Simultaneous Construction of Polymer Backbone and Side Chains by Three-Component Polycondensation. Synthesis of Polyethers with Allenyl Side Chains from Dialdehydes, Alkylene Bis(trimethylsilyl) Ethers, and Propargyltrimethylsilane

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ABSTRACT: Polyethers with the allenyl side chains were synthesized by the simultaneous acid-catalyzed reaction of dialdehydes **1**, alkylene bis(trimethylsilyl) ethers **2**, and 1-trimethylsilyl-2-butyne (**4b**). Before polymerization, Lewis acid-catalyzed three-component reactions of aldehydes, alkoxysilanes, and propargylsilanes were studied to find that **4b** was effective as an allenyl reagent in this reaction. The polycondensations of **1**, **2**, and **4b** were carried out in the presence of 10 mol % of triphenylmethyl perchlorate ($TrClO_4$) at −50 °C to yield the desired polyethers consisting of **1**, **2**, and **4b** with a molar ratio of 1:1:2 in good yields. This polyether was treated with a cationic catalyst such as BF_3OEt_2 to give a cross-linked polymer. This polymer synthesis is unusual in that it concurrently constructs both the polymer backbone and the functional side chains from three starting compounds.

Introduction

Synthesis of polymers having functional groups in the side chains is among the most significant accomplishments in polymer chemistry. This enables us to use polymer as not only fabrication materials but also the materials that work for many kinds of purposes. These polymers are usually synthesized by one of two methods,[1] either by grafting or by polymerization of monomers containing a functional group in the side chain. Recently, we have reported the three-component polycondensations of dialdehydes **1**, alkylene bis(trimethylsilyl) ethers **2**, and various silyl nucleophiles **3**. In these polymerizations, the use of triethylsilane as **3** gave ordinary polyethers,[2a] whereas the use of allyltrimethylsilane, cyanotrimethylsilane, and silyl enol ethers afforded polyethers having the allyl,[2b] cyano,[2c] and keto[2d,e] side chains, respectively. In the latter cases, we have demonstrated that the polyether backbone and the functional side chains are simultaneously constructed in one pot. Since the polyether backbone was produced from **1** and **2** and the side chains were introduced from **3**, the use of other **3**s would yield polyethers with other functional side chains. A polymer having the allenyl groups as functional side chains is expected to have substantial reactivity, because allene derivatives undergo a variety of reactions[3a] such as cycloaddition,[3b−d] radical addition,[3e,f] photooxygenation,[3g] and polymerization with transition metals,[3h−l] etc. These polymers are applicable to thermosetting resins or photocrosslinking polymers under mild conditions. A polymer having the allenyl side chains was synthesized by the polymerization of a monomer bearing the allenyl group,[4] but to the best of our knowledge, it has not been hitherto reported that the allenyl group is directly introduced to polymer by allenyl reagents. It has been reported that propargyltrimethylsilanes react with electrophiles such as acetals and aldehydes in the presence of Lewis acid to yield allenic derivatives.[5] However, the three-component reaction of propargylsilanes, aldehydes, and alkoxysilanes, where α-allenyl ethers would be obtained in one pot, has not been reported. Furthermore, this reaction would be applicable to the synthesis of polyethers having the allenyl side chains. In this paper, we develop the three-component condensation reaction of aldehydes **5**, alkoxytrimethylsilanes **6**, and propargylsilane **4**, and this reaction is applied to the synthesis of polyethers having the allenyl side chains as an extension of this work to the simultaneous construction of polymer backbone and side chains from three compounds (Scheme 1). Furthermore, cross-linking of the polyether is conducted to demonstrate the function of the allenyl side chains.

