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Simultaneous Construction of Polymer Backbone and Side Chains by Three-Component Polycondensation. Synthesis of Polyethers with Cyano Side Chains from Dialdehydes, Alkylene Bis(trimethylsilyl) Ethers, and Cyanotrimethylsilane[1]

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ABSTRACT: Polyethers with cyano side chains were synthesized by the simultaneous acid-catalyzed reaction of dialdehydes (**1**), alkylene bis(trimethylsilyl) ethers (**2**), and cyanotrimethylsilane (**4**). The reactions of **1**, **2**, and **4** were carried out in the presence of 10 mol % of triphenylmethyl (trityl) perchlorate at ambient temperature by the addition of **4** into the reaction mixture of **1**, **2**, and trityl perchlorate to yield polyethers having cyano groups in the side chains. When **1** was added to the mixture of **2**, **4**, and trityl perchlorate, a low-molecular-weight oligomer was formed. The observed deference is attributed to the fact that **4** was more reactive than **2** toward **1**, as shown in the model reactions using monofunctional analogues. This polyether synthesis is unusual in that it concurrently constructs both the polymer backbone and the functional side chains from three compounds.

Introduction

Polymers with functional groups in the side chains are usually synthesized by one of two methods,[2] either by grafting or by polymerization of monomers containing a functional group in the side chain. We have recently reported the simultaneous construction of a polymer backbone and functional side chains from three compounds as a novel approach to polymers with functional groups in the side chains. Thus, the reactions of aromatic dialdehydes (**1**), alkylene bis(trimethylsilyl) ethers (**2**), and allyltrimethylsilane (**3**) take place in the presence of catalytic amounts of triphenylmethyl (trityl) perchlorate to yield polyethers with allyl side chains (Scheme 1).[3] Furthermore, the three-component polycondensation of **1**, **3**, and trialkylsilane instead of **2** yields polyethers with arbitrary amounts of allyl side chains according to the feed ratios of **3** and trialkylsilane.[4]

Since the polyether backbone was produced from **1** and **2** and the side chains were introduced from **3** in the reaction of **1**, **2**, and **3**, use of other silyl nucleophiles instead of **3** would yield polyethers with other functional side chains. In this paper is described the three-component polycondensation of **1**, **2**, and cyanotrimethylsilane (**4**), which simultaneously constructs a polyether backbone and cyano side chains (Scheme 1). The polyethers with the cyano groups are expected to have the following two features. First, a side reaction where cleavage of the ether linkage of polyethers followed by a Friedel−Crafts reaction occurred would be depressed. In the three-component polycondensation of **1**, **2**, and **3** or trialkylsilane[5] at ambient temperature, the ether linkages of polyethers were cleaved by trityl cation to generate benzylic cations, which underwent electrophilic substitution of the aromatic protons to afford a cross-linked polymer. Introduction of the cyano group into the benzylic position would make the benzylic cation generated by the cleavage of the ether linkage unstable, so that the ether linkage would not be cleaved. Second, intramolecular charge transfer between the ether linkage and the cyano group would be expected. Since the cyano group is a strong electron-withdrawing group, charge transfer from the lone pair electrons on the oxygen of ether linkage to the cyano group could take place, and interesting physical properties might result.

