Macromolecules **1995,** *28,* 651−652

Lewis Acid-Promoted Anionic Polymerization of a Monomer with High Cationic Polymerizability. Synthesis of Narrow Molecular Weight Distribution Polyoxetane and Polyoxetane−Poly(methyl methacrylate) Block Copolymer with Aluminum Porphyrin Initiators

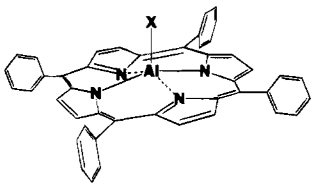
Daisuke Takeuchi, Yoshihiko Watanabe,
Takuzo Aida,* and Shohei Inoue*,†

Department of Chemistry and Biotechnology,
Faculty of Engineering, University of Tokyo, Hongo,
Bunkyo-ku, Tokyo 113, Japan

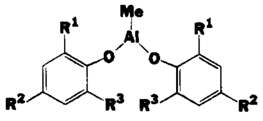
Received September 2, 1994
Revised Manuscript Received November 14, 1994

It has long been accepted that cyclic ethers with more than a four-membered ring are, in contrast with oxiranes, only cationically polymerizable due to the high basicities of their ether oxygen atoms. The cationic polymerization involves O-alkylation of the monomer to give a highly reactive cyclic oxonium ion as the growing species, which is regarded as the monomer activated for nucleophilic attack. From this standpoint, one can expect that even cyclic ethers with high basicities may undergo anionic ring-opening polymerization when they are activated by an electrophile.

Recently, we have found that the living anionic polymerizations of oxiranes and methacrylic esters initiated with aluminum porphyrins (**1**)[1] are dramatically accelerated upon addition of sterically hindered Lewis acids such as **5**,[2,3] where the monomers are coordinated to and activated for nucleophilic attack by the Lewis acids. In this case, the degradative attack of the nucleophilic growing species to the Lewis acid, which is usually inevitable, is prohibited due to the steric hindrance between the large porphyrin unit around the active site and the bulky phenoxide ligands attached to the Lewis acidic center.



1 X = Cl
2 X = $OCH_2CH_2CH_2Cl$
3 X = $OCH(CH_3)_2$
4 X = CH_3



5 $R^1 = R^3 = {}^{tert}Bu$, $R^2 = Me$
6 $R^1 = R^2 = {}^{tert}Bu$, $R^3 = H$

Herein we report results of successful extension of this method to the living anionic polymerization of oxetane (Scheme 1).[4,5] A typical example of the polymerization of oxetane is as follows: To a 100-mL round-bottomed flask fitted with a three-way stopcock, containing a CH_2Cl_2 solution (2 mL) of (TPP)AlCl[6] (**1**, 0.10 mmol) and a Teflon-coated stirring bar under nitrogen, was added oxetane (10 mmol) by a syringe at room temperature (~20 °C). Although **1** is an excellent initiator for the living anionic polymerization of oxiranes, no polymerization of oxetane took place throughout the observation over a period of 3 h. On the other hand, when a CH_2Cl_2 (2 mL) solution of **5**[7] (0.6 mmol) was added to this flask, the polymerization did take place to attain 47.4 and 88.4% conversion in 0.5 and 3 h, respectively.[8] The produced polymer showed a sharp GPC chromatogram, where the M_n value[9] was increased proportionally to monomer conversion, retaining the narrow MWD ($M_w/M_n \sim 1.1$) (Figure 1). The degree of polymerization of the polymer was in good agreement with the mole ratio of the monomer reacted to the initiator, indicating that every initiator molecule produces one polymer molecule. When **6** was used as a Lewis acid at a higher initial monomer-to-initiator mole ratio such as 400, a narrow MWD polyoxetane with a higher molecular weight (M_n = 19 000 ($M_{n,theory}$ = 23 000), M_w/M_n = 1.11) was obtained at 100% conversion in 13.5 h.

