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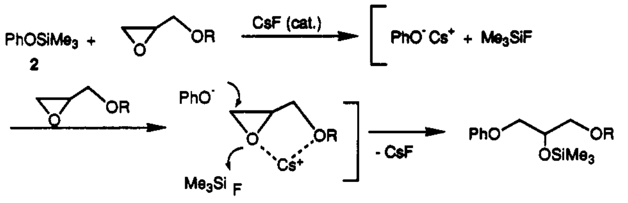
Controlled Polymerization of Alkyl Glycidyl Ether by a New Catalyst System, Aryl Silyl Ether/CsF

Controlled polymerization of vinyl monomers has been potentially developed by way of anionic,[1] cationic,[2] or group-transfer polymerization.[3] However, reports on the controlled ring-opening polymerization of epoxides are restricted for few examples such as the anionic polymerization of unsubstituted epoxide[4] or the immortal polymerization of substituted epoxides by metalloporphyrins.[5]

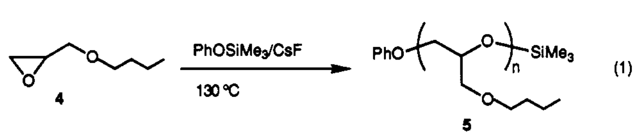
Very recently we have succeeded in the novel ring-opening reaction of glycidyl phenyl ether (**1**) by trimethyl silyl phenoxide (**2**) catalyzed by cesium fluoride (CsF) to produce the trimethyl silyl ether of secondary alcohol.[6] Adducts of **2** and various glycidyl-type epoxides were obtained by selective ring opening in high yield. However, alkyl- or haloalkyl-substituted epoxides were unreactive. Thus, the epoxides that could be activated through coordination to the cesium cation are susceptible for ring opening (Scheme I). This reaction seems to be attractive for its applicability to polymer synthesis, because the product again carries the silyl ether function that might be attacked by a fluoride ion.

Scheme I



We describe here the controlled polymerization of glycidyl ethers by a new catalyst system to produce polyethers with a narrow molecular weight distribution, developed from the newly found ring-opening reaction of epoxides with aryl silyl ethers.

Polymerization of some glycidyl ethers was carried out by use of catalytic amounts of silyl ether **2** and CsF. Although glycidyl ether **1** or glycidyl methacrylate (**3**) did not polymerize even under severe conditions, *n*-butyl glycidyl ether (**4**) gave a polyether (**5**) with a narrow molecular weight distribution (1.15) in high conversion at 130 °C for 30 min in the evacuated sealed tube (Table I; eq 1). Glycidyl methyl ether (**6**) also gave a good result. Thus, alkyl glycidyl ethers which might be activated potentially through effective coordination to the cesium ion were polymerized by this new catalyst system.



The polymerization of glycidyl ether **4** by silyl ether **2** (2 mol %) and CsF (1 mol %) at 130 °C proceeds rapidly as shown in Figure 1. Figure 2 demonstrated that a good correlation was obtained between the number-average molecular weight of polymer ($\bar{M}_n$) and conversion under various reaction conditions, and the molecular weight distribution was kept narrow throughout the polymerization.

Control of molecular weights was examined by use of this new catalyst system (Figure 3). $\bar{M}_n$ of polyether **5** showed a fair proportionality with the molecular weight calculated by the mole ratio of consumed monomer to silyl ether ($\bar{M}_{ncal}$) as shown in Figure 4, whereas $\bar{M}_n$ did not depend on the molar ratio of monomer to CsF. These results indicate that silyl ether **2** participates as an initiator and CsF as a catalyst in this living-type polymerization. On the other hand, polymerization by cesium phenoxide resulted in insufficient control for both the degree of polymerization and molecular weight distribution (Figure 4).

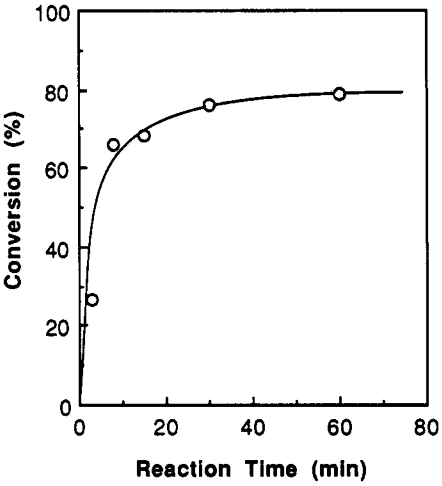


Figure 1. Polymerization of glycidyl ether **4** catalyzed by **2**/CsF (2/1 mol %) at 130 °C.

