 ppm, and the ratio of signal intensities of olefinic and methyl protons was 1:3. These spectral data indicate that the resulting polymers consist of one unit formed by selective addition of the thiol group of BDT or MPS to only the terminal double bond of **1**.

Newly formed carbon–carbon double bonds in the polymers contained both *E* and *Z* structure, the ratio of which was estimated by ^{1}H NMR using the ratio of signal areas for the two different types of methyl protons. The assignment of stereochemistry has been made on the basis that in the carbon–carbon double bond assigned as *Z*, the methyl and olefinic protons appear at lower field in the NMR. The ^{1}H NMR spectrum of the model compound, obtained by the radical addition of benzenethiol to allenyl benzyl ether, was similar to that of the polymers, and a strong correlation in 500-MHz ^{1}H NOESY NMR spectrum was observed between the methyl protons at lower field and the olefinic proton at lower field, indicating the signals for *Z* isomer (Figures 1 and 2). And this assignment agreed very closely with the calculated data. The *E*/*Z* ratio of the double bonds in the polymer obtained from both BDT and MPS was changed from ca. 1/1 to 1/9 with reaction time, and similar tendency was also observed in the model reaction of **3** with benzenethiol.

However, when the polyadditions of flexible aliphatic dithiols such as ethanedithiol, 1,3-propanedithiol, and 1,4-butanedithiol of **1** were carried out, the cross-linked polymers were obtained in all cases. On the basis of the

model reaction, the produced polymer could be expected to have the end groups dithiane, but the addition of dithiols to the carbon–carbon double bonds of different polymer chain would also proceed to afford cross-linked polymers.



Furthermore, the polyaddition of aromatic dithiol to the flexible diallene **2** gave also cross-linked polymer. This is probably because **2** is thermally unstable and undergoes

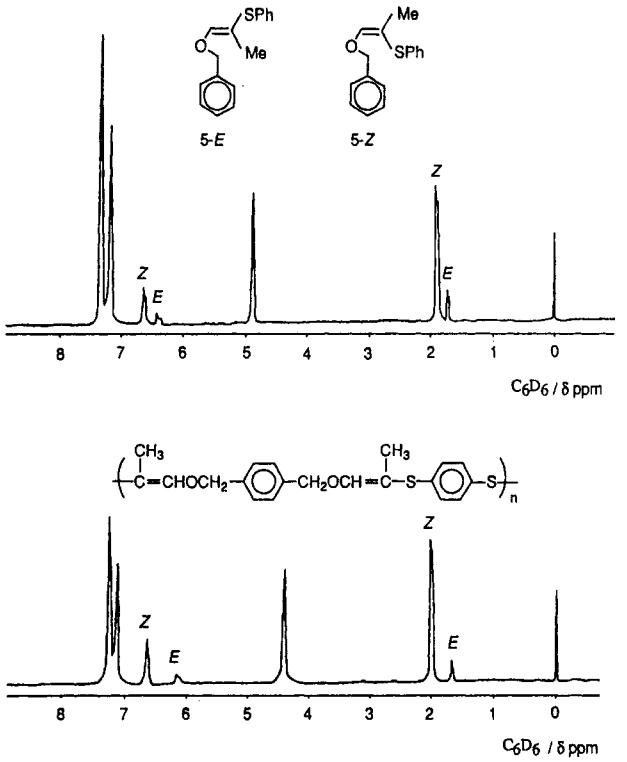


Figure 1. 60-MHz ^{1}H NMR spectrum of the model compound (*E*- and *Z*-**5**) and the polymer in C_6D_6.