Results and Discussion

Three-Component Reaction for α-Allenyl Ethers. We first studied the reaction of benzaldehyde dimethylacetal **7** with propargylsilanes such as 1-trimethylsilyl-2-propyne (**4a**) and 1-trimethylsilyl-2-butyne (**4b**) (Scheme 2),[6] because acetals were found to be an intermediate in the Lewis acid-catalyzed reactions of aldehydes, alkoxysilanes, and silyl nucleophiles.[2] The results are shown in Table 1. When **4a** was used, the reaction barely proceeded with 5 mol % of triphenylmethyl perchlorate ($TrClO_4$)[7] to yield α-allenyl ether **8a** in very low yield and recover **7** in 45% yield (entry 1). The use of 50 mol % of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf)[8] resulted in complete consumption of **7**, but **8a** was not obtained though α-propargyl ether **9** was afforded in low yield (entry 2). Surprisingly, the reaction of **4b** with **7** smoothly proceeded by 5 mol % of $TrClO_4$ to yield **8b** in quantitative yield (entry 3). It should be noted that the reaction of methyl-substituted **4b** with **7** was totally different from that of unsubstituted **4a** with **7**, and the former reaction gave selectively α-allenyl ether **8b**.

We next carried out the three-component condensation of benzaldehyde **5**, methoxytrimethylsilane **6**, and **4b** in the presence of 5 mol % of $TrClO_4$ or Me_3SiOTf (Table 2). Both reactions gave **8b** in good yields; both catalysts were effective for this reaction. The fact that

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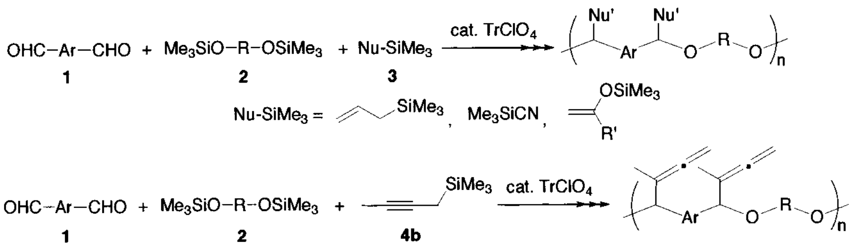
Scheme 1



Scheme 2

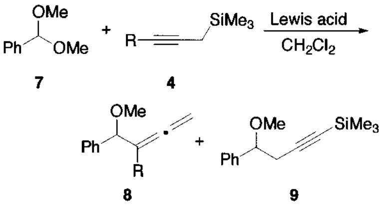


Table 1. Reaction of 7 with 4

entry	R in **4**	temp (°C)	time (h)	yield (%)[c]	
				8	**9**
1[a]	H: **4a**	−78	4.0	2	0
2[b]	**4a**	−78	7.5	0	3
3[a]	Me: **4b**	−50	2.0	100[d]	0

[a] The reaction was carried out with 5 mol % of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{7}]_0 = [\mathbf{4}]_0 = 0.5$ M). [b] The reaction was carried out with 50 mol % of Me_3SiOTf in CH_2Cl_2 ($[\mathbf{7}]_0 = [\mathbf{4a}]_0 = 0.67$ M). [c] Isolated yield. [d] Determined by ^1H NMR using an internal standard (1,1,2,2-tetrachloroethane).

Table 2. Reaction of 5, 6, and 4b[a]

catalyst	time (h)	yield of **8b** (%)[b]
$TrClO_4$	18	95
Me_3SiOTf	24	97

[a] The reaction was carried out with 5 mol % of catalyst in CH_2Cl_2 ($[\mathbf{5}]_0 = [\mathbf{6}]_0 = [\mathbf{4b}]_0 = 0.5$ M) at −78 °C. [b] Determined by GC.

Scheme 3

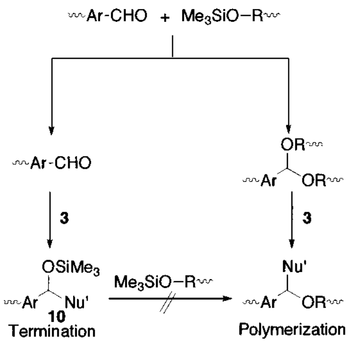


Table 3. Three-Component Polycondensation of 1a, 2a, and 4b[a]

catalyst (mol %)	yield (%)[b]	polymer composition[d]		
		M_n[c]	M_w/M_n[c]	**1a**:**2a**:**4b**
Me_3SiOTf (10)	25	6300	2.76	39:36:25
$TrClO_4$ (10)	64	6600	2.85	24:25:51
$TrClO_4$ (5)	60	6100	1.88	25:25:50

[a] The polymerization was carried out in CH_2Cl_2 ($[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = 0.5$ M, $[\mathbf{4b}]_0 = 1.0$ M) at −50 °C for 24 h. [b] Polymer insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards using THF as solvent. [d] Determined by ^1H NMR.

