Synthesis of Hyperbranched Polymers by the Anionic Ring-Opening Polymerization of 3,3-Bis(hydroxymethyl)oxetane

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ABSTRACT: The anionic ring-opening polymerization of 3,3-bis(hydroxymethyl)oxetane (BHO) was carried out using t-BuOK as an initiator in the presence of 18-crown-6-ether (18-C-6) in NMP at $180\,^\circ$C, affording the corresponding hyperbranched polyethers, poly(BHO)s containing an oxetanyl group and many hydroxyl groups at the ends in 83–98% yields. Since the resulting poly(BHO)s were insoluble in common organic solvents, the poly(BHO)s were treated with acetic anhydride to obtain poly(BHO-Ac)s containing acetyl groups at the ends. The M_ns and degree of branching (DB) of poly(BHO-Ac)s were in the range of 2600–4400 estimated by SEC and 0.09–0.55 calculated by ^{13}C NMR spectroscopy, respectively. The cationic copolymerization of poly(BHO-Ac) and 3-ethyl-3-phenoxymethyloxetane (EPO) was examined using BF_3OEt_2 as an initiator in CHCl$_3$ at $0\,^\circ$C for 24 h, affording pseudo dendritic polymers, poly-[poly(BHO-Ac)/EPO]s with $M_n = 11000$–15000 in 58–65% yields. Furthermore, the obtained poly[poly(BHO-Ac)/EPO] was hydrolyzed with KOH to afford the poly[poly(BHO)/EPO] containing many hydroxyl groups.
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    KEY WORDS   Oxetane / Hyperbranched Polymer / Anionic Ring-Opening Polymerization / Cationic Polymerization / Hydrolysis /

Oxetanes with 4-membered ring are well known to be polymerized with cationic initiators, due to their high basicity.[1] Vandenberg *et al.*[2] reported the synthesis of the polyethers by the cationic ring-opening polymerization of 3-ethyl-3-hydroxymethyloxetane (EHO) in the presence of aluminum complexes as cationic initiators. Recently, Hult *et al.*[3] reported the synthesis of hyperbranched polyethers by the cationic ring-opening polymerization of EHO using various cationic initiators. Penczek *et al.*[4] reported that the cationic ring-opening polymerizations of 3,3-bis(hydroxymethyl)oxetane (BHO), and the copolymerization of BHO with EHO were performed to give medium molecular-weight polymers in good yields.

Meanwhile, we have developed many new reactions of oxetanes with various protonic reagents such as phenols,[5] thiophenols,[6] carboxylic acids,[7] and thioesters[8] in the presence of quaternary onium salts or crown ether complexes as catalysts. These new reactions have been applied to the synthesis of polymers such as polyethers,[5] polyesters,[7,9] polyphosphonates,[10] and poly(silyl ether)s.[11] Furthermore, we have found anionic alternating ring-opening copolymerization of oxetanes with carboxylic anhydrides in the presence of the quaternary onium salts as initiators.[12] Inoue and Endo *et al.* preformed the living anionic polymerization of oxetanes using metal complexes as catalysts.[13–17]

More recently, we reported a new anionic ring-opening polymerization of EHO and 3-methyl-3-hydroxymethyloxetane (MHO) containing hydroxyl groups using potassium *tert*-butoxide (t-BuOK) and 18-crown-6-ether (18-C-6), affording the hyperbranched polyether containing an oxetanyl group and many hydroxyl groups at the end (Scheme 1).[18,19] Furthermore, we achieved the synthesis of a pseudo dendritic polymer with many pendant hydroxyl groups by the cationic ring-opening polymerization of the poly(EHO) derivative.[19] These synthesized polymers poly(EHO), poly(MHO), and pseudo dendritic polymers are expected as useful functional materials, because they have many hydroxyl groups at the ends.
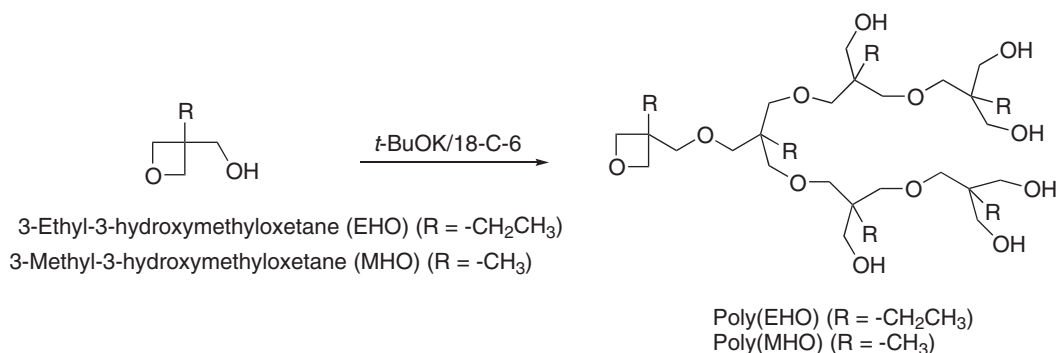
In a series of the study for the synthesis of hyperbranched polyether by the anionic ring-opening polymerization of the oxetane with hydroxyl groups in this article, we examined the reaction of BHO containing two hydroxyl groups in the presence of t-BuOK in several conditions in detail. Furthermore, we also examined the reaction of the resulting polymers for the synthesis of new branched polymers containing pendant many hydroxyl groups.