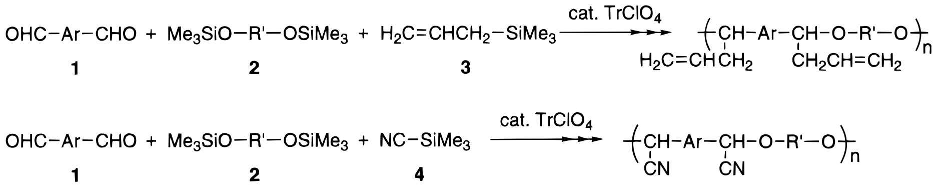
Results and Discussion

Model Reaction. The three-component coupling reactions of aldehydes, alkoxytrimethylsilanes, and **4** have not been reported, although similar reactions of aldehydes, alkoxytrimethylsilanes, and trialkylsilanes[6] or **3**[7] are known, where unsymmetrical ethers and homoallyl ethers were obtained, respectively. Accordingly, the reaction of benzaldehyde (**5**), 1-octyl trimethylsilyl ether (**6a**), and **4** was carried out in the presence of a catalytic amount of Lewis acid as a model reaction of polymerization. Into a solution of **5**, **6a**, and 5 mol % of trityl perchlorate ($TrClO_4$) or trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) in CH_2Cl_2 was slowly added a solution of **4** in CH_2Cl_2 at room temperature, and the mixture was stirred for 1 h to yield the desired three-component coupling product **7a** in high yields irrespective of Lewis acids (Scheme 2, Table 1). It should be noted that the yields of **7a** hardly changed for 24 h even at room temperature. In the reaction of **5** with 2 equiv of dimethylphenylsilane in the presence of a catalytic amount of $TrClO_4$ at room temperature, the desired dibenzyl ether was obtained quantitatively in 1 h, but its yield decreased to less than 50% after 24 h.[8] The observed decrease in yield was caused by the fission of the ether linkage of the product with $TrClO_4$ to generate benzyl cation, followed by the electrophilic substitution of the phenyl group (Friedel−Crafts reaction).[5] Consequently, no decrease of the yield of **7a** in the reaction of **5**, **6a**, and **4** indicates that the undesirable Friedel−Crafts reaction would not occur in the polymerization of **1**, **2**, and **4**, as previously described.

Polymerization Conditions. The addition methods of the reagents were first studied by the polymerization of isophthalaldehyde (**1a**), 1,8-bis(trimethylsiloxy)octane

S0024-9297(97)01544-1 CCC: $15.00

Scheme 1



Scheme 2

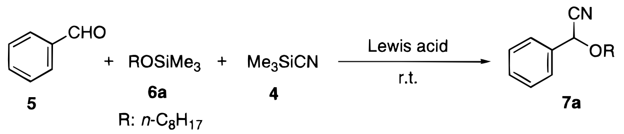


Table 1. Reaction of 5, 6a, and 4[a]

catalyst[b]	time, h	yield of **7a**, %[c]
$TrClO_4$	1	92
	24	97
Me_3SiOTf	1	98
	24	91

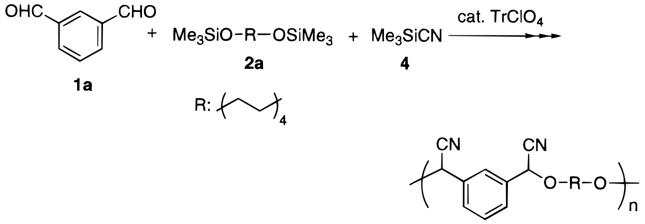
[a] The reaction was carried out in CH_2Cl_2 ($[\mathbf{5}]_0 = [\mathbf{6a}]_0 = [\mathbf{4}]_0 =$ 0.33 M) at 25 °C for 1 h. [b] 5 mol %. [c] Determined by ^1H NMR using internal standard (1,1,2,2-tetrachloroethane).

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

reaction temp, °C	time, h	M_n[b]	M_w/M_n[b]	polymer composition[c] **1a**:**2a**:**4**
−23	3	9000	1.39	25:25:50
	24	7800	1.37	25:25:50
0	0.25	11000	1.48	25:25:50
	0.50	11000	1.40	25:25:50
	1	11000	1.45	25:25:50
	3	11000	1.45	25:25:50
	6	11000	1.47	25:25:50
	24	12000	1.70	25:25:50
25	0.25	12000	1.59	25:25:50
	0.50	12000	1.57	25:25:50
	1	12000	1.59	25:25:50
	3	12000	1.41	25:25:50
	6	13000	1.52	25:25:50
	24	13000	1.63	25:25:50
	144	15000	1.70	25:25:50

[a] The polymerization was carried out with 10 mol % of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = 0.50$ M, $[\mathbf{4}]_0 = 1.0$ M). [b] Estimated by GPC based on polystyrene standards in DMF. [c] Estimated by ^1H NMR.

Scheme 3



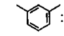
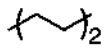
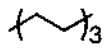
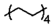
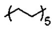
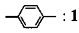
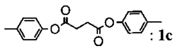
(**2a**), and **4**. The reactions were carried out in CH_2Cl_2 at ambient temperature by the addition of **4** into the mixture of **1a**, **2a**, and $TrClO_4$ (method A) or by the addition of **1a** into the mixture of **2a**, **4**, and the catalyst (method B). The order of addition of reagents dramatically affected polymer formation. Thus, method A yielded the desired polyether consisting of **1a**, **2a**, and **4** with a molar ratio 1:1:2, and the number-average molecular weight (M_n) was 13 000. On the other hand, no polymer was obtained and only a small amount of **2a** was recovered by method B. The ^1H NMR spectra of the product by method B showed the characteristic signal of the benzylic proton of cyanohydrin trimethylsilyl ether at δ 5.60 ppm, implying that the reaction of **1a** with **4** could also take place without the participation of **2a**. Other catalysts, Me_3SiOTf and trimethylsilyl iodide (Me_3SiI), were also used in the polymerization by method A. However, the M_n of polymers was lower than that of the polymer obtained with $TrClO_4$.