Table 4. Three-Component Polycondensation of 1a, 2a, and 4b[a]

temp (°C)	yield (%)[b]	M_n[c]	M_w/M_n[c]	polymer composition[d]
				1a:**2a**:**4b**
rt[e]	23	3400	2.30	44:41:15
0	18	4500	2.14	28:45:27
−20	21	4000	1.51	26:30:44
−50	60	6100	1.88	25:25:50
−78	42	5200	1.65	28:28:44

[a] The polymerization was carried out with 5 mol % of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = 0.5$ M, $[\mathbf{4b}]_0 = 1.0$ M) for 24 h. [b] Polymer insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards using THF as solvent. [d] Determined by ^1H NMR. [e] rt = room temperature.

no α-allenyl alcohol was produced as a result of a direct attack of **4b** on **5** shows that the reaction of **4b** with an intermediate acetal, which is generated by **5** and **6**, proceeds selectively even in the presence of **5** in the reaction mixture. That is important when this reaction is applied to three-component polycondensation. In the previous article,[2d] we revealed the reaction mechanism of the three-component polycondensation of **1**, **2**, and **3** (Scheme 3). All of the silyl ethers react with half the amount of the formyl group to generate the acetal group: the formyl group and the acetal group are present in a molar ratio of 1:1. Then, **3** reacts with the acetal group afforded the desired polyether. However, the direct reaction of the formyl group with **3**, leading to **10**, causes termination, since **10** cannot react further with silyl ether.

Polymerization. On the basis of the three-component reaction developed above, polycondensation was studied by the use of dialdehydes **1** and alkylene bis(trimethylsilyl) ethers **2** instead of aldehydes and silyl ethers, respectively. In this polymerization, however, the allenyl side chains may cause overreactions with $TrClO_4$, because it has been known that allenic derivatives polymerize by Lewis acids.[9] To establish the optimal conditions for yielding the polyethers having the allenyl side chains, the polymerization of isophthalaldehyde (**1a**), 1,10-bis(trimethylsiloxy)decane (**2a**), and **4b** was carried out under different conditions.

We first studied the polymerization with 10 mol % of $TrClO_4$ and Me_3SiOTf, respectively (Table 3). These Lewis acids did not affect the number-average molecular weight (M_n) of the polymer obtained. In the polymerization with $TrClO_4$, however, the polymer consisting of **1a**, **2a**, and **4b** with a molar ratio of 1:1:2 was obtained in higher yield. The decrease of the amount of $TrClO_4$ up to 5 mol % resulted in narrower molecular weight distribution (M_w/M_n), implying that higher concentration of the catalyst might cause a reaction between polymer chains through the allenyl groups.

The polymerization was next carried out with 5 mol % of $TrClO_4$ at −78 °C to room temperature (Table 4). All of the polymerizations proceeded homogeneously. In the polymerization at −50 °C, the yield and M_n of

Table 5. Three-Component Polycondensation of 1a, 2a, and 4b[a]

				polymer composition[d]
time (h)	yield (%)[b]	M_n[c]	M_w/M_n[c]	**1a**:**2a**:**4b**
0.25	28	5400	4.73	26:24:50
0.5	38	6800	2.21	25:24:51
1	41	6800	2.10	25:24:51
3	49	6500	2.08	24:25:51
6	45	6600	2.96	26:24:50
24	64	6600	2.85	24:25:51
48	53	6400	2.60	27:26:47
72	43	6700	2.86	22:31:47

[a] The polymerization was carried out with 10 mol % of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = 0.5$ M, $[\mathbf{4b}]_0 = 1.0$ M) for 24 h. [b] Polymer insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards using THF as solvent. [d] Determined by ^1H NMR.

