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Hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) via anionic polymerization

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Abstract

Anionic polymerization of 3-ethyl-3-hydroxymethyl oxetane was achieved using NaH with coinitiators benzyl alcohol (BA) or trimethylol propane (TMP). Pendent hydroxyls facilitate a multibranching polymerization. NMR confirmed the presence of linear, dendritic, and terminal repeat units. For TMP initiated polymerizations there was an acetone soluble portion which was more branched (DB = 0.48) than the acetone insoluble portion (DB = 0.20). Polymers were not soluble in water, ether or THF, but were partially soluble in acetone and completely soluble in methanol, benzene, chloroform, and DMSO. MALDI-TOF analysis showed relatively low molecular weights (around 500) and confirmed the presence of both cyclic and TMP endgroups. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic ring-opening polymerization; 2-Ethyl-2-hydroxymethyl oxetane; Hyperbranched

1. Introduction

Hyperbranched polymers are typically prepared by one-pot polymerizations, offering cost and time saving advantages over multistep syntheses of dendritic polymers. For example, ring-opening multibranching polymerizations using cyclic AB_2 monomers have led to the controlled synthesis of hyperbranched polyglycerols [1,2]. Slow addition of glycidol to a triol-initiating core that had been activated with base gave hyperbranched polyethers with good polydispersities and complete initiator incorporation. These hyperbranched polyols are easily modified [3], as demonstrated by conversion of any linear segments (one pendent hydroxyl) into dendritic segments (completely substituted) using a postsynthetic modification strategy [4], block copolymerization with propylene oxide [5], and selective core-shell modifications [6].

Oxetanes undergo cationic ring-opening polymerization using cationic photoinitiators [7–9], and traditional cationic initiators including boron trifluoride diethyletherate, trifluoromethanesulfonic acid [10,11], and benzyltetramethylenesulfonium hexafluoroantimonate [12]. Cationic polymerizations of the multifunctional 2-ethyl-2-hydroxymethyl oxetane gave hyperbranched polyol structures analogous to hyperbranched glycerols [12–14]. A review on hyperbranched materials was published by Kakimoto and Jikei [15]. These polymers have enormous potential for further reaction to give a wide variety of derivatives with unique properties, especially if alternative one-pot synthetic methods could be developed.

While oxetanes have generally been classified as monomers that will polymerize only cationically, some anionic polymerizations of unsubstituted oxetane have been accomplished using bulky aluminum-based catalysts with added Lewis acids [16,17]. However, other strongly basic species such as potassium *tert*-butoxide at 60 °C [18]. or potassium phenolate at 80 °C in the presence of crown ethers [19], failed to give polymer. Substituted oxetanes, while not undergoing polymerization, have been shown to open when treated with extremely strong nucleophiles, such as the azide anion [20], or under redox conditions with lithium 4,4′-di-*tert*-butylbiphenylide [21]. In this report, we describe the anionic ring-opening polymerization of 3-ethyl-3-hydroxymethyloxetane (EHO) to a hyperbranched polyol using sodium hydride as a strong base.

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Table 1
Results from ^{13}C NMR, and SEC for fractionated and unfractionated samples of poly(EHO)

Sample	TMP/OX	Polymerization conditions	NMR			SEC		
			DB	DP_n	M_n	M_n	M_w	PDI
1	1:20	Unfractionated by precipitation	0.33	11.2	1300	533	590	1.11
2	1:20	Fractionated-acetone insoluble	0.20	12.3	1427	–	–	–
3	1:20	Fractionated-acetone soluble	0.48	11.2	1300	498	423	1.15

2. Experimental

For a typical polymerization, an oven-dried flask was equipped with a dried addition funnel and placed in a preheated oil bath (>100 °C). To this flask, trimethylol propane (0.578 g, 4.31 mmol) was added as three-armed core initiator, or benzyl alcohol (0.67 g, 5.9 mmol) as monofunctional initiator. A strong nitrogen purge was used to remove residual moisture, and a slight positive pressure maintained to keep the system dry. NaH (~10 mol% based on alcohol initiator) was added and gas evolution was observed. EHO (10.0 g, 86.2 mmol)[1] was added at a rate of approximately one drop per minute. The mixture was allowed to stir for 40 h at a temperature greater than 100 °C. All polymerizations were quenched by addition of methanol and the product isolated by precipitation into water. Yields ranged from 3.14 g (31.4%) to 4.3 g (43%); polymers were not soluble in THF, water and ether but were soluble in methanol, benzene, $CHCl_3$ and DMSO. Both ^{13}C and ^{1}H NMR spectra showed that the fraction that did not precipitate in water was a combination of oligomers that could not be filtered and unreacted monomer. For one polymerization (Samples 2 and 3, Table 1), the polymerization was quenched with methanol and precipitated into acetone giving a small amount of precipitate. The acetone solution was concentrated by rotary evaporation and precipitated into water giving an acetone soluble fraction.

