Metal-Free Ring-Opening Polymerization of Glycidyl Phenyl Ether by Tetrabutylammonium Fluoride

Hisatoyo Morinaga,[†] Bungo Ochiai,[‡] and Takeshi Endo*,[†]

Molecular Engineering Institute, Kinki University,
11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan,
and Department of Polymer Science and Engineering,
Faculty of Engineering, Yamagata University,
4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

Received February 14, 2007
Revised Manuscript Received May 14, 2007

Introduction

Metal-free polymerization has been developed to construct polymerization systems without possible contamination of metallic initiators or catalyst residues that often degrade the resulting polymers. Numerous interests have been devoted to metal-free ring-opening polymerization of cyclic monomers, such as ϵ-caprolactone,[1,2] aliphatic cyclic carbonates,[3] ethylene oxide,[4] and lactide,[5] whose polymers are applicable as biomaterials, resist materials, and electronic materials.

Ring-opening polymerization of glycidyl phenyl ether (GPE), a common epoxide widely used as a monofunctional diluent in epoxy resins and a modifier for dyes and fibers, has been investigated by many researchers as a model polymerization for constructing effective curing systems.[6] For curing, metal initiators are often responsible for low insulation abilities and rust out. It should also be mentioned that the polymerization of GPE is accompanied by frequent side reactions (i.e., chain transfer and termination reactions) that limit the increase in the molecular weights of poly(GPE).[7] In order to increase the molecular weights, controlled anionic polymerization of epoxides including GPE and propylene oxide has been developed by the use of potassium *tert*-butoxide,[8] aryl silyl ether/CsF compounds,[9] metalloporphyrin,[10] potassium *tert*-butoxide/active methylene compounds,[11] alkali metal alkoxide/trialkylaluminum system,[12] double-metal cyanide compounds,[13] aluminum Lewis acids,[14] and tetraalkylammonium salts with trialkylaluminum as a cocatalyst.[15] Recently, a controlled anionic ring-opening polymerization of ethylene oxide was achieved using a metal-free phosphazene base *t*-BuP$_4$ catalyst (*p*-cresol/phosphazene *t*-BuP$_4$).[4] However, there is no report on the metal-free ring-opening polymerization of GPE with a controlled or living-like nature, which is in greatly demand owing to the scientific and industrial interests. A candidate initiator is a salt with a nucleophilic anion and an organic cation. For example, ammonium fluorides meet this requirement among commercially available reagents. This paper seeks the possibility of a controlled ring-opening polymerization of GPE using a commercially available metal-free initiator, tetrabutylammonium fluoride.

Experimental Section

Materials. Glycidyl phenyl ether (GPE) (Wako Pure Chemical Industries, Japan) was distilled from calcium hydride before use. Tetrabutylammonium fluoride was purchased from Sigma Chemical (St. Louis, MO) as tetrahydrofuran (THF) solution (1 M) and used as received.

Polymerization of GPE. Tetrabutylammonium fluoride (65.2 mg, 0.25 mmol) in THF solution (0.25 mL, 1.0 M) was added to a glass tube under argon gas. THF was evaporated off under vacuum, and GPE (750 mg, 5.0 mmol) was added. The polymerization was conducted at 50 °C for 6 h under argon gas equipped with a magnetic stir bar and was terminated with an excess amount of methanol. Monomer conversions were determined by ^{1}H NMR (nuclear magnetic resonance) spectroscopy (300.4 MHz). The conversion at the end of the polymerization was above 99%. The polymer was precipitated with a large amount of water and was dried at 50 °C for 24 h under reduced pressure ($M_{\mathrm{n(GPC)}} = 2500$, yield = 98%).

