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STUDY ON CATIONIC RING-OPENING POLYMERIZATION MECHANISM OF 3-ETHYL-3-HYDROXYMETHYL OXETANE

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ABSTRACT

Cationic ring-opening polymerization of 3-ethyl-3-hydroxylmethyl oxetane was carried out using $BF_3 \cdot O(C_2H_5)_2$ as initiator, and a branched polyether was formed. Typical SEC curves show that the polymer consists of two fractions: one has higher molecular weight ($11.\ 7 \times 10^4 \sim 9.2 \times 10^4$) and the other has lower molecular weight ($3.8 \times 10^3 \sim 4.0 \times 10^3$). This probably resulted from the chain-transfer reaction of two propagating polymer chains. The structure of the polyEHMO formed was characterized by ^{1}H and ^{13}C NMR spectra. The degree of branching is mainly affected by the propagation mechanism. As the molar ratio of $[I]_0/[EHMO]_0$ in feed increased, the degree of branching also increased.

Key Words: Cationic ring-opening polymerization; Branched polyether; Oxetane derivate; Polymerization mechanism; Degree of branching

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INTRODUCTION

Hyperbranched polymers have received increasing attention in recent years due to their special properties and potential applications.[1–4] The cationic [5] and free radical [6–8] living polymerizations have been used to synthesize hyperbranched polymers. However, only a few papers reported the synthesis of hyperbranched polymers by cationic ring-opening polymerization, [1,9–14] mainly the study on self-condensing ring-opening polymerization (SCROP) of 3-ethyl-3-hydroxylmethyl oxetane (EHMO).[1,12–14] Some preliminary results on this reaction were obtained by Kim, but only a low molar mass polyether was obtained.[1] By using $BF_3{\cdot}O(C_2H_5)_2$ and CF_3SO_3H as initiators, Penczek et al. [12] successfully prepared hyperbranched polyethers. Hult et al.[13] simultaneously reported thermally initiated cationic ring-opening polymerization of EHMO, obtaining hyperbranched polyethers with a degree of branching (DB) of 41%. In addition, Yan et al. carried out the cationic polymerization of a similar monomer, 3-methyl-3-hydroxylmethyl oxetane, and based on DSC curves, they deduced that the DB of resulting polymers might be dependent on the feed ratio of $[EHMO]_0{:}[I]_0$.[14] It is well recognized that two competitive mechanisms are responsible for the cationic ring-opening polymerization: (1) active chain end (ACE) mechanism (nucleophilic attack of the monomer on α-carbon of the tertiary oxonium ion); and (2) activated monomer (AM) mechanism (an attack of the hydroxyl group in the polymer on α-carbon of the protonated monomer). However, the effect of polymerization mechanism on a branching structure has not been discussed yet, and it is not clear whether the feed ratio and polymerization conditions affect DB and structure of the polymer obtained. In this paper, we report our results on these aspects.

EXPERIMENTAL

Materials

$BF_3{\cdot}O(C_2H_5)_2$ was distilled under reduced pressure prior to use. CH_2Cl_2 was purified by distillation over CaH_2. Petroleum ether was used as received.

EHMO was synthesized according to the procedure reported in the literature [15] and obtained in 80% yield by redistillation at 82°C/2.8 mm Hg after drying in molecular sieve for 48 hours.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (TMS, ppm) 0.88–0.95 (m, 3H $C\underline{H}_3$), 1.70–1.75 (m, 2H, $C\underline{H}_2CH_3$), 3.16 (s, 1H, $CH_2O\underline{H}$), 3.72 (s, 2H $C\underline{H}_2OH$), 4.41, 4.47 (m, 4H, -$C\underline{H}_2$-$OC\underline{H}_2$-C).

Typical Polymerization Procedure

A two-necked, round-bottom flask with a magnetic bar was evacuated and purged with pure nitrogen three times, into which EHMO and methylene chloride were added. The catalyst was injected with a syringe; after the polymerization was carried out for a prescribed time, excess phenol dissolved in CH_2Cl_2 was added by a syringe to quench the polymerization. The stirring continued for 3 hours, then the mixture was washed with distilled water until neutralization, and the crude product was purified by precipitation in petroleum ether. The purified polymer was then dried at 35°C under vacuum for 24 hours, and the conversion was determined by gas chromatography.

