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Influence of Reaction Conditions on Degree of Branching in Hyperbranched Aliphatic Polyethers from 3-Ethyl-3-(hydroxymethyl)oxetane

Heléne Magnusson, Eva Malmström, and Anders Hult*

Department of Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT: The cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane to form hyperbranched polyethers has been studied. The polymerizations have been performed in bulk using sulfonium salt initiators. To produce polymers of different degrees of branching, the reaction conditions (reaction temperature and initiator) have been varied. Polymerizations have also been performed in the presence of a trifunctional core molecule, trimethylolpropane. The conversion of monomer turned out to be the main factor determining the degree of branching in the resulting polymer. Polymers with degrees of branching ranging from 0.15 to 0.41 were synthesized. When 3-ethyl-3-(hydroxymethyl)oxetane was polymerized by slow addition of monomer to a core molecule, a lower degree of branching was obtained compared to the one-step synthesis with full conversion of monomer. The polydispersity was generally slightly lower when a core molecule was used than in the one-step homopolymerization of 3-ethyl-3-(hydroxymethyl)oxetane.

Introduction

The influence of macromolecular architecture on different material properties has gained increased interest in recent years. It has been found that several physical and mechanical properties are greatly affected by the organization of the monomer units in space, and by varying the architecture, new materials of desired properties can be produced. Dendritic polymers, hyperbranched polymers, and dendrimers are a class of structures that has found more and more applications due to their special properties.[1,2] Dendritic polymers are built from monomers with three or more functional groups which introduces one possible branch point in each repeating unit. The resulting polymer has many reactive end groups and is more compact than a linear polymer. While dendrimers are perfectly branched, monodisperse molecules and hyperbranched polymers are irregular and polydisperse structures that can be manufactured in simple one-step syntheses. Because of their compact structure and multitude of end groups, hyperbranched polymers have several properties different than their linear counterparts. For example, hyperbranched polymers show an increased solubility and a lower viscosity in solution and in the molten state. The highly branched structure prevents the formation of chain entanglements, and the mechanical properties of hyperbranched polymers are therefore generally poor.[3] Hyperbranched polymers have been used as processing additives and have been found to decrease the viscosity of polymer melts during processing.[4] They have also been useful in preventing the formation of sharkskin in extrusion of HDPE.[5] Furthermore, they have been used as toughening agents.[6,7]

The branching in hyperbranched polymers is described by the term average degree of branching, DB. The degree of branching relates the number of branched repeating units in the structure to the total number of repeating units. For the determination of the DB, two different expressions have been suggested. The first compares the relative amounts of the terminal and dendritic repeating units to all repeating units in the structure[8] while the more recent equation takes only the dendritic and linear repeating units into account.[9] For high molecular weight polymers, both expressions give the same value of DB while for low molecular weight polymers, the second expression is more suitable.

The synthesis of hyperbranched polymers by ring-opening polymerization has been studied by a few authors during the past years.[10−13] Unlike the traditional condensation polymerizations mostly used in the synthesis of hyperbranched polymers, the removal of a small molecule is not necessary in ring-opening polymerization, and polymer of high molecular weight can be obtained without driving the reaction to extremely high conversion. Polymerization of hydroxy functional oxetanes has been extensively studied by Vandenberg et al.[14,15] under different conditions. Vandenberg described the linear polymer from 3-ethyl-3-(hydroxymethyl)oxetane as a highly crystalline material with a melting point of 175 °C.[16] Later, a melting point of 163 °C was reported[17] while no glass transition temperature was reported. Hyperbranched polyethers from 3-ethyl-3-(hydroxymethyl)oxetane have also been reported by different authors.[18,19] The hyperbranched material was described as an amorphous polymer with a T_g of 54 °C.

