Synthesis of Polyethers of the Type $(A-O-B-O)_n$ via Insertion of Diol Bis(trimethylsilyl) Ethers into Polyethers of the Type $(A-O)_n$

Tsutomu Yokozawa,† Makoto Nishimori, Shigeo Mizukami, and Takeshi Endo*

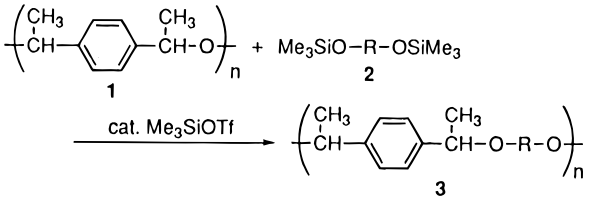
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan, and Department of Applied Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan

Received May 21, 1996

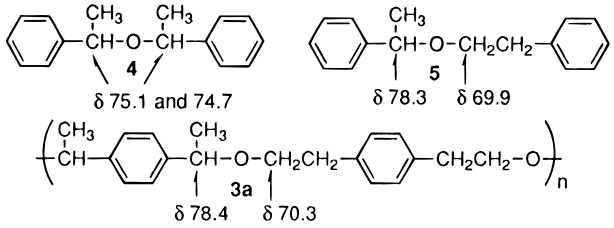
Revised Manuscript Received September 4, 1996

Copolymers with specifically desired properties can be synthesized by variations in the nature and relative amounts of the two monomer units in the copolymer product, where generally two monomers simultaneously have been polymerized. Recent advances in the insertion of monomers to the backbone of homopolymers afford another access to copolymers. For example, random copolymers are prepared by the insertion of epoxy compounds into polyesters,[1] by the insertion of cyclosiloxanes into polysiloxanes,[2] and by the insertion of acetylenes[3] or quinones[4] into polysilanes. Alternating copolymers, which are produced via complete insertion into all backbone linkage of homopolymers, are also synthesized by the insertion of isocyanides into oligosilanes,[5] by the insertion of ϵ-caprolactam into polycarbonates,[6] and by the insertion of thiiranes or oxiranes into polythioesters.[7]

We have recently reported the synthesis of poly(benzylic ether) **1** of the type $(A-O)_n$ by a catalytic polycondensation of bis(trimethylsilyl) xylylene ether, where one of the major problems is cleavage of the ether linkage of the polymer with the catalyst with elongation of reaction time.[8] However, Okuda and Yoshihara's observation[9] of montmorillonite-catalyzed conversion of dibenzyl ether into benzyl alkyl ether in the presence of alkyl alcohol suggested that the cleaved benzyl ether linkage of **1** could be converted into the benzyl alkyl ether linkage via insertion of an alkyl diol segment; this would be the first example of the insertion of monomers into polyethers. We wish to report our preliminary results on a new approach to polyethers **3** of the alternating copolymer type $(A-O-B-O)_n$ from the polyether **1** of the homopolymer type $(A-O)_n$ through the insertion of diol disilyl ether **2** into the polyether **1**.



The polyether **1** ($\bar{M}_n$ = 3200, $\bar{M}_w/\bar{M}_n$ = 1.46)[10] was prepared in situ by the reaction of α,α'-dimethylxylylene bis(trimethylsilyl) ether with 10 mol % of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) in diethyl ether at ambient temperature.[8] Into the reaction mixture was added 1,4-bis(2-(trimethylsiloxy)ethyl)benzene (**2a**) and 10 mol % of Me_3SiOTf, followed by stirring for 24 h at this temperature. The reaction was terminated with ammoniacal methanol, and the solution was poured into a large amount of methanol to yield a polymer ($\bar{M}_n$ = 4400, $\bar{M}_w/\bar{M}_n$ = 1.54)[10] in 20% yield.[11] To confirm the structure of the polymer obtained, model compounds, α-phenethyl ether (**4**) and α-phenethyl β-phenethyl ether (**5**), were prepared, and their ^{13}C NMR spectra were measured in $CDCl_3$. The carbon signals adjacent to an ether linkage of **4** were observed at 75.1 and 74.7 ppm as a diastereomeric mixture and the signals of **5** at 78.3 and 69.9 ppm. In the ^{13}C NMR spectrum of the polymer obtained, the carbon signals adjacent to an ether linkage were observed at 78.4 and 70.3 ppm, and the signals around 75 ppm were not observed. The comparison of the ^{13}C NMR spectra of the model compounds with that of the polymer indicated that the polymer did not contain the units of **1** but consisted of only the units of **3a**, that is, the polyether **1** of the type $(A-O)_n$ was reconstructed into the polyether **3a** of the type $(A-O-B-O)_n$ by the insertion of **2a** into the ether linkage of **1**.[12]



The insertion of a variety of compounds **2** into the polymer **1** was also carried out (Table 1).[13] The primary diol disilyl ethers effectively underwent insertion to yield the polyethers of the type $(A-O-B-O)_n$, although **2** with a long carbon chain resulted in contamination of a few $(A-O)_n$ units. When the secondary diol disilyl ethers were used, the insertion took place very slowly to afford the polymer containing a small amount of $(A-O-B-O)_n$ units, implying that the insertion into the polymer was strongly affected by the bulkiness of **2**.