Chromatography

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-500 nuclear magnetic resonance (NMR) spectroscopy with DMSO-d_6 or $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. Gas chromatography was carried out on a 102G gas chromatography (Shanghai Analysis Instrument Co., Shanghai, China). Size Exclusion Chromatography (SEC^3) measurements were as follows: A dual SEC detector (Model T60, Viscotek Corp.), with right angle laser light scattering (RALLS) and differential viscometer (DV) detectors in series, was combined online with a differential refractometer (RI, Model 410, Waters Corp.) coupled to a programmable HPLC pump (Model 590, Waters Corp.). Two chromatographic columns (American Polymer Standards Corp., Mentor, Ohio), measuring 30 cm in length and packed with 5 μm diameter PS gel, were used in series. THF was degassed ultrasonically and used as the mobile phase at a flow rate of 1.0 mL/min. The samples were dissolved in THF and filtered through 0.2 μm pore size membrane filters. Measurements were performed at 25°C, and injection volumes of the sample solutions were 100 μL. TriSEC software (Viscotek) was used to treat the data obtained. The setup of the SEC^3 system was described in a previous paper.[16]

RESULTS AND DISCUSSION

Cationic Ring-Opening Polymerization

EHMO was polymerized in a CH_2Cl_2 solution using $BF_3{\cdot}O(C_2H_5)_2$ as initiator. The representative results are given in Table 1.

According to our previous study, [17–19] and the mechanism reported,[20] the possible mechanisms of cationic ring-opening polymerization of EHMO in the presence of $BF_3{\cdot}O(C_2H_5)_2$ are proposed in Sch. 1. The initiation in-

Table 1. The Conditions and Results of Cationic Ring-Opening Polymerization of EHMO[a]

No	Molar Ratio of $[I]_0$/ $[EHMO]_0$	Reaction Time (min)	Conv.[b] (%)	M_n[c] (NMR) $\times 10^{-3}$	M_n (SEC^1)[d] $\times 10^{-3}$		M_n (SEC^3)[e] $\times 10^{-3}$		M_w/M_n (SEC^3)		Ratio of $I_{Ar}/I^f_{4.3}$	DB[i] (%)
					A[g]	B[g]	A	B	A	B		
1	1:30	15	48	3.9	55.7	2.6	91.9	4.0	4.92	1.16	5.0	34
2	1:50	30	41	3.5	64.6	1.7	153.6	5.0	2.10	1.09	1.3	28
3	1:100	720	70	3.7	71.5	2.1	117.7	3.8	3.36	1.26	0.5	18
4	1:100	360	36	2.6		1.1[h]					0.5	19
5	1:100	180	18	2.0		0.9[h]					0.4	19

[a] Polymerization conditions: Initiator: $BF_3.O(C_2H_5)_2$; Solvent: CH_2Cl_2; $[EHMO]_0$: 2mol/L; Temperature: 25°C.

[b] Conversion was determined by GC.

[c] Mn(NMR) was calculated by Eq.1.

[d] SEC^1 means SEC/RI.

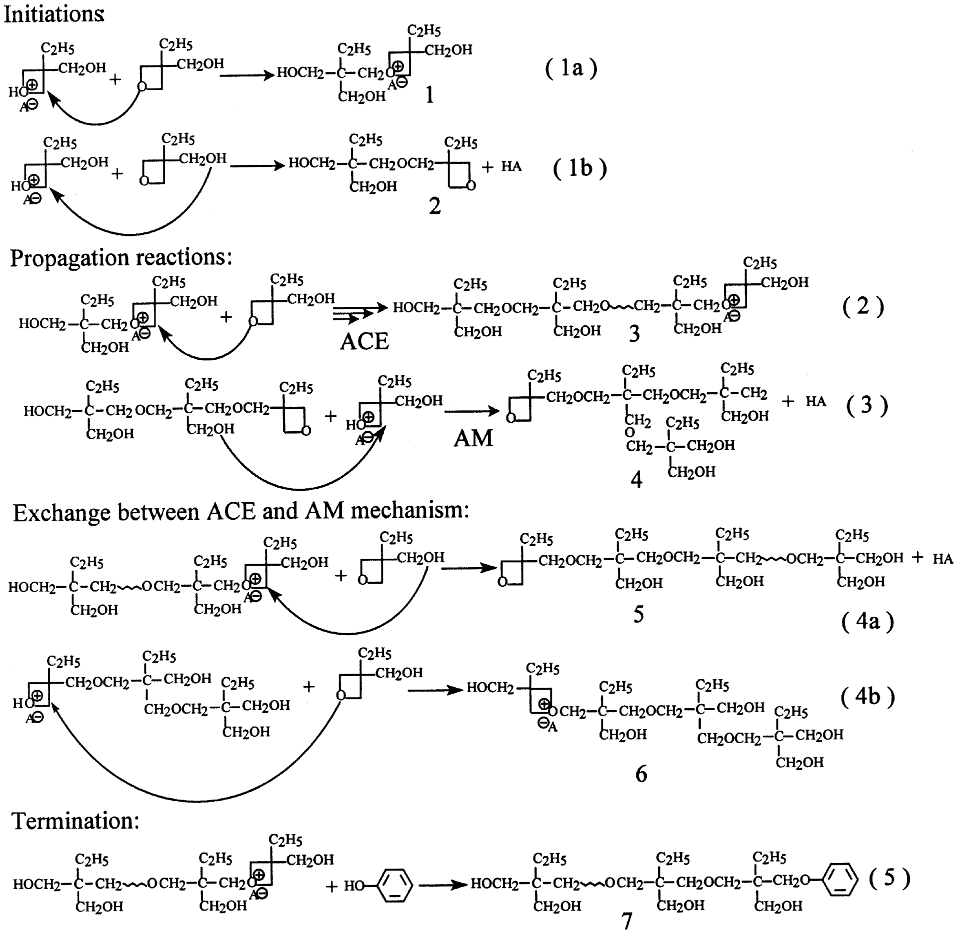
[e] SEC^3 means SEC/RI/RALLS/DV.

