Polymer Journal, Vol. 35, No. 1, pp 88—91 (2003)

SHORT COMMUNICATIONS

Synthesis of a Hetero Telechelic Hyperbranched Polyether. Anionic Ring-Opening Polymerization of 3-Ethyl-3-(hydroxymethyl)oxetane Using Potassium *tert*-Butoxide as an Initiator

Hiroto KUDO, Ayako MORITA, and Tadatomi NISHIKUBO[†]

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama, 221–8686 Japan

(Received September 6, 2002; Accepted October 29, 2002)

KEY WORDS Hetero Telechelic Hyperbranched / Anionic Polymerization / Polyethers / 3-Ethyl-3-(hydroxymethyl)oxetane /

Oxetanes with 4-membered ring are polymerized exclusively with cationic initiators, due to high basicity.[1] Vandenberg *et al.* reported that cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane (EHO) in the presence of aluminum complexes as cationic initiators produced linear polymers with high crystallinity and no glass transition temperature.[2,3] Hyperbranched polymers by cationic ring-opening polymerization of EHO using sulfonium salts as cationic initiators have been reported.[4–7] Inoue *et al.* performed living anionic polymerization of oxetanes using aluminum porphyrin/Lewis acid as catalyst.[8] The authors have developed useful reactions of oxetanes for synthetic organic chemistry and polymer synthesis.[9]

No research has been done on the anionic polymerization of oxetanes using common anionic initiators such as butyllithium (BuLi), sodium methoxide (MeONa), potassium *tert*-butoxide (*t*-BuOK) and etc.

Herein, we describe successful results of the anionic ring-opening polymerization of oxetane, 3-ethyl-(3-hydroxymethyl)oxetane (EHO), affording hetero telechelic hyperbranched polyethers, poly(EHO)s containing an oxetanyl and many hydroxyl groups at the ends.

EXPERIMENTAL

Materials

18-Crown-6-ether (18-C-6) was recrystallized twice from acetnitrile. *t*-BuOK was purified by the sublimation. 3-Ethyl-3-(hydroxymethyl)-oxetane (EHO) was donated from Toagosei Co., Ltd. and distilled over $MgSO_4$ before use.

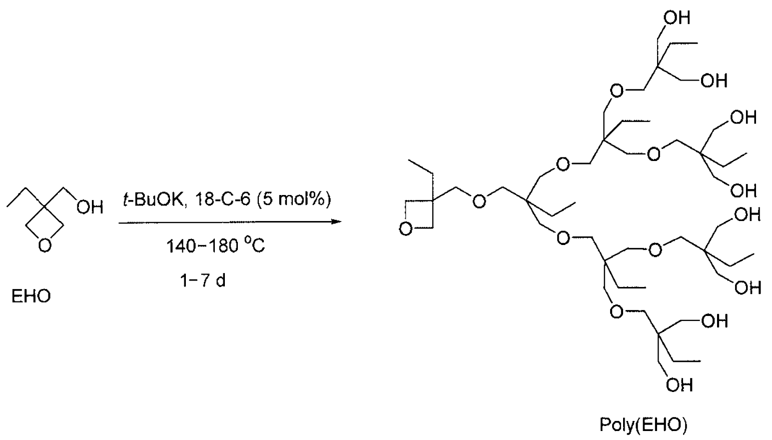
Instrumentation

Infrared (IR) absorption spectra were measured on a Jasco model IR-420 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL model JNM α-500 (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR) in DMSO-d_6 with Me_4Si (TMS) as internal standard. The degree of branching was calculated from relative intensity of the $-CH_2CH_3$ in proton decoupled, quantitative ^{13}C NMR spectra. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated by gel permeation chromatography (GPC; TOSOH model HLC-8020) on TSK gel Multipore Hxl-M columns calibrated by narrow molecular weight polystyrene standards and with solution of LiBr and phosphoric acid (20 mM) in dimethylformamide (DMF) as eluent without correction with a refractive index detector. T_g's were measured on a Seiko Electronic Instrument (SSC5200/DSC120) differential scanning calorimeter (DSC) at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. Thermal analysis was performed on a Seiko Electronic Instrument (TG/DTA 120) at a heating rate of 10 °C min^{-1} for thermogravimetric analysis (TGA) under nitrogen. Matrix-assisted laser desorption ionization time-of flight mass (MALDI-TOF-MS) experiments were performed SHIMAZU/KRATOS MALDI-TOF-MS using dihydroxy benzoic acid as matrix and chloroform as solvent.

Synthesis of Hyperbranched Polyethers by the Polymerization of 3-Ethyl-(3-hydroxymethyl)oxetane (EHO). A typical procedure for the polymerization of EHO is as follows: To EHO (0.58 g, 5 mmol) in a

---

[†] To whom correspondence should be addressed (E-mail: nishit02@kanagawa-u.ac.jp).