^{1}H and ^{13}C NMR were collected on a Varian 300 MHz NMR in both DMSO-d_6 and $CDCl_3$. Specific shifts, ^{1}H NMR ($CDCl_3$): $\delta = 0.8$m CH_2CH_3; 1.3m CH_2CH_3; 1.7m CH_2CH_3; 3.3–3.4m, 3.5s, 3.6m, 4.4m CH_2OCH_2, CH_2OH, or OH. ^{13}C NMR ($CDCl_3$): $\delta = 7.7$, 8.5 CH_2CH_3; 23.1, 27.2m CH_2CH_3; 43.3m C; 65.8m, 72.2m, 74.2, 78.5 CH_2OCH_2 or CH_2OH.

To get better resolution of the quaternary carbon, poly(EHO) (0.3 g) was dissolved in trifluroracetic anhydride (TFAA) (3 ml) and stirred at room temperature for 30 min. Excess TFAA was removed by rotary evaporation. The residue was dissolved in $CDCl_3$ for ^{13}C NMR. All chemicals were used as received with the exception of benzyl alcohol, which was distilled under vacuum from calcium hydride immediately prior to use.

MALDI-TOF analysis was performed by the New Orleans Center for MS research. Measurements were performed with a PerSeptive Biosystems Voyager-Elite MALDI-TOF. Dithranol was used as matrix. The ions were accelerated to 20.0 kV and measured in the reflection mode of the spectrometer. Only sodium-cationized ions ($M + Na^+$) were detected.

Molecular weights and polydispersities were determined using a size exclusion chromatography (SEC) system equipped with a Waters 515 HPLC pump, an Alcott 728 Autosampler (Alcott, Inc.), a 2410 Refractive Index Detector (Waters Corp.), and two sets of PLgel™ (Polymer Laboratories Inc.) 5 μm SEC columns in series. HPLC grade $CHCl_3$ served as a mobile phase and was delivered at a flow rate of 1.0 ml/min. The SEC columns were calibrated using a series of narrow polystyrene standards. PL Caliber® GPC software (Polymer Laboratories Inc.) was used to calculate molecular weights and polydispersities by converting the refractive index detector response of the sample into a molecular weight distribution based on the log M vs. elution time calibration curve. Thermal analyses were performed on a TA Instruments 9900 analyzer equipped with 952 thermal gravimetric analyzer cells using heating rates of 10 °C/min under nitrogen purge.

3. Results and discussion

Temperature was found to play a key role in the anionic reaction of EHO. Using NaH, anionic polymerization of EHO was achieved, but only at temperatures greater than 100 °C; ^{13}C and ^{1}H NMR spectra showed no signs of ring-opening when the reaction was attempted at 90 °C. This could be the result of a high energy of activation for the opening of the oxetane ring, or to contamination by strongly bound moisture, which inhibits formation of alkoxide groups needed for the ring-opening process. Slow addition of monomer to both tri- and monofunctional initiator resulted in hyperbranched polymers (Fig. 1). Polymers obtained were generally waxy in appearance, although a

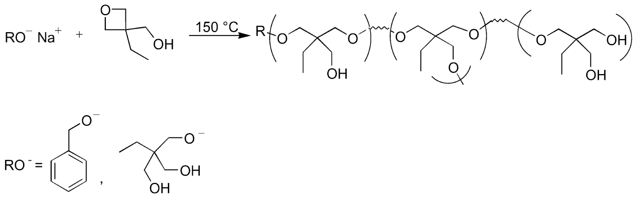

Fig. 1. Hyperbranching polymerization of EHO.

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[1] Available from Toagosei Co., Ltd, Toyko.

