Coexistence of Activated Monomer and Active Chain End Mechanisms in Cationic Copolymerization of Tetrahydrofuran with Ethylene Oxide

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ABSTRACT: Cationic copolymerization of tetrahydrofuran (THF) with ethylene oxide (EO) in the presence of diols proceeds with simultaneous participation of secondary and tertiary oxonium ions. This process comprises therefore some features of the *activated monomer* (AM) and the *active chain end* (ACE) mechanisms. The mechanism of copolymer formation was evaluated, and the kinetics of competing reactions involving both secondary and tertiary oxonium ions with nucleophiles present in the system was studied. The apparent rate constants were derived, allowing the estimation of the influence of copolymerization conditions on the composition and microstructure of copolymers.

Introduction

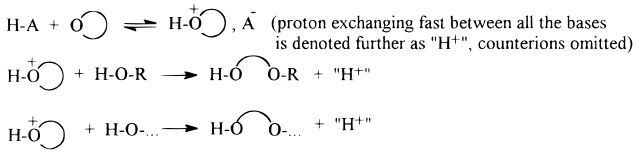
In a typical cationic ring-opening polymerization of cyclic ethers, propagation involves nucleophilic attack of an oxygen atom of the monomer molecule on the carbon atom in a position α to the oxygen atom in oxonium ion located at the growing chain end.[1] This mechanism is thus described as the *active chain end* (ACE) mechanism. In the polymerization proceeding by the ACE mechanism, due to the presence of an oxonium ion at the chain end, back-biting, leading to formation of cyclic fraction, can hardly be avoided. In some instances, however, e.g. in THF polymerization, it may be slow when compared to propagation. This may lead to essentially linear polymers, particularly if polymerization is terminated shortly after reaching the monomer−polymer equilibrium.[2]

An alternative mechanism of cationic polymerization of cyclic ethers operates, when polymerization is carried out in the presence of a sufficiently high concentration of compounds containing hydroxyl groups (alcohols, diols).[3−5] It was shown that conditions may be found, where a protonated monomer molecule reacts mainly with hydroxyl groups, without having the possibility of reacting with the next monomer molecule and initiating in this way propagation by the ACE mechanism, as shown schematically in Scheme 1.

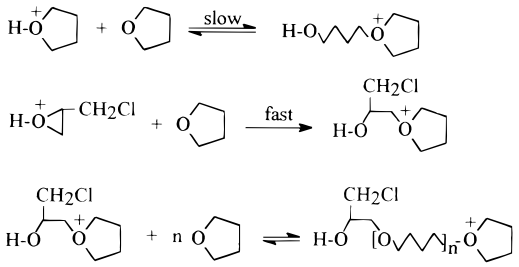
Reaction of a protonated monomer with a hydroxyl group leads to a larger molecule, containing one monomer unit more than the original one and still containing a hydroxyl group. Protons exchanging rapidly between all nucleophiles present in the system may protonate the next monomer molecule; thus the reaction between protonated (activated) monomer and a terminal hydroxyl group is a propagation reaction.

Hydroxyl groups are reproduced after each propagation step, and if a low molecular weight diol is used as the initiator (protonic acid HA being a catalyst), the product is oligodiol with $DP_n = ([M]_0 - [M]_t)/[HO-R-OH]_0$, providing that $[HO-R-OH]_0 \gg [HA]_0$. This method is, therefore, suitable for preparation of telechelic polyethers terminated with hydroxyl groups, essentially free of the cyclic fraction.[6−8] It cannot be, however, applied for THF homopolymerization, because protonic acids, in the presence of alcohols or diols, do not initiate the polymerization of THF. In the absence of hydroxyl group containing compounds, strong protonic acids (e.g., trifluoromethanesulfonic acid) initiate THF polymerization, although the rate constant of initiation is much lower than the rate constant of initiation by alkylating agents (e.g., trialkyloxonium ion) and is lower than the rate constant of propagation.[2] This stems from the much lower reactivity of the secondary oxonium ion (protonated THF) as compared to the tertiary oxonium ion (alkylated THF). In the presence of hydroxyl group containing compounds, hydrogen bonding leads apparently to further reduction of the reactivity of the secondary oxonium ions, and initiation becomes negligibly slow.