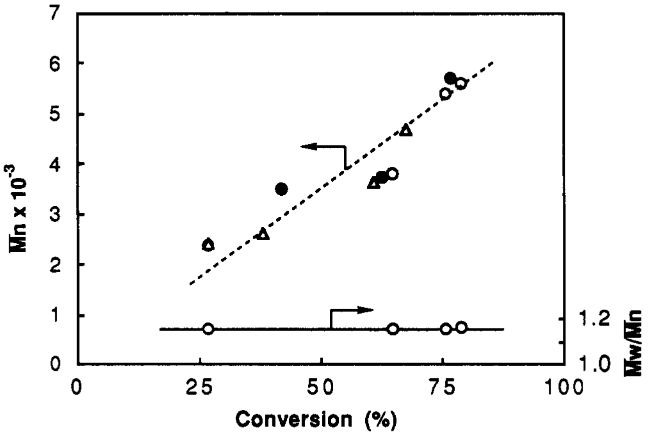


Figure 2. Plots of $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ vs conversion in the polymerization of glycidyl ether **4**: (○) 130 °C, PhOSiMe$_3$/CsF (2/1 mol %); (●) 130 °C, PhOSiMe$_3$/CsF (2/2 mol %); (△) 115 °C, PhOSiMe$_3$/CsF (2/2 mol %).

The structure of polyether **5** was confirmed by oligomerization. The oligoether **5** obtained by reaction of **4** with 10 mol % of silyl ether **2** and 1 mol % of CsF at 130 °C for 30 min has a molecular weight distribution of 1.15 and a $\bar{M}_n$ of 690. The ^{1}H NMR spectra of the oligomer **5**[8] in CCl$_4$ showed terminal phenoxy and silyloxy groups at 0.06 and 7.8–8.3 ppm, respectively, with integral values corresponding to the degree of polymerization.

A possible mechanism for polymerization is schematically represented in Scheme II. Path a is the group-transfer-type mechanism where the alkyl silyloxy group is once formed and activated for the propagation. Path b is the modified anionic polymerization mechanism where the polymerization was propagated by the attack of alkoxide anion to monomer and terminated by attack of the anion to trimethyl silyl fluoride to form the polymer with the terminal silyloxy group. In the latter path, termination would be significant only in the final stage of the polymerization; that is, the monomer is almost consumed, and the chain transfer or other termination reactions observed in the usual anionic polymerization[8] would be minimized by this termination.

In order to discuss the reaction mechanism, silyl ether **7** was synthesized as the end-group model.[9] When **7** was used as an initiator for the CsF-catalyzed polymerization

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Table I
Polymerization of Glycidyl Ethers by Various Catalyst Systems

epoxide	catalyst, mol %	temp, °C	time, min	conv, %	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]
1	2/CsF, 2/1	150	210	8		
3	2/CsF, 2/1	150	210	5		
4	2/CsF, 2/1	150	210	83	4750	1.19
4	2, 2	150	210	0		
4	2, 2	150	210	0		
4	2/CsF, 2/1	130	30	76	5390	1.15
6	2/CsF, 2/3	130	120	87	2520	1.19
4	2/CsF, 5/2	130	30	84	2490	1.10
4	2/CsF, 10/1	130	30	60	1040	1.13
4	2/CsF, 20/10	130	30	42	500	1.12
4	PhOCs, 2	130	30	100	5330	1.30
4	7/CsF, 2/1	130	30	8		

[a] Evaluated by GPC analysis based on polystyrene.

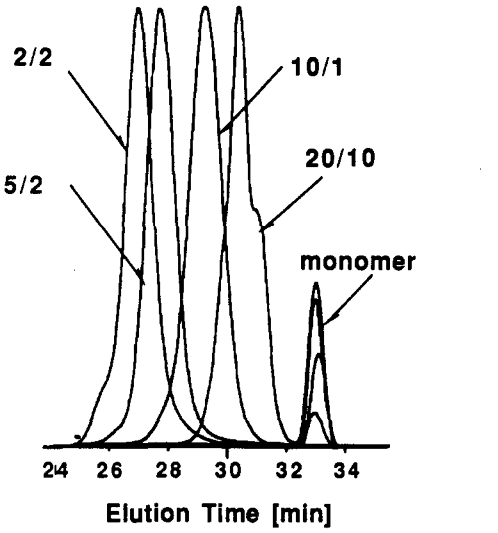


Figure 3. GPC curves of the products in the polymerization at 130 °C for 30 min monitored by RI detector. The numbers in the figure indicate the amount of catalysts **2**/CsF (in mol %).

