Multihydroxyl Branched Polyethers. 2. Mechanistic Aspects of Cationic Polymerization of 3-Ethyl-3-(hydroxymethyl)oxetane

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ABSTRACT: This paper, second in a series, reports the cationic polymerization of 3-ethyl-3-(hydroxymethyl)oxetane leading to branched polyethers containing exclusively methylol groups attached to the quaternary carbon atoms (primary hydroxyl groups). GPC chromatograms and MALDI TOF spectra of the isolated polymers demonstrated that intramolecular chain transfer to polymer occurred, providing a cyclic fragment of the macromolecule. This limited the chain growth and thus the molecular weight of resulting polymers. The phosphorus cation-trapping method showed that both secondary and tertiary oxonium ions were present in the polymerization mixture, indicating that both active chain end (ACE) and activated monomer (AM) mechanisms contributed to the chain growth. As a consequence of the coexistence of two propagation mechanisms and significant chain transfer, both molar mass and degree of branching depended only slightly on the polymerization conditions.

Introduction

In the first paper of this series, we described the synthesis of branched polyethers having exclusively primary hydroxyl groups at the multiple chain ends.[1] Similar results were reported by Hult et al.[2] and later by Yan et al.[3] These works are related to the earlier studies by Vandenberg et al.[4] on the polymerization of different hydroxymethyloxetanes.

Several years ago, our laboratory showed that in the cationic polymerization of cyclic ethers in the presence of compounds containing hydroxyl groups, propagation proceeds by an activated monomer (AM) mechanism involving successive additions of the protonated (activated) monomer molecules to the terminal hydroxyl groups of the growing macromolecules.[5] The kinetics of this process was studied, and the influence of the polymerization conditions on the contribution of both competing mechanisms of propagation, namely the conventional active chain end (ACE) mechanism, (i.e., involving reaction of monomer molecules with tertiary oxonium ion active species located at the end of growing macromolecule) and activated monomer mechanism in the polymerization of oxiranes was established by the kinetic method.[6,7]

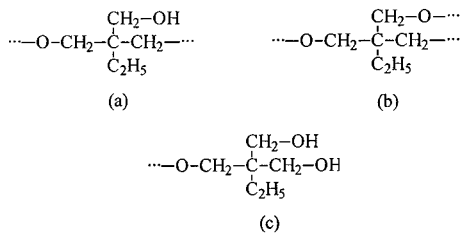
This turned our attention to the cationic polymerization of cyclic ethers containing both functions needed for the AM mechanism to operate, i.e., cyclic ethers containing hydroxyl substituents. The typical example of this class of monomers is glycidol ((hydroxymethyl)-oxirane). Our studies of cationic polymerization of glycidol revealed that both ACE and AM mechanisms contribute to the growth of macromolecules to produce branched polyethers,[8] like those prepared by anionic polymerization.[9,10] The influence of reaction conditions on the contribution of AM mechanism (leading to branched units) was studied, but was not fully explained.[11]

The branched polymers of glycidol contain both primary and secondary hydroxyl groups. Since this is a disadvantage, we have been exploring the polymerization of oxetanes substituted at the 3-position with hydroxymethyl groups.[1] Polymerization of these monomers, irrespectively of the propagation mechanism, leads to polymers containing exclusively $-CH_2-OH$ as pendant groups in the main chain and in branches. If one more substituent is present at the same 3-position, then $-CH_2-OH$ groups are connected exclusively to the quaternary carbon atom. Therefore, side reactions that can occur in polyglycidol, like elimination of water to form unsaturated end groups, are not possible.

Polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (EOX) in bulk or in CH_2Cl_2 solution proceeded smoothly at room temperature with typical cationic initiators like trifluorometanesulfonic (triflic) acid or BF_3−etherate, and nearly complete conversions were reached within a few hours, giving polymers with M_n's in the range of $(1-5) \times 10^3$, thus considerably lower than could have been expected for the process without transfer.[1] Polymers with similar molar masses were produced by bulk polymerization of EOX carried at 120 °C with benzyltetramethylenesulfonium hexafluoroantimonate as initiator.[2]

^{13}C NMR analysis detected both linear (Scheme 1a) and branched (Scheme 1b) units; it was thus concluded, that polymers are branched (one branch per 2−3 units).[1] No other units besides linear (Scheme 1a), branched (Scheme 1b) and terminal units (Scheme 1c) were detected by ^{13}C NMR.

Scheme 1



The aim of the present paper is to establish the polymer microstructure in more detail in order to identify chain breaking reactions preventing the forma-

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Table 1. M_n's of poly-EOX

no.	polymerization conditions[a]	monomer convn, %[b]	M_n(calcd)[c] $\times 10^{-4}$	M_n(obsd,GPC) $\times 10^{-3}$
1	bulk, 25 °C $[BF_3{\cdot}Et_2O]_0 = 3.2 \times 10^{-3}$ mol/L	80	25	1.47
2	bulk, 25 °C $[CF_3SO_3H]_0 = 5 \times 10^{-3}$ mol/L	68	13.6	1.25
3	methylene dichloride, 25 °C[d]	92	1.15	1.19
4	chloroform, 25 °C[d]	90	1.12	0.90
5	chloroform, 60 °C[d]	98	1.22	0.95
6	*o*-dichlorobenzene, 60 °C[d]	~90	1.12	1.12
7	*o*-dichlorobenzene, 130 °C[d]	~90	1.12	1.66