Scheme 1



Scheme 2



The low reactivity of protonated THF is due to the low ring strain of the five-membered ring. When the secondary oxonium ions involve a highly strained three-membered ring, their reactivity is considerably enhanced. Thus, oxiranes (e.g. epichlorohydrin) act as promoters of protonic acid initiated polymerization of THF, increasing considerably the rate of initiation (Scheme 2).[9]

Indeed although THF in bulk, in the presence of 10 mol % of ethylene glycol and up to 2 mol % of protonic

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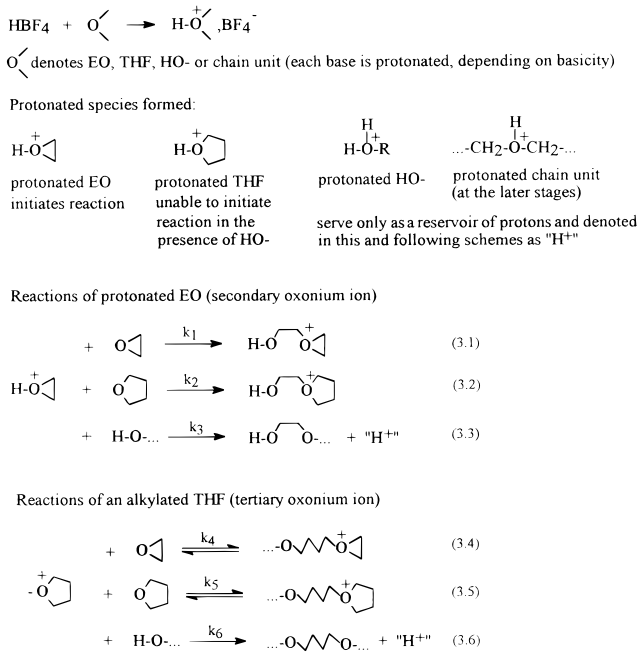
Scheme 3



acid (HBF_4·Et_2O) at room temperature, does not undergo any reaction for at least 14 days, the reaction starts upon addition of oxirane, e.g., epichlorohydrin (ECH), to the system, and the ECH−THF copolymer is formed for as long as there is still ECH present in the system.[10] Once ECH is consumed, the reaction stops.

The same behavior is observed for the ethylene oxide−tetrahydrofuran (EO−THF) system. Such a course of reaction may be explained by Scheme 3.

The characteristic feature of the mechanism shown in Scheme 3 is that both secondary oxonium ions (protonated oxirane) and tertiary oxonium ions (alkylated THF) participate in the reaction and undergo continuous interconversion. Thus, from the viewpoint of active species structure, the process combines the features of the *activated monomer* (AM) mechanism (secondary oxonium ion active species) and the *active chain end* (ACE) mechanism (tertiary oxonium ion active species).

Both secondary and tertiary oxonium ions may react, reversibly or irreversibly, with any nucleophile present in the system. Reactions, which have to proceed in order to form a copolymer other than the alternating copolymer are reactions 3.2, 3.5, and 3.6 in Scheme 3. According to such a scheme, oxirane is incorporated into copolymer by reaction of the secondary oxonium ion while THF propagates by reaction of the tertiary oxonium ion. Additionally, opening of an oxirane ring is practically irreversible while opening of the THF ring may be reversible. Therefore, the copolymer microstructure can be governed by simultaneously using the kinetic (slow addition of EO to keep its instantaneous concentration low) and thermodynamic (reversibility of THF propagation) control.