The theoretical number-average molecular weights based on the conversions are defined as follows:

$$M_{\mathrm{n}}(\mathrm{theor}) = \frac{[\mathrm{monomer}]_0}{[\mathrm{Bu_4NF}]_0} \times M_{\mathrm{monomer}} \times \mathrm{conv} + \mathrm{endo\ groups}\ (^{19}\mathrm{F} + {}^{1}\mathrm{H}) \quad (1)$$

where M_{monomer} is the molecular weight of the monomer and [monomer]$_0$ and [Bu$_4$NF]$_0$ are the initial concentrations of the monomer and Bu$_4$NF, respectively. ^{1}H NMR (CDCl$_3$, 300.4 MHz, δ, ppm): 3.18−3.32 (−O*H*); 3.49−3.89 (−OC*H*$_2$CH(CH$_2$OPh)O−), (−OCH$_2$C*H*(CH$_2$OPh)O−), and (FCH$_2$C*H*(O−)CH$_2$OPh); 3.89−4.22 (−OCH$_2$CH(C*H*$_2$OPh)O−) and (FCH$_2$CH(O−)C*H*$_2$OPh); 4.53 (FC*H*$_2$CH(CH$_2$OPh)O-, d, J = 47.0 Hz); 6.66−7.40 (aromatic ring). ^{13}C NMR (CDCl$_3$, 75.4 MHz, δ, ppm): 67.7 (−O*C*H$_2$CH(O−)CH$_2$OPh); 69.9 (−OCH$_2$CH(O−)*C*H$_2$OPh) and (FCH$_2$CH(O−)*C*H$_2$OPh); 78.1 (−OCH$_2$*C*H(O−)CH$_2$OPh); 78.6 (FCH$_2$*C*H(O−)CH$_2$OPh); 82.5 (F*C*H$_2$−, d, J = 170 Hz); 114.4, 120.7, and 129.3 (methine carbon in aromatic ring); 158.5 (quaternary carbon in aromatic ring). ^{19}F NMR (CDCl$_3$, 282 MHz, δ, ppm): −233.7 (*F*CH$_2$−, dt, J = 46.7 and 17.9 Hz).

Postpolymerization of GPE. When the monomer conversion reached 80% in the polymerization of GPE (750 mg, 5.0 mmol) conducted with the aforementioned procedure (20 equiv with respect to tetrabutylammonium fluoride), a 3.0 mmol amount of GPE (450 mg) was added to the glass tube containing the prepolymer mixture under argon gas. The polymerization was conducted at 50 °C for an additional 10.5 h and was terminated with an excess amount of methanol. The conversion determined by ^{1}H NMR spectroscopy was above 99%. The polymer was precipitated with an excess amount of methanol and was dried at 50 °C for 24 h under reduced pressure ($M_{\mathrm{n(GPC)}} = 4000$, yield = quantitative).

Measurements. ^{1}H (300.4 MHz), ^{13}C (75.4 MHz), and ^{19}F NMR (282 MHz) spectra were recorded on a JEOL AL300 spectrometer, using tetramethylsilane (^{1}H and ^{13}C) and hexafluorobenzene (^{19}F) as internal standards in CDCl$_3$. Molecular weights (M_{n} and M_{w}: number- and weight-average molecular weights) and molecular weight distribution ($M_{\mathrm{w}}/M_{\mathrm{n}}$) were estimated by size exclusion chromatography (SEC) on a Tosoh HLC-8120 system equipped with a refractive index detector and a polystyrene gel column (TSK-GEL Super HM-H, Tosoh Corp.) (6.0 mm i.d. × 15 cm; particle size: 3 μm; exclusion limit molecular weight: 4×10^8 g/mol) using THF as an eluent at 40 °C. The system was operated at a flow rate of 0.6 mL/min, and molecular weights were calibrated with polystyrene standards.

Results and Discussion

GPE was polymerized with tetrabutylammonium fluoride in bulk under an argon atmosphere. The reaction mixtures were homogeneous without any evidence of microscopic precipitation. When the polymerization of GPE was conducted at 100 °C for

---

* To whom correspondence should be addressed: Tel +81-948-22-7301; Fax +81-948-21-9130; e-mail tendo@ me-henkel.fuk.kindai.ac.jp.

[†] Kinki University.

[‡] Yamagata University.

10.1021/ma070386z CCC: $37.00

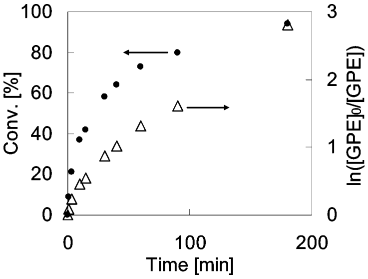


Figure 1. Time vs conversion and first-order kinetic plots for the polymerization of glycidyl phenyl ether initiated with tetrabutylammonium fluoride (5.0 mol %) in bulk at 50 °C.