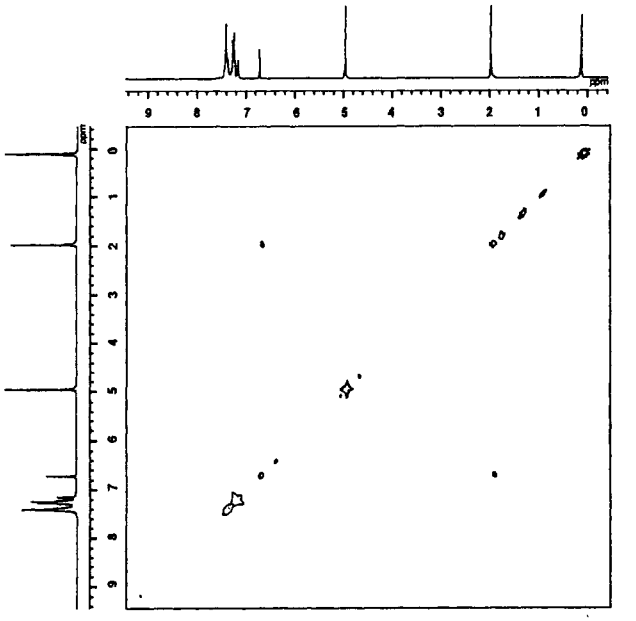
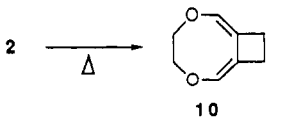


Figure 2. 500-MHz ^{1}H NMR NOESY spectrum of the model compound (*Z*-**5**) of the polymer in C_6D_6.

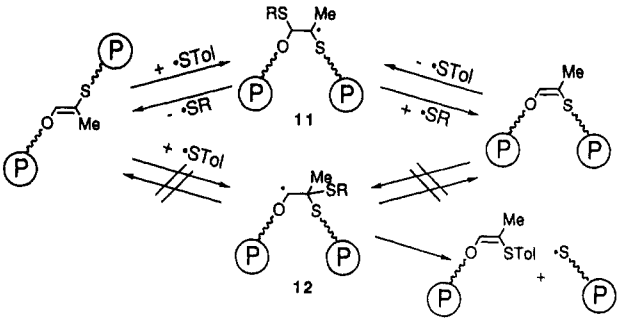
cyclization to **10**,[1] which may afford cross-linked polymer on the glass surface.

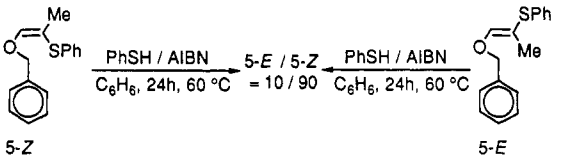


Isomerization Mechanism

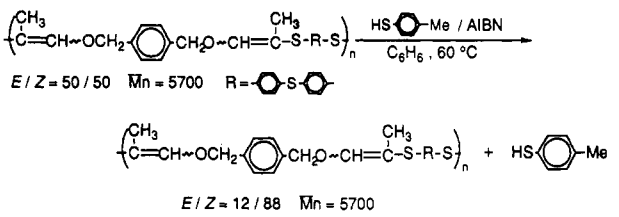
The model compounds, *E*-**5** or *Z*-**5** were treated with benzenethiol under the conditions for the radical addition to afford an *E*/*Z* mixture with the same ratio (*E*/*Z* = 10/90) in the both cases. These results clearly indicate that the isomerization of the products was not one-way traffic but traffic walking on the right-side facing.

Scheme I. Isomerization Mechanism of the Polymer Structure





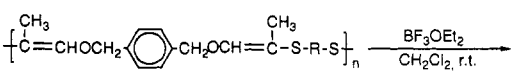
When the polymer with the ratio of *E*/*Z* = 54:46 was treated with *p*-toluenethiol in the presence of AIBN, the ratio was changed to 12:88, but the number average molecular weight was not changed and *p*-toluenethiol was quantitatively recovered. Furthermore, when the polymer was reacted with radical initiator in the absence of thiol in dark as blank test, the ratio of *E*/*Z* and number average molecular weight were not changed. These results suggest



that the isomerization takes place by virtue of the thiyl radical, and the thiyl radical attacks the α-carbon to afford **11** not the β-carbon to afford **12** (Scheme I). If the thiyl radical attacks the β-carbon, one would expect consumption of *p*-toluenethiol and a decrease of molecular weight of the polymer via intermediate **12**; these phenomena did not agree with the experimental results. Stereochemistry of the polymer structure would be determined via rotation of the intermediates **11**.

