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Reductive Polycondensation. Synthesis of Polyethers Consisting of One Unit from Dialdehydes and of Polyethers Consisting of Two Alternating Units from Dialdehydes and Alkylene Bis(trimethylsilyl) Ethers[1]

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ABSTRACT: Facile synthesis of polyethers of the type $(A{-}O)_n$ is achieved by triphenylmethyl (trityl) perchlorate-catalyzed reductive condensation of dialdehydes with triethylsilane, and the method was also extended to the synthesis of polyethers of the type $(A{-}O{-}B{-}O)_n$ by the reductive polycondensation of dialdehydes and alkylene bis(trimethylsilyl) ethers. The reductive polycondensation of isophthalaldehyde (**1a**) proceeded even at −50 °C to yield the polyether consisting of one unit derived from **1a**. Dialdehydes with weak electron-withdrawing groups such as ester, carbonate, and bromide also underwent the reductive polycondensation to yield the corresponding polyethers having such functional groups. Especially, bis(4-formylphenyl) succinate (**1b**) resulted in the polyether with the highest molecular weight of dialdehydes investigated. The reductive polycondensations of dialdehydes **1** and alkylene bis(trimethylsilyl) ethers **2** were carried out with dimethylphenylsilane to yield the polyethers consisting of alternating **1** and **2** units. Primary and secondary **2** were effective for obtaining polyethers of the type $(A{-}O{-}B{-}O)_n$ by the reductive polycondensation of **1** and **2**.

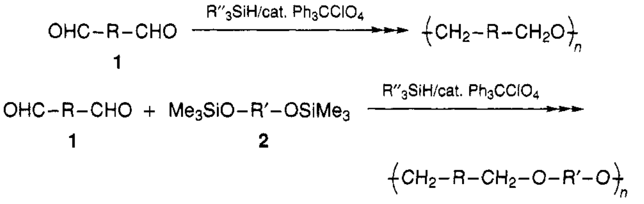
Introduction

Polyethers are one of the fundamental polymers in polymerization chemistry and in the field of material science. The preparation of polyethers is generally accomplished by ring-opening polymerization of cyclic ethers,[2] polycondensation of alkylene dihalides and sodium diphenoxides (Williamson ether synthesis),[3] polycondensation of bifunctional aromatic halides activated by electron-withdrawing groups and sodium diphenoxides,[4] and oxidative polymerization of phenol derivatives,[5] etc. Recently, the fluoride-catalyzed polycondensation of silylated diphenols and fluoroaromatics has been reported.[6] In general, polyethers of the type $(A{-}O)_n$ are obtained by the ring-opening polymerization of cyclic ethers and the oxidative polymerization of phenol derivatives, whereas polyethers of the type $(A{-}O{-}B{-}O)_n$ are obtained by the polycondensation of bifunctional nucleophilic and electrophilic monomers. However, there is no polyether synthetic method that yields both polyethers of the type $(A{-}O)_n$ by the homopolymerization and of the type $(A{-}O{-}B{-}O)_n$ by the copolymerization.

In recent organic chemistry, several methods have been reported for the preparation of ethers by the trialkylsilane reduction of carbonyl compounds or acetals by the promotion of protonic acids or Lewis acids under mild conditions.[7−14] Of these ether syntheses the triphenylmethyl (trityl) perchlorate-promoted reactions[10] gave both symmetrical ethers from carbonyl compounds (aldehydes and ketones) and unsymmetrical ethers from equimolar carbonyl compounds and alkoxytrimethylsilanes.

Accordingly, application of this chemistry to polymer synthesis would open the way to polyethers of the type $(A{-}O)_n$ by the reductive homopolymerization of bifunctional carbonyl compounds and of the type $(A{-}O{-}B{-}O)_n$ by the reductive copolymerization of the bifunctional carbonyl compounds and alkylene bis(trimethylsilyl) ethers. In the present article we study the reductive polycondensations of isophthalaldehyde (**1a**) with trialkylsilane under various conditions, and the condensations of a variety of dialdehydes **1** having functional groups are carried out under the optimal conditions to yield polyethers consisting of one unit. Furthermore, the condensations of dialdehydes **1** and alkylene bis(trimethylsilyl) ethers **2** are carried out to yield polyethers consisting of alternating **1** and **2** units.

These reductive polycondensations would serve as a complementary synthetic method for a broad variety of primary xylylene polyethers; the catalytic polycondensation of bis(trimethylsilyl) xylylene ethers reported in the preceding paper[15] are effective for the synthesis of secondary xylylene polyethers, but only low molecular weight primary xylylene polyethers are obtained along with a lot of cross-linked polymers.



$$\underset{\mathbf{1}}{OHC{-}R{-}CHO} \xrightarrow{R''_3SiH/cat.\ Ph_3CClO_4} {-}\!\!(CH_2{-}R{-}CH_2O)\!\!{-}_n$$

$$\underset{\mathbf{1}}{OHC{-}R{-}CHO} + \underset{\mathbf{2}}{Me_3SiO{-}R'{-}OSiMe_3} \xrightarrow{R''_3SiH/cat.\ Ph_3CClO_4} {-}\!\!(CH_2{-}R{-}CH_2{-}O{-}R'{-}O)\!\!{-}_n$$

Results and Discussion

Reductive Polycondensation of Isophthalaldehyde (1a). The reductive polycondensation of **1a** was carried out with 2 equiv of triethylsilane in the presence of 10 mol % of trityl perchlorate in dichloromethane. The polymers obtained were purified by precipitation in diethyl ether. In the polymerization at ambient temperature, the polymer was precipitated during reaction after 30 min, whereas the polymerization below 0 °C proceeded homogeneously even after 24 h. The results of the polymerization below 0 °C are summarized in Table 1. The average molecular weights of the polymers slightly increased with time at 0 °C, whereas they were almost constant at −20 and −50 °C.