EXPERIMENTAL

Materials

The solvents, chloroform (CHCl$_3$), tetrahydrofuran (THF), dimethylformamide (DMF), and *N*-methyl-

3-Ethyl-3-hydroxymethyloxetane (EHO) (R = -CH$_2$CH$_3$)
3-Methyl-3-hydroxymethyloxetane (MHO) (R = -CH$_3$)

Poly(EHO) (R = -CH$_2$CH$_3$)
Poly(MHO) (R = -CH$_3$)

Scheme 1.

pyrrolidinone (NMP) were purified in the usual way before use. Potassium *tert*-butoxide (*t*-BuOK) was purified by the sublimation. Potassium carbonate (K$_2$CO$_3$) and potassium hydroxide (KOH) were used without further purification. 18-Crown-6-ether (18-C-6) was recrystallized from acetonitrile. Pentaerythritol, diethyl carbonate, acetic anhydride and pyridine were used without further purification. 3-Ethyl-3-phenoxymethyloxetane (EPO) was donated from Toagosei Co., Ltd., and purified by distillation under reduced pressure before use. Boron trifluoride diethyl etherate (BF$_3$OEt$_2$) was purified by distillation under reduced pressure.

Measurements

Infrared (IR) absorption spectra were measured on a Jasco FT/IR-420 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-α-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) and JEOL JNM-α-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) in CDCl$_3$ with Me$_4$Si (TMS) as an internal standard. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) with the use of a TOSO HLC-8220 SEC equipped with refractive index and ultraviolet detectors using TSK gel columns [eluent: solution of LiBr and phosphoric acid (20 mM) in DMF]; calibrated with narrow molecular-weight polystyrene standards. The glass transition temperatures (T_gs) of the polymers were measured on a Seiko Instruments EXTAR 6000 DSC 6200 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min under nitrogen. Thermal analysis (TGA) was performed on a Seiko Instruments EXTAR 6000 TG-DTA 6200 at a heating rate of 10 °C/min under nitrogen.

Synthesis of 3,3-bis(hydroxymethyl)oxetane (BHO)

A mixture of pentaerythritol (50.0 g, 0.37 mol), diethyl carbonate (60.0 g, 0.50 mol) and K$_2$CO$_3$ (0.40 g, 3.0 mmol) was stirred for 24 h at 110 °C. The remaining diethyl carbonate and ethanol were re-

moved by distillation under atmospheric pressure. The residual product was distilled at vacuum pressure (0.8 mmHg, 147 °C), (reference: 1 mmHg, 148–160 °C).[4] Yield 42% (18.0 g). IR (neat, cm^{-1}): 3314 (ν OH), 1053 (ν C–O–C ether), 983 (ν C–O–C oxetane ring). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ ppm: 3.55 (d, 4.0H, $J = 5.4$ Hz, –C<u>H</u>$_2$OH), 4.27 (s, 4.0H, –CH$_2$–O–, oxetane ring), 4.75 (t, 2.0H, $J = 5.4$ Hz, –CH$_2$O<u>H</u>). ^{13}C NMR (125 MHz, DMSO-d_6, TMS) δ ppm: 44.9 (quaternary carbon), 62.0 (–CH$_2$OH), 74.0 (–CH$_2$–O–, oxetane ring).

Anionic Ring-Opening Polymerization of BHO

Typical Procedure. BHO (0.35 g, 3 mmol), *t*-BuOK (0.067 g, 10 mol% –OH equiv), and 18-C-6 (0.15 g, 10 mol% –OH equiv) were dissolved in NMP (0.6 mL), and the solution was stirred at 180 °C for 24 h under nitrogen. The resulting mixture was poured into an excess amount of methanol to precipitate the polymers. The insoluble polymers in methanol were filtered and then dried *in vacuo* at r.t. for 24 h. Yield 95% (0.33 g). IR (disk, cm^{-1}): 3311 (ν OH), 1107, 1055 (ν C–O–C ether), 983 (ν C–O–C oxetane ring).

The Esterification of Hydroxyl Groups of Poly(BHO) with Acetic Anhydride

Typical Procedure. To a solution of poly(BHO) (0.20 g) in pyridine (0.3 mL) was added acetic anhydride (3 mL) and the mixture was refluxed for 3 h. The resulting mixture was diluted with CHCl$_3$, washed with 1 N HCl solution and water. The organic phase was dried over MgSO$_4$ and concentrated by a rotary evaporator. The resulting mass was dried *in vacuo* at 50 °C for 12 h to obtain the oily product, poly-(BHO-Ac). Yield 98% (0.34 g). $M_n = 3700$, $M_w/M_n = 1.64$. IR (film, cm^{-1}): 1745 (ν C=O), 1109, 1053 (ν C–O–C ether), 983 (ν C–O–C oxetane ring). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ ppm: 1.99 (s, 3.0H, –C(O)–CH$_3$), 3.26–3.33 (m, 2.0H, –CH$_2$–O–), 3.96–4.03 (m, 2.0H, –CH$_2$O–C(O)–), 4.25 (s, 4.0H, –CH$_2$–O–CH$_2$–, oxetane ring), 4.46 (AB quar-
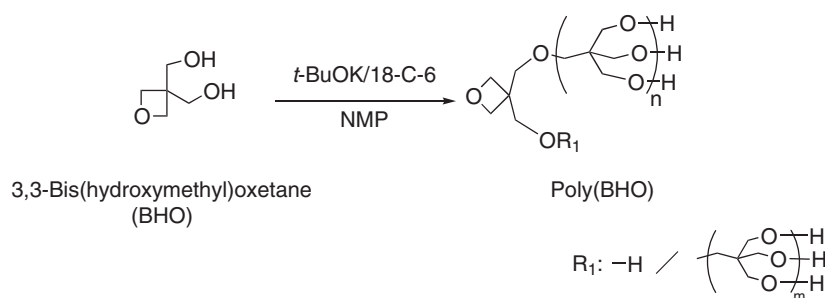
Scheme 2.

tet, 4.0H, –CH$_2$–O–CH$_2$–, oxetane ring). ^{13}C NMR (125 MHz, DMSO-d_6, TMS) δ ppm: 19.7 (–C(O)–$\underline{C}$H$_3$), 41.6–43.7 (quaternary carbon), 61.7–62.2 (–CH$_2$O–C(O)–), 68.8–69.3 (–CH$_2$O–), 74.6 (–CH$_2$O–, oxetane ring), 169.5 (–$\underline{C}$(O)–CH$_3$).