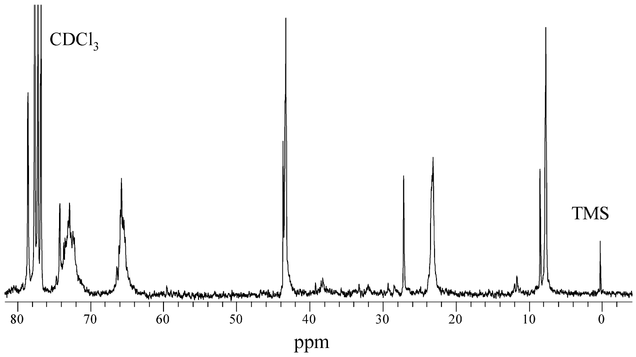

Fig. 2. ^{13}C NMR spectra of poly(EHO) (sample 3).

solid fraction could be obtained by precipitation into acetone, which amounted to about 21% of the total mass of polymer synthesized. Fig. 2 shows the ^{13}C NMR spectra for acetone soluble poly(EHO). When a monofunctional initiator was used, the entire fraction was soluble in acetone. Table 1 summarizes polymerization conditions, average degrees of branching and degrees of polymerization (by ^{13}C NMR), and molecular weight. The average DP was calculated using peak heights from of the quaternary carbon [2]. There is poor agreement between the calculated DP and M_n by SEC indicating the formation of cyclic species, or initiation by species other than the TMP core.

Initially, the difference in solubility and appearance was thought to be the result of difference in molecular weight between the two fractions, however, MALDI-TOF showed that both fractions had similar molecular weights. Fig. 3 shows the MALDI-TOF spectrum for acetone soluble poly(EHO). Although GPC of hyperbranched materials is often difficult, there was good molecular weight agreement with the MALDI-TOF results for the acetone soluble portion. Therefore, the differences in solubility is most likely due to the differences in the average degree of branching (DB), which was calculated for low molecular weight polymers according to Frey et al. [22] using the quaternary region of the ^{13}C NMR spectra. Polymers were treated with trifluoroacetic anhydride (TFAA) to convert pendent and terminal alcohol groups to trifluoroacetate moieties. This allows better NMR resolution of the various repeat unit structures generated. DEPT NMR confirmed the presence of the quaternary carbons from ring-opened monomer units, and peak assignments for terminal, dendritic, and linear segments were made according to the literature values [10,12,13], and corresponded to values obtained by the cationic polymerization of EHO in our laboratory. The acetone insoluble fraction had a DB = 0.20 and the acetone soluble fraction had a DB = 0.48. An additional peak in the quaternary region can be seen as a shoulder on the linear peak (Fig. 4A) or as a doublet of the linear peak (Fig. 4B) which does not correspond to the literature values, or to monomer peaks. This peak is due to cyclic endgroups resulting from initiation by an oxetane alkoxide.

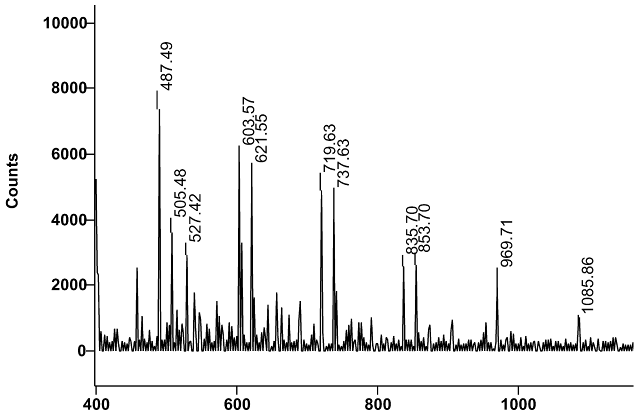

Fig. 3. MALDI-TOF for poly(EHO) (sample 3).