The IR spectra of the polymers showed the characteristic absorption of an ether linkage at 1140 cm^{-1}, and an absorption attributable to a carbonyl group around 1700 cm^{-1} was hardly observed. Figure 1 shows the ^{1}H

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Table 1. Reductive Polycondensation of 1a with Triethylsilane[a]

temp, °C	time, h	yield, %[b]	$\bar{M}_n$[c]
0	0.25	52	6500
	1	50	7800
	2	42	8600
	6	40[d]	10400[e]
−20	0.25	58	8800
	1	63	8600
	2	53	7500
	6	55	8800
	24	72	8500
−50	0.25	65	9700
	1	67	10600
	2	70	10700
	6	63	10300
	24	54	11400

[a] The polymerization of **1a** was carried out with 2 equiv of triethylsilane in the presence of 10 mol % of trityl perchlorate in dichloromethane. [b] Polymer insoluble in diethyl ether. [c] Estimated by GPC based on polystyrene standard. [d] A small portion of the polymer became insoluble in DMF after the precipitation. [e] GPC showed a shoulder at the high molecular weight region.

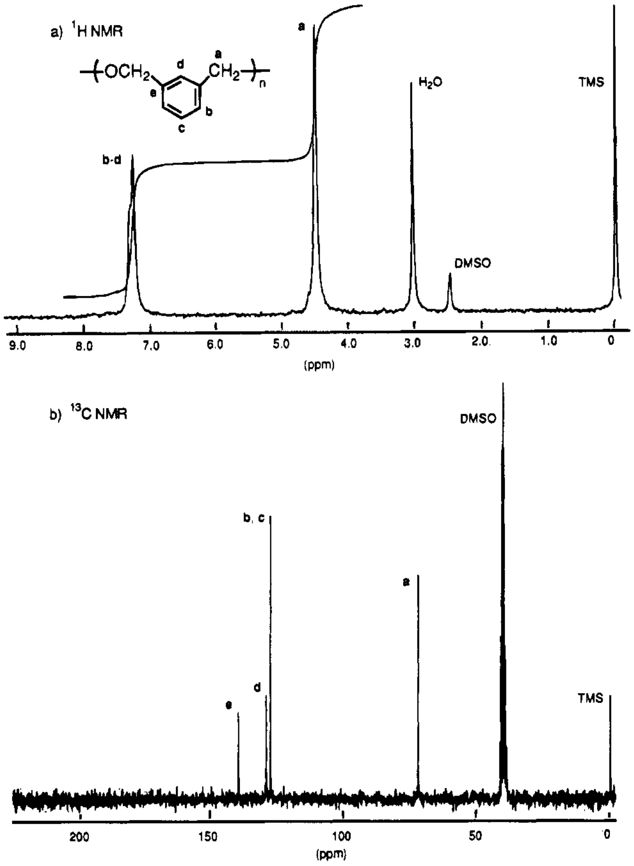


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of the polymer from **1a** in $(CD)_3SO$ at 80 °C.

and ^{13}C NMR spectra of the polymer with assignment for various signals. Only two signals corresponding to the aromatic protons at 7.23 ppm and corresponding to the benzyl methylene protons on a carbon atom adjacent to an ether linkage at 4.48 ppm were observed, and the intensity ratio of the two signals was 1:1. The ^{13}C NMR spectrum of the polymer (Figure 1b) shows the characteristic signals due to aromatic carbons at 138.5, 128.1, and 126.5 ppm and the signal corresponding to the benzyl carbon adjacent to an ether linkage at 71.6 ppm. The signal of the carbonyl carbon around 190 ppm was not observed. These spectral data indicate that **1a** was converted to polyether by triethylsilane reduction.

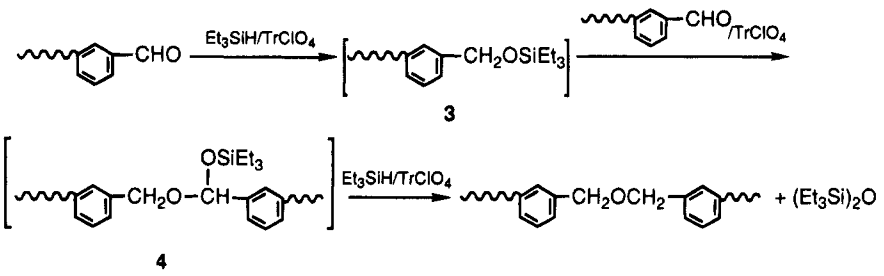
The polymerization process is considered in the following way, as shown in Scheme 1 according to the proposed mechanism in organic chemistry.[10] Alkoxysilane **3** is initially produced by reduction with triethylsilane, and **3** reacts with the formyl group faster than the triethylsilane does to give hemiacetal-type compound **4**, which is readily reduced with triethylsilane to form an ether linkage. In both steps, the trityl cation activates the formyl group and the hemiacetal moiety, respectively.