The Cationic Ring-Opening Copolymerization of Poly(BHO-Ac) with EPO

Typical Procedure. Poly(BHO-Ac) (0.56 g, 0.3 mmol) and EPO (0.29 g, 1.5 mmol) were dissolved in CHCl$_3$ (0.6 mL), and the solution was cooled at 0 °C under nitrogen. To the resulting solution was added BF$_3$OEt$_2$ (25 mg, 10 mol%) as catalyst, and the mixture was stirred at 0 °C for 24 h. After that, a small amount of NEt$_3$ was slowly added to the reaction mixture at room temperature. The resulting mixture was washed with water, 1 N HCl solution and water. The organic phase was dried over MgSO$_4$ and concentrated by a rotary evaporator. The resulting mixture was poured into large amount of methanol and viscous liquid polymers were separated. After that, the supernatant solution was decanted and the resulting polymer was dried *in vacuo* at room temperature for 24 h. Yield = 58% (0.49 g). $M_n = 11000$, $M_w/M_n = 1.28$. IR (film, cm^{-1}): 1745 (ν C=O), 1599, 1497 (ν C=C aromatic), 1243 (ν C–O–C ester), 1108, 1038 (ν C–O–C ether). ^{1}H NMR (600 MHz, CDCl$_3$, TMS) δ ppm: 0.64–0.86 (m, 3.0H, –CH$_2$C$\underline{H}_3$), 1.28–1.50 (m, 2.0H, –C$\underline{H}_2$CH$_3$), 2.05 (s, 3.0H, –C(O)–CH$_3$), 3.09–3.42 (m, 2.0H, –CH$_2$–O–), 3.81–3.97 (m, 2.0H, –CH$_2$O–Ph), 3.97–4.12 (m, 2.0H, –CH$_2$O–C(O)–), 6.65–7.35 (m, 5.0H, aromatic H).

Hydrolysis Reaction of the Poly[poly(BHO-Ac)/EPO]

The copolymer (poly(BHO-Ac):EPO = 1:9) (2.0 g, 6 mmol) and KOH (0.33 g, 6 mmol) were dissolved in H$_2$O/THF (1 mL/4 mL). The solution was stirred at 50 °C for 48 h. The crude mixture was poured into 1 N HCl solution to obtain the colorless solid. The obtained products were dissolved in THF and poured into *n*-hexane. The insoluble products in *n*-hexane were filtered and then dried *in vacuo* at r.t. for 24 h. Yield =

80% (1.53 g). $M_n = 14400$, $M_w/M_n = 1.31$. IR (film, cm^{-1}): 3291 (ν OH), 1599, 1497 (ν C=C aromatic), 1244 (ν C–O–C ester), 1105, 1036 (ν C–O–C ether). ^{1}H NMR (600 MHz, CDCl$_3$, TMS) δ ppm: 0.68–0.79 (m, 3.0H, –CH$_2$C$\underline{H}_3$), 1.35–1.45 (m, 2.0H, –C$\underline{H}_2$CH$_3$), 3.11–3.74 (m, 2.0H, –CH$_2$–O–), 3.81–3.97 (m, 2.0H, –CH$_2$O–Ph), 4.78 (broad s, 2.0H, –OH), 6.68–7.25 (m, 5.0H, aromatic H).

RESULTS AND DISCUSSION

Anionic Ring-Opening Polymerization of BHO

In our previous paper, we reported the synthesis of the hetero telechelic hypebranched polyether, poly(E-HO) containing an oxetanyl group and many hydroxyl groups at the ends by the anionic ring-opening polymerization of EHO.[18] In this paper, we examined the synthesis of hyperbranched poly(ether) by the anionic polymerization of BHO, containing two hydroxyl groups (Scheme 2).

The anionic ring-opening polymerization of BHO was examined using *t*-BuOK and 18-C-6 (10 mol%) in NMP for 24 h at various temperatures in the range between 100 and 180 °C. The results and conditions were summarized in Table I.

In all the cases, the reaction mixture was consistently homogeneous with all starting materials and products remaining in the solution. The reaction mixture was poured into methanol to precipitate white powdery compounds, which were dried *in vacuo* at r.t. for 24 h to obtain the polymers poly(BHO)s. However, the resulting poly(BHO)s were insoluble in common organic solvents. This indicates that many hydroxyl groups at the ends of the poly(BHO) form inter- and intra-hydrogen bonds. Therefore, we performed the esterification of the resulting poly(BHO). The reaction of poly(BHO) with acetic anhydride was carried out in pyridine to afford the corresponding poly(BHO-Ac) containing acetyl groups at the ends in a quantitative yield (Scheme 3).

It was found that poly(BHO-Ac) was soluble in the common organic solvents. As summarized in Table I, the molecular weight (M_n) and polydispersity ratios

Table I. The polymerization of BHO[a], and M_n and degree of branching (DB) of poly(BHO-Ac)[b]

Run	Temperature (°C)	Yield[c] (%)	M_n (SEC)[d,f]	M_n (NMR)[e,f]	M_w/M_n[d,f]	DB[f,g]
1	100	0	—[h]	—[h]	—[h]	—[h]
2	120	7	1100	1200	1.11	0.09
3	130	43	1800	3000	1.41	0.26
4	140	88	3100	—[h]	1.40	0.49
5	160	95	3500	—[h]	1.61	0.49
6	180	94	3700	—[h]	1.64	0.51

[a]The polymerization of BHO (3 mmol) was carried out in the presence of t-BuOK (0.6 mmol) and 18-C-6 (0.6 mmol) in NMP (0.6 mL) for 24 h at 100–180 °C. [b]The reaction of poly(BHO) and acetic anhydride was carried out in the presence of pyridine under reflux to afford the poly(BHO-Ac) quantitatively. [c]Insoluble parts in methanol. [d]Estimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). [e]Calculated by ^{1}H NMR. [f]For acetylated polymer. [g]Degree of branching was calculated by ^{13}C NMR. [h]Not determined.