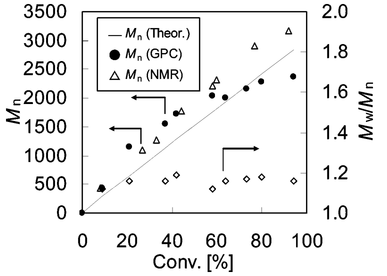


Figure 2. Conversion vs M_n (number-average molecular weights) and conversion vs M_w/M_n (molecular weight distribution) plots for the polymerization of glycidyl phenyl ether initiated with tetrabutylammonium fluoride (5.0 mol %) in bulk at 50 °C.

180 min with 5.0 mol % of tetrabutylammonium fluoride, 82% of GPE was consumed, and the corresponding polymer with a narrow and unimodal SEC profile ($M_n = 1700$, $M_w/M_n = 1.21$) was obtained. However, a significant decrease in the polymerization rate was observed after the conversion was 60%, probably due to some side reactions such as a backbiting reaction. In contrast, the polymerization at 50 °C consumed GPE quantitatively within 360 min to afford poly(GPE) with a narrow molecular weight distribution ($M_n = 2500$, $M_w/M_n = 1.12$). Accordingly, we selected the polymerization at 50 °C for further investigation on the controlled polymerization of GPE.

Figure 1 shows time vs conversion and first-order kinetic plots for the polymerization of GPE initiated with a 5.0 mol % amount of tetrabutylammonium fluoride. The conversion of GPE reached ~94% after 180 min and quantitative after 360 min. The polymer was obtained in an excellent yield (98% after purification by precipitation with water). The ln([GPE]$_0$/[GPE]) values, where [GPE]$_0$ and [GPE] represent the initial and the temporal concentrations of GPE, respectively, increased with time. This result indicates that the concentration of the propagating species is almost constant during polymerization. The slight decrease in the polymerization rate at the latter stage may be ascribed to the slight deactivation and/or the increased viscosity.

Figure 2 shows the conversion vs M_n and conversion vs M_w/M_n plots for the polymerization of GPE with 5.0 mol % of tetrabutylammonium fluoride at 50 °C. The M_n values calculated from the integral ratios of the ^{1}H NMR peaks of the methylene protons in the initiating end at 4.53 ppm and of the three protons of aromatic ring at 6.66−7.00 ppm increased linearly with the conversion. The M_n values estimated by SEC were consistent to the M_n values determined by ^{1}H NMR spectroscopy until the conversion reached 60%. The M_w/M_n values were kept narrow (<1.19) regardless of conversion. The narrow M_w/M_n values and the linear increase in the molecular weights suggest that this polymerization involves negligible chain transfer and termination reactions.

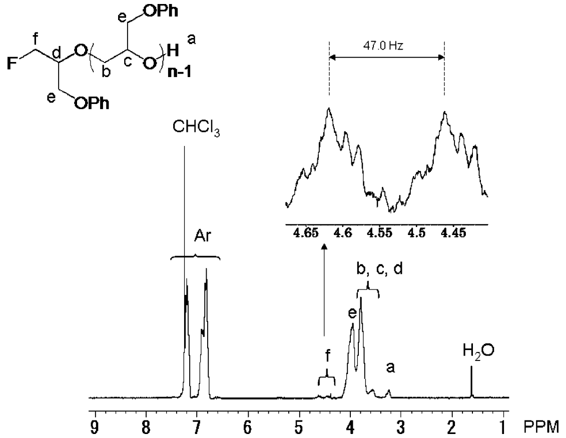
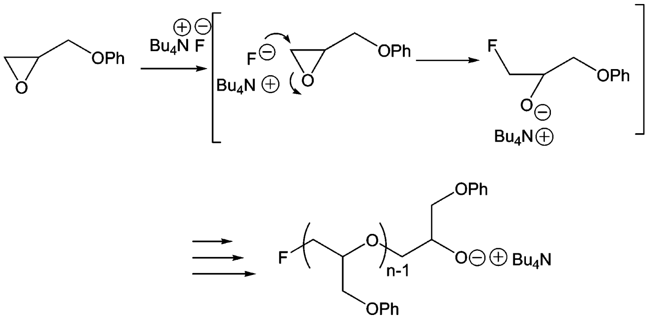


Figure 3. ^{1}H NMR spectrum of poly(glycidyl phenyl ether) (M_n = 2500).