In the present work, the kinetics and mechanism of cationic copolymerization of ethylene oxide with tetrahydrofuran in the presence of diols was studied, mainly in model systems, to determine the effect of reaction conditions on the contribution of competing reactions. In the subsequent paper of this series, the possibility of controlling the composition and the distribution of comonomer units in resulting telechelic copolyethers, will be described.[11]

Scheme 4

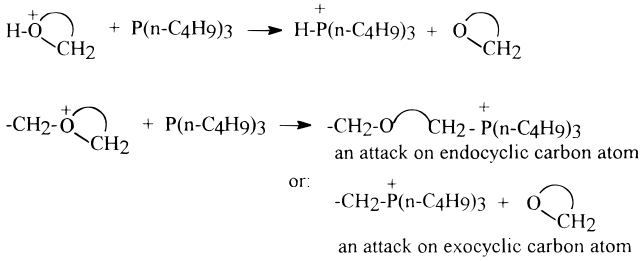


Table 1. Concentrations of the Secondary and Tertiary Oxonium Ions in Copolymerization of THF with EO in the Presence of $PhCH_2CH_2OH$ as Initiator[a]

$[ROH]_0$, mol/L	$[HBF_4$·$Et_2O]_0$, mol/L	convn of THF, %	[sec oxonium ions], mol %	[tert oxonium ions], mol %
0.5	0.1	16	52.5	47.5
0.25	0.1	22	41	59
0.25	0.1	36	42	59

[a] Conditions: $[THF]_0$ = 3.0 mol/L; $[EO]_0$ =1.5 mol/L; CH_2Cl_2; −78 °C.

Results and Discussion

Determination of Concentrations of Secondary and Tertiary Oxonium Ions in the Cationic Copolymerization of EO with THF in the Presence of Diols. The mechanism shown in Scheme 3 involves secondary and tertiary oxonium ions, simultaneously present in the reaction mixture and participating in formation of the copolymer.

To determine both types of oxonium ions in the system, the ion-trapping method, developed earlier in this laboratory,[12,13] was applied. The method is based on the fast, quantitative and irreversible transformation of oxonium ions into phosphonium ions in reaction with tertiary phosphine, as shown schematically in Scheme 4.

Secondary oxonium ions, reacting with tertiary phosphine, give tertiary phosphonium ions while tertiary oxonium ions give quaternary phosphonium ions. There is practically no exchange between these species, and separate narrow signals corresponding to both types of phosphonium ions are observed by ^{31}P NMR. Integration of the signals, with respect to the signal corresponding to a known excess of the unreacted phosphine, allows determination of concentrations of both species. A typical ^{31}P NMR spectrum of the copolymerizing mixture, after addition of an excess (with respect to the concentration of catalyst) of tri-*n*-butylphosphine, is shown in Figure 1.

Signals of both kinds of phosphonium ions are clearly distinguished in the spectrum, indicating the presence of both secondary and tertiary oxonium ions in the copolymerizing mixture. Table 1 summarizes the results obtained from two model experiments in which copolymerization was carried out in solution with relatively high concentration of a monofunctional alcohol. Due to the sensitivity of aliphatic tertiary phosphines to oxidation, these model experiments were conducted in sealed ampules and sealed NMR tubes (cf. Experimental Part). The required amount of EO was introduced in one portion; therefore, its concentration in the system was considerably higher than in the systems when EO was

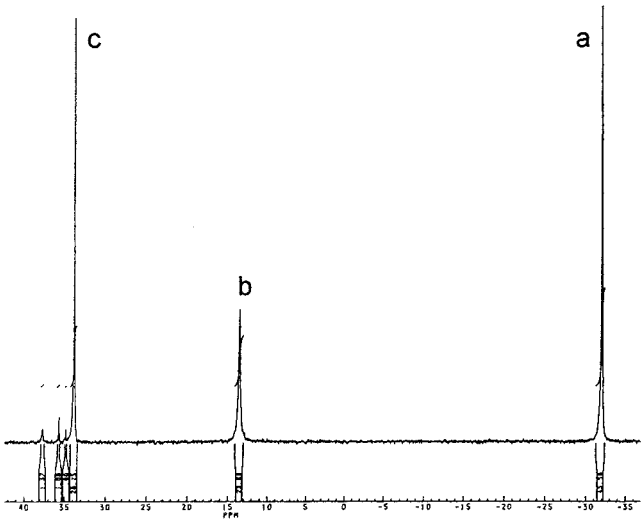
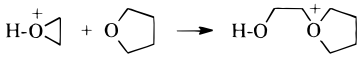