It has been found that hyperbranched polymers with different degrees of branching differ in their rheological and thermal behavior. While hyperbranched aliphatic polyethers with low degree of branching were semicrystalline, those with higher degree of branching were amorphous and had a lower melt viscosity.[20] In this paper, the polymerization of 3-ethyl-3-(hydroxymethyl)oxetane, TMPO, in bulk is studied. The possibility of tailoring the DB and thereby the properties of hyperbranched polymers from TMPO by varying the reaction conditions has been examined. Polymerizations have been performed using different sulfonium salt initiators at different reaction temperatures. TMPO has been

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Table 1

rxn	initiator	concn	temp (°C)	core	comment
1	p-$CH_3BTSSbF_6$	0.20 mol %	100		structure buildup
2	p-$CH_3BTSSbF_6$	0.20 mol %	60		structure buildup
3	$BTSSbF_6$	0.20 mol %	80		structure buildup
4	$BTSSbF_6$	0.20 mol %	100		structure buildup
5	$BTSSbF_6$	0.20 mol %	80		structure buildup
6	$BTSSbF_6$	0.20 mol %	80		structure buildup
7	p-$CH_3BTSSbF_6$	0.20 mol %	160		
8	p-$CH_3BTSSbF_6$	0.20 mol %	100		dry monomer core
9	$BTSSbF_6$	0.20 wt %	140	TMP	
10	$BTSSbF_6$	0.20 wt %	100	TMP	slow addition
11	$BTSSbF_6$	0.20 wt %	100	TMP	slow addition
12	$BTSSbF_6$	0.20 wt %	100	TMP	slow addition
13	$BTSSbF_6$	0.20 wt %	100	TMP	slow addition

polymerized in bulk both in one-pot processes and by the slow addition of monomer to a trifunctional core molecule, trimethylolpropane (TMP).

Results and Discussion

Synthesis of Poly-TMPO. The cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) was performed in bulk at temperatures from 60 to 160 °C (Table 1). The initiator was quickly dissolved in the monomer, a clear, nonviscous liquid. At 60 °C, the viscosity increased after 30−40 min stirring, and the mixture turned opaque. The mixture remained opaque and became more and more waxy during the course of reaction. At 100 °C, on the other hand, the viscosity of the reaction mixture increased after a few minutes stirring, and no or very little precipitation was observed. If present, the precipitate disappeared after a short period of time, and the mixture became clear and tough. According to ^{13}C NMR data, mainly linear polymer was formed at early stages of the polymerization. It is known from literature[16] that the linear poly(TMPO) is highly crystalline, and we therefore believe that the precipitate appearing in the reaction mixture at low conversions is due to precipitation of the formed crystalline, linear polymer. When the conversion increased, the degree of branching in the polymer increased, and it became more soluble. It was found that the precipitation was more apparent in reaction mixtures at low temperature, 60 °C, and almost not visible at all at high temperature (100−160 °C) where the solubility of the linear polymer was higher. Samples from the reaction mixtures also differed in solubility in DMSO-d_6. To keep the more linear samples in solution, all ^{13}C NMR measurements were performed at 40 °C.

Samples were taken out continuously from the reaction mixture during the course of reaction for analysis with respect to molecular weight by SEC, MALDI-TOF, and ^{13}C NMR (Table 1, reactions 1−6). The monomer conversion was monitored by quantitative, proton-decoupled ^{13}C NMR where the methylene carbon from the ethyl group gave rise to distinct singlets from the monomer and the dendritic, linear, and terminal repeating units (Figure 1). Reactions at different temperatures (60−100 °C) and using different initiators ($BTSSbF_6$ and p-$CH_3BTSSbF_6$) were studied.

SEC data showed an increase in polydispersity of the polymer with increasing conversion and molecular weight. The polydispersity is slightly higher for polymerizations performed at 100 °C than at 80 °C. The increasing trend of the molecular weight and the polydispersity were similar for both temperatures (Figures 3 and 4). To investigate whether the molecular weight of the hyperbranched polymer was limited due to water present in the system, the polymerization was performed under argon using dried monomer (Table 1, reaction 8). However, the molecular weight, as measured by MALDI-TOF and SEC, and polydispersity of the polymer were not affected by those precautions.