The polymerizations of **1a**, **2a**, and **4** by method A were carried out at −23 to +25 °C. The M_n, molecular weight distributions (M_w/M_n), and polymer compositions with time are summarized in Table 2. The polymerization proceeded homogeneously at −23 to 25 °C to yield quantitatively polymers consisting of **1a**, **2a**, and **4** with a molar ratio 1:1:2 (Scheme 3). The M_n hardly increased with time in 24 h at any polymerization temperature, but increased with temperature; the M_n of polymers obtained at ambient temperature were slightly higher than those at 0 °C. It should be noted that the increase of the M_n of polymer in the polymerization at ambient temperature for 6 days without the formation of cross-linked polymer was distinct from the polymerization behaviors of **1**, **2**, and **3**[3] or trialkylsilane, where M_n decreased and cross-linked polymer was obtained at room temperature.[5] This result also showed that the cleavage of the ether linkage was depressed in the polymerization of **1**, **2**, and **4**.

The IR spectrum of the polymer obtained from **1a**, **2a**, and **4** showed the characteristic absorption of a cyano group at 2254 cm^{-1} and of an ether linkage at 1086 cm^{-1}. The carbonyl group absorption around 1700 cm^{-1} was not observed. The ^1H NMR spectrum of polymer showed the signal assignable to the benzyl methine proton on a carbon between the cyano group and the ether linkage at δ 5.30 and 5.27, the signals of the aromatic protons of **1a** at δ 7.59−7.46, and the aliphatic protons of **2a** at δ 3.83−3.54, 1.80−1.50, and 1.50−1.20. On the basis of the signal intensities of aromatic protons, aliphatic protons, and the cyano group-substituted methine proton, the molar ratio of **1a**, **2a**, and **4** was determined to be 1:1:2. In the ^{13}C NMR spectrum, the signal corresponding to the cyano group at δ 117.1 and the signal corresponding to the benzyl carbon adjacent to an ether linkage at δ 70.5 were observed besides the signals assigned to the aromatic and aliphatic carbons derived from the **1a** and **2a** units, respectively. When the signal intensities of the aromatic carbons, the aliphatic carbons, and the cyano carbons were measured with the ^{13}C NMR NNE mode, the molar ratio of **1a**, **2a**, and **4** was also 1:1:2. These spectra of the polymer are consistent with the structure in Scheme 3.

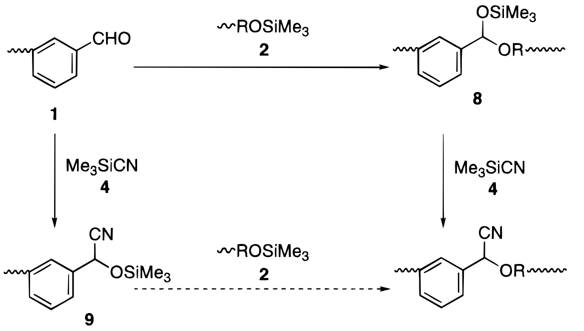
Polymerization of a Variety of 1, 2, and 4. According to the results above, a variety of **1**, **2**, and **4** were polymerized in the presence of 10 mol % of $TrClO_4$ in CH_2Cl_2 at 25 °C for 24 h (Table 3). The polymerizations proceeded quantitatively, but the yields are shown as the methanol-insoluble part after precipitation to

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

R in **1**	R' in **2**	yield, %[b]	M_n[c]	M_w/M_n[c]	polymer composition[d] **1**:**2**:**4**
 : **1a**		0 (100)[e]	1800[e]	1.42	[f]
1a		6	3100	3.09	25:25:50
1a		40	12000	2.05	25:25:50
1a	 : **2a**	38	13000	1.63	25:25:50
1a		6	7000	2.22	25:25:50
1a		0 (100)[e]	1500[e]	1.31	[f]
1a	 : **2b**	0 (80)[e]	2200[e]	1.65	[f]
 : **1b**	**2a**	39	4100	3.06	25:25:50
 : **1c**	**2a**	49	9200	2.28	25:25:50

[a] The polymerization was carried out with 10 mol % of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.33$ M, $[\mathbf{4}]_0 = 0.66$ M) at ambient temperature for 24 h. [b] Polymer insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards in DMF. [d] Estimated by ^1H NMR. [e] MeOH-soluble part. [f] Not determined.