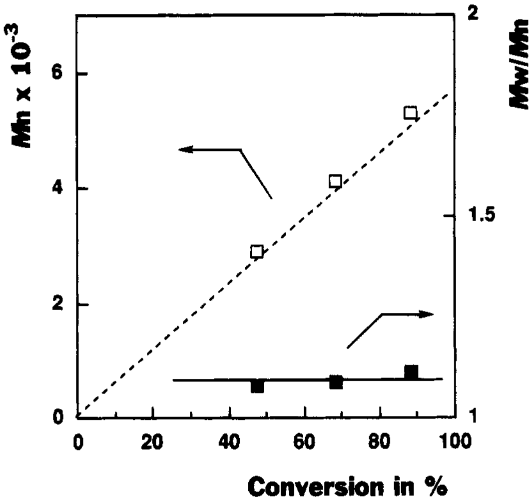
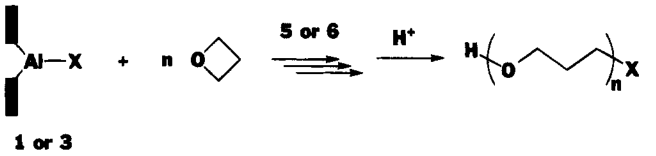


Figure 1. Polymerization of oxetane with the **1**/**5** system in CH_2Cl_2 at room temperature (~20 °C) ($[oxetane]_0/[\mathbf{1}]_0/[\mathbf{5}]_0$ = 100/1/6). M_n (M_w/M_n) − conversion relationship.

Scheme 1



In order to confirm the living character of polymerization, the two-stage polymerization of oxetane with **1** as initiator in the presence of **5** was investigated. Thus, after the completion of the first-stage polymerization of oxetane ($[oxetane]_0/[\mathbf{1}]_0/[\mathbf{5}]_0$ = 50/1/3) in CH_2Cl_2 at room temperature, 150 equiv of oxetane with respect to **1** was newly added to the system, whereupon the second-stage polymerization ensued, and the M_n of the polymer was increased from 2900 (M_w/M_n = 1.09) to 8300, retaining the narrow MWD (M_w/M_n = 1.22).

Very recently, Amass *et al.* reported that **1** alone is capable of initiating the polymerization of oxetane at an elevated temperature such as 55 °C, but the polymerization was slow.[5] A preliminary ^1H NMR study at 22 °C on a CD_2Cl_2 solution of a mixture of oxetane and **1** (10/1) in the absence of **5** indicated the formation of a one-to-one adduct (**2**: δ −1.43 (t), −1.26 (m), 0.82 (t)), without any polymeric products. Upon addition of **5** to this system, the polymerization was started. In conformity with this observation, a (porphinato)aluminum alkoxide such as **3** (0.1 mmol) as initiator in the presence of **5** (0.3 mmol) under similar conditions initiated the polymerization of oxetane (10 mmol) to give at 100% conversion a polymer with M_n and M_w/M_n,

---

[†] Present address: Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.

0024-9297/95/2228-0651$09.00/0

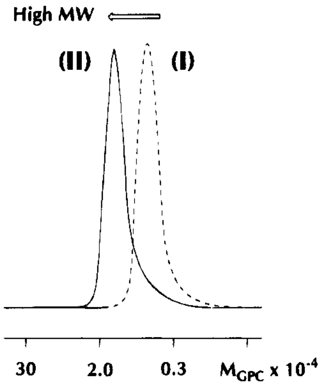


Figure 2. Block copolymerization of methyl methacrylate (MMA) and oxetane with the **4/5** system ($[\mathrm{MMA}]_0/[\mathrm{oxetane}]_0/[\mathbf{4}]_0/[\mathbf{5}]_0 = 100/50/1/6$). GPC chromatograms of the prepolymer of MMA (**I**, $M_n = 6500$, $M_w/M_n = 1.13$) and the block copolymer of MMA and oxetane (**II**, $M_n = 15\,000$, $M_w/M_n = 1.20$).

respectively, of 8900 and 1.24. ^{1}H NMR analysis of the polymer, after hydrolytic workup, showed the presence of a 2-propoxy end group (δ 1.15, CH_3 (d)) originating from **3** but no phenoxy group from **5**.

By using the aluminum porphyrin/Lewis acid system, we attempted the synthesis of a narrow MWD block copolymer from oxetane and methyl methacrylate (MMA). Methacrylic monomers are polymerizable radically and anionically but not cationically, so polyoxetane–poly(methyl methacrylate) block copolymer has never been synthesized. As already reported, methacrylic monomers undergo accelerated living anionic polymerization with the (TPP)AlCH$_3$ (**4**)^6–**5** system via a (porphinato)aluminum enolate as the growing species. Thus, at the first stage, MMA (5 mmol) was polymerized with **4** (0.1 mmol) in the presence of **5** (0.6 mmol) in CH_2Cl_2 (6 mL)[10] (PMMA at 100% conversion: $M_n = 6500$ ($M_{n,\mathrm{theory}} = 5000$), $M_w/M_n = 1.13$ [Figure 2 (**I**)]), and then oxetane (15 mmol) was added to this system, whereupon the second-stage polymerization ensued and attained 100% monomer conversion within 14 h, affording the corresponding block copolymer in almost quantitative yield.[11] The GPC analysis (Figure 2) showed a sharp elution peak (**II**: $M_n = 15\,000$ ($M_{n,\mathrm{theory}} = 11\,000$), $M_w/M_n = 1.20$) in the higher molecular weight region than that of the PMMA prepolymer (**I**).[12,13] The successful formation of the PMMA–polyoxetane block copolymer demonstrates that the polymerization of oxetane initiated with **1** in the presence of **5** is *anionic*.