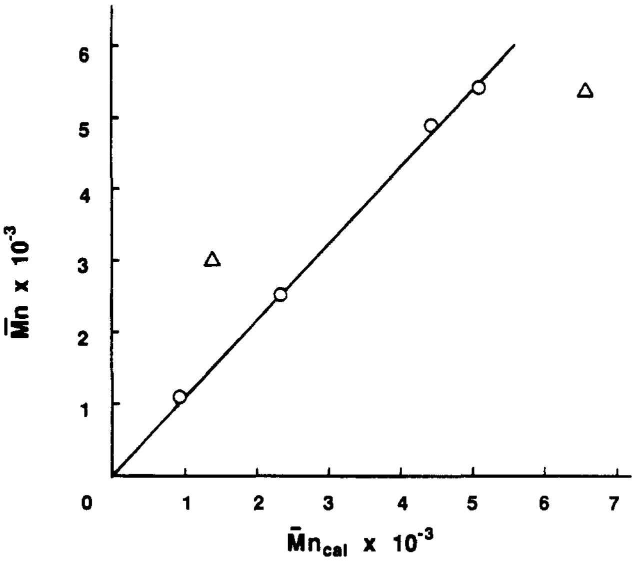
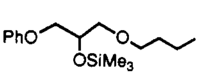


Figure 4. Plots of $\bar{M}_n$ vs $\bar{M}_{n,cal}$ for polyethers polymerized by PhOSiMe$_3$ (○) or PhOCs (△).



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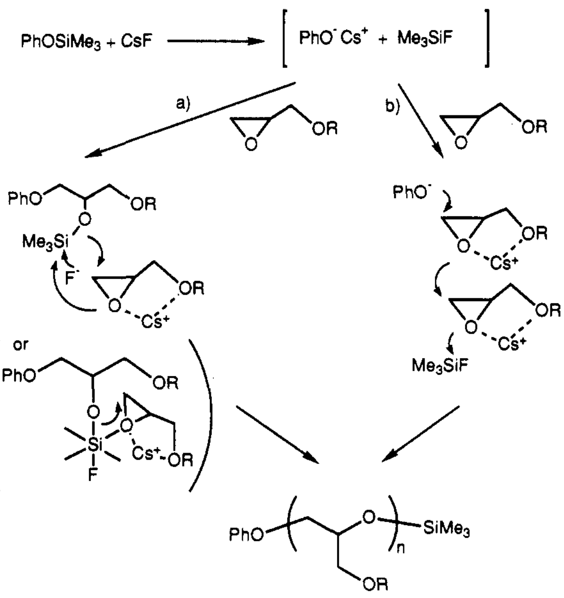
Scheme II



of **2** under the same reaction conditions, the conversion remained very low (Table I). Therefore, the polymerization is suggested to proceed in path b.

In conclusion we could present the first example of a ring-opening polymerization by a silyl ether/CsF system to result in the molecular weight controlled polymerization of substituted epoxides. These findings have potential prosperity in view of both the methodology and the property of products.

References and Notes

(1) Szwarc, M. *Adv. Polym. Sci.* **1983**, *178*, 1168.
(2) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693.
(3) Webster, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(4) Price, C. C.; Carmelite, D. D. *J. Am. Chem. Soc.* **1966**, *88*, 4039.
(5) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162.
(6) Nambu, Y.; Endo, T. *Tetrahedron Lett.* **1990**, *31*, 1723.
(7) Simons, D. M.; Verbanc, J. J. *J. Polym. Sci.* **1960**, *44*, 303.
(8) ^{1}H NMR spectra of **5** (CCl$_4$): δ 0.06 (Me$_3$SiO), 0.8–1.9 (CH$_3$CH$_2$CH$_2$), 3.3–4.1 (OCH$_2$CHO, CH$_2$O), 7.8–8.3 (Ph).
(9) Silyl ether **7** was prepared by the CsF-catalyzed ring opening of **4** with **2** and purified by column chromatography (silica gel column, eluent CH$_2$Cl$_2$) and distillation. Bp: 114–115 °C (0.23 mmHg). The structure was confirmed by ^{1}H NMR

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