Precipitation of the polymer during the polymerization at ambient temperature may be interpreted in terms of cross-linking between aromatic rings by the trityl perchlorate-assisted Friedel−Crafts reaction: the ether linkage of the polyether was cleaved by trityl cations to generate benzyl cations, which underwent electrophilic substitution of aromatic protons. The IR spectrum of the precipitated polymer showed not only absorptions of a 1,3-disubstituted benzene ring at 905, 800, and 710 cm^{-1} but also absorptions attributable to a trisubstituted benzene ring at 890 and 750 cm^{-1}, although the IR spectra of soluble polymers showed only the absorptions of the 1,3-disubstituted benzene ring. In the model reaction of benzaldehyde with triethylsilane in the presence of trityl perchlorate at room temperature, the ^1H NMR spectrum showed a decrease of the benzylic protons of the ether linkage at 4.57 ppm and an increase of the methylene protons between aromatic rings at 3.90 ppm with reaction time, indicating that the ether formed was converted to the diphenyl methylene groups by the Friedel−Crafts reaction (Scheme 2). Therefore, the slight increase of the molecular weight of the polymer with time at 0 °C may be ascribed to some cross-linking by the Friedel−Crafts reaction, because the gel permeation chromatogram (GPC) of the polymer obtained after 6 h showed a discernible shoulder in the high molecular weight region, and a small portion of the polymer became insoluble even in *N,N*-dimethylformamide (DMF) after precipitation. Since these phenomena were not observed in the polymerization below −20 °C, the undesirable Friedel−Crafts reaction is thought to be almost depressed below −20 °C.

The almost constant molecular weight at −20 and −50 °C seems to imply that all the formyl groups reacted with triethylsilane or alkoxysilane **3** during 15 min, and the polymer ends became the alkoxysilyl groups. Actually, the signal of the formyl group was not observed in the ^1H NMR spectra of the polymer and ether-soluble part in the polymerization for 15 min even at −50 °C. Furthermore, the IR spectra of the polymers obtained after precipitation showed the weak characteristic absorption of a hydroxy group at 3500 cm^{-1}.

As mentioned in Scheme 1, alkoxysilane **3** reacts with the formyl group faster than the triethylsilane does in the polymerization; otherwise the dialdehyde **1** would be converted to only dialkoxysilane by triethylsilane reduction. Accordingly, the molecular weight of the polymer is considered to be strongly dependent on the rate of the reaction of **3** with the formyl group in comparison with the rate of the formation of **3** via triethylsilane reduction; if the latter became slower, the molecular weight would increase. The polymerization was then carried out with bulky silanes instead of triethylsilane at −20 °C for 1 h in order to decrease the rate of the formation of **3** with reduction (Table 2). However, the molecular weight did not dramatically increase, and further use of trihexylsilane, which is the most bulky silane, resulted in a decrease of both the molecular weight and the polymer yield. This may be because the rate of the reaction of **3**, which became bulky with bulky silane reduction, with the formyl group

Scheme 1



Scheme 2

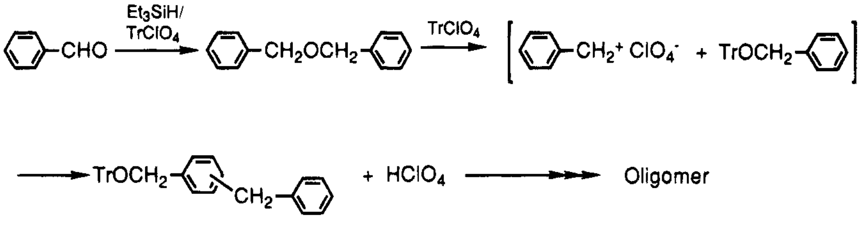


Table 2. Reductive Polycondensation of 1a with Some Silanes[a]

silane	yield, %[b]	$\bar{M}_n$[c]
Et_3SiH	63	8600
n-Hex_3SiH	24	5600
$PhMe_2SiH$	63	9200
Ph_3SiH	23[d]	9900

[a] The polymerization was carried out at −20 °C for 1 h. [b] Polymer insoluble in diethyl ether. [c] Estimated by GPC based on polystyrene standard. [d] The precipitation was repeated three times to remove hexaphenyldisiloxane.

also became slower.

Reductive Polycondensation of Various Dialdehydes 1. Since the reductive polycondensation of **1a** proceeded under mild conditions, various functional groups, which are unable to be introduced by Williamson ether synthesis, are expected to be introduced to polyethers. Etherifications of substituted benzaldehydes were first studied to learn possible functional groups introduced by the reductive etherification of aldehydes.