Scheme 1.

Table I. Polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane[a]

Run	Reaction Time (h)	Reaction Temperature (°C)	Yield[b] (%)	$M_n(M_w/M_n)$[c]	$M_{n,\,\mathrm{MALDI}}$[d]	$M_{n,\,\mathrm{NMR(DP)}}$[e]	T_g[f]	T_{d10}[g]	DB (Fréchet)[h]	DB (Frey)[i]
1	24	100	0	–[j]	–[j]		–[j]	–[j]	–[j]	–[j]
2	24	120	32	620 (1.41)	–[j]	533.6 (4.6)	69	294	0.30	0.25
3	24	140	61	850 (1.60)	–[j]	788.8 (6.8)	72	301	0.21	0.15
4	24	160	82	1280 (1.81)	–[j]	1345.6 (11.6)	72	306	0.24	0.20
5	24	180	85	3120 (4.33)	3280	3178.4 (27.4)	78	319	0.18	0.14
6	48	180	89	3750 (4.09)	3520	–[k]	75	312	0.20	0.15
7	168	180	95	4120 (4.03)	4200	–[k]	73	310	0.27	0.23

[a]Conditions: 3-ethyl-3-(hydroxymethyl)-oxetane (5.0 mmol), potassium *tert*-butoxide (10 mol%), 18-Crown-6-ether (10 mol%), in NMP (1.0 mL), for 24 h. [b]*n*-Hexane-insoluble parts. [c]Estimated by GPC based on polystyrene standards; eluent: solution of LiBr and phosphoric acid (20 mM) in DMF. [d]Molar masses determined with MALDI-TOF-MS. [e]Calculated by ^{1}H NMR. DP: Degree of polymerization. [f]Determined by DSC. [g]Determined by TGA. [h]Determined by ^{13}C NMR. Calculated by Fréchet *et al.* See ref 11. [i]Determined by ^{13}C NMR. Calculated by Frey *et al.* See ref 12. [j]Not determined. [k]Signals of polymer ends not observed.

polymerization tube were introduced 5 mol% *t*-BuOK, 18-Crown-6-ether (18-C-6) and subsequently dry *N*-methylpyrroridone (1.0 mL). The mixture was stirred at 180 °C for 48 h under nitrogen. The reaction mixture was consistently homogeneous. The mixture was poured into 1 N hydrogen chloride solution to obtain a colorless solid which was dissolved in chloroform and poured into *n*-hexane to precipitate the polymers. The *n*-hexane-insoluble polymers were filtered with a membrane filter (0.45 µm) and dried *in vacuo* at 60 °C for 12 h. Yield = 0.516 g (89%). M_n = 3750, M_w/M_n = 4.09. IR (film, cm^{-1}) : 3356 (ν OH), 1110 (ν C–O–C ether), 1047 (ν C–O–H), 984 (ν C–O–C of oxetane ring). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ = 0.77–0.81(*m*, –CH_3), 1.23–1.26(*m*, –CH_2CH_3), 1.66(*q*, J = 7.4, –CH_2CH_3, polymer end), 2.71–3.35(*m*, –OCH_2, –CH_2OH), 3.42(*s*, –CH_2O–, polymer end), 4.16(*s*, –CH_2OH), 4.21, 4.33(AB quartet, J = 5.9, –CH_2O, oxetane ring) ppm. ^{13}C NMR (125 MHz, DMSO-d_6, TMS) δ = 8.04 (–CH_3), 22.0–23.2 (*t*, –CH_2CH_3), 43.3 (>C<), 62.0 (–CH_2OH), 71.6 (–CH_2O–) ppm.

RESULTS AND DISCUSSION

Polymerization of EHO was performed in the presence of *t*-BuOK and 18-C-6 in NMP (Scheme 1).

When polymerization of EHO was carried out at 100 °C in NMP for 24 h, no polymer was obtained (run 1). By the polymerization of EHO in NMP at 120 °C, a polymer was obtained in 32% yield with low molecular weight (M_n = 620, M_w/M_n = 1.41) (run 2). As reaction temperature and time increased, M_ns and yields of poly(EHO)s increased (runs 3–6). Poly(EHO) with M_n = 4120 (M_w/M_n = 4.03) was obtained in 95% yield by polymerization of EHO in NMP at 180 °C for 7 d (run7). In all cases, the reaction mixtures were consistently homogeneous with products remaining in solution. The conditions and results are summarized in Table I.