[a] At the applied conditions 50% conversion was reached within a few hours. Because of solidification of the reaction mixture, further reaction was slow. Therefore, to achieve high monomer conversion, the reaction mixture was kept for 24−48 h. [b] Determined by ^{1}H NMR. [c] $M_n(\text{calcd}) = 116 \times ([M]_0 - [M]_t)/[I]_0$. [d] $[M]_0 = 2.15$ mol/L, $[BF_3{\cdot}Et_2O]_0 = 2 \times 10^{-2}$ mol/L.

tion of the higher molar mass polymers. Chain transfer can be determined from the chain ends. We used MALDI TOF mass spectroscopy, giving the absolute values of molar masses of individual macromolecules to identify end groups. Then, to understand the origin of the observed structures, some mechanistic aspects of EOX polymerization were studied, in particular, the contribution of a secondary (involved in propagation by AM mechanism) oxonium ions and tertiary oxonium ions (involved in propagation by ACE mechanism) to chain growth.

Experimental Section

3-Ethyl-3-(hydroxymethyl)oxetane (EOX) was synthesized from 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (Perstorp Polyols) according to our previous procedure.[1] Purity after two fractionating distillations (bp = 108 °C/10 Torr) was ~ 99% according to ^{1}H NMR. Bis[(3-ethyl-3-oxetanyl)methyl] ether was synthesized from bis[(2,2-dihydroxymethyl)butyl] ether (ditrimethylolopropane) (Perstorp Polyols) by the same procedure. Boron trifluoride etherate $BF_3{\cdot}O(C_2H_5)_2$ (Aldrich, purified, redistilled) and triflic acid CF_3SO_3H (Aldrich, purity = 98%) were used as supplied. CH_2Cl_2 (POCh, Gliwice, Poland) was purified by heating for 24 h with concentrated sulfuric acid to remove unsaturated compounds. The organic layer was then separated, washed with distilled water, 5% aqueous Na_2CO_3 and two times with water. CH_2Cl_2 was subsequently dried over $CaCl_2$ for 24 h, heated over CaH_2 and distilled. The fraction boiling at 39.9−40 °C was collected. $CHCl_3$ (POCh) and o-dichlorobenzene (Aldrich) were purified by distillation (fractions boiling at 60−61 and 178−180 °C, respectively, were collected). Tri-*n*-butyl phosphine (Aldrich, purity = 99%) was purified by vacuum distillation (bp = 150 °C/50 Torr).

Polymerizations were carried out in bulk or in solvent (CH_2Cl_2, $CHCl_3$, or *o*-dichlorobenzene) under argon atmosphere at 25, 60, or 130 °C with 0.2−1 mol % of initiator. Below, we describe experimental procedures for typical bulk and solution polymerizations.

Bulk polymerization of EOX (no. 1 in Table 1) was performed by placing 10 g (0.086 mol) of EOX in a two-neck flask fitted with neutral gas inlet and magnetic stirrer. Argon (Poligaz, Lodz, Poland, purity > 99.99%) was used as neutral gas. The flask was placed in a thermostating bath at 25 °C, and after purging with argon, 4 μL of BF_3−etherate (3.2×10^{-5} mol, 3.2×10^{-3} mol/L) was introduced by syringe. The viscosity of the polymerization mixture increased gradually, and after about 0.5 h, the content of the flask could no longer be stirred. At this stage, the polymerization mixture was a viscous liquid which solidified during the later stages of the reaction. After 48 h, a solid mass was withdrawn from the flask, crushed, and stirred with 100 mL of a 1% solution of sodium methoxide in methanol to deactivate the catalyst. After filtration, the polymer was dried on vacuum line for 4 h. In some cases, crude product was further purified by placing it in a Soxhlet apparatus and extracting it with CH_2Cl_2. (see Results and Discussion). The polymer was then precipitated from hot CH_2Cl_2 into cold diethyl ether.

Solution polymerization of EOX (no. 6 in Table 1) was performed by placing 6 mL of *o*-dichlorobenzene in a three-neck flask fitted with neutral gas inlet, dropping funnel and magnetic stirrer. Argon (Poligaz, Lodz, Poland, purity > 99.99%) was used as a neutral gas. The flask was placed in a thermostating bath at 60 °C, and after purging with argon, 20 μL of BF_3−etherate (1.6×10^{-4} mol, 2×10^{-2} mol/L) was indroduced by syringe. The content of the flask was stirred and 2.0 g (1.7×10^{-2} mol) of EOX was subsequently added from dropping funnel within 0.5 h. Already, at an early stage, polymer started to precipitate. After 5 h, the heating was discontinued and the reaction mixture was kept at 25 °C for 24 h. Solid polymer separated from the solvent by filtration was stirred with 20 mL of a 1% solution of sodium methoxide in methanol to deactivate the catalyst. After filtration, the polymer was dried on vacuum line for 4 h.