The reaction of *p*-anisaldehyde **5a** with triethylsilane was carried out in dichloromethane at −50 °C. Although **5a** was consumed quickly, the corresponding ether **6a** was not obtained at all. Since the ^1H NMR spectrum of the product showed the signal of the methylene protons between aromatic rings at 3.90 ppm, as described also in the preceding sections, similar Friedel−Crafts products shown in Scheme 2 were ascertained to be formed. The stable *p*-methoxybenzyl cation and the activated *p*-methoxyphenyl group would be responsible for the easily occurring Friedel−Crafts reaction.

In the reaction of *m*-nitrobenzaldehyde (**5b**) at 25 °C, the corresponding ether **6b** was obtained as well as *m*-nitrobenzyl alcohol and triphenylmethane, and Friedel−Crafts products were not formed. The production of *m*-nitrobenzyl alcohol and triphenylmethane implied that the formation of a hemiacetal-type intermediate like **4** or reduction of it with triethylsilane was slow, and hence the trityl cation as a catalyst was reduced by triethylsilane.

Additionally, the reaction of acetophenone (**5c**) was also carried out at 0 °C, resulting in the recovery of **5c** and formation of triphenylmethane. Consequently, weak electron-withdrawing groups are suitable for substituents of aldehydes, and ketones cannot be used in the reductive polycondensation.

On the basis of the model reactions the reductive polycondensations of dialdehydes **1b**−**1e** were carried out with triethylsilane (Table 3). The condensations of aldehydes having an ester or carbonate moiety, except for **1c**, yielded polyethers with high molecular weights compared to isophthalaldehyde (**1a**); lower yield and molecular weight in the condensation of **1c** may be ascribed to the low solubilities of **1c** and the polymer in dichloromethane. The higher molecular weights of the polymers from **1b** and **1d** compared to those from

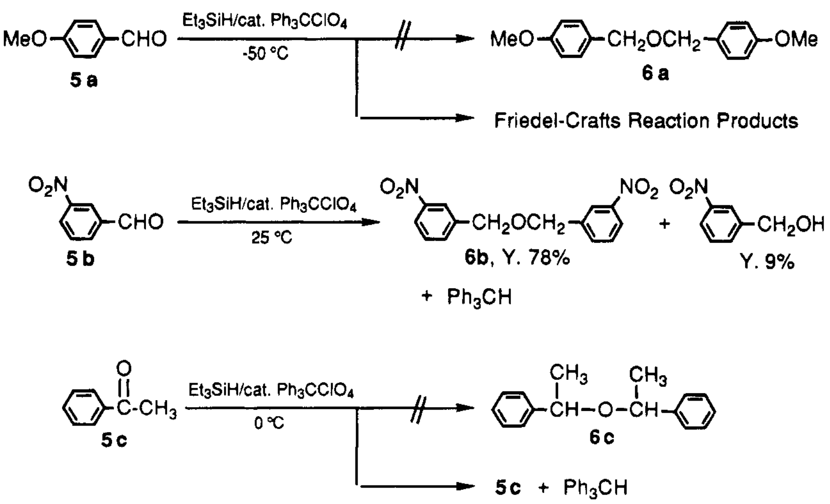
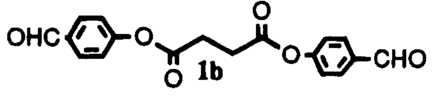
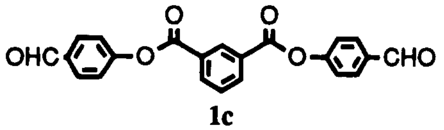
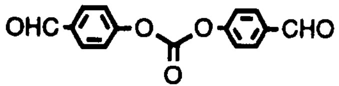
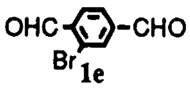


Table 3. Reductive Polymerization of 1 with Triethylsilane[a]

1	temp, °C	yield, %[b]	$\overline{M}_n$[c]
 1b	-20	61	38000
 1c	-20	17	4900
 1d	-20	97	23700
 1e	-20	69	5500
	0	58	6200

[a] The polymerization of 1 was carried out with 2 equiv of triethylsilane and 10 mol% of trityl perchlorate in CH_2Cl_2 for 2 h. [b] Polymer insoluble in diethyl ether. [c] Estimated by GPC based on polystyrene standard.

Scheme 3

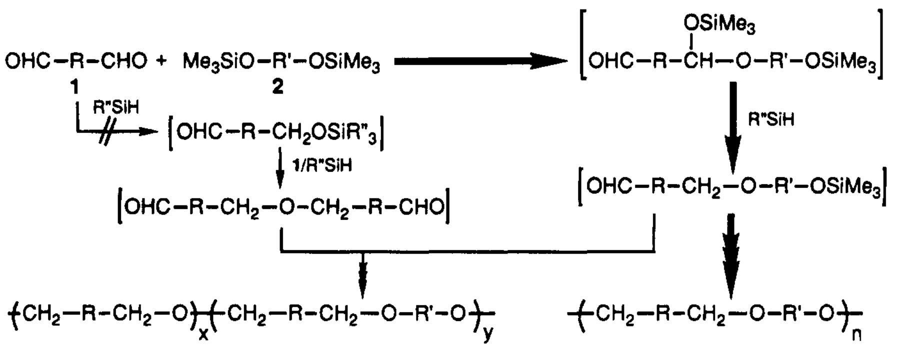
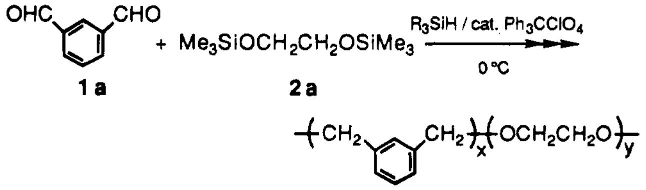