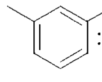
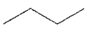
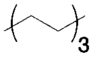
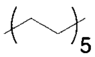
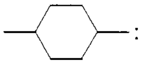
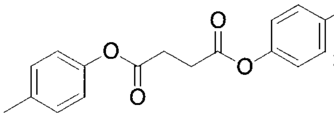
polymer were the highest, and the polyether consisted of **1a**, **2a**, and **4b** with a molar ratio of 1:1:2. When the reaction temperature increased to room temperature, the yield and M_n of polymer decreased and the M_w/M_n became broad, and the unit of **4b** in polymer decreased. Furthermore, in the IR spectrum of the polymer obtained at room temperature, the characteristic absorption of an allenyl group at 1958 cm^{-1} was weaker than that of the polymer obtained at −50 °C. These results suggest that the allenyl groups in the side chains reacted to some extent at higher temperature than −50 °C.

Furthermore, we studied the effect of reaction time in the polymerization of **1a**, **2a**, and **4b** at −50 °C. The results are summarized in Table 5. The polymer yield gradually increased until 24 h had passed, although the reaction time did not affect the M_n and M_w/M_n. The composition of obtained polymers was almost 25:25:50, irrespective of time. The IR spectrum of the polymer obtained from **1a**, **2a**, and **4b** showed the characteristic absorption of an allenyl group at 1958 cm^{-1} and an ether linkage at 1100 cm^{-1}. The ^1H NMR spectrum of the polymer showed the signal assignable to the benzyl methine proton on a carbon adjacent to the ether linkage at δ 4.83, the signals of the aromatic protons of **1a** at δ 7.26, and the aliphatic proton of **2a** at δ 3.51−3.36, 1.62−1.59, and 1.29, respectively. And the signals of the terminal methylene and the methyl group of the allenyl side chains were also observed at δ 4.69−4.68 and δ 1.51, respectively.

With the optimized conditions in hand, we carried out the polymerization of a variety of **1**, **2**, and **4b** with 10 mol % of $TrClO_4$ at −50 °C for 24 h. The results are summarized in Table 6. Long carbon-chain **2c** and **2a** yielded polymers with similar M_n in good yields, whereas ethylene glycol disilyl ether **2b** afforded polymer in very poor yield. This low yield can be accounted for by the formation of a stable cyclic acetal, 1,3-dioxolane, from the formyl group and **2b**; the reaction of **4b** with the cyclic acetal would be very slow. Actually, the ^1H NMR spectrum of the methanol-soluble part showed the signals assignable to 1,3-dioxolane protons at δ 5.88 and 5.84. When secondary **2d** was used, the polymer yield and M_n also decreased. Furthermore, dialdehyde **1b** containing the ester linkage afforded polymer in the highest yield. In all of these polymerization, the polymer compositions of **1**, **2**, and **4b** were almost 25:25:50, indicating that these polymers have the desired structure as shown in Scheme 1. The polymerizations proceeded quantitatively, but the yields are shown as the methanol-insoluble part after precipitation to remove the catalyst. The ^1H NMR spectrum of the methanol-soluble part showed the signals of the desired polyethers and of trace amount of the formyl group. Consequently, the methanol-soluble part contained polyethers of low molecular weight.

Cross-Linking of the Polyether from 1a, 2a, and 4b. To demonstrate the function of the polyether having the allenyl groups in the side chains, cross-linking of the polymer obtained from **1a**, **2a**, and **4b** was carried out (Scheme 4). The results are summarized in Table 7. When the polyether was treated with 10 mol % of $TrClO_4$ as a cationic catalyst in CH_2Cl_2 at room temperature, cross-linked polymer was not obtained. When 10 mol % of BF_3OEt_2 was used as a cationic catalyst, cross-linked polymer was obtained in 30% yield after washing gel with CH_2Cl_2 in a Soxhlet extractor. Furthermore, photocross-linking of the resulting polymer was carried out by using 26 mol % of bis[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluorophosphate) (DPSP)[10] as a photoacid generator. After irradiation of UV for 80 min, the conversion of the allenyl groups reached 60%,