Cross-Linking of the Polymer

Cross-linking of the obtained polymer was carried out with BF_3OEt_2 by utilizing the reactive electron-rich carbon–carbon double bonds in the backbone. To a solution of the polymer in dichloromethane was added 3 mol % of BF_3OEt_2 at room temperature to give a cross-linked polymer in 30 s, quantitatively (eq 3). Since characteristic absorptions of a double bond in the polymer at 1640 and 814 cm^{-1} disappeared almost completely in the IR spectrum of the resulting cross-linked polymer, the reactive electron-rich double bonds in the backbone of different polymer chain may undergo cationic polymerization to afford the cross-linked polymer. In summary,



Crosslinked polymer (3)

the present work has demonstrated that a functional-group-substituted diallene such as 1 can be utilized for selective radical polyaddition of dithiols. Furthermore, the obtained polymers have high solubility in common organic solvents and contain reactive electron-rich double bonds, by which cross-linking can take place with Lewis acid and other functions will be able to be introduced. Further work on the polyadditions of dithiols to other diallenes as well as applications of the resulting polymers as functional materials are in progress.

Experimental Part

^1H, ^{13}C NMR, and ^1H NMR NOESY spectra were recorded on JEOL PMX 60S, EX-90, and GX-500 spectrometers, using tetramethylsilane (TMS) as an internal standard in CCl_4, $CDCl_3$, and C_6D_6 at 27 °C. FT IR spectra were obtained with a JASCO FT/IR-3 at 25 °C. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$, number and weight average molecular weights) and its distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with polystyrene gel columns, using tetrahydrofuran as solvent (flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors).

Solvents were purified by distillation according to the usual methods.

Preparation of 1,4-Bis(propargyloxy)xylene. To the mixture of xylylene dichloride (30.0 g, 171 mmol), propargyl alcohol (21.2 g, 378 mmol), tetrabutylammonium bromide (TBAB 0.6 g, 2 mmol), dimethylformamide (34.0 mL), and water (4.3 mL) was added solid sodium hydroxide (17.1 g 428 mmol) at room temperature. After the reaction mixture was vigorously stirred for 24 h, the solution was poured into a large amount of water. The solution was extracted with diethyl ether and washed with 5% ammonium chloride aqueous solution. The organic layer was dried over magnesium sulfate. After the solvent was removed under reduced pressure, the residue was distilled to obtain 34.2 g (93%) of the title compound: bp 113–119 °C (0.12 mmHg); ^1H NMR(CCl_4) δ 7.25 (s, 4H), 4.52 (s, 4H), 4.07 (d, J = 2.4 Hz, 4H), 2.31 (t, J = 2.4 Hz, 2H); IR (neat) 1198, 2118 cm^{-1}.

Preparation of 1,4-Bis(allenyloxy)xylene (1). To the solution of potassium *tert*-butoxide (3.16 g, 28 mmol) in 15 mL of dry tetrahydrofuran (THF) was added the mixture of 1,4-bis(propargyloxy)xylene (10.0 g, 47 mmol) in 40.0 mL of dry THF at room temperature. After the mixture was stirred at room temperature for 24 h, the reaction mixture was poured into a large amount of water. The solution was extracted with diethyl ether and washed with 5% ammonium chloride aqueous solution. The organic layer was dried over magnesium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 300 mesh) to obtain 5.8 g (58%) of 1; ^1H NMR (CCl_4) δ 7.27 (s, 4H), 6.81 (t, J = 6.2 Hz, 2 H), 5.43 (d, J = 6.2 Hz, 4H), 4.57 (s, 4H); IR (neat) 1199, 1955 cm^{-1}.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.52; H, 6.59. Found: C, 77.88; H, 6.60.

Preparation of 1,2-Bis(proparglyoxy)ethane. To the mixture of ethylene glycol (9.31 g, 150 mmol), propargyl bromide (39.26 g, 330 mmol), TBAB (0.15 g, 0.5 mmol), and water (3.8 mL) was added solid sodium hydroxide (15.0 g, 375 mmol) at room temperature, and the mixture was vigorously stirred for 5 h. After the reaction mixture was kept at 50 °C for 3 h, the solution was poured into a large amount of water. The solution was extracted with diethyl ether and washed with 5% ammonium chloride aqueous solution. The organic layer was dried over magnesium sulfate. After the solvent was removed under reduced pressure, the residue was distilled to obtain 13.5 g (65%) of the title compound, bp 79–80.5 °C (7 mmHg); ^1H NMR (CCl_4) δ 4.20 (d, J = 2.6 Hz, 4H), 3.73 (s, 4H), 2.42 (t, J = 2.6 Hz, 2H); IR (neat) 1098, 2118 cm^{-1}.