[f] The ratio of $I_{Ar}/I_{4.3}$ was calculated from ^{1}H-NMR data: Ratio $(I_{Ar}/I_{4.3}) = (I_{Ar}/I_{4.3}) \times 2/5$.

[g] A, B means two portions of the resulting polymer with higher and lower molecular weight respectively.

[h] This data was detected by only one SEC detector.

[i] DB = Degree of branch was calculated based on Eq. (2).



Scheme 1.

volves the protonation of oxygen in the oxetane ring, followed by successive ring-opening reaction due to nucleophilic attack of the oxygen in a second monomer, or due to nucleophilic attack of hydroxyl group in the monomer, leading to the product 1 (see reaction 1a) or product 2 (see reaction 1b), respectively. The tertiary oxonium ion was successively attacked by the oxygen in EHMO, and the polymerization proceeded via the so-called active-chain-end mechanism (ACE); a linear polymer 3 was obtained (see reaction 2). When the nucleophilic attack of hydroxyl group in EHMO unit of polymer chain on the protonated monomer occurred, the polymerization proceeded according to so-called activated monomer mechanism (AM), a branching polymer 4 was produced (see reaction 3). For propagation of a polymer chain, it may undergo AM mechanism in a certain period, and in another period, it may proceed via ACE mechanism (see reactions 4a and

4b). Whatever mechanism is involved in the propagation process, one end group in the resulting polymer chain must be two hydroxyl groups and the other one must be oxetane ring or oxonium ion. For the sake of obtaining a stable product and quantitatively calculating the amount of terminal groups, excess phenol was added to quench the polymerization. As we discussed, when propagating via the ACE mechanism, the oxonium ion at the end of polymer chain will open its ring by the attack of excess phenol, forming the polymer with structure 7.[21]

In order to identify whether the cationic ring-opening polymerization of EHMO proceeds via Sch. 1, the ^{1}H-NMR spectra of the polymers are shown in Fig. 1. Signals at 0.8 and 1.2 ppm are ascribed to the methyl and methylene protons of the EHMO unit of polyethers. Two small signals at 6.8 and 7.1 correspond to the aromatic protons, indicating that the ring opening of oxetane due to the attack of phenol really occurs. Two small signals at 4.2 and 4.3 ppm belong to the methylene protons of the oxetane ring since the

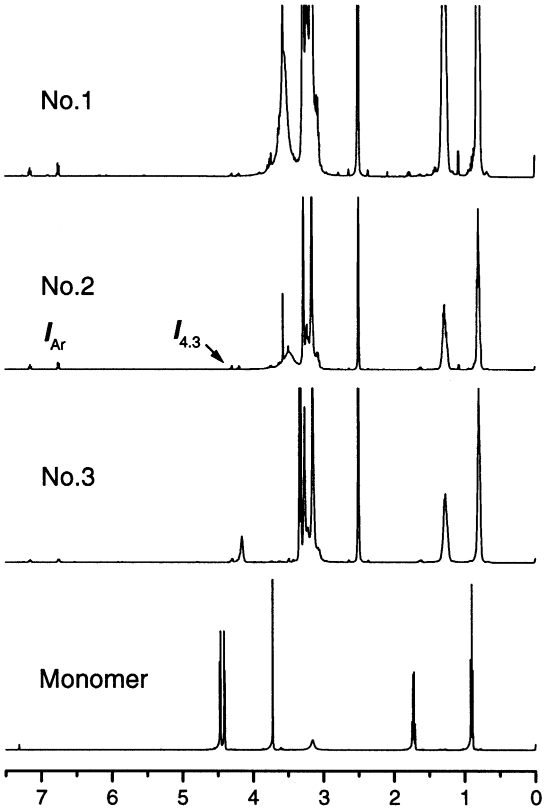


Figure 1. ^{1}H-NMR spectra of the monomer and the resulting polymers (No. 1–3) obtained from different feed ratio of $[EHMO]_0/[I]_0$, which is 30:1 (No. 1), 50:1 (No. 2), and 100:1 (No. 3), respectively.