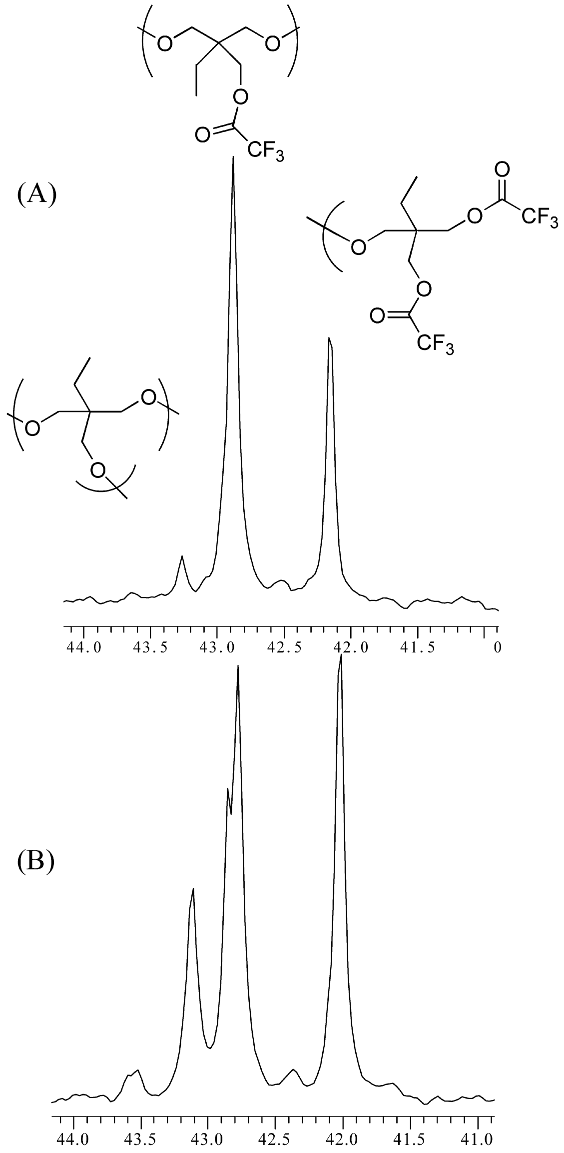

Fig. 4. ^{13}C NMR of TFAA treated poly(oxetane). (A) Acetone insoluble fraction (sample 2); (B) acetone soluble fraction (sample 3).

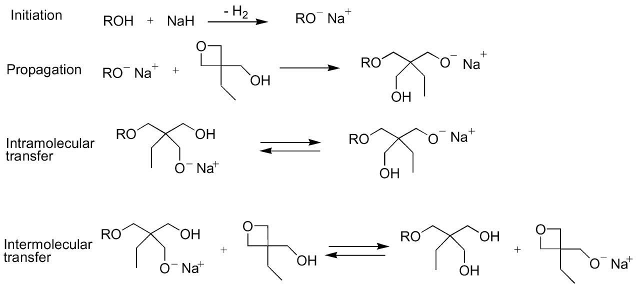

Fig. 5. Mechanism for ring-opening multibranching polymerization of EHO with side-reaction generating terminal oxetane units.

Using benzyl alcohol as an initiator gave higher yields (43%) of polymer, but it was completely soluble in acetone indicating either a lower molecular weight or increased branching. NMR indicates a higher DB and confirms the incorporation of the benzyl group.

The polymers were less thermally stable than the polyglycidols and cationically prepared oxetanes, degrading at 220 °C; however, these materials were not end-capped to prevent thermal depolymerization by back-biting of the various alcohol groups on ether linkages.

Fig. 5 gives a proposed mechanism for hyperbranched anionic polymerization of this substituted oxetane based on the mechanism suggested for the anionic polymerization of glycidol [2]. As there are no tertiary hydrogens in the 3 position of the monomer and repeat units, dehydration cannot occur to give chain terminating double bonds. We suggest that, if the methoxy oxetane salt were generated by proton exchange of initiator or propagating anion, it could initiate polymerization and remain as an unreacted end-group. This would account for the additional peak in the quaternary region. Additional peaks in the ^{13}C NMR at approximately 8.2, 26.9, 73.2, and 79.5 ppm that do not shift when acylated are consistent with cyclic terminal units. MALDI analysis showed two sets of peaks, one corresponding to TMP initiated poly(EHO) and one corresponding to poly(EHO) with no TMP initiator fragment. This results from a cyclic oxetane endgroup, or macrocyclic species. Two sets of peaks were also seen in the polymerization of glycidols if monomer addition was too rapid [2].

Sodium hydride was shown to be a suitable base for ring-opening polymerization of 3-ethyl-3-hydroxymethyl oxetane to give highly branched products. The resulting polymers possessed varying degrees of branching and a high percentage of cyclic endgroups. This provides a simple route to hyperbranched polyether-polyols free of difficult to handle catalyst. Most interesting is the possibility of direct (one-pot) conversion of the initially formed polymer to blocky copolymers (addition of a second monomer) or functional derivatives (addition of electrophilic reagents) in a second step, along with the increased functionality of a reactive cyclic endgroup. Initial results indicate facile substitution reactions with allyl bromides giving allyl ethers.

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