Table 4. Reductive Polycondensation of 1a and 2a with Some Silanes[a]

silane	yield, %[b]	polymer content[c] 1a:2a	$\overline{M}_n$[d]
Et_3SiH	41	60:40	7600
$PhMe_2SiH$	58	54:46	7600
n-Hex_3SiH	38	66:34	4700
$C_6H_{11}Me_2SiH$	54	56:44	6400
Ph_3SiH	18	54:46	11800

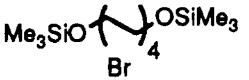
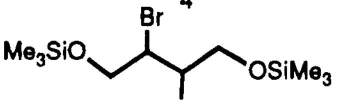
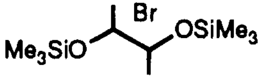
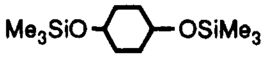
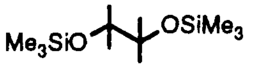
[a] The polymerization was carried out in CH_2Cl_2 at 0 °C for 24 h. [b] Polymer insoluble in hexane. [c] Estimated by ^1H NMR. [d] Estimated by GPC based on polystyrene standard.



1a are ascribed to depression of cleavage of the ether linkage because of the destabilizing of the benzylic cation generated by the cleavage by means of the electron-withdrawing groups on the benzene rings. It should be noted that these reductive polycondensations yield polyethers having ester, carbonate, and halogen substituents directly from dialdehydes having such groups without protecting methodology, contrary to Williamson ether synthesis. Incidentally, the reductive polycondensation of aliphatic dialdehydes could not be carried out because the aliphatic dialdehydes are generally unstable and can be obtained only as aqueous solutions.

Reductive Polycondensation of Dialdehydes 1 and Alkylene Bis(trimethylsilyl) Ethers 2. In order to prepare polyethers consisting of two alternating units by the reductive polycondensation of 1 and 2, 2 should react with 1 considerably faster than 1 is reduced with trialkylsilane. Otherwise, trialkylsilyl ether formed by the reduction of 1 would react with 1 to afford the polyether containing successive ether units derived from 1 (Scheme 3). When a bulky trialkylsilane is used, the reduction of 1 would become slow, resulting in an increase of the relative rate of the reaction of 1 with 2. Therefore, the polycondensations of 1a and ethylene bis(trimethylsilyl) ether 2a were carried out with various bulky trialkylsilanes at 0 °C (Table 4). When triethylsilane was used, the polyether rich in 1a was obtained. However, when bulkier silanes, except for trihexylsilane, were used, the polyethers consisted of 1a and 2a with a ratio of nearly 1:1. The structure would be alternating, as shown in Scheme 3, because 2a alone does not polymerize under these conditions. Of these bulky trialkylsilanes, dimethylphenylsilane was the most suitable for obtaining relatively high molecular weight polymer in good yield.

Table 5. Reductive Polycondensation of 1 and 2[a]

1	2	yield, %[b]	polymer content[c] 1:2	$\overline{M}_n$[d]
1a		47	54:46	7600
1a		59	51:49	11100
1a		52	53:47	5200
1a		31	55:45	4500
1a		73	50:50	9200
1a		14	*e*	4900
1b	**2a**	95	53:47	19100
	**2a**	71	54:46	8900

[a] The polymerization was carried out with 2 equiv of $PhMe_2SiH$ and 10 mol% of trityl perchlorate at 0 °C in CH_2Cl_2 for 24 h. [b] Polymer insoluble in hexane. [c]Estimated by ^1H NMR. [d]Estimated by GPC based on polystyrene standard. [e]Polymer was not soluble in common solvents for NMR.

On the basis of the above results, the reductive condensations of a variety of **1** and **2** were carried out with dimethylphenylsilane at 0 °C (Table 5). The condensations of **1a** with primary or secondary alkylene bis(trimethylsilyl) ethers yielded polyethers consisting of **1** and **2** with the ratio 1:1, whereas the condensation of **1a** with the tertiary ether did not proceed effectively, giving a polymer with poor solubility. The observed difference in the reaction with the tertiary **2** may be interpreted in terms of low nucleophilicity of the bulky tertiary **2** and of possible generation of carbocation from the tertiary **2** with trityl perchlorate, resulting in cross-linking between the phenyl groups by the Friedel–Crafts reaction. When the aldehyde **1b** with an electron-withdrawing group was used, higher molecular weight polymer was obtained, similarly to the reductive polycondensation of **1b** alone. Although terephthalaldehyde resulted in an insoluble polyether by its polycondensation, the copolymerization of it with **2a** yielded a soluble polyether.