methylene protons in the oxetane ring of the monomer appear at 4.41 and 4.67 ppm, and the methylene protons next to the hydroxyl group could not be found in Fig. 1, demonstrating that the remaining EHMO in the polymer would be negligible. This verifies that some EHMO monomers underwent the initiation reaction 1b. As we discussed, the terminal oxonium ion is the result of initiation 1a and propagation via the ACE mechanism, while the terminal oxetane ring is due to initiation 1b and propagation via the AM mechanism. The integration ratio of the peaks at 6.8 and 7.1 (I_{Ar}) to that at 4.3 ($I_{4.3}$) should reflect the activities of ACE and AM mechanisms at the same feed ratio of $[EHMO]_0/[I]_0$. Figure 2 shows that the integration ratio of $I_{Ar}/I_{4.3}$ decreased from 5 to 0.5 as the feed ratio of $[EHMO]_0/[I]_0$ increased from 30 to 100, implying that more oxonium ions reacted with phenol at a higher ratio of $[EHMO]_0/[I]_0$. When the feed ratio of initiator to EHMO increases, the active monomer increases, but free EHMO decreases since the total amount of EHMO keeps constant. The propagation reactions according to

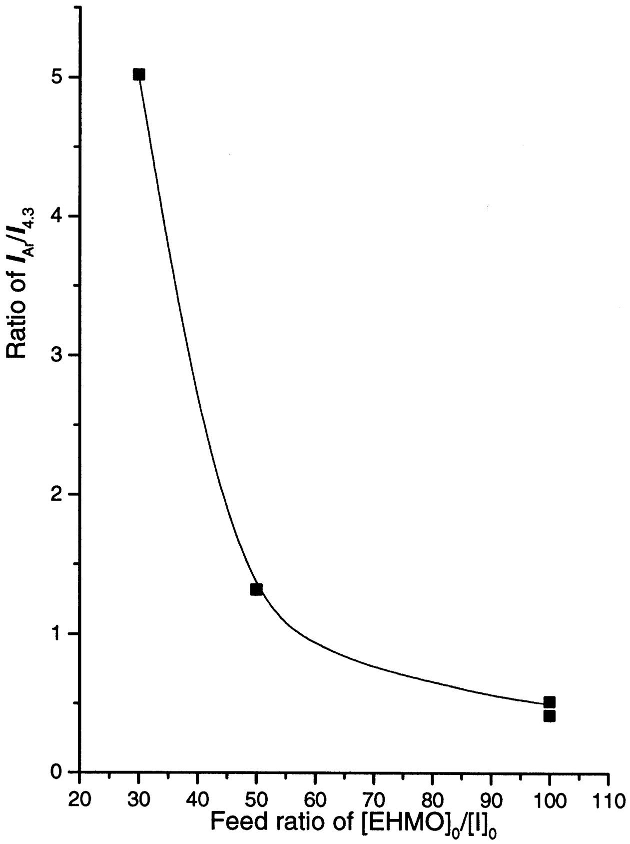


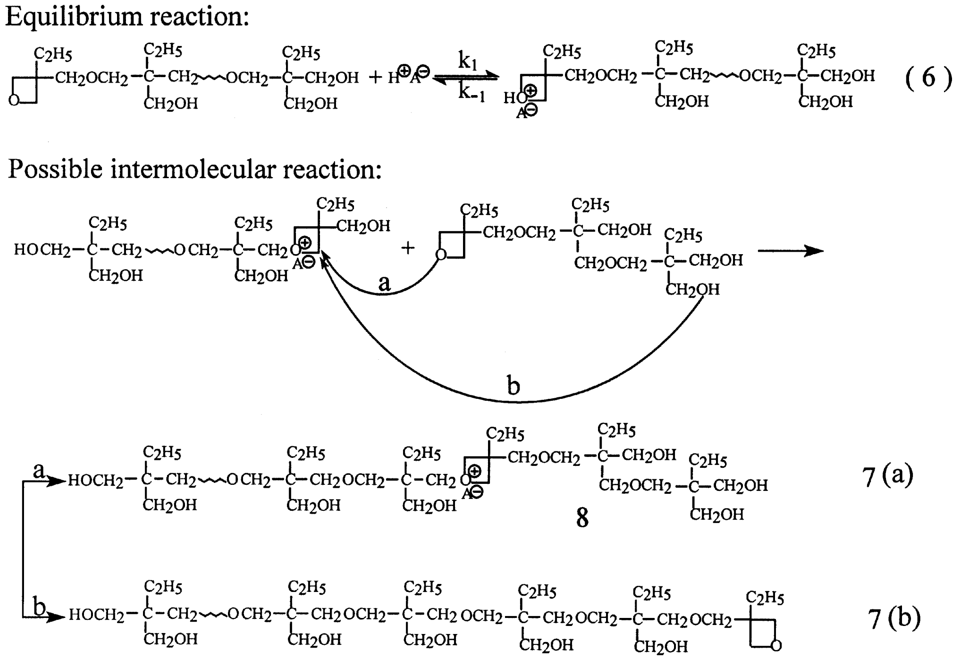
Figure 2. The relationship of the feed ratio of $[EHMO]_0/[I]_0$ with the ratio of $I_{Ar}/I_{4.3}$ calculated based on ^{1}H-NMR data.

ACE and AM mechanisms are competitive reactions. The reduction of free EHMO might reduce the rate of ACE propagation, leading to less terminal oxonium ions in the polymer chains, which is contrary to the phenomenon observed. Therefore, an equilibrium between the terminal oxetane and its oxonium ion (see reaction 6 in Sch. 2) has to be considered. As the amount of initiator increases, more terminal oxetane groups are protonated, and as a result, the terminal phenyl groups increase.

In any case, the terminal group of the polymer obtained is oxetane or oxonium ion. Thus, based on the ^{1}H-NMR data, the number-average molecular weight Mn(NMR) can be calculated according to Eq. (1):