Scheme 1



The mechanism of this polymerization was elucidated from NMR spectroscopic analysis. In the ^{1}H NMR spectrum of poly(GPE) (M_n = 2500), the signal of the protons assignable to FCH$_2$− group was observed at 4.53 ppm (Figure 3). The absence of peaks assignable to *n*-butyl groups suggests that the initiations with *n*-butyl or other alkyl anions did not take place. In the ^{19}F NMR spectrum of poly(GPE) ($M_n = 1100$), a signal was clearly observed at −233.7 ppm, which is assignable to a fluorine in an alkyl fluoride moiety in place of a signal of tetrabutylammonium fluoride at −132 ppm (Figure S1). The ^{1}H−^{19}F coupling constants of the ^{19}F NMR signal are ^2J(H,F) = 46.7 Hz (average) and ^3J(H,F) = 17.9 Hz (average), which are consistent with the reported values for monofluoroalkyl groups.[16] The ^2J(H,F) value of the ^{1}H NMR signals for FCH$_2$− groups at 4.53 ppm is 47.0 Hz, and it supports the presence of the FCH$_2$− initiating end. Furthermore, two signals in the ^{13}C NMR spectrum of poly(GPE) at 81.5 and 83.7 ppm are assignable to the F*C*H$_2$− group with a 170 Hz of ^{13}C−^{19}F coupling constant, which is consistent to the reported value for ^1J(C,F) (Figure S2, Supporting Information).[16] These observations indicate that a fluorine atom is connected at the polymer chain end. The good accordance between the $M_{n(NMR)}$ values and the theoretical M_n values suggests that the initiation from the fluoride anion proceeded effectively. Scheme 1 illustrates a plausible mechanism for the ring-opening polymerization of GPE initiated with tetrabutylammonium fluoride. A fluoride anion nucleophilically attacks the methylene of GPE and subsequently ring-opens GPE to form a tetrabutylammonium alkoxide. Then, a continuous anionic polymerization with tetrabutylammonium counter cation will give poly(GPE) bearing a FCH$_2$− initiating end. The termination with an excess amount of CH$_3$OH substitutes the tetrabutylammonium alkoxide ends to the hydroxyl groups by the exchange between the alkoxides and alcohols.

In order to confirm the stability of propagating ends in poly(GPE), a postpolymerization experiment was carried out. The SEC profiles of the prepolymer and the postpolymer are shown

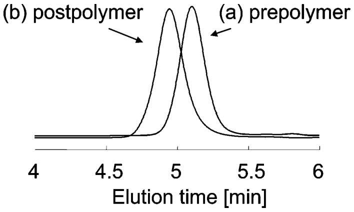


Figure 4. SEC profiles of (a) prepolymer ($M_n = 2300$, $M_w/M_n = 1.12$) and (b) postpolymer ($M_n = 4000$, $M_w/M_n = 1.19$) in a postpolymerization experiment.

in Figure 4. After the first stage polymerization of GPE (20 equiv with respect to tetrabutylammonium fluoride) at 50 °C for 90 min to consume 80% of GPE, an additional portion of GPE (12 equiv) was fed and polymerized for 10.5 h. The added monomer was consumed completely. The SEC profile of the postpolymer shows a unimodal elution peak that shifted to a higher molecular weight region from that of the prepolymer, while maintaining a narrow M_w/M_n. This result supports the stability of the propagating species in this polymerization that enables a living-like polymerization and that achieves a molecular weight of $M_n = 4000$ by negligible chain transfer and termination.

In conclusion, a metal-free living-like polymerization of glycidyl phenyl ether (GPE) was attained using tetrabutylammonium fluoride, by which poly(GPE) having controlled molecular weight can be obtained in high yield. The attainable molecular weight in this metal-free polymerization ($M_n = 4000$) is competitive with the previously reported controlled polymerizations with metal initiators. The propagating end of the poly(GPE) is stable enough to conduct a postpolymerization experiment. This metal-free GPE polymerization system with tetrabutylammonium fluoride is facile because the initiator is commercially available. The initiating system with tetraalkylammonium fluoride is advantageous over conventional initiating systems that cannot attain high molecular weight without metal initiators.