Poly(BHO)   Acetic anhydride   Poly(BHO)-Ac
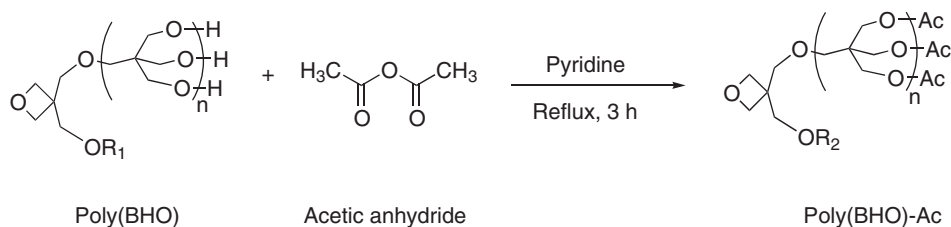
Scheme 3.

(M_w/M_n) were estimated by SEC. Poly(BHO) could not be obtained by the polymerization at 100 °C (run 1 in Table I). At more than 120 °C, poly(BHO) was obtained in 7–94% yields (runs 2–6 in Table I). It was observed that the yields and M_ns of the obtained poly(BHO)s increased with increasing the reaction temperature. Furthermore, the structure of poly-(BHO-Ac) was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopies. The IR spectrum of poly-(BHO-Ac) showed some characteristic absorption signals at 1745, 1109, 1053, and 983 cm^{-1} due to C=O, C–O–C, and C–O–C oxetane ring, respectively. Figure 1 illustrates the ^{1}H NMR spectrum of poly-(BHO-Ac) (run 3 in Table I). This figure shows two types of signals assignable to cyclic ethers, type A and type B of oxetane moieties at polymer end at 4.25 and 4.42–4.49 ppm, respectively. Scheme 4 illustrates a plausible mechanism of the anionic ring-opening polymerization of BHO. At first, the proton-exchange reaction between hydroxyl groups of BHO and t-BuOK would occur to produce the alkoxy anion intermediate of BHO (Scheme 4, initiator). Next, the anion exchange reaction between the produced primary alkoxy anion of BHO dimer and a hydroxyl group would take place inter- or intramolecularly to produce types A and B of poly(BHO) with branching structure.

Furthermore, the ^{13}C NMR spectrum supported this structure as illustrated in Figure 2. It is well known

from the literature,[4] that the degree of branched (DB) of the polymer obtained by the cationic polymerization of BHO can be calculated by methylene signals of ethyl groups corresponding to double dendritic (DD), single dendritic (SD), linear (L) and terminal (T) repeating units in the range between 42.5 and 44.5 ppm in ^{13}C NMR analysis. However, no DD was confirmed in our synthesized poly(BHO-Ac) (Figure 2). This result indicated that DD units could not be obtained by the steric hindrance effect in the anionic ring-opening polymerization of BHO. The DB of the obtained poly(BHO-Ac) was estimated here according to the equation introduced by Frey et al.[20] It was observed that the DB increased with M_n, as summarized in Table I. These results showed that the poly(BHO) was heterotelechelic hyperbranched polymer containing an oxetanyl group and many hydroxyl groups at the ends.