Experimental Section

^1H NMR spectra were obtained on a JEOL FX-200 operating in the pulsed Fourier-transform (FT) modes and a Hitachi R-24B, using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Hitachi 270-30. Elemental analysis was performed on a Yanaco CHNcorder MT-2. The number-average molecular weights ($\overline{M}_n$) of the polymers obtained 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 (2 × GMH_{XL} and 2 × $G2000H_{XL}$).

Isophthalaldehyde and terephthalaldehyde were recrystallized from water and vacuum dried in a desiccator. Triethylsilane, trihexylsilane, cyclohexyldimethylsilane, dimethylphenylsilane, and triphenylsilane were used as received. Triphenylmethyl (trityl) perchlorate was prepared from triphenylmethanol and 70% perchloric acid according to the reported procedure[16] and used without recrystallization. Dichloromethane was purified by distillation over P_2O_5. Tetrahydrofuran (THF) was distilled over sodium just before use. Pyridine was purified by distillation over CaH_2.

Preparation of Bis(4-formylphenyl) Succinate (1b). Into the mixture of *p*-hydroxybenzaldehyde (6.10 g, 50 mmol) and triethylamine (7.7 mL, 55 mmol) in dry dichloromethane (140 mL) was added a solution of succinyl chloride (4.26 g, 27.5 mmol) in dichloromethane (20 mL) at 0 °C. After 43 h of stirring at room temperature, the mixture was washed with saturated $NaHCO_3$ solution and dried over $MgSO_4$. Upon evaporation of dichloromethane and recrystallization of the residue from hexane, **1b** was obtained in 42% yield: mp 87–90 °C; IR (KBr) 3068, 2936, 1756, 1688, 1600, 1500, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.10 (s, 2H), 8.05 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.4 Hz, 4H), 3.10 (s, 4H).

Preparation of Bis(4-formylphenyl) Isophthalate (1c).[17] Into the mixture of *p*-hydroxybenzaldehyde (6.10 g, 50 mmol) and triethylamine (7.7 mL, 55 mmol) in dry dichloromethane (140 mL) was added a solution of isophthaloyl dichloride (5.60 g, 27.5 mmol) in dichloromethane (20 mL) at 0 °C. After 96 h of stirring at room temperature, the mixture was washed with saturated $NaHCO_3$ solution and dried over $MgSO_4$. Upon evaporation of dichloromethane and recrystallization of the residue from methanol, **1c** was obtained in 50% yield: mp >300 °C; IR (KBr) 3068, 2868, 1740, 1688, 1504, 1424, 906, 802, 716 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.05 (s, 2H), 8.83 (s, 1H), 8.51 (d, J = 7.81 Hz, 2H), 8.04 (d, J = 7.79 Hz, 4H), 7.87 (t, J = 7.81 Hz, 1H), 7.59 (d, J = 7.79 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 191.1, 162.0, 154.0, 134.5, 133.9, 130.5, 129.5, 129.3, 122.1.

Preparation of Bis(4-formylphenyl) Carbonate (1d). A solution of triphosgene (1.20 g, 4.0 mmol) in dichloromethane (20 mL) was added into the mixture of *p*-hydroxybenzaldehyde (2.44 g, 10 mmol), NaOH (0.80 g, 20 mmol), and tetrabutylammonium bromide (0.032 g, 0.10 mmol) in water (20 mL) at ambient temperature. After 1 h of stirring at that temperature, the mixture was extracted with dichloromethane. The dichloromethane layer was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the crude product was recrystallized from cyclohexane to afford **1c** in 35% yield: mp 148–151 °C; IR (KBr) 3070, 2854, 1773, 1698, 1600, 1500, 813 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.05 (s, 2H), 8.00 (d, J = 9.0 Hz, 4H), 7.50 (d, J = 9.0 Hz, 4H).

Preparation of Bromoterephthalaldehyde (1e). $NaBH_4$ (2.95 g, 78 mmol) and dry THF (70 mL) were placed in a reaction flask under argon. A solution of bromoterephthalic acid (9.57 g, 39 mmol) in THF (40 mL) was added via dropping funnel. After 30 min of stirring at room temperature, a solution of BF_3OEt_2 (12.8 mL, 104 mmol) in THF (50 mL) was added and the mixture was stirred for 24 h. The reaction mixture was poured into water, extracted with ether, and then washed with water. After drying over $MgSO_4$, the ether layer was concentrated in vacuo to afford the crude bromo-*p*-xylene diol (9.07 g). In a round-bottomed flask was placed dry pyridine (122.4 mL, 1.5 mol), and chromium(VI) oxide (15.0 g, 150 mmol) was added in small portions. After 1 h of stirring, excess pyridine was removed by decantation, and the residue was washed with hexane by decantation several times. Upon filtration and drying of the precipitate, chromium(VI) oxide–pyridine complex ($CrO_3{\cdot}2Py$, 29.78 g) was obtained in 79% yield. The bromo-*p*-xylene diol (9.07 g), $CrO_3{\cdot}2Py$ (29.0 g), and dichloromethane (160 mL) were placed in a round-bottomed flask and refluxed for 18 h. Diethyl ether was added to the reaction mixture, and the ether layer was collected by decantation several times. Evaporation of the ether and column chromatography of the residue on SiO_2 yielded **1e** in 32% yield: mp 69–72 °C [lit.[18] 75 °C from water]; IR (KBr) 3072, 2928, 1708, 792, 546 cm^{-1}; ^1H NMR (acetone-d_6) δ 10.35 (s, 1H), 10.10 (s, 1H), 8.30–8.00 (m, 3H).