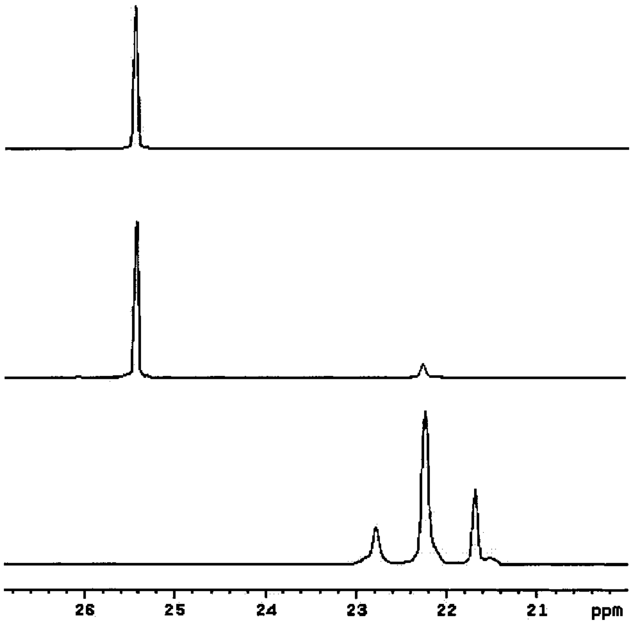


Figure 1. Proton-decoupled ^{13}C NMR spectra of three samples from the reaction mixture during the course of polymerization of TMPO. The first sample contains TMPO only (above). At low conversions, some linear repeating units have formed (middle). At full conversion (below), all TMPO units are incorporated in the polymer. From left to right the peaks corresponding to the dendritic, linear, and terminal repeating units are seen.

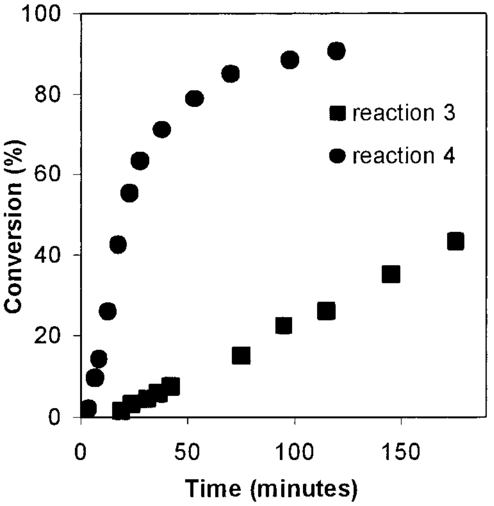


Figure 2. Conversion as a function of reaction time in cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane at 80 and 100 °C.

Structure Buildup. To examine whether the degree of branching, DB, was influenced by the reaction conditions, polymerizations were performed at different temperatures and using different sulfonium salt initiators, benzyltetramethylenesulfonium hexafluoroantimonate ($BTSSbF_6$) and p-methylbenzyltetramethylenesulfonium hexafluoroantimonate (p-$CH_3BTSSbF_6$) (see Scheme 1).

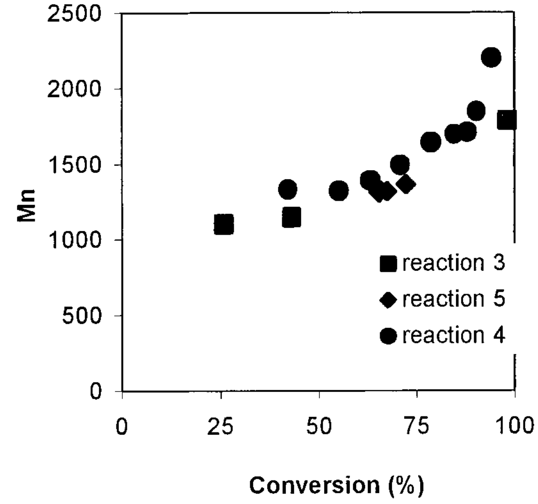


Figure 3. Number-average molecular weight, M_n, as a function of monomer conversion at 80 and 100 °C.

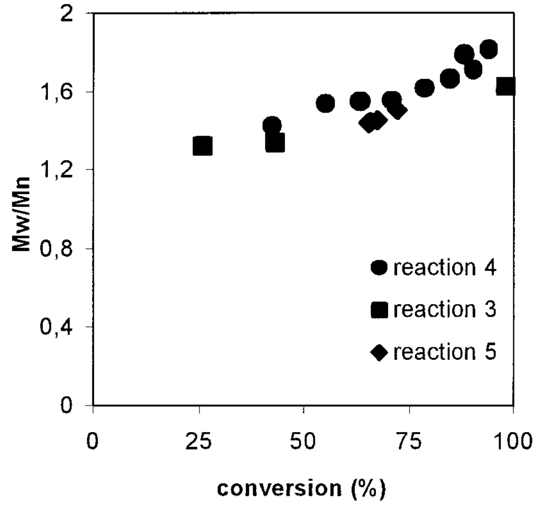


Figure 4. Polydispersity as a function of monomer conversion at 80 and 100 °C.