The structure of poly(EHO) was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of poly(EHO) (M_n = 3120, M_w/M_n = 4.33, run 5 in Table I) showed signals assignable to cyclic ether and ethyl groups of oxetane moieties at polymer ends at 4.20–4.31 and 1.65 ppm, respectively (Figure 1). In the

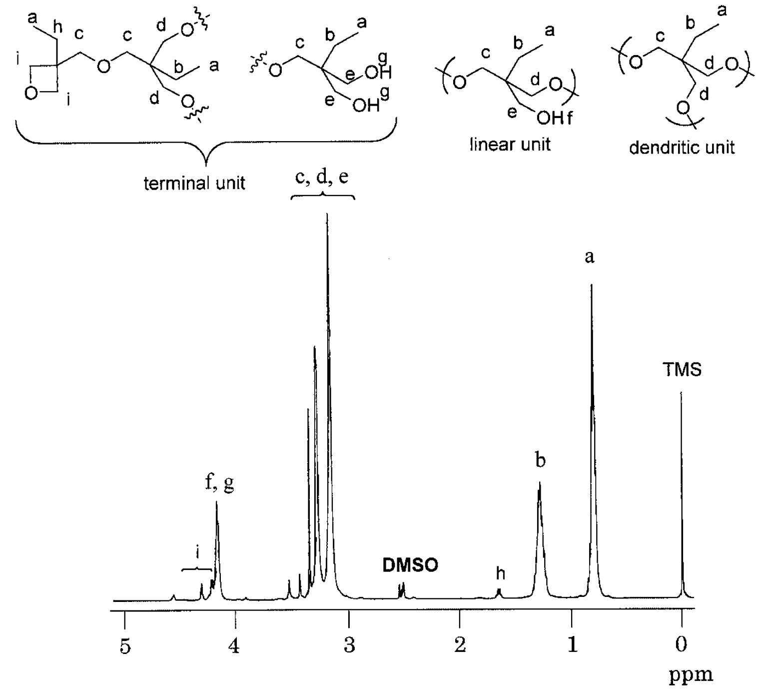


Figure 1. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of poly(EHO) (M_n = 3120, M_w/M_n = 4.33, run 5 in Table I).

IR spectrum of this polymer, characteristic absorption peaks were observed at 3356, 1110, and 984 cm^{-1} due to OH, C–O–C (ether) and C–O–C (oxetane), respectively. These results showed that poly(EHO) was a hetero telechelic hyperbranched polymer with an oxetanyl group and many hydroxyl groups at the ends with the structure shown in Scheme 1. The ^{13}C NMR spectrum supported this structure.[10] The value of GPC for hyperbranched polymers is often claimed to be too low since hydrodynamic volume of a hyperbranched polymer is smaller than that of a polystyrene used for calibration. In this study, the polymers were analyzed by MALDI-TOF mass spectra. Molecular weights estimated by GPC well agreed with those measured by MALDI-TOF. The degree of polymerization of poly(EHO) (M_n = 620–3120, runs 2–5 in Table I) was 4.6–27.4 by ^{1}H NMR integration of the signal methylene protons of the polymer end at 1.65 ppm and methyl protons at 0.81 ppm. These values also agree with those estimated by GPC (Table I). Figure 2 showed the MALDI-TOF mass spectrum of the poly(EHO) (M_n = 3280, run 5 in Table I). Mass differences in peaks were exactly the molar mass of the 3-ethyl-(3-hydroxymethyl)oxetane repeating unit (M = 116). It was impossible to discriminate molar mass fraction of polymers with M_ns = 620, 850, 1280 (runs 2–4 in Table I) by the MALDI-TOF mass spectra.

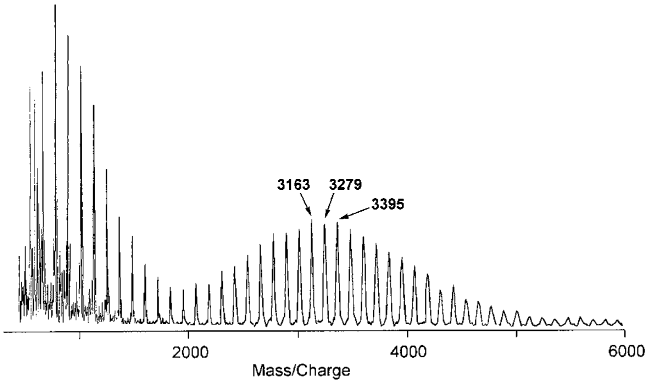


Figure 2. MALDI-TOF mass spectrum of poly(EHO) (M_n = 3120, M_w/M_n = 4.33, run 5 in Table I).