Analysis of products was performed as follows. GPC measurements were performed with ConstaMetric 4100 pump equipped with Phenogel 5 500 Å and Phenogel 5 50 Å columns, with an RI detector using THF as the solvent with a flow rate of 0.7 mL/min at 25 °C. Molecular weights were calculated on the basis of calibration with polystyrene standards. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using Bruker AC 200 or Bruker MSL 300 spectrometers. MALDI TOF analysis was performed with Voyager Elite spectrometer using dihydroxybenzoic acid as matrix and NaI as cationating agent. Nitrogen laser desorption at a wavelength equal to 337 nm, an accelerating voltage of 20 kV, and an analyzer pressure of 10^{-7}−10^{-8} Torr were applied. The sample for analysis was prepared by mixing solutions of polymer (1 mg/mL) and dihydroxybezoic acid (10 mg/mL) in tetrahydrofuran with a solution of NaI (10 mg/mL) in acetone in a 10:10:1 volume ratio, and the resulting solution was loaded onto a sample plate and solvents were evaporated. The plate was then inserted into the ionization chamber.

Results and Discussion

Molar Mass of poly-EOX. Table 1 lists the results of a series of EOX polymerizations. Poly-EOX is poorly soluble in the solvents used, and it precipitated in the course of polymerization.

The reported molar masses are based on GPC measurements (polystyrene calibration) for polymer samples purified by precipitation from hot CH_2Cl_2 into diethyl ether. Because calibration with linear polystyrene is not applicable for determining the correct values of M_n for branched polyethers, the values shown in Table 1 may differ from the real M_n values. However, results show that irrespective of the polymerization conditions, only medium molar mass polymers are obtained. The upper values of M_n that can be reached are independent of the reaction conditions.

If the cationic polymerization of EOX proceeded exclusively by the ACE mechanism with quantitative initiation and without transfer or termination, the M_n values should be equal to $M_n = 116([EOX]_0 - [EOX]_t/[H^+])$. These theoretically calculated values are given in Tables 1 and 2 as M_n(calcd). If, on the other hand, polymerization proceeded exclusively by an AM mech-

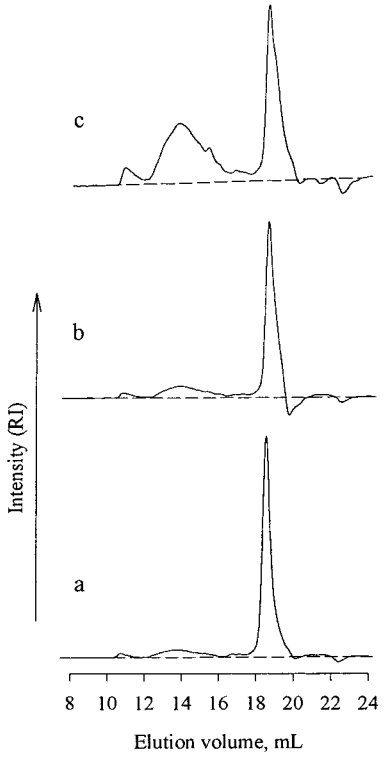


Figure 1. GPC curves for samples of polymerization mixture withdrawn at monomer conversion (determined independently by ^{1}H NMR): (a) 15%; (b) 25%; (c) 60%. Polymerization conditions: bulk polymerization of EOX at 25 °C. $[BF_3{\cdot}O(C_2H_5)_2]_0 = 3.2 \times 10^{-3}$ mol/L. The signal at an elution volume of about 19 mL corresponds to monomer.

Table 2. M_n of Poly-EOX at Various Monomer Conversions: Bulk Polymerization, 25 °C, $[BF_3{\cdot}Et_2O]_0 = 3.2 \times 10^{-3}$ mol/L

time, min	monomer convn, %	M_n(calcd)[a] $\times 10^{-4}$	M_n(obsd,GPC) $\times 10^{-3}$	polydispersity
15	11	3.4	1.39	
45	15	4.6	1.53	1.30
315	25	7.7	1.48	1.27
1680	60	18.5	1.45	1.34
2 d	80	25.00	1.47	

[a] Cf. Table 1.

anism (i.e., with acid acting as catalyst and not as initiator), then DP_n should increase with conversion as in polyaddition, reaching very high values at high conversion.

The observed molar masses are evidently lower than expected with either exclusively ACE mechanism or exclusively AM mechanism (or both mechanisms contributing to the chain growth) assuming no chain transfer. Therefore, some additional reactions that restrict chain length proceed in the system.

To determine the evolution of molar masses with conversion, samples of polymers isolated at different monomer conversion, without any purification, were analyzed by GPC. Results are shown in Figure 1 and in Table 2.

Three peaks appeared in the GPC chromatograms. The elution volumes at which the peaks appear did not change with increasing monomer conversions; only the relative intensities of signals changed. The peak at highest elution volume was assigned to the unreacted monomer on the basis of the elution volume observed independently for the monomer. The other two peaks correspond to polymeric products with peak molar masses corresponding to about 1700 and 30000. The components of the sample isolated at the final stage of polymerization were separated by extraction of the solid mass with hot CH_2Cl_2. Figure 2 shows the GPC traces of the individual fractions.