The effect of the reaction time on the anionic ring-opening polymerization of BHO was investigated using t-BuOK and 18-C-6 (10 mol%) in NMP at 180 °C. As summarized in Table II, the yield of poly(BHO) reached to 83% for 6 h. The M_n and yield of poly-(BHO-Ac) increased gradually with increasing the reaction time, and reacted to 4400 (for the acetylated polymer) and 98% at 72 h, respectively. The degree of branching (DB) of the resulting poly(BHO-Ac) increased with increasing the reaction time, and the values were in the range between 0.42 and 0.55.
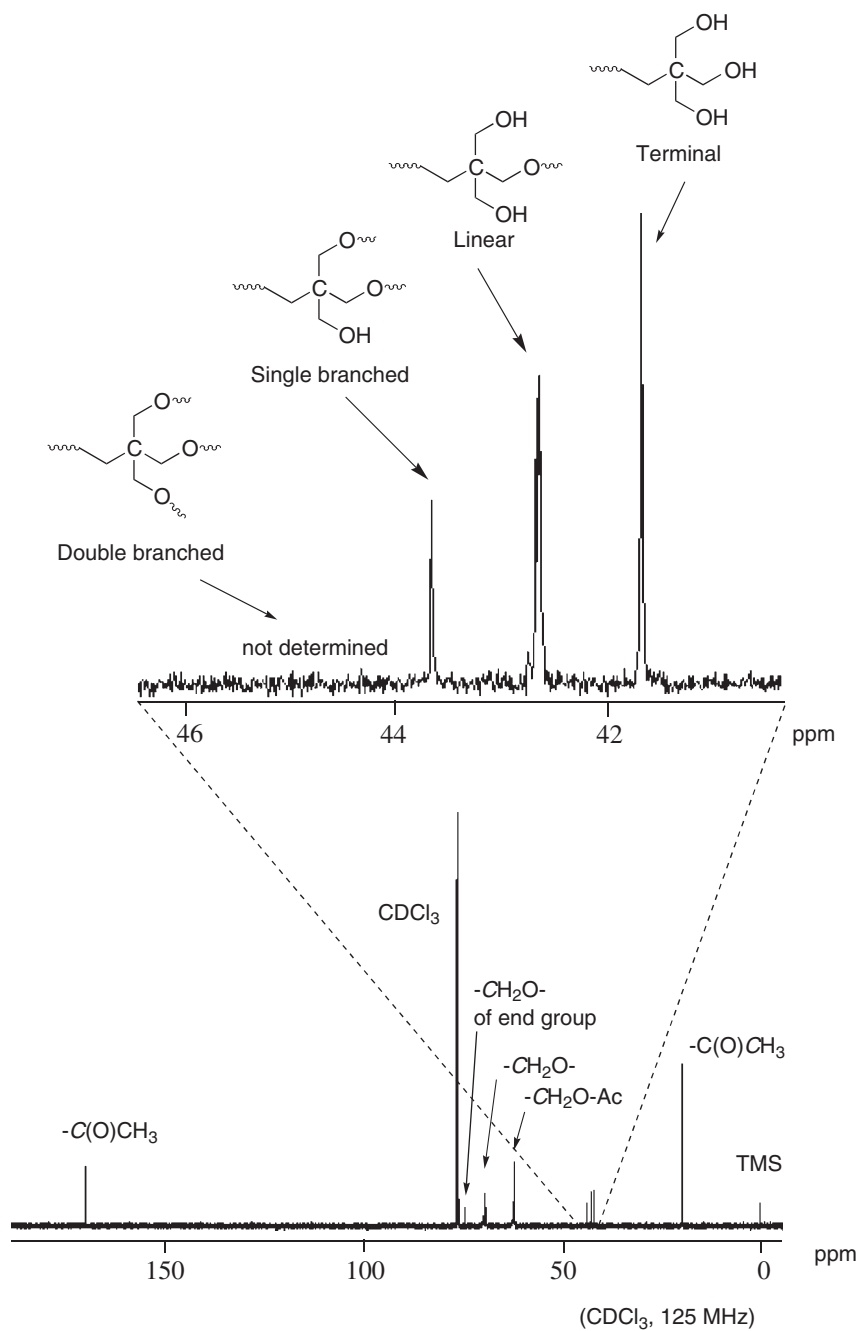
Poly(BHO-Ac) ($M_n = 1800$, Type A : Type B = 2 : 1)
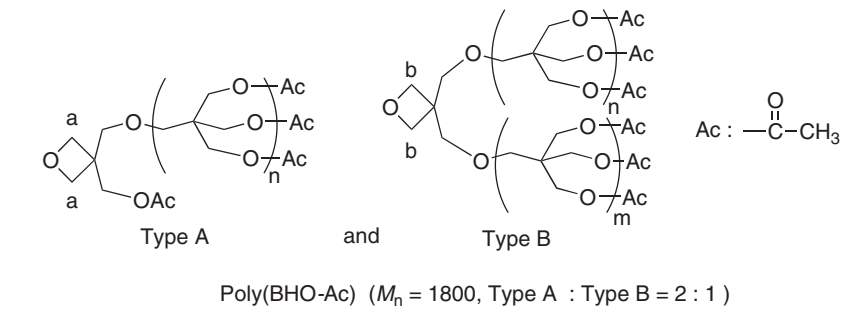
Figure 1. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of poly(BHO-Ac) ($M_n = 1800$, $M_w/M_n = 1.41$, run 3 in Table I).
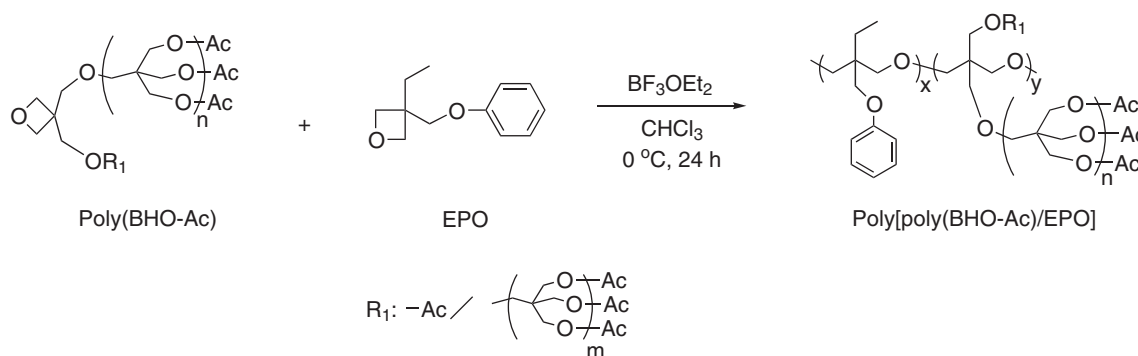

Scheme 4.