Furthermore, it is known from the literature,[6] that the degree of branched (DB) of poly(EHO) obtained by the cationic polymerization of EHO can be calculated by methylene signals of ethyl groups corresponding to dendritic (D), linear (L), and terminal (T) repeating units at 23.0, 22.5, and 21.9 ppm, respectively, in ^{13}C NMR analysis.[10] The degree of branching (DB) of poly(EHO) was found here by equations introduced by Frechet *et al.*[11] and Frey *et al.*[12]

Ten percent weight-loss of temperature (T_{d10}) and grass transition temperature (T_g) of poly(EHO) were observed at 294–319 °C in TGA and 69–78 °C in DSC, respectively. As M_ns and yields of poly(EHO)s increased, DB was observed. The thermal stability of poly(EHO)s decreased with increase of DB of poly(EHO). DBs of poly(EHO) obtained under different reaction conditions for polymerization were different. Poly(EHO)s (M_n = 850–4120, M_w/M_n = 1.60–4.33) were soluble in common organic solvents, such as dimethyl sulfoxide, dimethylformamide, chloroform, and dichloromethane, but insoluble in water, methanol and ethanol. The film-forming ability of poly(EHO) was very good.

On the other hand, the polymerization of EHO was carried out with MeOK (5 mol%) as initiator in the presence of 18-C-6 (5 mol%) in NMP at 180°C for 48 h to obtain the oligomer with M_n = 2800, M_w/M_n = 4.66 in 88% yield. Furthermore, the polymerization of 3-ethyl-3-phenoxymethyloxetane with *t*-BuOK (5 mol%) was carried out in the presence of 18-C-6 (5 mol%) in NMP at 180°C for 24 h, to afford the corresponding linear polymer with low molecular weight (M_n = 430, M_w/M_n = 1.12) in 52% yield. It might be indicated that the anionic ring-opening polymerization of EHO could proceed smoothly due to hydroxyl groups. The mechanistic studies on ring-opening polymerization of EHO using anionic initiators are now underway.

This paper presents the first example of polymerization of oxetanes anionically using a common anionic initiator, hetero telechelic hyperbranched polymers, poly(EHO)s containing an oxetanyl and many hydroxyl groups at the ends. Dendritic unit ratios and thermal stabilities of poly(EHO) decreased with M_ns. Wide application of poly(EHO) as a reactive hyperbranched polymer should be possible owing to the oxetane moiety and many hydroxyl groups.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, in Japan (No. 14655351) from the Ministry of Education, Culture, Sports, Science and Technology, which is gratefully acknowledgement.

REFERENCES

1. For example:
   S. Inoue and T. Aida, in "Ring-Opening Polymerization", 2nd ed, K. J. Ivin, T. Saegusa, Ed., Elsevier Applied Science, London, 1984, vol. 1, pp 185–298.
2. E. J. Vandenberg, J. C. Mullis, and R. S. Juvet, Jr., *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3083 (1989).
3. E. J. Vandenberg, J. C. Mullis, R. S. Juvet, Jr., T. Miller, and R. A. Nieman, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3113 (1989).
4. M. Bendnarek, T. Biedron, J. Helinski, K. Kaluzynski, P. Kubisa, and S. Penczek, *Macromol. Rapid Commun.*, **20**, 369 (1999).
5. H. Magnusson, E. Malmstrom, and A. Hult, *Macromol. Rapid Commun.*, **20**, 453 (1999).
6. H. Magnusson, E. Malmstrom, and A. Hult, *Macromolecules*, **34**, 5786 (2001).
7. H. Magnusson, E. Malmstrom, A. Hult, and M. Johansson, *Polymer* **43**, 301 (2002).
8. D. Takeuchi, Y. Watanabe, T. Aida, and S. Inoue, *Macromolecules*, **28**, 651 (1995).
9. For example:
   T. Nishikubo and A. Kameyama, *Prog. Polym. Sci.*, **18**, 963 (1993).
10. Spectroscopic data of poly(EHO) (M_n = 3120, M_w/M_n = 4.33, run 5 in Table I): ^{13}C NMR (DMSO-d_6, 125 MHz); δ = 7.60 (–CH_3), 8.04 (–CH_3, oxetane), 21.9 (–CH_2CH_3, terminal), 22.5 (–CH_2CH_3, linear), 23.0 (–CH_2CH_3, dendritic), 26.5 (–CH_2CH_3, oxetane), 40.0 (quaternary carbon, oxetane), 43.3 (quaternary carbon), 62.0 (–CH_2OH, polymer end), 71.6 (–CH_2O–), 73.4 (C–*C*–O, polymer end), 77.0 (*C*–O, oxetane) ppm.
11. The DB value was calculated by the following equations.
    DB(Fréchet) = (D + T)/(D + T + L) × 100
    Where D, T, and L are the values of the integration ratios of dendritic, terminal, and linear repeating units measured by the ^{13}C NMR spectroscopy.
    References:
    C. J. Hawker, R. Lee, and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **113**, 4583 (1991).
12. DB (Frey) = 2D/(2D + L) × 100
    References:
    D. Holter, A. P. Burgath, and H. Frey, *Acta Polym.* **48**, 30 (1997).