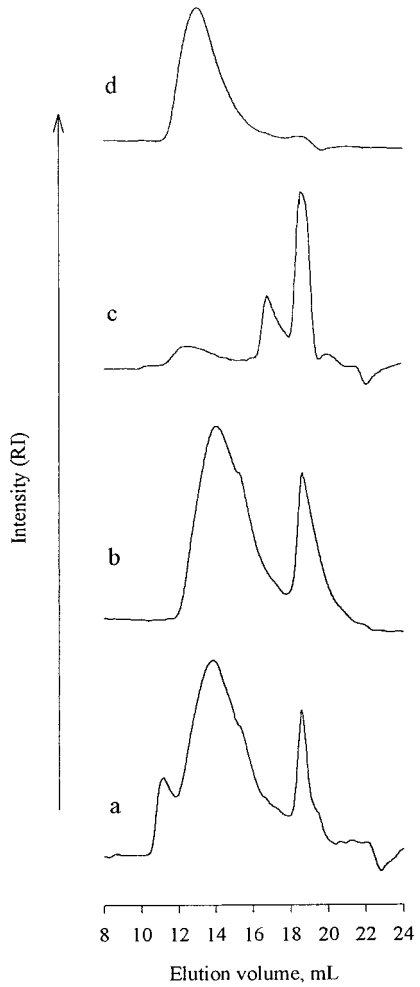


Figure 2. GPC curves of products of EOX polymerization isolated at 80% monomer conversion at different stages of purification. Polymerization conditions as in Figure 1. Key: (a) crude polymerization mixture; (b) fraction soluble in hot CH_2Cl_2; (c) fraction insoluble in hot CH_2Cl_2; (d) fraction soluble in hot CH_2Cl_2 after precipitation from hot CH_2Cl_2 into cold diethyl ether.

Two fractions were isolated. The CH_2Cl_2-soluble fraction contained medium molar mass polymer and some unreacted monomer (Figure 2 b). The CH_2Cl_2-insoluble part contained a lower molar mass oligomer (probably dimer) and some medium molar mass polymer (Figure 2c). Neither fraction contained the highest molar mass component giving the peak at M_n about 30 000 in the GPC of the original sample (Figure 2a). Since this fraction disappeared during the workup, it is evidently due to the relatively stable aggregates, presumably hydrogen-bonded, formed under the polymerization conditions. Further purification of the polymer by precipitation from hot CH_2Cl_2 into diethyl ether led to a product with a nearly unimodal molar mass distribution, although it still contained a small amount of unreacted monomer (Figure 2d).

Our hypothesis that the highest molar mass peak is due to relatively stable aggregates of individual macromolecules linked by multiple hydrogen bonds is corroborated by the fact that it also disappeared upon

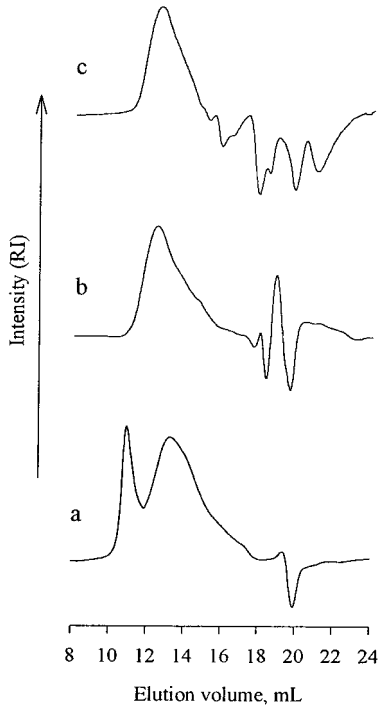


Figure 3. GPC curves of poly-EOX isolated at ~100% monomer conversions (polymerization conditions as in Figure 1): (a) crude product after polymerization; (b) reaction mixture after silylation with *N*,*O*-bis(trimethylsilyl)acetamide (BSA); (c) reaction mixture after esterification with trifluoroacetic anhydride (TfA). (Reaction mixtures b and c contained an excess of BSA or TfA and low molar mass side products of silylation and esterification giving a deviation from the baseline at elution volumes above 18 mL.)

esterification of the hydroxyl groups in the original (i.e., prior to any workup) sample with trifluoroacetic anhydride or after silylation with BSA, as shown in Figure 3.

Structure of the End Groups by MALDI TOF Analysis. Since the low observed M_n's indicate that polymerization proceeds with some transfer reactions restricting the molar masses, the nature of the end groups was studied by MALDI TOF mass spectroscopy.

Branched macromolecules have several end groups, in contrast to the linear ones, containing two end groups. In the following discussion, by end groups in branched poly-EOX we mean only units formed by initiation and termination (transfer).

Figure 4 shows a typical MALDI TOF spectrum of a purified polymer isolated at the later stage of polymerization (monomer conversion > 80%).

The main series signals appearing in the spectra are separated by 116 Da which is the molar mass of the EOX unit. The observed molar masses of the main series correspond exactly to the multiplicity of the molar mass of the EOX units (monomer) and are equal to $M = n116.141 + 22.99$ (NaI was used as the cationating agent). Thus, signal corresponding to decamer appears at $m/z = 1184$ while M calculated is equal to 1184.41.