$$\mathrm{Mn(NMR)} = [(I_{1.2}/2)/(I_{Ar}/5 + I_{4.3}/2)] \times 116 \tag{1}$$

where 116 is the molecular weight of EHMO. The molecular weight and molecular weight distribution (MWD) were characterized by the SEC^3 technique. All the results are listed in Table 1. We can see that the conversion and molecular weight increase as polymerization time increases. When the molecular weight of hyperbranched polymers is measured by SEC^1 using polystyrene standards in the calibration, the lower molecular weight than its actual molecular weight is generally observed. Comparing the values measured by SEC^1, molecular weights measured by SEC^3 (see Table 1) are much larger; indicating the formation of hyperbranched polyether. Typical SEC



Scheme 2.

curves of the resulting polymers are shown in Fig. 3. There are two portions of branched polyethers in the SEC curve of No. 3, one has higher molecular weight and the other lower molecular weight. Possible reactions are suggested as shown in Sch. 2. Once intermolecular reactions 7a–b occur, the resulting polymer chain has more hydroxyl groups statistically; its propagation rate will be faster than that of the polymer chain with low molecular weight. At a higher conversion, intermolecular reactions 7a–b should be considered. Comparing with propagation reactions of polymer chains with EHMO, the molecular weight of polymer chain increases faster. As conversion increases, intermolecular reactions become more important, leading to the formation of higher molecular weight polyether. In order to confirm this explanation, the cationic ring-opening polymerization of EHMO was carried at various conversions. The SEC curves of the resulting polyethers obtained at conversions of 18% (sample 5) and 70% (sample 3) are shown in Fig. 3. Comparing sample 3 with sample 5 in Fig. 3, the difference is obvious. One small peak at higher molecular weight position is observed in the SEC curve of sample 3, while several peaks with relatively lower molecular weight appear