A. MORITA, H. KUDO, and T. NISHIKUBO
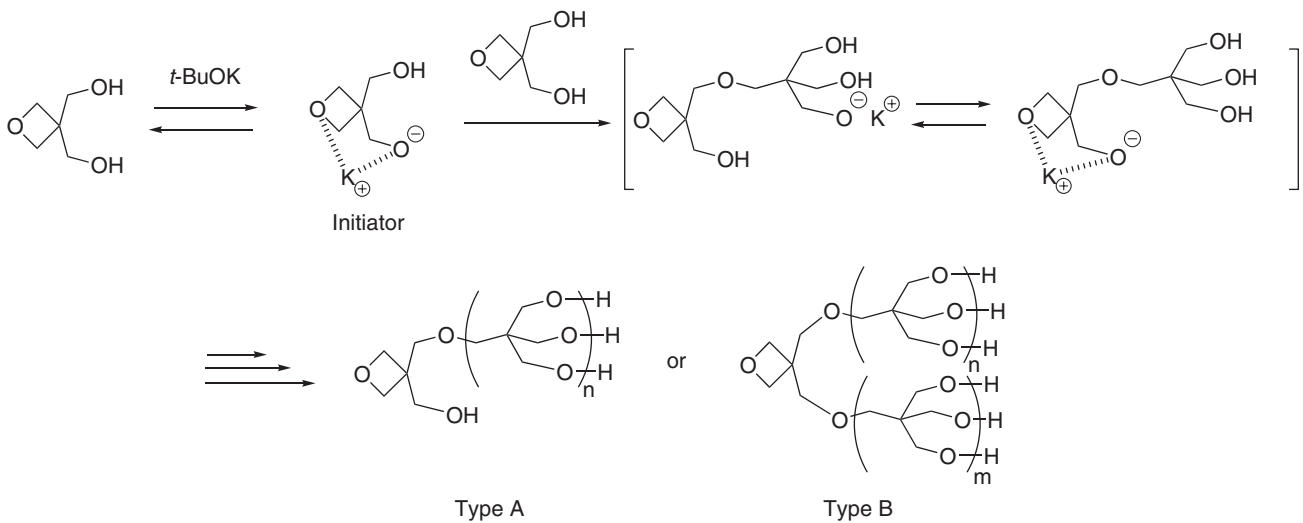
Figure 2. ^{13}C NMR spectrum (125 MHz, CDCl$_3$) of poly(BHO-Ac) ($M_n = 1800$, $M_w/M_n = 1.41$, run 3 in Table I).

Table II. The polymerization of BHO[a], and M_n and degree of branching (DB) of poly(BHO-Ac)[b]

Run	Time (h)	Yield[c] (%)	M_n[d,e]	M_w/M_n[d,e]	DB[f]
1	6	83	2600	1.38	0.42
2	12	92	3200	1.61	0.48
3	24	95	3700	1.64	0.51
4	48	97	4000	1.63	0.51
5	72	98	4400	1.68	0.55

[a]The polymerization of BHO (3 mmol) was carried out in the presence of *t*-BuOK (0.6 mmol) and 18-C-6 (0.6 mmol) in NMP (0.6 mL) for 6–72 h at 180 °C. [b]The reaction of poly(BHO) and acetic anhydride was carried out in the presence of pyridine under reflux to afford the poly(BHO)-Ac quantitatively. [c]Insoluble parts in methanol. [d]Estimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). [e]For acetylated polymer. [f]Degree of branching was calculated by ^{13}C NMR.

Scheme 5.

Table III. The cationic polymerization of poly(BHO-Ac) with EPO[a]

Run	Feed Molar Ratio Poly(BHO-Ac)/EPO	Yield[b] (%)	Copolymer Composition[c] Poly(BHO-Ac)/EPO	M_n[d,e]	M_w/M_n[d,e]
1	1/0	0	1/0	—	—
2	1/5	58	1/5	11000	1.28
3	1/10	63	1/9	15000	1.34

[a]The polymerization of poly(BHO-Ac) with various feed ratios of EPO was carried out in the presence of BF_3OEt_2 in $CHCl_3$ for 24 h at 0 °C. [b]Insoluble parts in methanol. [c]Calculated by ^1H NMR. [d]Estimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). [e]For acetylated polymer.

The Cationic Polymerization of Poly(BHO-Ac)

As described in the introduction, oxetanes are polymerized with cationic initiators. The poly(BHO) had an oxetanyl group at the end. Therefore, we examined the synthesis of new branched polymers by the cationic polymerization of poly(BHO-Ac) (Scheme 5).

When the cationic ring-opening polymerization of poly(BHO-Ac)[21] was carried out using BF_3OEt_2 as an initiator at 0 °C in $CHCl_3$ for 24 h, the polymerization of poly(BHO-Ac) did not proceed. However, the cationic ring-opening copolymerization of poly(BHO-Ac) with 3-ethyl-3-phenoxymethyloxetane (EPO) in feed molar ratios of poly(BHO-Ac)/EPO = 1/5 and 1/10 proceeded smoothly to afford the corresponding polymers with M_ns = 11000 and 15000, in 58 and 63% yields, respectively. These results and conditions were summarized in Table III.

Figure 3 illustrates the SEC profiles of poly(BHO-Ac) (M_n = 1500) and the copolymers obtained by the polymerization of poly(BHO-Ac) with EPO. The latter showed a higher M_n than the former, and no absorption corresponding to the original poly(BHO-Ac). As shown in Figure 4A, the ^1H NMR spectrum of the obtained polymer showed both signals based on poly-(BHO-Ac) and EPO units. These results showed that the copolymerization of poly(BHO-Ac) and EPO proceeded to afford new hyperbranched polymers. The unit ratio of poly(BHO-Ac) and EPO was calculated from the integration ratio of the methyl proton signal of acetyl groups of poly(BHO-Ac) unit at 2.05 ppm and the aromatic proton signals of EPO unit at
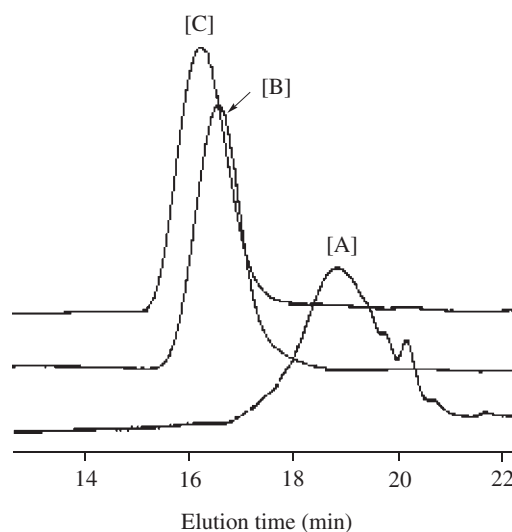

Figure 3. SEC profiles of poly(BHO-Ac) and poly[poly-(BHO-Ac)/EPO]. [A] poly(BHO-Ac) (M_n = 1500, M_w/M_n = 1.35) obtained by Ref 13. [B] poly[poly(BHO-Ac)/EPO] (M_n = 11000, M_w/M_n = 1.28, run 2 in Table III). [C] poly[poly(BHO-Ac)/EPO] (M_n = 15000, M_w/M_n = 1.34, run 3 in Table III).