Table 6. Three-Component Polycondensation of 1, 2, and 4b[a]

					polymer composition[d]
Ar in **1**	R in **2**	yield (%)[b]	Mn[c]	Mw/Mn[c]	**1** : **2** : **4b**
 : **1a**	 : **2b**	2	4000	1.52	24 : 28 : 48
1a	 : **2c**	44	5000	1.90	25 : 25 : 50
1a	 : **2a**	64	6600	2.85	24 : 25 : 51
1a	 : **2d**	52	3400	1.89	25 : 25 : 50
 : **1b**	**2a**	70	5200	2.98	25 : 25 : 50

[a] The polymerization was carried out with 10 mol % of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.5$ M, $[\mathbf{4b}]_0 = 1.0$ M) at −50 °C for 24 h. [b] Polymer insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards using THF as solvent. [d] Determined by ^1H NMR.

Scheme 4

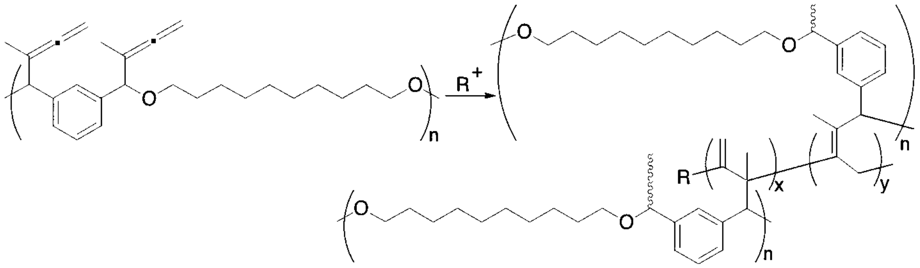


Table 7. Cross-Linking of Polyether from 1a, 2a, and 4b

reagent (mol %)	solvent	conditions	yield (%)[a]
$TrClO_4$ (10)[b]	CH_2Cl_2	rt,[e] 30 h	0
BF_3OEt_2 (10)[b]	CH_2Cl_2	rt,[e] 90 min	30
DPSP[c] (26)	neat	rt,[e] UV, 80 min	60[d]

[a] Isolated yield after purification with Soxhlet extraction with CH_2Cl_2. [b] $[\text{polyether}]_0 = 0.42$ M. [c] Bis[4-(diphenylsulfonio)phenyl-]sulfide bis(hexafluorophosphate). [d] Conversion of allenyl group. [e] rt = room temperature.

which was estimated by the IR spectrum, and cross-linked polymer was obtained. In the IR spectrum of the cross-linked polymer, the absorption of an allenyl group at 1958 cm^{-1} became weak, whereas the characteristic absorption of a terminal methylene at 1719 cm^{-1} appeared, implying that cross-linking would proceed via the cationic polymerization of the allenyl groups.

Conclusion. The present work has demonstrated that 1-trimethylsilyl-2-butyne **4b** was available for the Lewis acid-catalyzed three-component condensation reactions for α-allenyl ethers. The reaction of **1**, **2**, and **4b** in the presence of a catalytic amount of $TrClO_4$ simultaneously constructed the polyether backbone and the allenyl side chains. In this polymerization, when the polymerization was carried out at lower temperature such as −50 and −78 °C, the polymers with higher M_n were obtained in higher yield, in comparison to the polymers obtained at −20 °C and higher. The polymer obtained at −50 °C yielded the desired polyether consisting of **1**, **2**, and **4b** with a molar ratio of 1:1:2. Furthermore, these polyethers afforded cross-linked polymers via the polymerization of the allenyl groups with BF_3OEt_2 or DPSP as cationic catalysts. Further work on the simultaneous construction of polymer backbone and functional side chains using other silyl nucleophiles is in progress.