The samples from the reaction mixture were analyzed with respect to the distribution of different repeating units by ^{13}C NMR (Figure 5).

Figure 5 shows the fraction of dendritic and linear repeating units as a function of conversion of monomer during polymerization. At conversions up to 30% almost exclusively linear repeating units were formed. At higher conversions more and more dendritic repeating units were formed, leading to an increase in degree of branching with increased conversion (Figure 5). This suggests that neither reaction temperature nor type of initiator affects the structure buildup of the polymer.

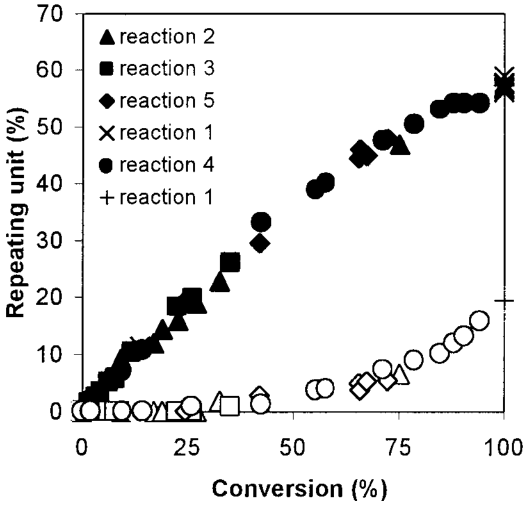
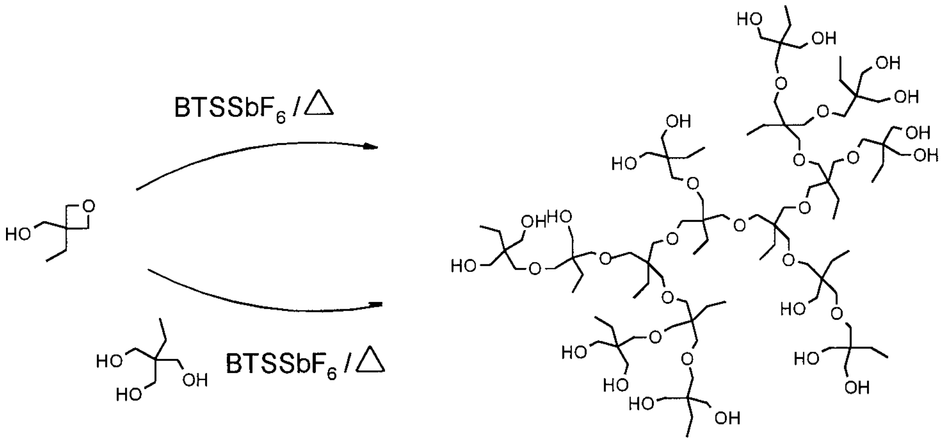


