Notes

Effect of Reaction Temperature on Degree of Branching in Cationic Polymerization of 3-Ethyl-3-(hydroxymethyl)oxetane

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Introduction

The degree of branching (DB) is one of the most important molecular parameters for branched polymers. It exerts a tremendous influence on the physical and chemical properties of polymer materials. However, it is difficult to control the DB of the resulting polymer in a conventional polymerization. Recently, Hult et al.[1−3] and Penczek et al.[4−6] independently reported the cationic polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane (EHO). Yan and co-workers[7] observed that the DB of the resulting polyether can be controlled by the monomer-to-catalyst ratio in the cationic polymerization of 3-methyl-3-(hydroxymethyl)oxetane (MHO). Furthermore, Hult and co-workers[2] carefully investigated the influence of reaction conditions on the DB of the hyperbranched polyether prepared from EHO. In their work, the cationic polymerization of EHO was carried out in bulk at different reaction temperatures above 60 °C. The DB of the resulting polymer (PEHO) depended on the rate of adding monomer and the monomer conversion but evidently was not affected by the reaction temperature. It seems necessary to further check the influence of reaction temperature on the DB of PEHO over a wider temperature range. This work performed the cationic polymerization of EHO with $BF_3{\cdot}O(C_2H_5)_2$ and CH_2Cl_2 as the initiator and the solvent, respectively, and the reaction temperature ranged from −50 to +30 °C. The products were characterized by SEC and ^{13}C NMR spectroscopy. It was found that the DB increases with increasing reaction temperature at the lower temperature range. This finding may facilitate the preparation of PEHO with desirable architecture.

Experimental Section

Materials. $BF_3{\cdot}O(C_2H_5)_2$ (Aldrich) was used as supplied. CH_2Cl_2 was purified as described.[8] 3-Ethyl-3-(hydroxymethyl)-oxetane was prepared according to a literature procedure.[9]

Polymerization. The cationic polymerization of EHO was conducted under a constant stream of nitrogen in a four-necked round-bottomed flask with a PTFE stirrer, a funnel, and a thermometer. Prior to performing the reaction, the system was heated to about 100 °C and was degassed using nitrogen for at least 20 min. Then 80 mL of CH_2Cl_2 and 6.4 mL of $BF_3{\cdot}OEt_2$ (0.05 mol) were added to the flask via syringe, respectively. The monomer (0.1 mol, 11.6 mL) was introduced through the funnel within 5 min, and the reaction temperature was kept constant throughout the polymerization process. After 48 h, the polymerization was quenched with ethanol. The product was precipitated in distilled water. The white solid sample was dried at 80 °C under high vacuum. The yields of all products were determined by gravimetry and given in Table 1.

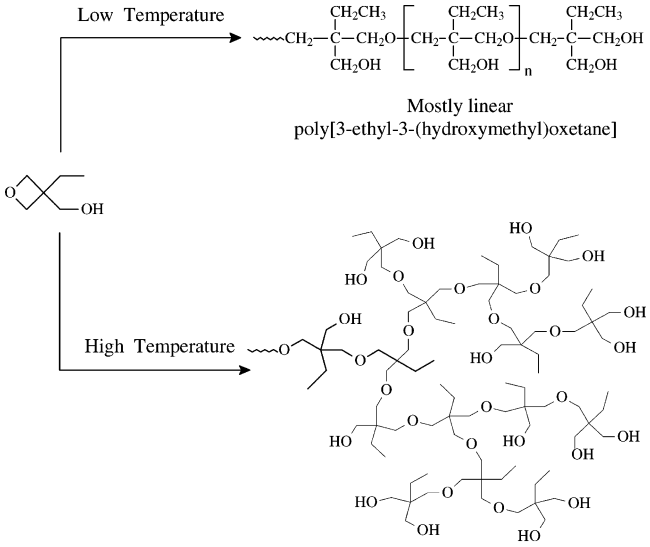
Characterizations. The molecular weights of the products were measured by size exclusion chromatography (SEC) on a Perkin-Elmer Series 200 system at 70 °C (100 μL injection column, PL gel 10 μm 300 × 7.5 mm mixed-B columns, polystyrene calibration). DMF was used as the solvent, and the flow rate was 1.0 mL/min. The DB values were determined by quantitative ^{13}C NMR, and all NMR measurements were performed on a Varian MERCURYplus 400 spectrometer at 20 °C. DMSO-d_6 was used as the solvent.

Table 1. Polymerization Conditions[a] and Characterization of PEHO

samples	reaction temp (°C)	yield in %	SEC $M_n \times 10^{-3}$	polydispersity	DB %
1	−50	84	5.425	1.33	9
2	−40	83	4.987	1.57	11
3	−30	89	4.890	1.54	15
4	−20	85	5.243	1.38	22
5	−10	86	5.412	1.46	31
6	0	90	4.731	1.61	36
7	10	87	5.266	1.45	39
8	20	90	5.374	1.42	41
9	30	91	5.078	1.60	42

[a] The molar ratio of the catalyst to the monomer equals 1/2.