Experimental Section

^{1}H NMR spectra were obtained on a JEOL A-500 and FX-200 operating in the pulsed Fourier transform (FT) modes, using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were also obtained on a JEOL A-500 and FX-200 operating in the FT modes using TMS as an internal standard. IR spectra were recorded on a JASCO FT/IR-410. In the photo-cross-linking reaction, samples were irradiated with UV light with a HOYA-SCHOTT EX-250 at 250 W using a high-pressure mercury lamp, and IR spectra were recorded on a BIO−RAD RT/IR FTS 3000. The M_n of polymers were measured with a TOSOH HLC-8120 gel permeation chromatography (GPC) unit (eluent, tetrahydrofuran (THF); calibration, polystyrene standards) using two TSK-gel columns (2 × Multipore H_{XL}-M). Isophthalaldehyde (**1a**) was recrystallized from water and vacuum-dried in a desiccator. Bis(4-formylphenyl) succinate (**1c**) was prepared from *p*-hydroxybenzaldehyde and succinyl chloride as previously reported.[2] Alkylene bis(trimethylsilyl) ethers **2** were prepared from the corresponding diols, 1,1,1,3,3,3-hexamethyldisilazane, and a catalytic amount of chlorotrimethylsilane as previously reported.[2] 1-Trimethylsilyl-2-propyne (**4a**) and 1-trimethylsilyl-2-butyne (**4b**) were prepared according to the previous literature.[11] $TrClO_4$ was prepared from triphenylmethanol and 70% perchloric acid according to the reported procedure.[2] Benzaldehyde (**5**), methoxytrimethylsilane (**6**), Me_3SiOTf, BF_3OEt_2, and DPSP were used as received. Commercially available dry dichloromethane was used as received.

Three-Component Reaction of 5, 6, and 4b. A round-bottomed flask, equipped with a three-way stopcock, was charged with $TrClO_4$ (18 mg, 0.025 mmol) and purged with argon. Dry CH_2Cl_2 (1.0 mL) was added to the flask, followed by cooling the solution to −78 °C. A solution of **5** (0.106 g, 1.0 mmol), **6** (0.108 g, 1.0 mmol), and 1,3-dichlorobenzene as an internal standard (0.050 g, 0.34 mmol) in CH_2Cl_2 (0.5 mL) was added at the −78 °C. After 5 min, a solution of **4b** (0.145 g, 1.0 mmol) in CH_2Cl_2 (0.25 mL) was added. The mixture was stirred at −78 °C, and the yield of **8b** was determined by GC. The reaction mixture was quenched with a few drops of ammoniacal methanol and concentrated in vacuo, and the residue was purified by column chromatography on silica gel to afford the corresponding α-allenyl ethers **8b**: IR (neat): 2931, 2823, 1959, 1601, 1092, 741, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.34 (bs, 5 H), 4.77−4.74 (m, 2 H), 4.73 (s, 1 H), 3.37 (s, 3 H), 1.52 (t, $J = 3.0$ Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 207.1, 140.5, 128.1, 127.7, 126.4, 99.1, 84.5, 74.9, 56.5, 13.2.

Typical Procedure for Polymerization of 1, 2, and 4b. A round-bottomed flask equipped with a three-way stopcock was charged with $TrClO_4$ (18 mg, 0.05 mmol) and purged with argon. After the addition of dry CH_2Cl_2 (0.5 mL) and after $TrClO_4$ dissolved, the solution was cooled to −50 °C, and a solution of **1** (0.5 mmol) and **2** (0.5 mmol) in CH_2Cl_2 (0.25 mL) was added slowly via a syringe. After this mixture was stirred for 5 min, a solution of **4** (0.130 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was added, and the reaction mixture was stirred for 24 h at −50 °C. The polymerization was terminated with ammoniacal methanol at −50 °C, and the solution was poured into a large amount of methanol (30 mL). The precipitated pale yellowish viscous polymer was collected and dried in vacuo.

Polyether from 1a, 2b, and 4b. ^{1}H NMR ($CDCl_3$): δ 7.25 (br, 4 H), 4.94 (bs, 2 H), 4.80−4.62 (m, 4 H), 3.82−3.58 (m, 4 H), 1.68−1.40 (m, 6 H).