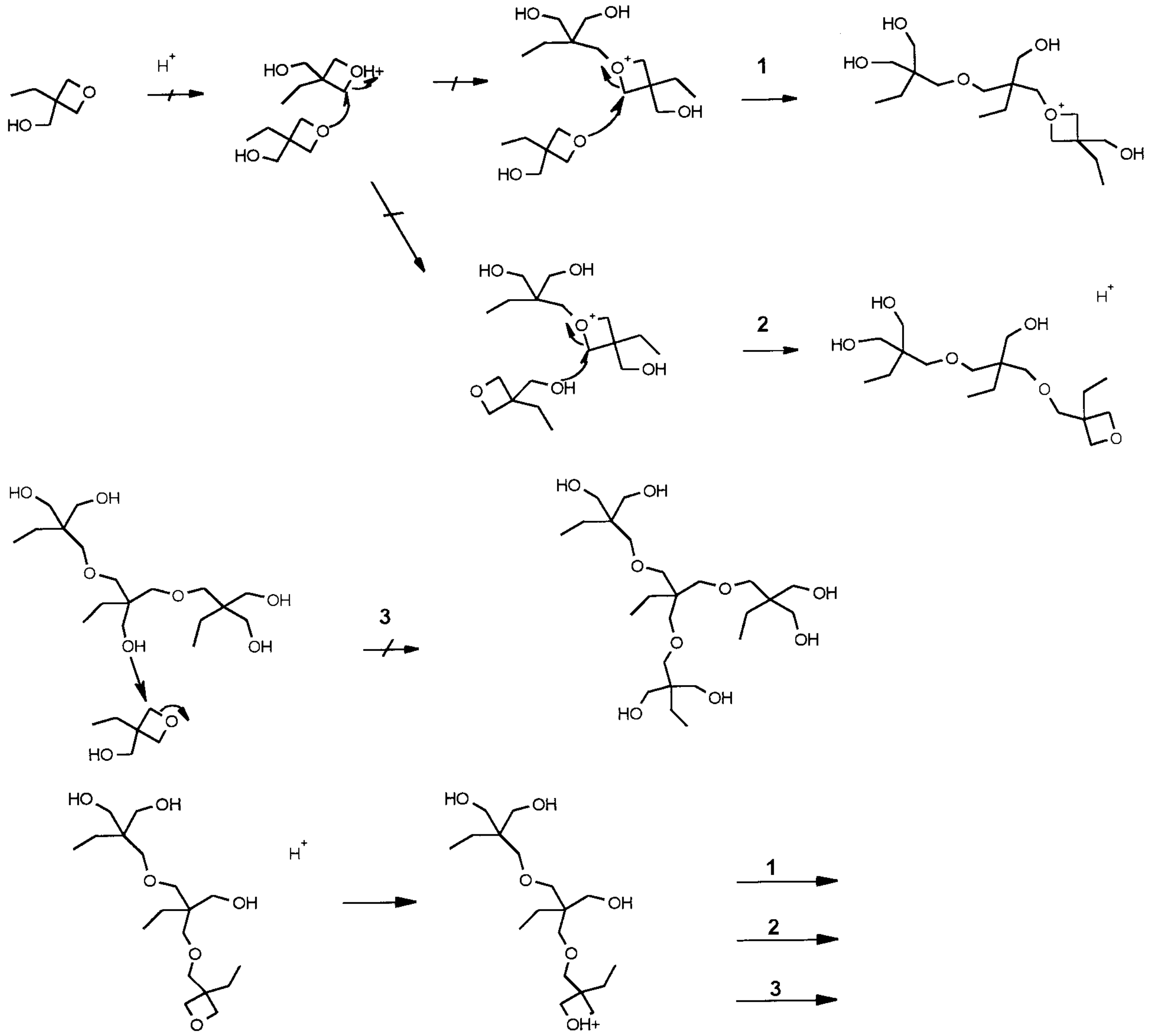
Figure 5. Fractions of linear (filled) and dendritic (unfilled) repeating units in the polymer at different conversions at 60, 80, and 100 °C.

One possible explanation to the increased formation of dendritic repeating units at higher conversions is a change in reaction mechanism. Oxetanes may react by either of two mechanisms: the activated chain-end mechanism (ACE) and the activated monomer mechanism (AM)[21] (Scheme 2). Furthermore, in the case of TMPO both the hydroxyl oxygen and the ring oxygen may act as nucleophiles. To examine whether a change in mechanism took place, $1/(1 - p)$ was plotted as a function of the time of reaction (Figures 6 and 7). Both plots exhibited a shift in slope in the curve which may indicate a change in mechanism. At 80 °C, the shift occurred at 20–25% conversion and at 100 °C at about 25% conversion. This corresponds well to the conversion where dendritic repeating units starts to form. At low conversions, where linear chain growth dominates, a lot of monomer is still present in the mixture. Reactions 1 and 2 in Scheme 2 dominate. At higher conversions, on the other hand, the long linear segments act as core molecules for further polymerization. The pendant hydroxyl groups along the main chain starts to play a more and more important role in the propagation (Scheme 2, reaction 3). In the early stages of the reaction where mainly linear repeating units are formed,

Scheme 1



Scheme 2



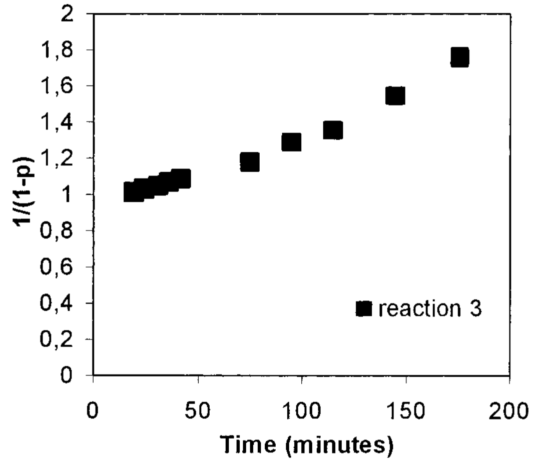


Figure 6.