Scheme 1



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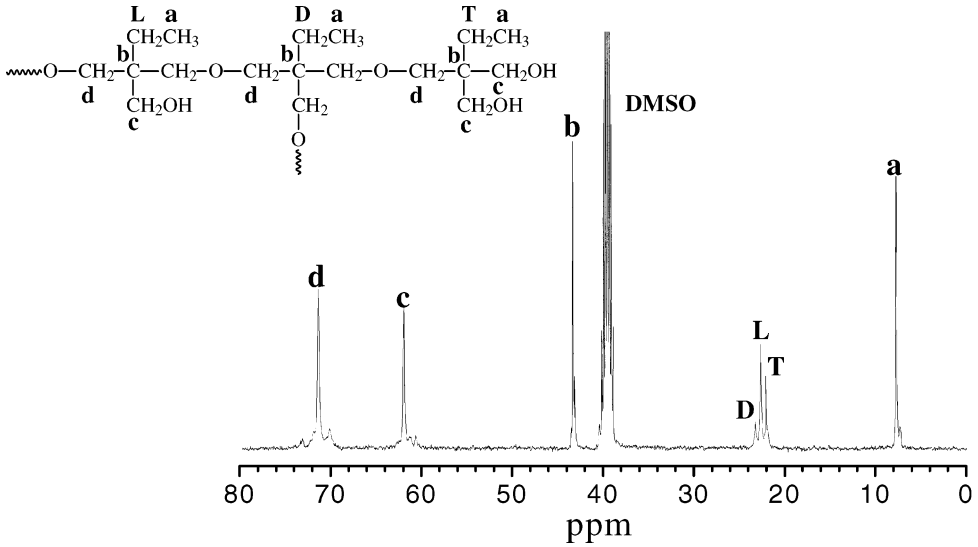

Figure 1. ^{13}C NMR spectrum of PEHO.

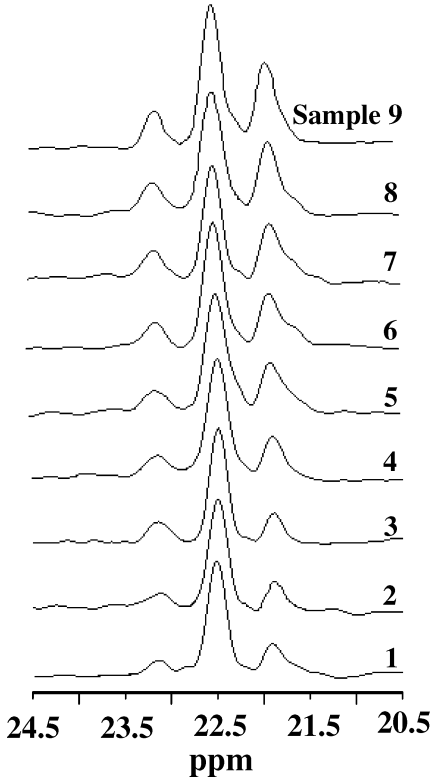

Figure 2. Variation of the three peaks near 22.50 ppm in ^{13}C NMR spectra of various PEHO samples.

Results and Discussion

The PEHO samples obtained were characterized by SEC and ^{13}C NMR measurements. The reaction conditions and the characterization results are listed in Table 1. The molecular weights of the PEHO samples are close to those reported previously.[1−6]

One of the ^{13}C NMR spectra of PEHO samples is given in Figure 1. The three peaks near 22.50 ppm are attributed to the carbon atoms of methylene in the ethyl groups of the dendritic unit (D), the linear unit (L), and the terminal unit (T). The peaks near 43.5 ppm from quaternary carbon atoms overlap into a single peak (b) due to the low resolution. The DB value can be determined by integration of signals of different ethyl groups. The ^{13}C NMR spectra near 22.50 ppm of various PEHO samples synthesized at different temperatures are shown in Figure 2. The DB values determined from Figure 2 are listed in Table 1. The corresponding plot of DB versus reaction temperature is presented in Figure 3. Evidently, the architecture of the resulting polyether depends on the reaction temperature. Penczek et al.[5] have discussed the mechanism of the cationic polymerization of EHO. We believe that there are two competitive addition reactions in the polymerization process; that is, the oxetane group of an inimer or a species adds to a terminal unit of other species forming a new linear unit, and the oxetane group aforementioned adds to a linear unit of other species generating a dendritic unit. At low temperature, the linear addition is preferred, which leads to mostly linear products; at higher temperatures, the addition reaction becomes a random process (the two addition manners are comparable) resulting in hyperbranched polymers (Scheme 1). Figure 3 demonstrates that only a little change in DB can be observed when the reaction temperature is higher than 20 °C. This may be why Hult et al.[2] could not observe a significant relationship between DB and reaction temperature because they performed the polymerizations of EHO at 60 °C or higher temperatures.

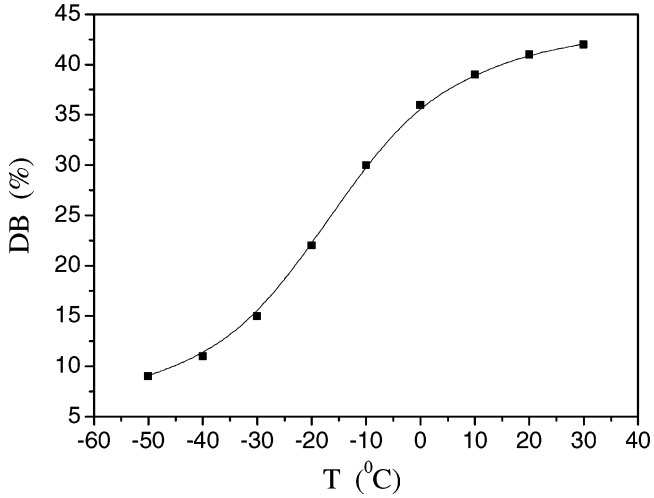

Figure 3. Relationship between DB and polymerization temperature.

Conclusion

The PEHO samples with various DBs were obtained in the cationic polymerization of EHO at −50 to +30°C. It was found that the DB determined by ^{13}C NMR increases with increasing reaction temperature. Only a little change in DB can be observed when the reaction temperature is higher than 20 °C. This may be why Hult and co-workers could not observe the dependence of DB on the reaction temperature because they performed the polymerizations of EHO at 60 °C or higher temperatures.

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