Preparation of 1,2-Bis(allenyoxy)ethane (2). To the solution of potassium *tert*-butoxide (1.22 g, 11 mmol) in 4 mL of dry THF was added the mixture of 1,2-bis(propargyloxy)-ethane (3.0 g, 22 mmol) in 3.0 mL of dry THF at room temperature. After the mixture was stirred at room temperature for 3 h, the reaction mixture was poured into a large amount of water. The solution was extracted with diethyl ether and washed with 5% ammonium chloride aqueous solution. The organic layer was dried over magnesium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 200 mesh) to obtain 2.1 g (70%) of 2: ^1H NMR (CCl_4) δ 6.78 (t, J = 6.0 Hz, 2H), 4.74 (d, J = 6.0 Hz, 4H), 3.79 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 201.0, 121.7, 91.2, 66.9; IR (neat) 1108, 1953 cm^{-1}.

The Addition Reaction of Ethanethiol to (Benzyloxy)-allene (3). The addition reaction of ethanethiol (127 mg, 2 mmol) to 3 (300 mg, 2 mmol) in the presence of azobis(isobutyronitrile) (AIBN, 10 mg, 3 mol %) was carried out at 60 °C for 24 h in a sealed tube in benzene (0.4 mL) under reduced pressure. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 300 mesh) to obtain 420 mg (98%) of *E*- and *Z*-5: *E*-5 ^1H NMR (CCl_4) δ 7.28 (s, 5H), 6.15 (q, J = 1.4 Hz, 1H), 4.78 (s, 2H), 2.66 (q, J = 7.22 Hz, 2H), 1.77 (d, J = 1.4 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H); *Z*-5 ^1H NMR (CCl_4) δ 7.28 (s, 5H), 6.45 (q, J = 1.4 Hz, 1H), 4.78 (s, 2H), 2.46 (q, J = 7.2 Hz, 2H), 1.88 (d, J = 1.4 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H); IR (neat) 1262, 1641 cm^{-1}.

The Addition Reaction of Benzenethiol to 3. The addition of benzenethiol (220 mg, 2 mmol) to 3 (300 mg, 2 mmol) in the presence of AIBN (10 mg, 3 mol %) was carried out at 60 °C for 24 h in a sealed tube in benzene (0.4 mL) under reduced pressure. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 300 mesh) to obtain 518 mg (99%) of *E*- and *Z*-5: *E*-5 ^1H NMR (CCl_4) δ 7.33 (s, 5H), 7.15 (s, 5H), 6.37 (q, J = 1.6 Hz, 1H), 4.90 (s, 2H), 1.73 (d, J = 1.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 147.1, 137.2, 137.0, 129.6, 128.6, 128.5, 127.6, 127.4, 125.4, 105.6, 74.1, 18.9; *Z*-5 ^1H NMR (CCl_4) δ 7.33 (s, 5H), 7.17 (s, 5H), 6.60 (q, J = 1.6 Hz, 1H), 4.90 (s, 2H), 1.90 (d, J = 1.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 151.5, 137.2, 137.0, 128.8, 128.7, 128.2, 128.0, 127.3, 125.9, 106.2, 74.3, 15.8; IR (neat) 1264, 1641 cm^{-1}.

The Addition Reaction of Excess Ethanethiol to 3. The addition of excess ethanethiol (249 mg, 4 mmol) to 3 (150 mg, 1 mmol) with AIBN (45 mg, 10 mol %) was carried out in a sealed tube in benzene (2.0 mL) under reduced pressure at 60 °C for 48 h. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 300 mesh) to obtain 261 mg (97%) of 6: ^1H NMR ($CDCl_3$) δ 7.42–7.27 (m, 5H), 4.94–4.47 (m, 3H), 3.30–3.02 (m, 1H), 2.75–2.51 (m, 4H), 1.47–1.15 (m, 9H).