6.77–7.23 ppm. The copolymers showed nearly the same unit ratios as expected from the feed ratios.

Hydrolysis of Poly[poly(BHO-Ac)/EPO]

Poly[poly(BHO-Ac)/EPO] (M_n = 15000, run 3 in Table III) was treated with KOH solution (THF/H_2O = 4/1) to afford the hydrolyzed polymer poly-[poly(BHO)/EPO] containing many hydroxyl groups with M_n = 14400 in a 80% yield (Scheme 6).
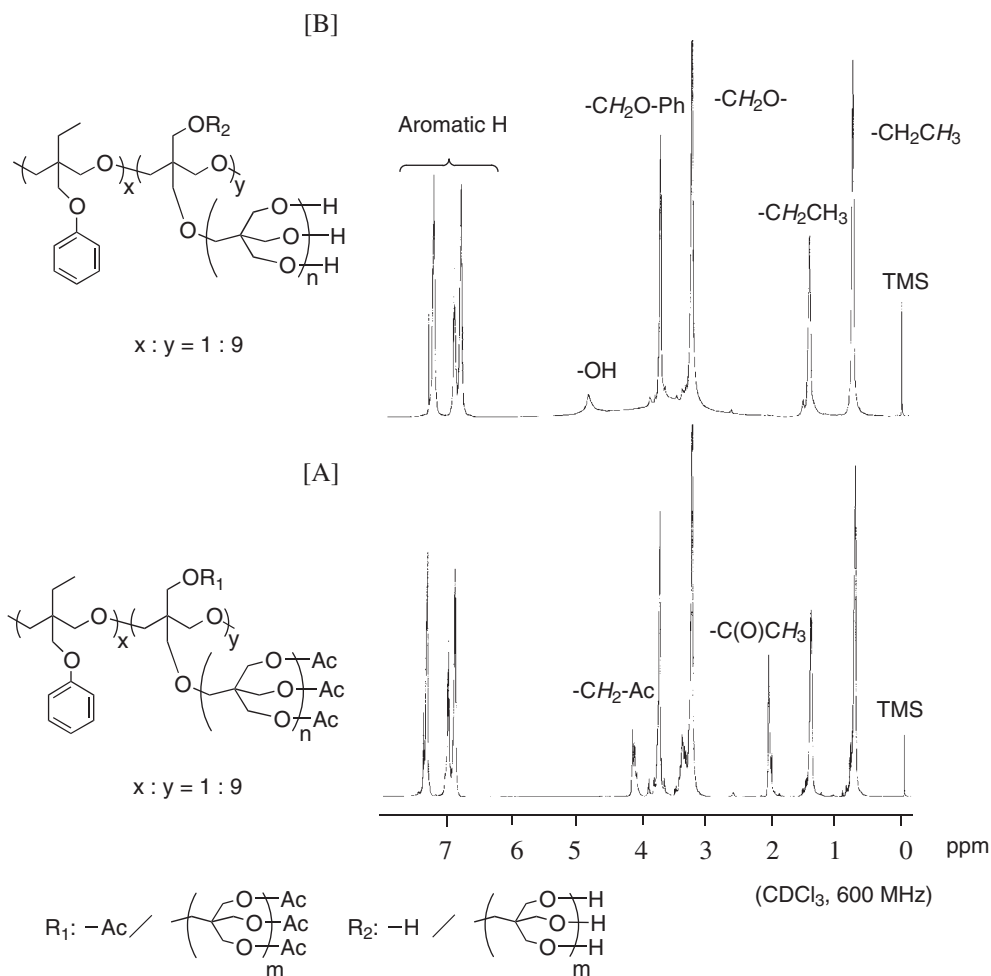
Figure 4. ^{1}H NMR spectra (500 MHz, CDCl$_3$) of poly[poly(BHO-Ac)/EPO] before and after hydrolysis reaction. [A] Before hydrolysis reaction; poly[poly(BHO-Ac)/EPO] ($M_n = 15000$, run 3 in Table III). [B] After hydrolysis reaction; poly[poly(BHO)/EPO] ($M_n = 14400$).
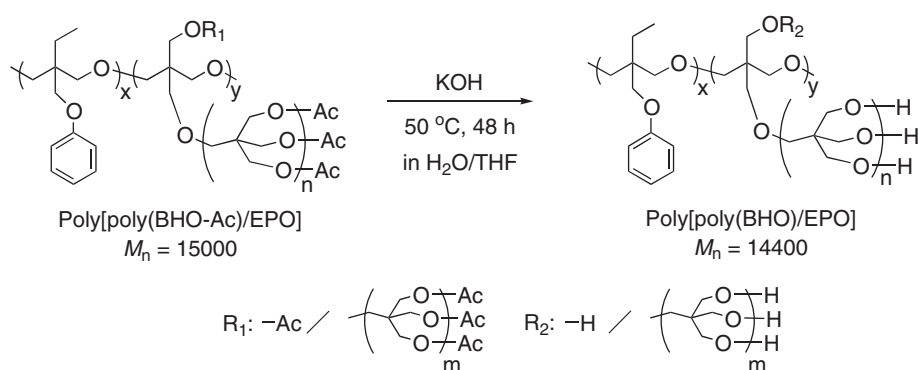
Scheme 6.