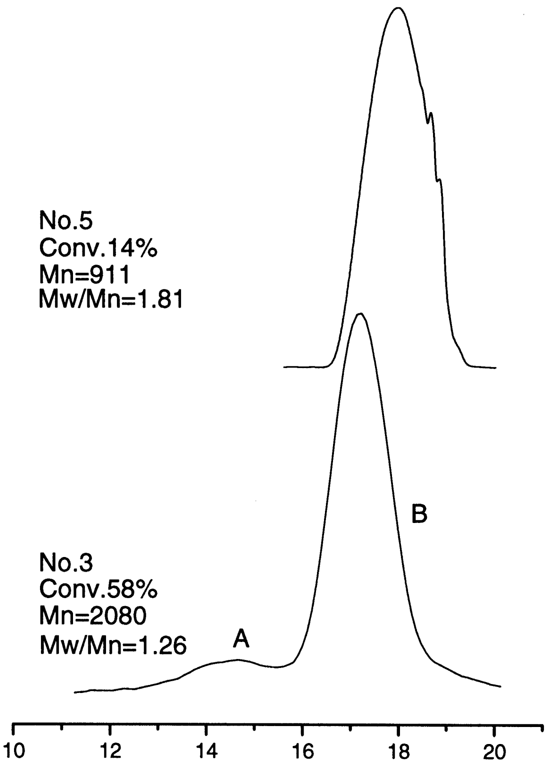


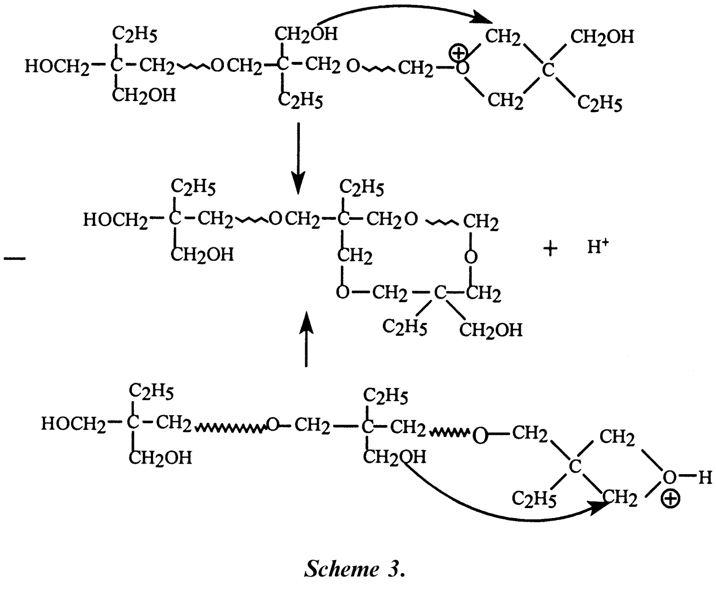
Figure 3. The effect of conversion on GPC curves of the resulting polymers with the same feed ratio of $[EHMO]_0/[I]_0$ (100:1).

in that of sample 5. At low conversion, polymerization takes place mainly according to reaction 2 and 3 (see Sch. 1). The oligomer chains with higher degree of polymerization (DP) has much higher possibility of propagation reaction than that with lower DP oligomer. Therefore, the peaks appeared at lower molecular weight positions are reasonable (see sample 5 in Fig. 3). When conversion increases, more and more intermolecular reactions occur, and the higher the molecular weight of the polymer chain, the higher the possibility of the reactions between polymer chains with higher DP. As a result, a small peak appears at a higher molecular weight (see No. 3 of Fig. 3), and the difference in molecular weights between the two peaks is big (see Table 1).

In addition, macromolecules growing by either ACE or AM mechanism may undergo intramolecular cyclization according to Sch. 3. Possibly, this is another reason why the low molecular weight polyether was formed.

Degree of Branching

In hyperbranched polymers, there are three different kinds of repeating units: dendritic (D), linear (L), and terminal units (T). In 1991, Fréchet et al. introduced the term average degree of branching to describe hyperbranched polymers.[22] The DB is a measure of the fraction of the repeating units that form branch points or terminal groups and was defined as the ratio of the amount of terminal and dendritic units to the sum of all repeating units, as shown in Eq. (2).



Scheme 3.