Supporting Information Available: ^{19}F NMR spectra of poly(GPE) and tetrabutylammonium fluoride (Figure S1) and ^{13}C NMR spectrum of poly(GPE) (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Endo, T.; Shibasaki, Y.; Sanda, F. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2190−2198.
(2) Cerrai, P.; Tricoli, M.; Andruzzi, F.; Paci, M.; Paci, M. *Polymer* **1989**, *30*, 338−343.
(3) (a) Yu, F.; Zhuo, R. *Polym. J.* **2004**, *36*, 28−33. (b) Morinaga, H.; Ochiai, B.; Mori, H.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1985−1996. (c) Morinaga, H.; Ochiai, B.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6633−6639.
(4) Schlaad, H.; Kukula, H.; Rudloff, J.; Below, I. *Macromolecules* **2001**, *34*, 4302−4304.
(5) Myers, M.; Connor, E. F.; Glauser, T.; Mock, A.; Nyce, G.; Hedrick, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 844−851.
(6) (a) Kirino, M.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3428−3433. (b) Kim, M.; Sanda, F.; Endo, T. *J. Appl. Polym. Sci.* **2001**, *81*, 2347−2351. (c) Suzuki, K.; Horii, H.; Sugita, Y.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4276−4283. (d) Morikawa, H.; Sudo, A.; Nishida, H.; Endo, T. *J. Appl. Polym. Sci.* **2005**, *96*, 372−378. (e) Morikawa, H.; Sudo, A.; Nishida, H.; Endo, T. *Macromol. Chem. Phys.* **2005**, *206*, 592−599.
(7) (a) Stolarzewicz, A. *Makromol. Chem.* **1986**, *187*, 745−752. (b) Stolarzewicz, A.; Grobelny, Z. *Macromol. Chem.* **1992**, *193*, 531−538. (c) Banks, P.; Peter, R. H. *J. Polym. Sci., Part A* **1970**, *8*, 2595−2610. (d) Tänzer, W.; Büttner, K.; Ludwig, I. *Polymer* **1996**, *37*, 997−1003.
(8) (a) Price, C.; Carmelite, D. *J. Am. Chem. Soc.* **1966**, *88*, 4039−4044. (b) Mendrek, A.; Mendrek, S.; Trzebicka, B.; Kuckling, D.; Walach, W.; Adler, H.-J.; Dworak, A. *Macromol. Chem. Phys.* **2005**, *206*, 2018−2026.
(9) Nambu, Y.; Endo, T. *Macromolecules* **1991**, *24*, 2127−2128.
(10) (a) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162−1166. (b) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1166−1169. (c) Aida, T.; Sanuki, K.; Inoue, S. *Macromolecules* **1985**, *18*, 1049−1055.
(11) Hino, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5407−5412.
(12) Billouard, C.; Carlotti, S.; Desbois, P.; Deffieux, A. *Macromolecules* **2004**, *37*, 4038−4043.
(13) (a) Ooms, P.; Hofmann, J.; Steinlein, C.; Ehlers, S. PCT Int Appl WO 0134297, 2001. (b) Ostrowski, T.; Harre, P.; Zehner, P.; Müller, J.; Stutzer, D.; Grosch, G. H.; Winkler, J. PCT Int Appl WO, 0162826, 2001.
(14) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64−68.
(15) Carlotti, S.; Billouard, C.; Gautriaud, E.; Desbois, P.; Deffieux, A. *Macromol. Symp.* **2005**, *226*, 61−68.
(16) (a) Hesse, M.; Meier, H.; Zeeh, B. In *Spectroscopic Methods in Organic Chemistry*, 1st ed.; Linden, A., Murray, M., Eds.; Thieme Medical Pub.: Stuttgart, Germany, 1995; p 364. (b) Hooper, D. L.; Sheppard, N.; Woodman, C. M. *J. Mol. Spectrosc.* **1967**, *24*, 277−283. (c) Purrington, S. T.; Pittman, J. H. *Tetrahedron Lett.* **1988**, *29*, 6851−6852.

MA070386Z