In addition to the main series of signals, additional series of much lower intensity are observed in the MALDI TOF spectrum. As shown in Figure 4 (inset), at least three additional series appear, with molar masses lower by 12 Da and higher by 18 and 34 Da than the molar mass of the main series. These series may be attributed to macromolecules terminated with water and cationated with Na^+ (m/z higher by18 Da) and with

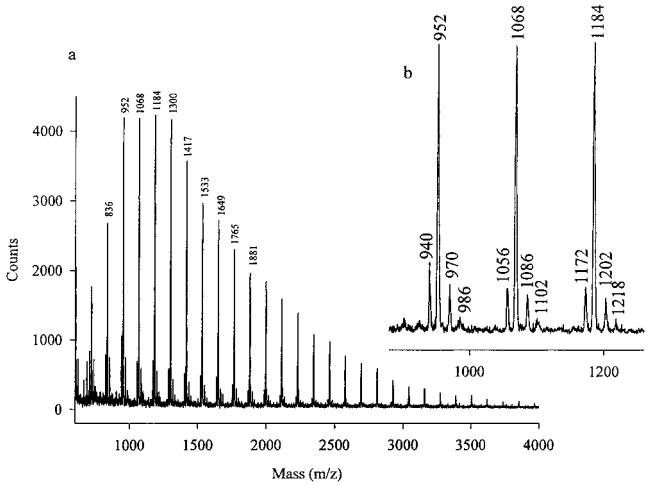


Figure 4. MALDI TOF spectrum of poly-EOX (a) (fraction d from Figure 2) with enlarged region corresponding to spectra of octamer, nonamer, and decamer (b).

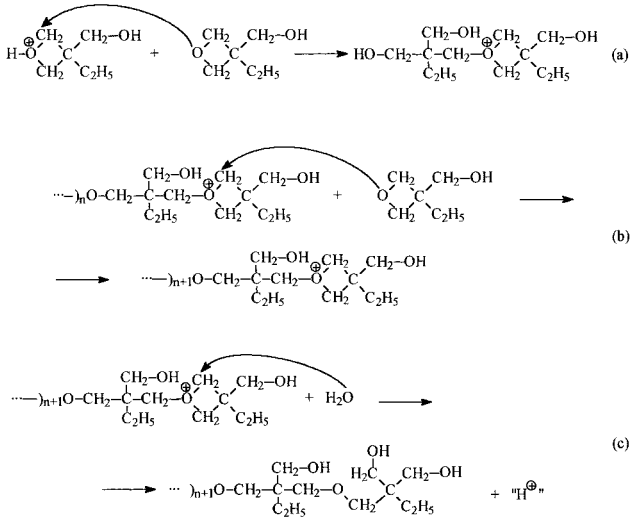
K^+ (m/z higher by 34 Da) and to macromolecules that underwent an unknown transformation which is not understood at present (m/z lower by 12 Da).

Intensities of signals of the additional series are considerably lower than the intensities of the main series signals; therefore, the results of the MALDI TOF analysis show that isolated polymer is composed mainly of macromolecules with molar masses exactly equal to the multiplicity of the molar mass of the EOX repeating unit. This indicates that in the macromolecules belonging to the main series either there are no end groups formed by initiation and termination; i.e., macromolecules contain a cyclic fragment or the end groups are isomerized monomeric units.

Below the corresponding structural possibilities are analyzed.

a. Macromolecules growing by the ACE mechanism should have the structure shown in Scheme 2.

Scheme 2

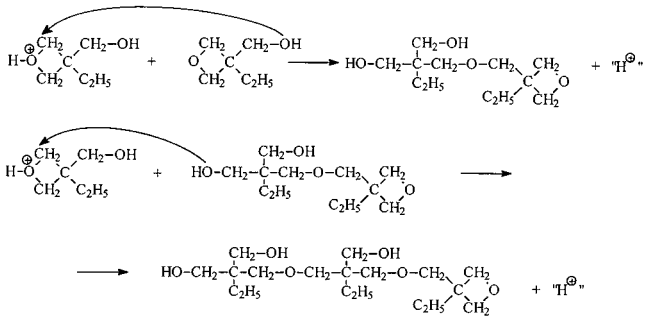


The headgroups are HO− groups formed by reaction of the first protonated monomer molecule with an oxygen atom of the oxetane ring of the second monomer molecule (Scheme 2a) while the tail groups are formed by deactivation of the cyclic tertiary oxonium ion. Whatever the deactivating agent is, some end groups,

related to this deactivating agent, would be incorporated into macromolecule, e.g., the −OH group if water acted as an deactivating agent (Scheme 2c). Termination with water should therefore provide macromolecules with molar masses equal to $M = n$ (molar mass of monomeric units) + 18 (sum of molar masses of H− and −OH) i.e., differing by 18 Da from the observed molar masses of the major series of peaks in the MALDI TOF spectra.

b. Macromolecules growing by AM mechanism should have the structure shown in Scheme 3.

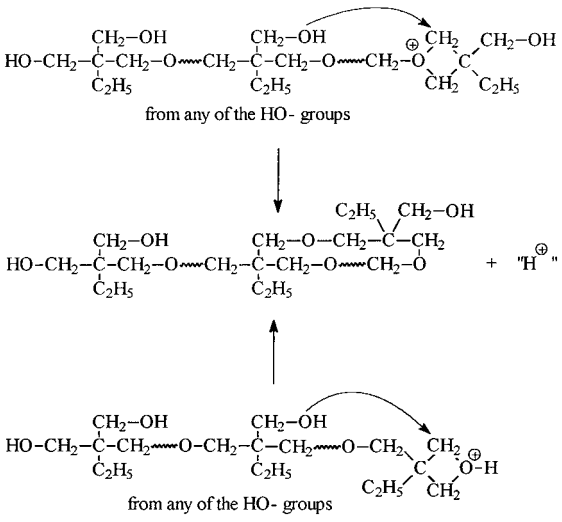
Scheme 3



One of the end groups should be a substituted oxetane ring formed by reaction of the first protonated monomer molecule with HO− groups of the other monomer molecule, while the other end group should be the HO− group. The molar mass of the macromolecule should be equal to $M = nM$ (monomeric units) i.e., equal to the molar mass observed by MALDI TOF mass spectrometry.