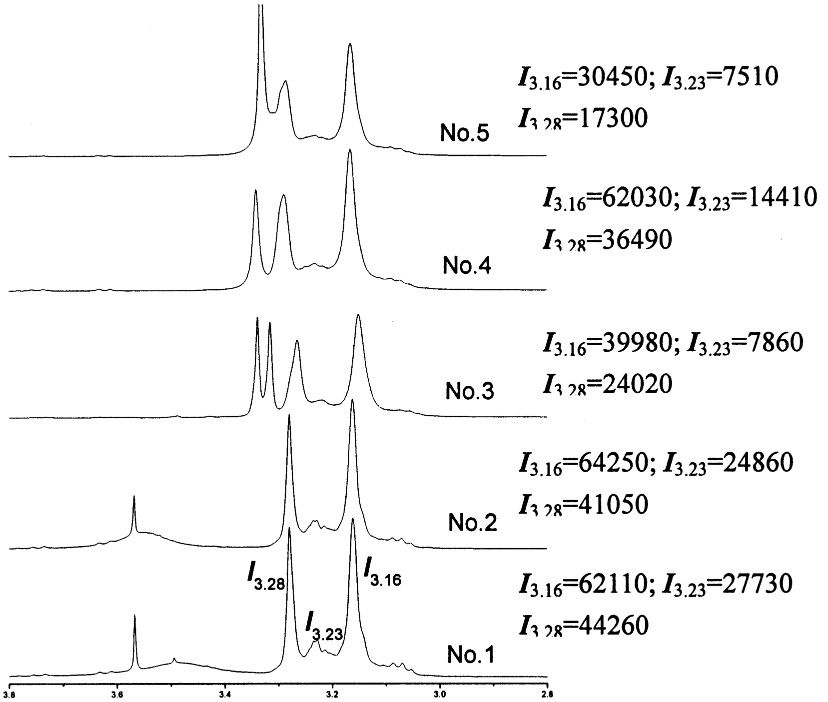
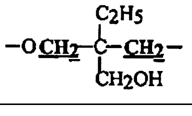
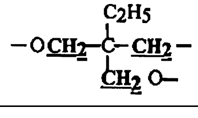
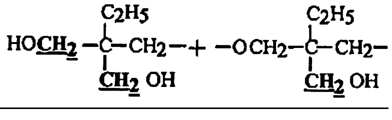


Figure 4. ^{1}H-NMR spectra in the range of 3.0 to 3.3 ppm for the polyethers No. 1–5 in Table 1.

$$DB = \frac{D + T}{D + L + T} \tag{2}$$

To estimate the DB, the signals in the range of 3.3 and 3.3 ppm corresponding to methylene protons adjacent to hydroxyl group and ether oxygen were magnified as shown in Fig. 4. The assignment of the three signals is listed in Table 2. The integration ratio of the peaks at 3.28 ($I_{3.28}$) to 3.23 ($I_{3.23}$) and 3.16 ($I_{3.16}$) ppm is 1:2.1, very close to the ratio of their proton numbers. From this assignment, the parameters in Eq. (2) are: $D = I_{3.23}/6$, $L = I_{3.16}/4$, and $T = [I_{3.28} - (I_{3.16}/4) \times 2]/4$. Therefore, the DB of the polymers

Table 2. Assignment of Methylene Groups Between 3.0 and 3.3

Structural units	 $-O\underline{CH_2}-\overset{C_2H_5}{\underset{CH_2OH}{\overset{\vert}{\underset{\vert}{C}}}}-\underline{CH_2}-$	 $-O\underline{CH_2}-\overset{C_2H_5}{\underset{\underline{CH_2}\,O-}{\overset{\vert}{\underset{\vert}{C}}}}-\underline{CH_2}-$	 $HO\underline{CH_2}-\overset{C_2H_5}{\underset{\underline{CH_2}\,OH}{\overset{\vert}{\underset{\vert}{C}}}}-CH_2- + -OCH_2-\overset{C_2H_5}{\underset{\underline{CH_2}\,OH}{\overset{\vert}{\underset{\vert}{C}}}}-CH_2-$
Chemical shifts (ppm)	3.16	3.23	3.28