As a model reaction, the ether **4** was reacted with bis(trimethylsiloxy)ethane (**2b**) and 15 mol % of Me_3SiOTf in ether at room temperature for 7 days. Surprisingly, however, the insertion of **2b** into **4** did not occur at all. Taking into account the presence of hexamethyldisiloxane in the insertion of **2** into the polyether **1** prepared in situ, the model reaction above was then carried out in the presence of 1 equiv of hexamethyldisiloxane for 6 days to yield the oxyethyleneoxy-inserted ether **6** in 31% yield (46% conversion). Consequently, hexamethyldisiloxane was ascertained to be required for the cleavage of the benzylic ether linkage with Me_3SiOTf in diethyl ether; the exact reaction mechanism remains unclear at present.[14]

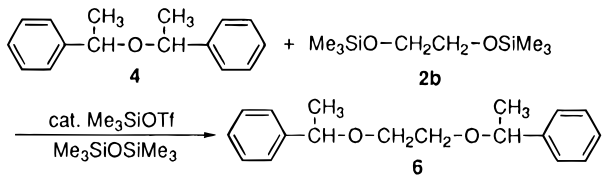
Table 1. Insertion of 2 into Polyether 1[a]

		3		
R of **2**[b]	$\bar{M}_n$ of **1**[c]	yield, %[d]	mol % of **2**[e]	$\bar{M}_n$[c]
1,4-$(CH_2CH_2)_2C_6H_4$[f]	3200	20	50	4400
$(CH_2)_2$	3000	11	50	2000
$(CH_2)_8$	2200	16	41	2000
$CH(CH_3)CH(CH_3)$	2600	20	g	3300
1,4-C_6H_{10}	3000	16	16	3400

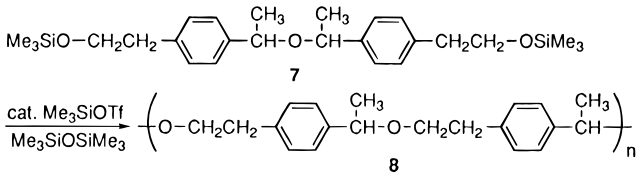
[a] Reaction was carried out in Et_2O at room temperature for 7 days. [b] Two equivalents. [c] Estimated by SEC based on polystyrene standards. [d] Polymer insoluble in MeOH. [e] Estimated by ^1H NMR. [f] One equivalent of **2** was reacted with **1** for 24 h. [g] Not determined.

† Kanagawa University.

S0024-9297(96)00751-6 CCC: $12.00



The formation of polyethers of the type $(A-O-B-O)_n$ from the polyether **1** of the type $(A-O)_n$ via insertion of **2** seems to be attributed to the rapid cleavage of the benzylic ether linkages compared to the benzylic alkyl ether linkages. To clarify this phenomenon, bis(trimethylsiloxy)benzylic ether **7** was treated with 10 mol % of Me_3SiOTf in the presence of hexamethyldisiloxane to yield polyether **8** ($\bar{M}_n = 730$, $\bar{M}_w/\bar{M}_n = 1.22$),[10] which would be formed by cleavage of the benzylic ether linkage, resulting in generation of the benzylic cation before attack of the siloxy group.[15]



In summary, the present work has demonstrated a new access to polyethers of the type $(A-O-B-O)_n$ from polyethers of the type $(A-O)_n$ by virtue of insertion of diol segment B. This system could serve as endowment of function into polyethers by using the diol segment B containing functional structures.

References and Notes

(1) Nishikubo, T.; Shimokawa, T.; Hirano, T.; Shiina, A. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2519.

(2) (a) Swint, S. A.; Buese, M. A. *Macromolecules* **1990**, *23*, 514. (b) Dvornic, P. R.; Govedarica, M. N.; Jovanvic, J. D.; Gerov, V. V. *Polym. Bull.* **1995**, *35*, 539.

(3) (a) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (b) Yamashita, H.; Tanaka, M. *Chem. Lett.* **1992**, 1547.

(4) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Macromolecules* **1993**, *26*, 2143.

(5) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899.

(6) Wurm, B.; Keul, H.; Höcker, H. *Macromolecules* **1992**, *25*, 2977.

(7) Kameyama, A.; Murakami, Y.; Nishikubo, T. *Macromolecules*, in press.

(8) Yokozawa, T.; Nishimori, M.; Endo, T. *Macromol. Chem. Phys.* **1996**, *197*, 1361.

(9) Okuda, Y.; Yoshihara, M.; Maeshima, T.; Fujii, M.; Aida, T. *Yukagaku* **1989**, *38*, 153.

(10) Number-average molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were determined by size exclusion chromatography (SEC) based on polystyrene standards in THF.

(11) IR (KBr) 3450, 2950, 2850, 1510, 1440, 1365, 1100, 1060, 1020, 835 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.10 (br, 8H), 4.36 (q, 2H), 3.45 (t, 4H), 2.74 (t, 4H), 1.37 (d, 6H); ^{13}C NMR (acetone-d_6) δ 114.2, 138.0, 129.6, 126.9, 78.4, 70.3, 37.0, 24.2.

(12) The polymer in the methanol-soluble part contained the polyether **1**; therefore, all of **2a** did not undergo insertion into **1**.

(13) For effective insertion of **2** into polyether **1**, 2 equiv of **2** was used, which may be responsible for the decrease of the molecular weight of the polyethers of the type $(A-O-B-O)_n$.

(14) The observation that the insertion of **2b** into **4** took place with thioanisole implies that the cleavage of the benzylic ether linkage with Me_3SiOTf seems to require the compound being more nucleophilic than diethyl ether and alkoxytrimethylsilane.

(15) The structure of **8** was ascertained by the ^{13}C NMR spectra of the polymer showing the signals on a carbon adjacent to an ether linkage at 78.5 and 70.1 ppm, compared to the signal of an ether linkage of **7** at 75.0 ppm.

MA960751E