Preparation of Alkylene Bis(trimethylsilyl) Ethers 2. A round-bottomed flask equipped with a reflux condenser fitted with a $CaCl_2$ drying tube is charged with diol (50 mmol) and 1,1,1,3,3,3-hexamethyldisilazane (11.6 mL, 55 mmol). Chlorotrimethylsilane (0.64 mL, 5 mmol) was added, and the reaction mixture was refluxed for 3.5–5.5 h until consumption of the diol. After an excess of the hexamethyldisilazane was removed under reduced pressure, the residue was distilled to give **2**.[19] When pinacol was used, **2** was further purified by column chromatography on Al_2O_3 after distillation.

Ethylene Bis(trimethylsilyl) Ether 2a (99% yield): bp 53–55 °C/9 Torr [lit.[20] 165–166 °C]; IR (neat) 2956, 1254, 1101 cm^{-1}; ^1H NMR (CCl_4) δ 3.55 (s, 4H), 0.10 (s, 18H).

Octamethylene Bis(trimethylsilyl) Ether (98% yield): bp 70–76 °C/0.15 Torr [lit.[21] 73–74 °C/0.15 Torr]; IR (neat) 2932, 2860, 1252, 1098 cm^{-1}; ^1H NMR (CCl_4) δ 2.70–2.30 (m, 4H), 1.30 (bs, 12H), 0.00 (s, 18H).

2,3-Dibromo-1,4-butanediol Bis(trimethylsilyl) Ether[22] (90% yield): bp 88 °C/0.3 Torr; IR (neat) 1254, 1092, 590 cm^{-1}; ^1H NMR (CCl_4) δ 4.31 (t, 7.0 Hz, 2H), 3.84 (d, 7.0 Hz, 4H), 0.67 (s, 18H).

2,3-Butanediol Bis(trimethylsilyl) Ether (99% yield): bp 58–59 °C/8 Torr [lit.[23] 62–64 °C/12 Torr]; IR (neat) 2956, 2878, 1157, 1110 cm^{-1}; ^1H NMR (CCl_4) δ 3.70–3.25 (m, 2H), 1.30–0.80 (m, 6H), 0.00 (s, 18H).

1,4-Cyclohexanediyl Bis(trimethylsilyl) Ether (91% yield): bp 50 °C/0.3 Torr [lit.[24] mp 53–54 °C]; IR (neat) 2938, 2860, 1251, 1098 cm^{-1}; ^1H NMR (CCl_4) δ 3.75–3.15 (m, 2H), 1.95–0.85 (m, 8H), 0.00 (s, 18H).

Pinacol Bis(trimethylsilyl) Ether (5% yield): [lit.[25] bp 80 °C/12 Torr]; IR 2956, 1251, 1038 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (s, 12H), 0.00 (s, 18H).

Reductive Condensation of Benzaldehyde. A round-bottomed flask equipped with a three-way stopcock was charged with trityl perchlorate (0.068 g, 0.2 mmol) and purged with argon. A solution of benzaldehyde (0.212 g, 2.0 mmol) in dry dichloromethane (2 mL) was added at 0 or 25 °C via a syringe. After 5 min of stirring, a solution of triethylsilane (0.233 g, 2.0 mmol) in dichloromethane (2 mL) was added, and the reaction mixture was stirred at that temperature. The reaction was quenched with triethylamine, and the solvent was evaporated. The yield of dibenzyl ether was estimated by the ^1H NMR spectrum of the residue (0 °C and 5 min, 86% yield; 0 °C and 24 h, 71% yield; 0 °C and 48 h, 75% yield; 25 °C and 24 h, 20% yield): ^1H NMR (CCl_4): δ 7.49–6.95 (m, 10H), 4.58 (s, 4H).

Reductive Condensation of *m*-Nitrobenzaldehyde (5b). A round-bottomed flask equipped with a three-way stopcock was charged with trityl perchlorate (0.068 g, 0.2 mmol) and purged with argon. A solution of *m*-nitrobenzaldehyde (0.302 g, 2.0 mmol) in dry dichloromethane (2 mL) was added at 0 °C via a syringe. After 5 min of stirring, a solution of triethylsilane (0.233 g, 2.0 mmol) in dichloromethane (2 mL) was added, and the reaction mixture was stirred at 25 °C for 73 h. After the reaction was quenched with triethylamine, the reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on SiO_2.