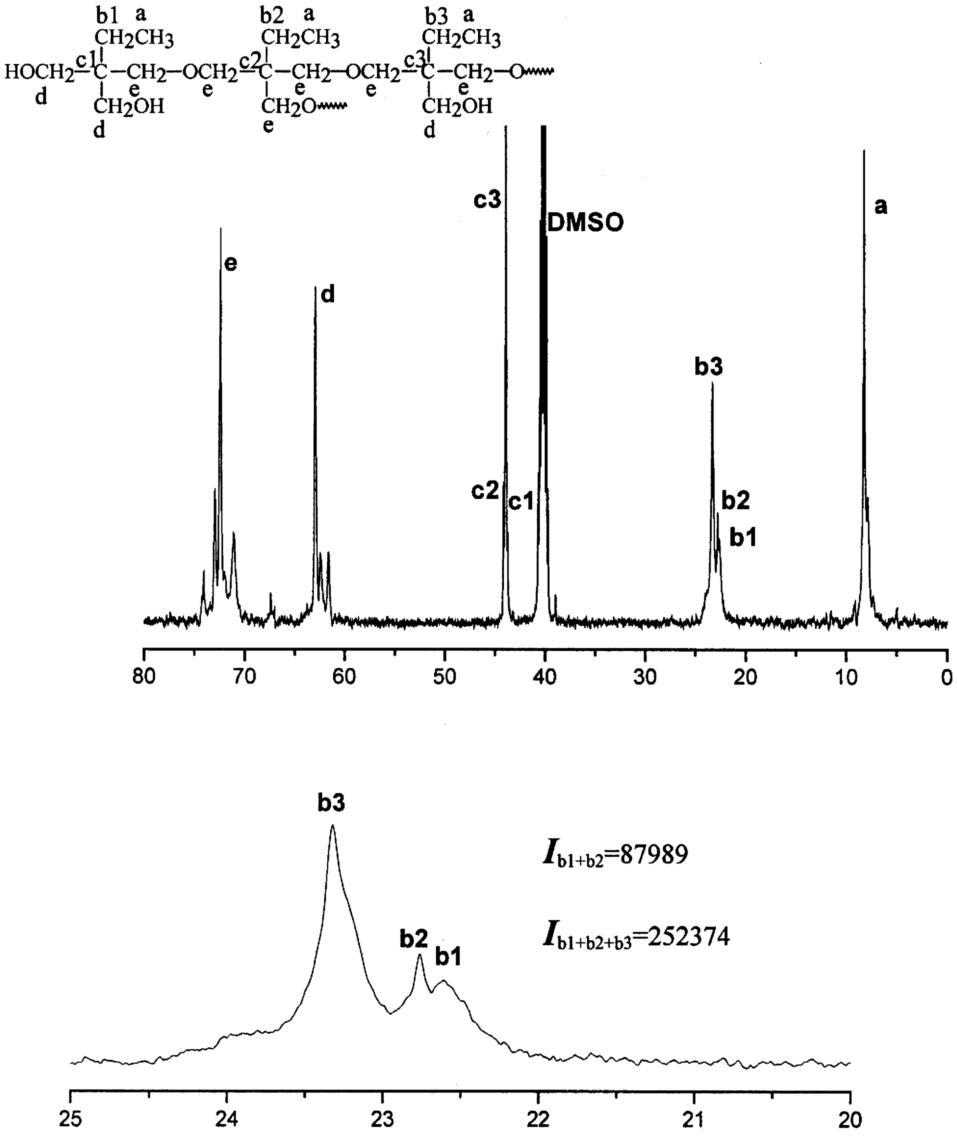


Figure 5. ^{13}C-NMR spectrum of sample No. 1 measured by DMX500M NMR spectroscopy.

obtained can be calculated based on Eq. (2), and the results are listed in Table 1.

For further examining the DB of the polymer, ^{13}C-NMR spectrum was analyzed. A typical ^{13}C-NMR spectrum and the assignment of each peak is shown in Fig. 5 (Sample 1 in Table 1). Three peaks at 22.6, 22.8, and 23.3 ppm correspond to the methylene carbons b1, b2, and b3, respectively (see Fig. 5). Also, another three peaks at 43.7, 43.9, and 44.1 are ascribed to the quaternary carbons c1, c3, and c2. Signals at δ 63 and 73 ppm belong to the methylene carbons adjacent to the hydroxyl group and ether oxygen, respectively. From the integrations of signals of various methylene carbons (b1, b2, and b3), the parameters in Eq. (2) are: $D + T = I_{b1+b2}$, $D + T + L = I_{b1+b2+b3}$, the DB can be calculated with a result of 35%, which is close to the result (DB = 34%) calculated from the ^{1}H-NMR spectrum.

The influence of the feed ratio of $[I]_0/[EHMO]_0$ on the DB of the polymer was investigated. DB increased with increasing the feed ratio of $[I]_0/[EHMO]_0$. Actually, initiation reactions 1a and 1b, and propagation reactions 2 and 3 are all competitive reactions. In comparison with chain transfer reactions 1b and 3, the activation energies of reaction 1a and 2 are lower and the k_ps are bigger. When more initiator is used, the amount of protonated oxonium ion would also increase, while the amount of hydroxyl groups remains unchanged during the polymerization. This will be favorable for the reactions 1b and 3 and also for the formation of the branched polymers.

CONCLUSION

EHMO can undergo cationic ring-opening polymerization via AM and ACE mechanisms using $BF_3 \cdot O(C_2H_5)_2$ as initiator. Two portions of branched polyether were obtained. The higher molecular weight polymer is the result of intermolecular reactions. Polymerization via ACE mechanism produces linear polyether. Branched polymer is formed only by the reaction of hydroxyl groups in the middle of polymer chain with oxonium ions. The terminal hydroxyl groups react with oxonium ion to afford linear polyether. The DB of the resulting polymers can be examined by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The DB of polyether increases with the increase of the initial ratio of $[I]_0/[EHMO]_0$.

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