Scheme 4

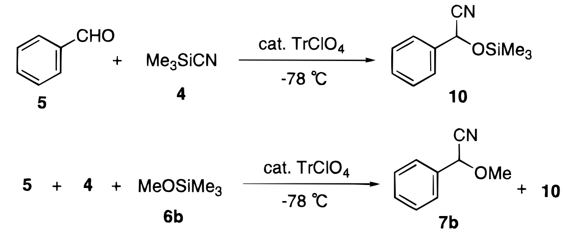


remove the condensation byproduct, hexamethyldisiloxane. When long carbon-chain primary **2**'s were used, polymers with higher M_n values were obtained and the molar ratios of **1**, **2**, and **4** were 1:1:2. Short carbon-chain primary **2**'s and secondary **2**'s resulted in low molecular weight polymers. The reactions with other dialdehydes such as terephthalaldehyde (**1b**) and dialdehyde **1c** containing the ester linkage yielded polymers with molar ratios of 1:1:2. Of the polymers obtained, only the polymer from **1a**, **2b**, and **4** showed an absorption attributable to a charge-transfer complex at $\nu_{max} = 315$ cm^{-1} in the UV spectrum.

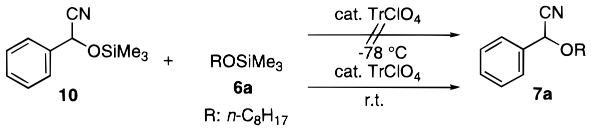
Polymerization Pathway. The proposed pathway of the polymerization by method A is shown in Scheme 4 according to the proposed mechanism of the polymerization of **1**, **2**, and **3**.[3] Initially, aldehyde **1** reacts with silyl ether **2** to give the hemiacetal-type compound **8**, which is subject to attack by cyanotrimethylsilane **4** with the subsequent elimination of hexamethyldisiloxane to form both the carbon–oxygen and carbon–carbon bonds. In both steps, trityl cation activates the formyl group and the hemiacetal moiety, respectively.

The production of oligomers having the cyanohydrin trimethylsilyl ether moiety by method B is accounted for by the occurrence of the reaction of **1** with **4** to give cyanohydrin trimethylsilyl ether **9**, which would not further react with **2**. This suggests that **4** reacts with **1** as fast or faster than **2** does, contrary to the reaction of **1**, **2**, and **3**.[3] The relative reactivities of **2** and **4** toward **1** and the reactivity of **9** toward **2** were confirmed by model reactions using monofunctional compounds. The reaction of benzaldehyde **5** with **4** was carried out at −78 °C in the presence of 5 mol % of $TrClO_4$. The reaction was completed in 5 min to yield cyanohydrin trimethylsilyl ether **10** quantitatively. In the reaction of **5**, **4**, and methoxytrimethylsilane (**6b**) by method B, the conversions of **5** and **4** attained 100% in 5 min, while about 30% of **6b** was consumed in that time. The products were **7b** and **10** (Scheme 5). These results indicate that cyanotrimethylsilane **4** reacts with aldehyde **5** faster than alkoxysilane **6b** does. Furthermore, **10** obtained from the reaction of **5** and **4** did not react with **6b** at −78 °C for 1 h, and **10** was recovered. Consequently, the reaction of **1** with **4** leading to **9** is considered to take place as a termination reaction to give low-molecular-weight oligomer in the polymerization of **1**, **2**, and **4** by method B.