In conclusion, the Lewis acid-promoted living anionic polymerization of oxetane is realized by utilizing aluminum porphyrin as the nucleophilic initiator in conjunction with Lewis acid as the monomer activator.

Acknowledgment. The present work was partly supported by Grant-in-Aid No. 04204006 for Scientific Research on Priority Area, the Ministry of Education, Science and Culture, Japan. T.A. also thanks Asahi Glass Foundation for financial support.

References and Notes

(1) Recent reviews: (a) Aida, T. *Prog. Polym. Sci.* **1994**, *19*, 469. (b) Inoue, S.; Aida, T. Controlled Polymer Synthesis with Metalloporphyrins. In *Molecular Design of Polymeric Materials*; Vogl, O., Hatada, K., Eds.; Dekker: New York, in press.

(2) (a) Kuroki, M.; Watanabe, T.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1991**, *113*, 5903. (b) Sugimoto, H.; Kuroki, M.; Watanabe, T.; Kawamura, C.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 3403. (c) Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 3672. (d) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013. (e) Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2820.

(3) Inoue, S.; Aida, T. *CHEMTECH* **1994**, *24*, 28.

(4) Examples of the polymerization of oxetane by organometallic initiators: (a) Hirano, T.; Nakayama, S.; Tsuruta, T. *Makromol. Chem.* **1975**, *176*, 1897. (b) Vandenberg, E. J.; Mullis, J. C.; Juvet, R. S., Jr.; Miller, T.; Nieman, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3113. (c) Vandenberg, E. J.; Mullis, J. C. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1421.

(5) A part of this work was presented in the annual meeting of the Society of Polymer Science, Japan Nagoya, May 1994: Japan, *Polym. Prepr. Jpn.* **1994**, *43*, 171. Concurrently, Amass *et al.* reported the polymerization of oxetane with (TPP)AlCl (**1**) alone at an elevated temperature (55 °C): Amass, A. J.; Perry, M. C.; Riat, D. S.; Tighe, B. J.; Colclough, E.; Steward, M. J. *Eur. Polym. J.* **1994**, *30* (5), 641.

(6) For the preparation of **1**, **3**, and **4**, see refs 2b and 2e.

(7) For the preparation of **5** and **6**, see ref 2b.

(8) Mixing of oxetane (15 mmol) with **5** (0.3 mmol) in CH_2Cl_2 (3 mL) in the absence of **1** under similar conditions resulted in the polymerization of oxetane, where the monomer conversion, however, was stopped at 61.4% (2 h), affording a broad MWD, high polymer ($M_n \sim 10^5$, $M_w/M_n = 1.93$) together with some cyclic oligomers.

(9) Narrow MWD polyoxetanes prepared with the **3/5** system, having defined M_ns by ^{1}H NMR end group ($OCH(CH_3)_2$) analysis, were used as standards for GPC calibration for evaluating M_ns and M_w/M_n ratios of other polyoxetane samples.

(10) **5** was added after a 3-h irradiation (xenon arc light, $\lambda >$ 420 nm) of the mixture of MMA and **4** at 30 °C.

(11) The polymerization mixture was poured into hexane, and the precipitates, collected and dried in vacuo at room temperature, were weighed to determine the polymer yield.

(12) The block copolymer was soluble in a large volume of MeOH, a poor solvent for PMMA.

(13) ^{1}H NMR ($CDCl_3$): δ 3.45 (OCH_2), 1.82 (CH_2) [polyoxetane segment], δ 3.59 (OCH_3), 0.5–1.2 (CH_3), 1.55–2.2 (CH_2) [PMMA segment]. Integration of the signals at δ 3.45 and 3.59 gave the oxetane and MMA contents respectively of 32 and 68%, which are in good agreement with those expected from the feed mole ratio of these two monomers (33 and 67%) and those from the molecular weights (GPC) of polyoxetane and PMMA segments (29 and 71%).

MA9411585