If, however, macromolecules growing by either ACE or AM mechanism underwent intramolecular cyclization according to Scheme 4, the same macrocyclic structures would be formed and also in this case the molecular weight would correspond to the observed ones by MALDI TOF.

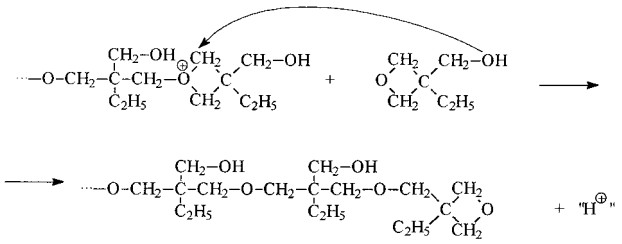
Scheme 4



Therefore, the results of the MALDI TOF analysis indicate that the isolated polymer may be composed either of macromolecules which had grown exclusively by the AM mechanism (cf. Scheme 3) or macromolecules growing by either mechanism and terminated by intramolecular cyclization (cf. Scheme 4) or a mixture of both.

One can also imagine that the growing tertiary oxonium ions react with the monomer in the "wrong way" i.e., with a hydroxyl group (cf. Scheme 5). Then, a macromolecule with an oxetane end group is formed, and also in this case, molar masses are equal to the observed ones.

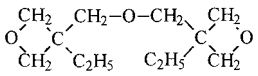
Scheme 5



Therefore, for the chain growth by AM mechanism or by ACE mechanism with transfer by "wrong monomer addition", each macromolecule should contain one oxetane ring whereas for the chain growth by ACE with intramolecular cyclization, macromolecules should be devoid of the oxetane rings.

Studies of ^{1}H NMR spectra of the polymer samples were undertaken in order to see whether the oxetane rings were present in the macromolecules. The polymer was purified from the unreacted monomer by precipitation from hot solution in CH_2Cl_2 into cold diethyl ether, spectra were recorded and compared with spectrum of a model compound: bis[(3-ethyl-3-oxetanyl)methyl] ether (Scheme 6).

Scheme 6



In the spectrum of the model compound, signals corresponding to the $-CH_2-$ groups in the ethyl group appear as a quartet at 1.69−1.77 ppm and the signal of the $-CH_2-$ groups in the ring appears as a multiplet (A_2B_2) at 4.40−4.51 ppm. Neither of these signals was detected in the NMR spectra of the isolated and purified polymers. In a separate experiment, the ^{1}H NMR spectrum of a mixture of the model compound (cf. Scheme 6) and a polymer was analyzed. It was shown that the corresponding signals should be clearly detectable even if proportion of oxetane end groups corresponded to about 10 mol % of all macromolecules with molar masses of approximately 1500, i.e., if only one macromolecule out of 10 contained oxetane groups.

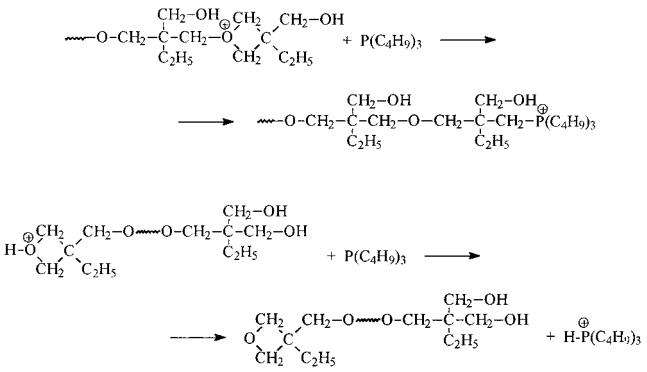
This result, coupled with the results of MALDI TOF analysis, indicate that the polymer is composed mainly of macromolecules which have undergone intramolecular cyclization (chain transfer) and contain cyclic fragment, as shown in Scheme 4.

MALDI TOF spectra of polymers isolated at lower monomer conversion (samples isolated at 11, 15 and 25% conversion) were essentially identical with MALDI TOF spectra of the polymers isolated at high monomer conversion. It may be therefore concluded, that the polymer isolated at any stage of polymerization is composed mainly or exclusively (at least 90 mol %) of macromolecules incorporating macrocyclic fragment resulting from intramolecular chain transfer to polymer involving −OH groups of its own macromolecule.

Structure of the Propagating Species. According to the findings described in the previous paragraph, the majority or all of the macromolecules in the polymer isolated at the final stage of polymerization had already undergone termination by intramolecular chain transfer to polymer (cyclization). As shown in Scheme 4, this process leads to identical structures for the macromolecules irrespective of the mechanism of propagation, i.e., independent of whether macromolecules grow by the ACE mechanism of propagation (as shown in Scheme 2) or according to the AM mechanism of propagation (as shown in Scheme 3). Therefore, MALDI TOF analysis of the final samples does not give any indication concerning the structure of macromolecules at the stage when they were still growing.