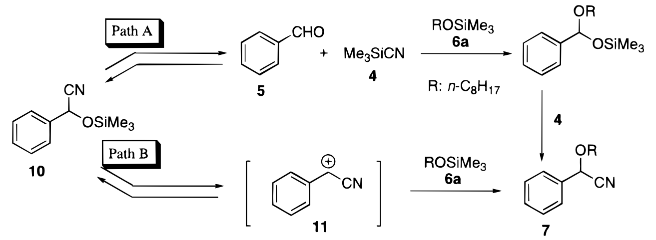
Scheme 5



Scheme 6



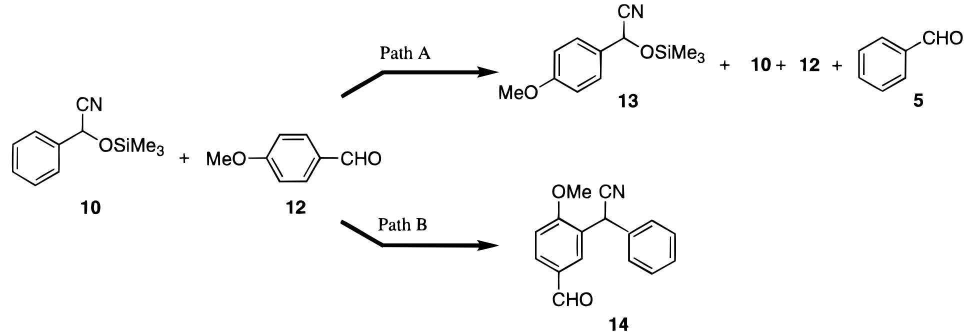
Scheme 7



However, the reaction of **10** with **6a** slowly proceeded at room temperature for 1 h to yield **7a** in 20% yield (Scheme 6). This result may be responsible for increase of the M_n of polymer with temperature in the polymerization of **1**, **2**, and **4** by method A. Thus, a small amount of end group **9** formed, even if it were by method A, could react with the siloxy end group at room temperature to form the ether linkage and increase the M_n of polymer.

Two alternative mechanisms for the reaction of **10** with **6a** at room temperature might be proposed, with the first one based on the regeneration of aldehyde **5** and **4**, followed by the successive reaction of **5** with **6a** and **4** (path A in Scheme 7), and the second one based on the generation of benzylic cation **11**, which reacts with **6a** (path B in Scheme 7). Accordingly, the reaction of **10** with *p*-anisaldehyde **12** was carried out in the presence of catalytic amount of $TrClO_4$. If the reaction proceeds through path A, cyanohydrin trimethylsilyl ether **13** from **12** would be formed as well as **10**, **5**, and **12**. If path B were correct, the Friedel–Crafts product **14** would be produced because of the activated benzene ring of **12** toward electrophilic substitution. The reaction at ambient temperature for 1 h gave **14** in 19% yield with 80% of **12** being recovered. Consequently, the reaction of **10** with **6a** at room temperature seems to involve the generation of benzylic cation **11**. This result

Scheme 8



seems to be in conflict with the model reaction containing no Friedel–Crafts reaction described above. However, the observed difference is ascribed to the strong electron-donating methoxy group on the benzene ring of **12**.

Conclusion

The reaction of **1**, **2**, and **4** in the presence of a catalytic amount of $TrClO_4$ simultaneously constructs the polyether backbone and cyano side chains. The addition of **4** into the solution of **1**, **2**, and the catalyst was found to be important for the production of polymer. When **1** was added to the solution of **2**, **4**, and the catalyst, a cyanohydrin trimethyl silyl ether moiety was formed as an end group, and the reaction of the end group with **2** proceeded much slower even at ambient temperature to yield oligomer. The observed deference by the addition method is accounted for by the higher reactivity of **4** toward **1** compared **2**. Further work on the simultaneous construction of polymer backbone and functional side chains using other silyl nucleophiles is in progress.

Experimental Section

^1H NMR spectra were obtained on a JEOL FX-200 operating in the pulsed Fourier-transfer (FT) modes and a HITACHI R-24B, using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-200 operating in the pulsed FT modes, using TMS as an internal standard. IR spectra were recorded on a HITACHI 270–30. The number-average molecular weights (M_n) of polymers were measured with a TOSOH HLC-8020 gel permeation chromatography (GPC) unit (eluent, *N*,*N*-dimethylformamide (DMF); calibration, polystyrene standards) using four TSK-gel columns (two GMH_{XL} and two $G2000H_{XL}$). Conversions of **4**, **5**, and **6b** in model reactions were determined by Shimazu gas chromatography GC-14BF with chlorobenzene as an internal standard. Isolation of products in model reactions was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform) using JA1GEL-1H and 2H columns.