The Addition Reaction of Bis(4-mercaptophenyl) Sulfide (MPS) to 3. The addition of bis(4-mercaptophenyl) sulfide (275 mg, 1 mmol) to 3 (300 mg, 2 mmol) in the presence of AIBN (5 mg, 3 mol %) was carried out at 60 °C for 24 h in a sealed tube in benzene (0.4 mL) under reduced pressure. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 300 mesh) to obtain 553 mg (99 %) of *E*- and *Z*-7: ^1H NMR ($CDCl_3$) δ 7.47–7.04 (m, 18H), 6.62 for *Z* isomer and 6.43 for *E* isomer (2q, J = 1.4 Hz, 2H), 4.88 (s, 4H), 1.90 for *Z* isomer and 1.76 for *E* isomer (2d, J = 1.4Hz, 6H); IR (neat) 1264, 1643 cm^{-1}.

Addition Reaction of Ethanedithiol to 3. The addition of ethanedithiol (94 mg, 1 mmol) to 3 (300 mg, 2 mmol) in the presence of AIBN (5 mg, 3 mol %) was carried out at 60 °C for 48 h in a sealed tube in benzene (0.4 mL) under reduced pressure. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (activated alumina, 300 mesh) to obtain 240 mg (49%) of *E*- and *Z*-8 and 120 mg (24%) of 9: *E*-8 ^1H NMR (CCl_4) δ 7.37–710 (m, 10H), 6.20 (q, J = 1.2 Hz, 2H), 4.79 (s, 4H), 2,45 (s, 4H), 1.78 (d, J = 1.2 Hz, 6H); *Z*-8 ^1H NMR (CCl_4) δ 7.37–7.10 (m, 10H), 6.34 (q, J = 1.2 Hz, 2H), 4.79 (s, 4H), 2.45 (s, 4H), 1.85 (d, J = 1.2 Hz, 6H); ^{13}C NMR (C_6D_6) δ 148.9, 137.1, 128.5, 128.0, 127.3, 106.6, 73.8, 15.6; IR (neat) 1288, 1640 cm^{-1}; 9, ^1H NMR (CCl_4) δ 7.42–7.25 (m, 5H), 5.07–4.75 (m, 3H), 3.59–2.48 (m, 5H), 1.48–1.15 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 137.4, 128.4, 128.3, 127.9, 75.6, 69.7, 42.0, 30.2, 23.8, 19.4.

The Polyaddition of 1,4-Benzenedithiol (BDT) or MPS to 1,4-Bis(allenyloxy)xylene (1). Equimolar amounts of BDT

or MPS and 1 were heated at 60 °C in benzene with a catalytic amount of AIBN (5 mg, 3 mol %) in a sealed tube under reduced pressure. After the polymers were purified by dissolution in benzene followed by precipitation in hexane, they were filtered off and dried in vaccuo. Often dissolved in benzene, they were freeze-dried. The result are summarized in Table I. ^{1}H NMR is shown in Figure 1.

The Isomerization reaction of 5. *E*-**5** or *Z*-**5** (50 mg, 2 mmol) and benzenethiol (22 mg, 0.2 mol) were heated at 60 °C in C_6D_6 with a catalytic amount of AIBN (1 mg, 3 mol %) in sealed NMR tubes under reduced pressure. The *E*/*Z* ratio of **5** was directly estimated at the appropriate time by ^{1}H NMR.

The Isomerization Reaction of the Polymer. The polymer (0.2 mg) and *p*-toluenethiol (87 mg, 0.7 mmol) were heated at 60 °C in C_6D_6 (0.4 mL) with a catalytic amount of AIBN (3 mg, 3 mol %) in a sealed NMR tube under reduced pressure. The *E*/*Z* ratio of the polymer was directly evaluated at the appropriate time by ^{1}H NMR. After reaction for 24 h, the yield of *p*-toluenethiol was determined by gas chromatography with an internal standard as CH_2Cl_2 (10 μL) and then the reaction mixture was purified by precipitation in hexane.

The Cross-Linking Reaction of the Polymer. The cross-linking reaction of the polymer ($\bar{M}_n$ = 6000) was carried out at room temperature in CH_2Cl_2 with a catalytic amount of BF_3OEt_2 (2.3 mg, 3 mol %). After a stirring bar was could not rotate, the reaction was terminated with NH_3/MeOH and then the reaction mixture was poured into a large amount of CH_2Cl_2. The precipitated polymer was collected by filtration, washed several times with water, extracted with CH_2Cl_2 using a Soxhlet extractor, and dried under vacuo.

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