In the former mechanism, propagation involves tertiary oxonium ions while in the latter secondary oxonium ions (protonated oxetane rings) are involved. The phosphorus ion trapping method that we developed and used successfully for many ring-opening and vinyl ionic polymerizations may distinguish between these two structures.[12] As shown previously, tertiary oxonium ions in reaction with phosphines give quaternary phosponium ions while secondary oxonium ions give tertiary phosphonium ions (protonated phosphine) (cf. Scheme 7). Reaction with tributylphosphine is fast, quantitative,

Scheme 7



and irreversible.[13] Thus, the reaction mixture at different stages of polymerization was terminated with about a 2-fold excess of tributylphosphine (under vacuum line conditions) and ^{31}P NMR spectra were recorded.

Figure 5 shows the ^{31}P NMR spectrum of polymerization mixture terminated with tributylphosphine at 30% monomer conversion.

The chemical shifts of tributylphoshine and the corresponding tertiary and quaternary phosphonium ions are as follows: −32.3 ppm, tributylphosphine (used in excess); 11,3 ppm, tertiary phoshonium ion; 34.0 ppm, quaternary phosphonium ion. Other signals present in the spectrum may be attributed to the products of oxidation of tributylphosphine (e.g., the signal at 54.6 ppm corresponds to the phosphine oxide), which could not be avoided even in the high vacuum system.

On the basis of the known initial concentration of tributylphosphine, by comparing the integrations of signals of phosphine and phosphonium ions, it was confirmed that the sum of the concentrations of phosphonium ions is close to the concentration of catalyst (initiator) used ([phosphonium ions] = 1.08 [initiator]). The fractions of tertiary and quaternary phosphonium ions were equal to 95 and 5 mol %, respectively. This means that before termination with phosphine more

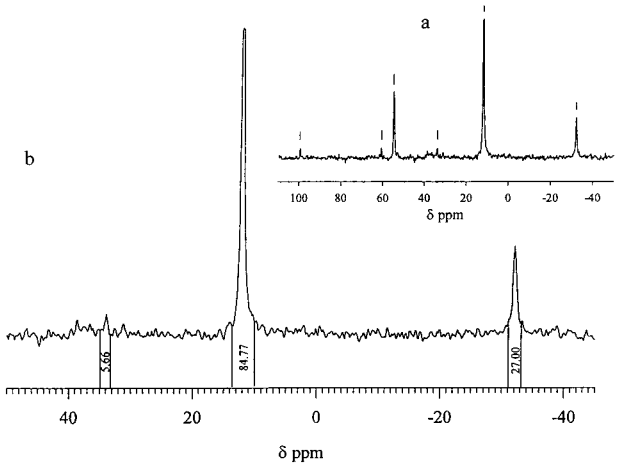


Figure 5. ^{31}P NMR spectrum of polymerization mixture terminated with an excess of tributylphosphine: (a) complete spectrum; (b) enlarged region of phosphonium ions absorption. Polymerization conditions: solution polymerization in CH_2Cl_2 at 25 °C, $[EOX]_0 = 2.2$ mol/L, $[BF_3{\cdot}O(C_2H_5)_2]_0 = 2 \times 10^{-2}$ mol/L, and $[(C_4H_9)_3P] = 4.2 \cdot 10^{-2}$ mol/L. Spectrum recorded at −70 °C. Assignments of the signals: −32.3 ppm, tributylphosphine (used in excess); 11,3 ppm, tertiary phoshonium ion; 34.0 ppm, quaternary phosphonium ion.

than 95 mol % of all ions existed as secondary oxonium ions and only approximately 5% mol % existed as tertiary oxonium ions.

The measured concentration of tertiary oxonium ions corresponds to the real concentration of species able to participate in propagation by the ACE mechanism. The measured concentration of the secondary oxonium ions corresponds to the sum of concentrations of different secondary oxonium ions which may exist in the system, namely protonated monomer, protonated HO− groups, and protonated ether chain units. Only the former ones may participate in propagation by the AM mechanism.

Distribution of protons among all these three basic sites in the system is governed by their relative basicities. The exact pK_B values are not known; the known pK_B values of the similar compounds may, however, be used to estimate the contribution of the protonated monomer. The basicity of unsubstituted oxetane is only slightly higher than that of aliphatic hydroxyl groups;[14] the corresponding pK_B value for oxetane is equal to 3.13.[15] Therefore, at the early stages of polymerization when contribution of the protonated ether units in macromolecules can still be neglected, protonated monomer may constitute more than 50% of all secondary oxonium ions observed. Thus, the concentration of the protonated monomer may be even 10 times higher than the concentration of tertiary oxonium ions. For the two types of oxonium ions considered, which may participate in two modes of propagation, the secondary oxonium ions are therefore much more abundant. This however does not necessarily mean, that propagation proceeds by the AM mechanism, because the rate constants of propagation by both mechanisms are not known and in general secondary oxonium ions are much less reactive toward nucleophiles (here hydroxyl groups in monomer molecules) than the tertiary ones. Thus, although again these results do not give any final conclusion, the simultaneous presence of both secondary and tertiary oxonium ions in the system has to be taken into account.