Isophthalaldehyde (**1a**) and terephthalaldehyde (**1b**) were 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.[5] 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;[5] 1,4-bis(trimethylsiloxy)cyclohexane was a cis and trans mixture, since the corresponding diol was also a cis and trans mixture. Cyanotrimethylsilane (**4**) was used as received. Triphenylmethyl (trityl) perchlorate ($TrClO_4$) was prepared from triphenylmethanol and 70% perchloric acid according to the reported procedure[5] and used without recrystallization. Dichloromethane (CH_2Cl_2) was distilled over P_2O_5.

Model Reaction of 5, 6a, and 4. A round-bottomed-flask equipped with a three-way stopcock was charged with $TrClO_4$ (9 mg, 0.025 mmol) and purged with argon, and dry CH_2Cl_2 (0.5 mL) was added to the flask via a syringe. When Me_3SiOTf was used, a solution of Me_3SiOTf (4.8 μL, 0.025 mmol) in dry CH_2Cl_2 (0.5 mL) was added to the flask, which was previously purged with argon. A solution of **5** (0.053 g, 0.5 mmol) and **6a** (0.101 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was slowly added at room temperature. After 5 min, a solution of **4** (0.050 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was added, and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with a few drops of triethylamine and concentrated in vacuo. Into the flask was added weighed 1,1,2,2-tetrachloroethane (about 0.5 mmol) as an internal standard, and the yield of **7a** was determined by ^1H NMR: ^1H NMR ($CDCl_3$) δ 7.65–7.17 (m, 5H), 5.24 (s, 1H), 3.82–3.49 (m, 2H), 1.48–1.12 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H).

Typical Procedure for Polymerization of 1, 2, and 4. A round-bottomed-flask equipped with a three-way stopcock was charged with $TrClO_4$ (34 mg, 0.1 mmol) and purged with argon. After the addition of dry CH_2Cl_2 (1.0 mL) and dissolving $TrClO_4$, a solution of **1** (1.0 mmol) and **2** (1.0 mmol) in CH_2Cl_2 (1.0 mL) was added at ambient temperature via a syringe. After this was stirred for 5 min, a solution of **4** (0.20 g, 2.0 mmol) in CH_2Cl_2 (1.0 mL) was added, and the reaction mixture was stirred for 24 h. The polymerization was terminated with methanol containing a small amount of ammonia, and the solution was poured into a large amount of methanol (60 mL). The precipitated orange-colored polymer was collected and dried in vacuo.

Polyether from 1a, Tetramethylene Bis(trimethylsilyl) Ether, and 4. IR (neat): 2920, 2248, 1071 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.53–7.26 (m, 4H), 5.30 and 5.27 (2s, 2H), 3.90–3.40 (br, 4H), 1.79 (bs, 4H). ^{13}C NMR ($CDCl_3$): δ 134.8, 129.9, 128.5, 125.9, 117.1, 70.5, 70.1, 26.0.

Polyether from 1a, Hexamethylene Bis(trimethylsilyl) Ether, and 4. IR (neat): 2920, 2260, 1083 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.59–7.26 (m, 4H), 5.27 (s, 2H), 3.83–3.55 (m, 4H), 1.88–1.55 (br, 4H), 1.42 (bs, 4H). ^{13}C NMR ($CDCl_3$): δ 134.9, 129.8, 128.4, 125.8, 117.1, 70.5, 29.1, 25.7.

Polyether from 1a, 2a, and 4. IR (neat): 2860, 2254, 1086 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.59–7.46 (m, 4H), 5.30 and 5.27 (2s, 2H), 3.83–3.54 (m, 4H), 1.80–1.50 (br, 4H), 1.50–1.20 (br, 8H). ^{13}C NMR ($CDCl_3$): δ 134.9, 129.7, 128.3, 125.8, 117.1, 70.6, 70.5, 29.2, 29.1, 25.8.

Polyether from 1a, Decamethylene Bis(trimethylsilyl) Ether, and 4. IR (neat): 2860, 2254, 1086 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.80–7.27 (m, 4H), 5.27 (s, 2H), 3.83–3.54 (m, 4H), 1.85–1.50 (br, 4H), 1.29 (bs, 12H). ^{13}C NMR ($CDCl_3$): δ 135.0, 129.9, 128.4, 125.9, 117.2, 70.8, 70.5, 29.5, 29.3, 26.0.