Figure 4 illustrates the ^{1}H NMR spectra of the polymers before and after hydrolysis. The signals of acetyl groups disappeared completely and hydroxyl proton signals appeared at 4.78 ppm after hydrolysis.

Furthermore, the thermal properties of the poly(BHO), poly(BHO-Ac), poly[poly(BHO-Ac)/EPO], and poly[poly(BHO)/EPO] were examined by DSC and TGA. These results were summarized in Table IV. It was observed that T_g and T_d^{10} of the polymer with pendant hydroxyl groups poly(BHO) and poly[poly(BHO)/EPO] were larger than those of poly(BHO-Ac) and poly[poly(BHO-Ac)/EPO], respectively. These results show that the thermal properties of the polymers are depended on the structures of

Table IV. The thermal stability of the poly(BHO), poly(BHO-Ac), poly[poly(BHO-Ac)/EPO], and poly[poly(BHO)/EPO]

Polymer	T_g [a] (°C)	T_d [10b] (°C)
Poly(BHO) [obtained by the reference 15, yield = 41%]	132	352
Poly(BHO-Ac) [obtained by the reference 15, M_n = 1900]	−20	341
Poly[poly(BHO-Ac)/EPO] [M_n = 15000, run 3 in Table III]	−12	419
Poly[poly(BHO)/EPO] [obtained by hydrolysis, M_n = 14400]	70	441

[a]Determined by DSC. [b]Determined by TGA.

the ends. That is, hydrogen bonding of the terminal hydroxyl groups enhanced strongly rising the T_g of the hyperbranched polymers.

SUMMARY

The anionic ring-opening polymerization of BHO as an AB3 monomer was examined using *t*-BuOK as an initiator in the presence of 18-C-6 in NMP at 180 °C, affording the corresponding hyperbranched polyether (poly(BHO)) in good yields. Poly(BHO) had an oxetanyl group and many hydroxyl groups at the ends. After that, poly(BHO-Ac) containing acetyl groups at the ends was obtained by the reaction of poly(BHO) and acetic anhydride. The cationic copolymerization of poly(BHO-Ac) with EPO was performed using BF_3OEt_2 as an initiator in $CHCl_3$ at 0 °C for 24 h, affording pseudo dendritic polymer, poly[poly(BHO-Ac)/EPO]. Furthermore, the poly[poly(BHO-Ac)/EPO] was hydrolyzed with KOH to afford the corresponding products poly[poly(BHO)/EPO]. The wide applications of the obtained poly[poly(BHO)/EPO] are expected due to the many pendant hydroxyl groups in the side chain.

REFERENCES

1. For example: S. Inoue and T. Aida, In "Ring-opening polymerization," K. J. Ivin and T. Saegusa, Ed., Elsevier, London, 1984, Vol. 1, pp 185–298.
2. a) E. J. Vandenberg and J. C. Mullis, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3083.
   b) E. J. Vandenberg and J. C. Mullis, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3113 (1989).
3. H. Magnusson, E. Malmstrom, and A. Hult, *Macromolecules*, **34**, 5786 (2001).
4. Y. Chen, M. Bednarek, P. Kubisa, and S. Penczek, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 1991 (2002).
5. T. Nishikubo, A. Kameyama, T. Nakajima, and H. Miyazaki, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2781 (1999).
6. T. Nishikubo, A. Kameyama, M. Ito, and A. Suzuki, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 2873 (1998).
7. T. Nishikubo, A. Kameyama, and A. Suzuki, *React. Funct. Polym.*, **37**, 19 (1998).
8. T. Nishikubo and K. Sato, *Chem. Lett.*, **1991**, 697.
9. H. Kudo, T. Kurakata, M. Sasaki, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, (2004) in press.
10. S. Minegishi, S. Tsuchida, M. Sasaki, A. Kameyama, H. Kudo, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 3835 (2002).
11. S. Minegishi, M. Ito, A. Kameyama, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 2254 (2000).
12. A. Kameyama, K. Ueda, H. Kudo, and T. Nishikubo, *Macromolecules*, **35**, 3792 (2002).
13. S. Inoue, IUPAC 35th International Symposium on Macromolecules, Akron, OH, Abstracts, 1994, p 60.
14. S. Inoue, T. Aida, M. Kinugawa, M. Isoda, and D. Takeuchi, *Macromol. Symp.*, **98**, 163 (1995).
15. D. Takeuchi, Y. Watanabe, T. Aida, and S. Inoue, *Macromolecules*, **28**, 651 (1995).
16. D. Takeuchi and T. Aida, *Macromolecules*, **29**, 8096 (1996).
17. D. Takeuchi, T. Aida, and T. Endo, *Macromol. Rapid Commun.*, **20**, 646 (1999).
18. H. Kudo, A. Morita, and T. Nishikubo, *Polym. J.*, **35**, 88 (2003).
19. H. Kudo, A. Morita, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, submitted.
20. D. Holter, A. P. Burgath, and H. Frey, *Acta Polym.*, **48**, 30 (1997).

$$DB = 2D + SD/\{2/3 \times (3D + 2SD + L)\}$$

Where D, SD, and L are the values of the integration ratios of double dendritic, single dendritic, and linear repeating units measured by ^{13}C NMR spectroscopy.

21. Poly(BHO) was synthesized by the anionic ring-opening polymerization in NMP at 130 °C for 24 h in 41% yield. The resulting poly(BHO) was treated with acetic anhydride to obtain the corresponding poly(BHO-Ac) with M_n = 1500, M_w/M_n = 1.35 in quantitative yield.