Polyether from 1a, 2c, and 4b. IR (neat): 2935, 2859, 1957, 1606, 1097, 848, 764, 707 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.26 (br, 4 H), 4.82 (bs, 2 H), 4.78−4.58 (m, 4 H), 3.60−3.30 (m, 4 H), 1.78−1.34 (m, 14 H). ^{13}C NMR ($CDCl_3$): δ 207.3, 140.8, 128.8, 127.8, 125.4, 99.7, 82.8, 74.8, 68.9, 29.8, 26.3, 13.4.

Polyether from 1a, 2a, and 4b. IR (neat): 2927, 2854, 1958, 1606, 1100, 845, 761, 706 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.26 (br, 4 H), 4.83 (s, 2 H), 4.69−4.68 (m, 4 H), 3.51−3.36 (m, 4 H), 1.62−1.59 (m, 4 H), 1.51 (t, $J = 3.0$ Hz, 6 H), 1.29 (bs, 12 H). ^{13}C NMR ($CDCl_3$): δ 207.3, 140.8, 127.8, 125.4, 124.7, 99.7, 82.7, 74.7, 68.9, 29.9, 29.7, 29.6, 26.4, 13.4.

Polyether from 1a, 2d, and 4b. IR (neat): 2941, 2864, 1957, 1605, 1071, 849, 765 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.26 (br, 4 H), 5.00 (bs, 2 H), 4.79−4.58 (m, 4 H), 3.64−3.38 (m, 2 H), 2.20−1.77 (m, 8 H), 1.77−1.30 (br, 6 H). ^{13}C NMR ($CDCl_3$): δ 207.4, 141.1, 127.7, 125.4, 124.7, 100.1, 79.6, 74.8, 74.6, 74.0, 72.7, 28.4, 28.3, 27.6, 27.5, 13.6.

Polyether from 1b, 2a, and 4b. IR (neat): 2927, 2858, 1959, 1759, 1604, 1134, 849 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37

(d, J = 8.5 Hz, 4 H), 7.06 (d, J = 8.5 Hz, 4 H), 4.83 (s, 2 H), 4.71 (br, 4 H), 3.54−3.51 (m, 2 H), 3.50−3.39 (m, 2 H), 2.97 (s, 4 H), 1.66−1.60 (m, 4 H), 1.52 (t, J = 3.1 Hz, 6 H), 1.40−1.25 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ 207.2, 170.7, 149.6, 138.7, 127.4, 120.9, 99.2, 82.1, 74.7, 68.8, 29.7, 29.5, 29.4, 29.3, 26.3, 13.0.

Cross-Linking of Polyether Obtained from 1a, 2a, and 4b with BF_3OEt_2. A round-bottomed flask equipped with a three-way stopcock was purged with argon. A solution of the polymer from **1a**, **2a**, and **4b** (0.096 g, 0.25 mmol) in CH_2Cl_2 (0.35 mL) was added to the flask. After the solution was cooled to −50 °C, a solution of BF_3OEt_2 (3 μL, 0.025 mmol) in CH_2Cl_2 (0.25 mL) was added at −50 °C via a syringe, and the solution was warmed to room temperature and stirred for 90 min. The resultant gel was washed with CH_2Cl_2 in a Soxhlet extractor for 6 h. The residual gel was collected and dried in vacuo to yield a brownish glassy solid (0.030 g, 31% yield). IR (KBr): 2927, 2854, 1719, 1100, 795, 712 cm^{-1}.

Cross-Linking of Polyether Obtained from 1a, 2a, and 4b with DPSP. A solution of polymer from **1a**, **2a**, and **4b** (0.096 g, 0.25 mmol) and DPSP (0.056 g, 0.065 mmol) in $CHCl_3$ (0.25 mL) was placed on aluminum foil, followed by evaporation of $CHCl_3$, and UV irradiation of the polymer. After predetermined intervals, IR spectra were measured for determination of the conversion of allenyl groups by comparison with absorption areas between allenyl groups at 1958 cm^{-1} and terminal methylene at 1719 cm^{-1}. After 80 min, the conversion of allenyl groups reached 60%, and the cross-linked polymer was obtained as a brownish glassy plate. IR (neat): 2930, 2855, 1958, 1720, 1102, 845, 795, 710 cm^{-1}.

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