TMPO acts as a difunctional monomer instead of a trifunctional monomer. This is probably one factor contributing to the narrow polydispersity in the polymer (Figure 4).

In three cases, reactions 1, 6, and 12, both the precipitated polymer and crude product were analyzed by ^{13}C NMR. The degree of branching changed very little, 8% at the most, on precipitation. Properties of hyperbranched poly(TMPO) of different DB have been compared elsewhere.[20]

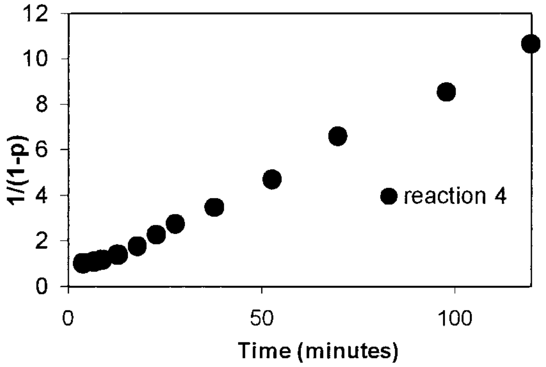


Figure 7.

Polymerization in the Presence of a Core Molecule. To examine the effect on the DB of a core molecule, the polymerization was performed in the presence of a trifunctional core molecule, trimethylolpropane (TMP) (Tables 1 and 2, reaction 9). The DB of the product is 0.34, which is slightly lower than expected as compared to the other polymers.

Table 2

no.	M_{n}^{1}	M_{n}^{2}	M_{n}^{3}	M_{n}^{4}	$M_{\mathrm{w}}/M_{\mathrm{n}}^{5}$	$M_{\mathrm{w}}/M_{\mathrm{n}}^{6}$	generation	DB
1	2574	2017	3893		2.57	1.51		0.41
7	2549	1986	1908		2.12	1.74		0.40
8	1997	2391	1602		1.67	1.61		0.41
9		1790	1827	5336		1.45	4	0.34
10	1236	1398	749	5336	1.41	1.25	4	0.20
11	1096	1419	616	2552	1.37	1.30	3	0.15
12	942	1465	594	1160	1.35	1.26	2	0.28
13	1538	2072	1000	5336	1.86	1.58	4	0.40

To investigate whether the molecular weight and polydispersity could be controlled by the slow addition of monomer to the core molecule and to examine the effect on the DB of the resulting polymer, slow addition experiments were performed. Hyperbranched polymers of theoretical generations 2−4 were synthesized by the slow addition of monomer to the melt of the core molecule with dissolved initiator. In reactions 10−12 the monomer was added dropwise at a rate of approximately 1.6 mmol/min, and in reaction 13 0.08 mmol was added per minute. To examine whether unreacted TMP was present in the reaction mixture at the end of reaction, a sample was taken from reaction mixture 12 before precipitation, for analysis by ^{13}C NMR. According to the ^{13}C NMR spectrum, some amount of unreacted TMP was present in the sample. Approximately 80% of the TMP core had been incorporated in the hyperbranched structure. In the reaction mixtures where no core molecule was added, no TMP was detected by ^{13}C NMR, which indicates that no TMP was formed during the reaction.

The DB values of the resulting polymers 10−12 were very low (Table 2). This may be expected, because new monomer was continuously added to the mixture and the conversion of monomer was kept low for a long time. Therefore, the reaction mixture was kept at a conversion low enough for mainly linear chain growth to occur during the main part of the reaction. Though the aim was to add the monomer at exactly the same rate in experiments 10−12, this was very difficult to achieve in practice. The differences in DB between polymers 10−12 may therefore be explained by differences in rate of monomer addition.

In reaction 13, the monomer was added at a much slower rate than in reactions 10−12. Under those conditions, almost all monomer was likely to be consumed before the next addition. Conversion was therefore kept high through the reaction, and a high DB and polydispersity was obtained.

Both SEC and MALDI-TOF results show that the polydispersity was slightly lower in polymers 10−12, synthesized by the slow addition of TMPO to a core molecule, than without the core (Table 2).