Mechanistic Aspects of EOX Polymerization Relevant to Polymer Structure. The phenomena

observed in cationic polymerization of EOX and reported in this paper can be summarized as follows:

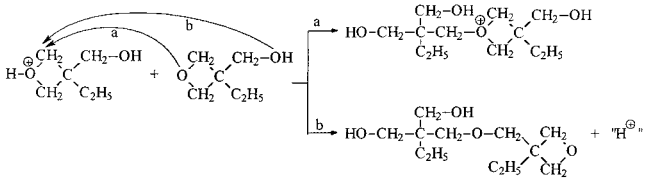
a. Both secondary and tertiary oxonium ions are present in the polymerizing system, the former ones being more abundant.

b. Cationic homopolymerization of EOX at the employed conditions leads only to medium molar mass polymers. The molar mass of the polymer does not substantially change with increasing conversion of monomer and is essentially the same at low (about 10%) and high (about 80%) conversions.

c. Molar masses of macromolecules are exactly multiplets of molar mass of the monomeric unit; thus, macromolecules do not contain end groups resulting from initiation and termination (transfer) but contain cyclic fragments formed in intramolecular chain transfer.

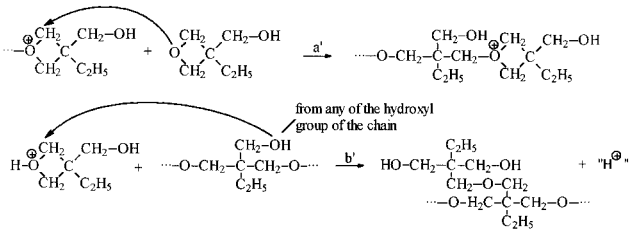
On the basis of these major facts, the following mechanism of the polymerization may be envisaged: polymerization is initiated by protonation of the monomer molecule (protons come either from CF_3SO_3H or are formed from BF_3 and the HO− groups). The monomer has two sites which may be protonated; due to the relatively high basicity of the ether oxygen in the four-membered ring, a significant fraction of protonic acid protonates the oxetane ether oxygen. The carbon atom in the α-position relative to an oxygen bearing formally the positive charge in the protonated monomer may either be attacked by ether oxygen or by the hydroxyl group oxygen atom of the next monomer molecule, as shown in Scheme 8.

Scheme 8



Route a represents initiation of the ACE polymerization while route b represents initiation by AM polymerization. In each subsequent step the same competition (a′ vs b′) may take place (Scheme 9).

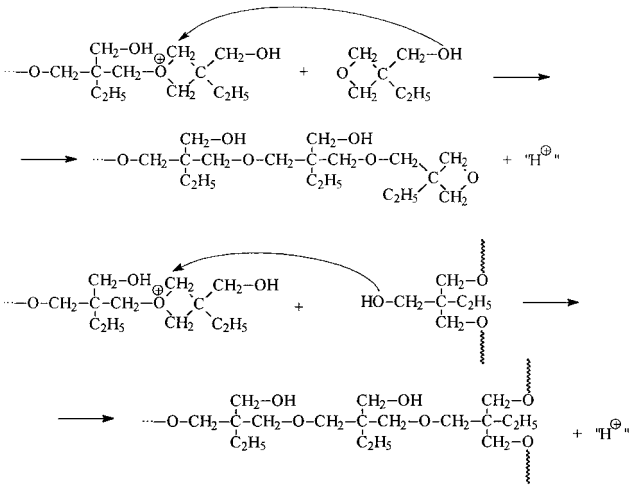
Scheme 9



Moreover, the tertiary oxonium ion active species may be converted into the secondary oxonium ions by its reaction with the −OH group of monomer or another polymer molecule, as shown in Scheme 10.

Processes shown in Schemes 8−10 (propagation by ACE or AM mechanism or coupling of the chains) lead to the chain growth. Chain growth proceeds only to a certain limit at which intramolecular chain transfer occurs. According to MALDI TOF analysis, termination of the growth of an individual macromolecule proceeds via an intramolecular chain transfer to polymer leading to formation of macrocyclic fragments. This process apparently occurs when there is enough of monomeric

Scheme 10



units in the branched chains to allow one of the HO− groups to appear in a favorable position to react either with the tertiary oxonium ion or with protonated oxetane end group (for ACE or AM processes respectively).

All our data strongly indicate that there is no substantial intermolecular chain transfer (chain coupling). Thus, it seems that during the growth the macromolecules change their conformation in such a way that the polyether chain is exposed to the outside and hydroxyl groups, due to formation of intramolecular hydrogen bonds, which are embedded inside the macromolecular coil becoming unavailable for reaction. For conformational reason, the molar mass is restricted at any stage of polymerization and does not depend on the polymerization conditions. Some of these macromolecules physically trap the other ones by hydrogen bonding and form labile aggregates, described in the previous section.

Conclusion

Cationic polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane (EOX) leads to branched macromolecules. M_n of poly-EOX does not practically change in the course of polymerization and is close to 1.5×10^3. MALDI TOF analysis has shown, that molar masses of macromolecules are multiplets of molar mass of monomer units, thus end groups provided by initiation/termination are absent. This fact strongly indicates, that the restricted molar masses are due to intramolecular chain transfer involving active species and hydroxyl groups from the same macromolecule. This leads to the final conclusion, that during the growth of the macromolecule, when more and more hydroxyl groups are accumulated, the conformation of the macromolecule, due to formation of intramolecular hydrogen bonds, changes in such a way that hydroxyl groups are becoming unavailable for reaction.

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