Polyether from 1b, 2a, and 4. IR (neat): 2926, 2260, 1092, 723 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.56 (s, 4H), 5.26 (s, 2H), 3.86–3.50 (m, 4H), 1.84–1.50 (br, 4H), 1.33 (bs, 8H). ^{13}C NMR ($CDCl_3$): δ 135.4, 127.8, 117.1, 70.6, 70.4, 29.3, 25.9.

Polyether from 1c, 2a, and 4. IR (neat): 2938, 2260, 1758, 1140, 732 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4 Hz, 4H), 5.23 (s, 2H), 3.84–3.50 (m, 4H), 3.00 (s, 4H), 1.80−1.50 (br, 4H), 1.32 (bs, 8H). ^{13}C NMR ($CDCl_3$): δ 170.5, 151.5, 131.6, 128.5, 122.2, 117.3, 70.4, 70.3, 29.2, 25.9.

Reaction of 5 with 4. A round-bottomed-flask equipped with a three-way stopcock was charged with trityl perchlorate (17 mg, 0.05 mmol) and purged with argon. After the addition of dry CH_2Cl_2 (0.5 mL) including weighed chlorobenzene as an internal standard, the flask was cooled to −78 °C, and a solution of **5** (0.106 g, 1.0 mmol) in CH_2Cl_2 (1 mL) was slowly added via a syringe. After this was stirred for 5 min, a solution of **4** (0.100 g, 1.0 mmol) in CH_2Cl_2 (1 mL) was added. After 5, 10, 15, and 60 min, the reaction mixture was sampled and the sample quenched with a few drops of triethylamine. The conversions of **5** and **4** were determined from their residual concentration measured by gas chromatography with chlorobenzene. **10:** ^{1}H NMR ($CDCl_3$) δ 7.45−7.25 (m, 5H), 5.50 (s, 1H), 0.23 (s, 9H).

Reaction of 5, 6b, and 4. A round-bottomed-flask equipped with a three-way stopcock was charged with trityl perchlorate (17 mg, 0.05 mmol) and purged with argon. After the addition of dry CH_2Cl_2 (0.5 mL) including weighed chlorobenzene as an internal standard, the flask was cooled to −78 °C, and a solution of **6b** (0.104 g, 1.0 mmol) and **4** (0.100 g, 1.0 mmol) in CH_2Cl_2 (1 mL) was slowly added via a syringe. After this was stirred for 5 min, a solution of **5** (0.106 g, 1.0 mmol) in CH_2Cl_2 (1 mL) was added. After 15, 30, 45, 60, and 180 min, the reaction mixture was sampled and the sample quenched with a few drops of triethylamine. The conversions of **5** and **4** were determined from their residual concentration measured by gas chromatography with chlorobenzene.

Reaction of 10 with 6a. A round-bottomed-flask equipped with a three-way stopcock was charged with trityl perchlorate (9 mg, 0.025 mmol) and purged with argon. Dry CH_2Cl_2 (0.5 mL) and a solution of **5** (0.053 g, 0.5 mmol) and **4** (0.050 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was successively added via a syringe. After this was stirred for 1 h, a solution of **6a** (0.101 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was added, and the reaction mixture was stirred for 1 h. The reaction mixture was quenched with a few drops of triethylamine and concentrated in vacuo. Into the flask was added weighed 1,1,2,2-tetrachloroethane (about 0.5 mmol) as an internal standard, and the yield of **7a** was determined by ^{1}H NMR.

Reaction of 10 with 12. A round-bottomed-flask equipped with a three-way stopcock was charged with trityl perchlorate (9 mg, 0.025 mmol) and purged with argon. Dry CH_2Cl_2 (0.5 mL) was added to the flask, which was cooled to 0 °C. A solution of **5** (0.053 g, 0.5 mmol) and **4** (0.050 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was successively added via a syringe. After this was stirred for 1 h, a solution of **12** (0.068 g, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was added, and the reaction mixture was stirred for 1 h. The reaction mixture was quenched with a few drops of triethylamine and concentrated in vacuo. Into the flask was added weighed 1,1,2,2-tetrachloroethane (about 0.5 mmol) as an internal standard, and the yield of **14** was determined by ^{1}H NMR. Friedel−Crafts product **14** was purified by preparative HPLC. IR (neat): 2260, 1698, 1602, 1515, 1026 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 10.0 (s, 1H), 7.91−7.87 (m, 2H), 7.65−7.45 (m, 5H), 6.99−6.92 (m, 1H), 5.50 (s, 1H), 3.84 (s, 3H).

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