Conclusions

The polymerization of 3-ethyl-3-(hydroxymethyl)oxetane was performed in bulk under different reaction conditions using onium salt initiators, and the possibility to synthesize polymers of different degree of branching (DB) was examined. Polymers of DB from approximately 0.15 to 0.41 were synthesized. The structure buildup during polymerization was studied by ^{13}C NMR. The type of initiator and the reaction temperature during polymerization did not influence the structure buildup in the hyperbranched structure. On the other hand, the conversion of monomer turned out to be an important factor determining the degree of branching in the polymer. At low conversions (<30%) almost exclusively linear repeating units were formed, and with increased conversion more and more dendritic repeating units were introduced in the structure. This opens the possibility to tailor the degree of branching of a polymer of this type by controlling the conversion of monomer.

Conversion studies suggest that a change in reaction mechanism occurs at low conversions, where dendritic repeating units starts to form.

The dropwise addition of monomer to a core molecule, TMP, gave a polymer of lower DB than the one-pot synthesis without a core. If the monomer was added very slowly to the core and initiator melt, so that the conversion of monomer was kept high during the course of reaction, a high DB was obtained. When the monomer was added at a moderately low rate to the reaction mixture, the polydispersity of the polymer was slightly lower than polymers from the one-pot synthesis.

The use of dried monomer and glassware and performing the reaction under argon did not give any increase in molecular weight of the polymer.

Experimental Section

Materials. 3-Ethyl-3-(hydroxymethyl)oxetane (TMPO) and trimethylolpropane (TMP) were kindly supplied by Perstorp AB and used as received. Benzyltetramethylenesulfonium hexafluoroantimonate ($BTSSbF_6$) and *p*-methylbenzyltetramethylenesulfonium hexafluoroantimonate (p-$CH_3BTSSbF_6$) were prepared according to literature procedures.[22]

Apparatus. The ^{1}H NMR spectra of the hyperbranched poly(3-ethyl-3-hydroxymethyl)oxetanes were performed on a Bruker 400 MHz spectrometer. All ^{13}C NMR experiments were performed on a Varian 600 MHz spectrometer at 40 °C. The degree of branching was calculated from the relative intensity of the $-CH_2CH_3$ peaks in proton decoupled, quantitative ^{13}C NMR spectra.[19] DMSO-d_6 was used as solvent in all NMR experiments. In the quantitative analysis, T1 was set to 12 s. Size exclusion chromatography (SEC) was performed with a Waters 6000A pump, a PL-EMD 960 light scattering evaporate detector, two PL gel 10 μm mixed-B columns (300 × 7.5 mm) from Polymer Labs, and one Ultrahydrogel linear column (300 × 7.8 mm) from Waters. All measurements were performed at 70 °C. DMF was used as solvent at a flow rate of 1 mL/min. Linear poly(ethylene oxide)s were used as standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) experiments were performed on a Hewlett-Packard G2025a MALDI-TOF system using dihydroxybenzoic acid as matrix and ethanol as solvent.

Synthesis of Hyperbranched Polyethers. In a typical experiment, no. 1, 15.0 g (129.3 mmol) of TMPO and 0.11 g (0.26 mmol) of p-$CH_3BTSSbF_6$ were added to a round-bottomed flask equipped with a stirrer bar. The flask was immersed in a preheated oil bath at 100 °C. The reaction was left for 30 min and then quenched with ethanol. The reaction mixture was dissolved in hot ethanol, precipitated in water and the hyperbranched polymer, a white solid, filtered, and dried under vacuum.

During the course of reaction, samples were taken out for analysis of molecular weight, conversion, and composition of the polymer by SEC and ^{13}C NMR (reactions 1−6). To prevent further reaction, the samples for SEC analyses were quenched with ethanol. The samples for ^{13}C NMR analysis were immediately dissolved in d_3-DMSO. Polymerizations were performed at 60, 80, 100, and 160 °C using $BTSSbF_6$ and p-$CH_3BTSSbF_6$ as initiators. At 60 °C the reaction was very slow and did not reach full conversion even after 24 h.