Bis(*m*-nitrobenzyl) Ether (6b) (78% yield): IR (neat) 3094, 2920, 1527, 1350, 1131, 801, 729, 672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.32–7.50 (m, 8H), 4.75 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 148.4, 139.8, 133.4, 129.5, 122.8, 122.3, 71.5.

***m*-Nitrobenzyl Alcohol (9% yield):** IR (neat) 3394, 3094, 2920, 1527, 1350, 1131, 801, 729, 672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.32–7.50 (m, 4H), 4.90 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ 148.4, 142.9, 133.4, 132.6, 129.4, 122.4, 64.0.

Typical Procedure for Reductive Polycondensation of 1. A round-bottomed flask equipped with a three-way stopcock was charged with trityl perchlorate (34 mg, 0.1 mmol) and purged with argon. A solution of **1** (1.0 mmol) in dry dichloromethane (1 mL) was added at −20 °C via a syringe. After 5 min of stirring, a solution of triethylsilane (0.233 g, 2.0 mmol) in dichloromethane (1 mL) was added, and the reaction mixture was stirred for 2 h at −20 °C. The polymerization was terminated with ammoniacal methanol, and the solution was poured into a large amount of diethyl ether. The precipitated white polymer was collected and dried in vacuo.

Polyether from 1a: IR (KBr) 2880, 1140, 905, 800, 710 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.21–7.00 (bs, 4H), 4.48 (bs, 4H); ^{13}C NMR (DMSO-d_6) δ 138.5, 128.1, 126.5, 71.6. Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 78.86; H, 7.05.

Polyether from 1b: IR (KBr) 3310, 3034, 2874, 1758, 1605, 1509, 1134, 801 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 4H), 7.05 (d, J = 8.4 Hz, 4H), 4.55 (bs, 4H), 2.95 (bs, 4H).

Polyether from 1c: IR (KBr) 3070, 2860, 1743, 1701, 1602, 1509, 1080, 801 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.10–7.10 (m, 12H), 4.65–4.45 (m, 4H).

Polyether from 1d: IR (KBr) 3070, 2860, 1770, 1602, 1089, 816 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.40 (d, J = 8.6 Hz, 4H), 7.31 (d, J = 8.6 Hz, 4H), 4.57 (bs, 4H); ^{13}C NMR (DMSO-d_6) δ 151.3, 150.2, 136.8, 128.7, 120.8, 71.5.

Polyether from 1e: IR (KBr) 3304, 3058, 2848, 1092, 531 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55–7.10 (m, 3H), 4.80–4.45 (m, 4H).

Typical Procedure for Reductive Polycondensation of 1 and 2. A round-bottomed flask equipped with a three-way stopcock was charged with trityl perchlorate (34 mg, 0.1 mmol) and purged with argon. A solution of **1** (1.0 mmol) and **2** (1.0 mmol) in dry dichloromethane (2 mL) was added at 0 °C via a syringe. After 5 min of stirring, a solution of dimethylphenylsilane (0.272 g, 2.0 mmol) in dichloromethane (1 mL) was added, and the reaction mixture was stirred for 24 h at 0 °C. The polymerization was terminated with ammoniacal methanol, and the solution was poured into a large amount of hexane (30 mL). The precipitated white polymer was collected and dried in vacuo.

Polyether from 1a and 2a: IR (KBr) 3310, 3034, 2860, 1722, 1101, 792 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (bs, 4H), 4.60 (bs, 4H), 3.70 (bs, 4H).

Polyether from 1a and Octamethylene Bis(trimethylsilyl) Ether: IR (KBr) 3304, 3028, 2926, 1101, 891, 791, 699 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.15 (bs, 4H), 4.45 (bs, 4H), 3.60–3.10 (m, 4H), 2.00–0.95 (m, 12H).

Polyether from 1a and Dibromo-1,4-butanediol Bis(trimethylsilyl) Ether: IR (KBr) 2864, 1488, 1156, 1080, 846, 702, 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43 (bs, 4H), 4.68 (bs, 6H), 3.89 (d, J = 8.0 Hz, 4H).

Polyether from 1a and 2,3-Butanediol Bis(trimethylsilyl) Ether: IR (KBr) 3310, 1716, 1092, 921, 792, 702 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.25 (bs, 4H), 4.55 (bs, 4H), 3.00–2.15 (m, 2H), 1.55–0.85 (m, 6H).

Polyether from 1a and 1,4-Cyclohexanediyl Bis(trimethylsilyl) Ether: IR (KBr) 3454, 3028, 2932, 1080, 906, 786, 699 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.40–6.80 (m, 4H), 4.60–4.20 (m, 4H), 3.60–3.00 (m, 2H), 2.00–1.00 (m, 8H).

Polyether from 1b and 2a: IR (KBr) 3310, 3034, 2926, 1758, 1134, 849 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.45 (d, J = 8.8 Hz, 4H), 7.10 (d, J = 8.8 Hz, 4H), 4.55 (bs, 4H), 3.65 (bs, 4H), 2.95 (bs, 4H).

Polyether from Terephthalaldehyde and 2a: IR (KBr) 3448, 2860, 1719, 1095, 810 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.23 (bs, 4H), 4.48 (bs, 4H), 3.64–3.16 (m, 4H).

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