Polymerization of Dried TMPO, Reaction 8. The monomer was dissolved in acetone and dried over magnesium sulfate for 3 days. The mixture was then filtered and the acetone evaporated. A round-bottomed flask and a stirrer bar were dried and equipped with a septum. The system was flushed with argon for 20 min before adding 15.0 g (129.3

mmol) of the dried TMPO and 0.11 g (0.26 mmol) of *p*-$CH_3BTSSbF_6$. The reaction vessel was then immersed into a preheated oil bath at 100 °C. The reaction was left for 30 min and then quenched with ethanol. The reaction mixture was dissolved in hot ethanol and precipitated in water. The product was filtered and dried under vacuum.

Fourth-Generation Hyperbranched Poly(TMPO) with a TMP Core, Reaction 9. 0.26 g TMP (1.9 mmol) was dissolved in 10.0 g of TMPO (86.2 mmol) in a round-bottomed flask equipped with a stirrer bar. The vessel was immersed in a preheated oil bath at 140 °C, and 0.02 g of $BTSSbF_6$ (0.05 mmol) was added after 5 min. The reaction was left for 2.5 h and then quenched with ethanol. The reaction mixture was dissolved in hot ethanol, precipitated in water, filtered, and dried under vacuum.

Fourth-Generation Hyperbranched Poly(TMPO) by Slow Addition of Monomer to a Core Molecule, Reactions 10−13. 0.13 g (0.96 mmol) of TMP and 0.010 g (0.024 mmol) of $BTSSbF_6$ were added to a round-bottomed flask equipped with a stirrer bar. The flask was immersed in a preheated oil bath at 100 °C. The monomer TMPO (5.0 g, 43.1 mmol) was added dropwise, on average 1 drop per 4 min. Because of the slow addition rate, the viscosity of the reaction mixture was quite high during the reaction. When all monomer was added, the mixture was left for another 3 h. It was then dissolved in ethanol, precipitated in water, and dried under vacuum (SEC, NMR, MALDI-TOF).

Hyperbranched poly(TMPO) of the second and third generation was prepared according to the directions above.

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References and Notes

(1) Kim, Y. H. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 1685.
(2) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453.
(3) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.
(4) Huber, T.; Pötschke, P.; Pompe, G.; Hässler, R.; Voit, B.; Grutke, S.; Gruber, V. *Macromol. Mater. Eng.* **2000**, *280*/*281*, 33.
(5) Hong, Y.; Cooper-White, J. J.; Mackay, M. E.; Hawker, C. J.; Malmström, E.; Rehnberg, N. *J. Rheol.* **1999**, *43*, 781.
(6) Glauser, T.; Hult, A.; Johansson, M.; Kornmann, X.; Berglund, L. *Macromol. Mater. Eng.* **2000**, *280*/*281*, 20.
(7) Boogh, L.; Pettersson, B.; Månsson, J.-A. E. *Polymer* **1999**, *40*, 2249.
(8) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
(9) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.
(10) Suzuki, M.; Ii, A.; Saegusa, I. *Macromolecules* **1992**, *25*, 7071.
(11) Huber, T.; Böhme, F.; Komber, H.; Kronek, J.; Luston, J.; Voigt, D.; Voit, B. *Macromol. Chem. Phys.* **1999**, *200*, 126.
(12) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240.
(13) Emrick, T.; Chang, H.-T.; Fréchet, J. M. J *Macromolecules* **1999**, *32*, 6380.
(14) Vandenberg, E. J.; Mullis, J. C.; Juvet, R. S., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3083.
(15) Vandenberg, E. J.; Mullis, J. C.; Juvet, R. S., Jr.; Miller, T.; Nieman, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3113.
(16) Vandenberg, E. J. *ACS Symp. Ser.* **1992**, *496*, 2.
(17) Parris, J. M.; Marchessault, R. H.; Vandenberg, E. J.; Mullis, J. C. J. *Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 749.
(18) Bednarek, M.; Biedron, T.; Helinski, J.; Kaluzynski, K.; Kubisa, P.; Penczek, S. *Macromol. Rapid Commun.* **1999**, *20*, 369.
(19) Magnusson, H.; Malmström, E.; Hult, A. *Macromol. Rapid Commun.* **1999**, *20*, 453.
(20) Magnusson, H.; Malmström, E.; Hult, A.; Johansson, M. Submitted to *Polymer*.
(21) Dworak, A.; Walach, W.; Trzebicka, B. *Macromol. Chem. Phys.* **1995**, *196*, 1963.
(22) Sundell, P.-E.; Jönsson, S.; Hult, A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1535.

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