Figure 1. ^{31}P NMR spectrum of the copolymerization reaction mixture terminated with an excess of tributyl phosphine. Conditions of copolymerization: $[THF]_0 = 3.0$ mol/L; $[EO]_0 = 1.5$ mol/L; $[C_6H_5CH_2CH_2OH]_0 = 0.5$ mol/L; $[HBF_4{\cdot}Et_2O]_0 = 0.1$ mol/L; −78 °C; CH_2Cl_2 solvent. After 35 min, at 16% conversion of THF (as determined by ^{1}H NMR), 0.18 mol/L of Bu_3P was added and the ^{31}P NMR spectrum was recorded at −78 °C. Assignments of signals: (a) unreacted excess of $P(C_4H_9)_3$ (−31.1 ppm); (b) tertiary phosphonium ion $H-P^+(C_4H_9)_3$ (13.4 ppm), (c) quaternary phosphonium ion: $-O-(CH_2)_4-P^+(C_4H_9)_3$ (33.7 ppm).

Scheme 5



continuously fed into reaction mixture with a rate corresponding to the rate of its consumption.

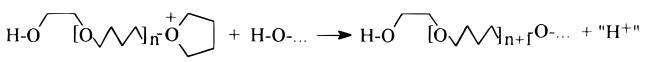
The differences in relative concentrations of ions in both experiments may be related to the different ratios of [THF]/[HO$^-$] used; the higher this ratio, the higher is the mole fraction of the tertiary oxonium ions.

The fraction of ions changes only slightly with increasing conversion of THF. Thus, apparently, at least within the observed range of reaction conditions, the steady-state exists; i.e., the rates of interconversion of the secondary into the tertiary oxonium ions and vice versa are equal to each other. The secondary oxonium ions are converted into tertiary ones in the reaction shown in Scheme 5.

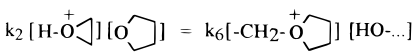
Because the concentration of EO in this particular model system is not negligibly low, formation of tertiary oxonium ions by reaction of protonated oxirane with EO should also be considered (reaction 3.1 in Scheme 3). This reaction, however, would lead to the formation of a tertiary oxonium ion involving a three-membered ring. In reaction with tertiary phosphine, such a tertiary oxonium ion would give a phosphonium ion differing from this formed by reaction of tertiary oxonium ion involving a five-membered ring $(-OCH_2)_2-PR_3^+$ vs $-O(CH_2)_4-PR_3^+$).

It was shown earlier, that these two structures, if present simultaneously, give two separate signals in the ^{31}P NMR spectrum, differing by about 0.5 ppm.[13] In the spectrum shown in Figure 1, there is essentially one signal in the region of quaternary phosphonium ions with a chemical shift corresponding to the product of the reaction of tertiary oxonium ion involving a five-membered ring with phosphine (33.70 ppm). Small

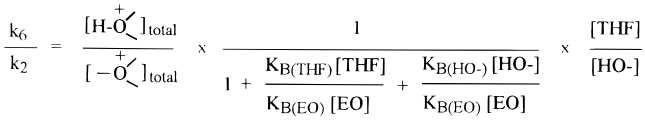
Scheme 6



Scheme 7



Scheme 8



signals in lower field are assigned to impurities (phosphine oxide and products of its reaction with oxonium ions).

Even, however, if one of these signals were due to the presence of the product of the reaction of phoshine with tertiary oxonium ion involving a three-membered ring, concentration of the corresponding tertiary oxonium ion would not exceed 3 mol % (based on integration) of the concentration of tertiary oxonium ions involving five membered rings. This indicates that reaction of protonated EO with EO may be neglected and that tertiary oxonium ions are formed practically only by the reaction shown in Scheme 5. Such a result may be explained by the lower concentration of EO and its lower nucleophilicity (basicity) as compared to THF (pK_B(EO) = 7.4; pK_B(THF) = 4.4[14]).

Tertiary oxonium ions are converted into secondary ones in the reaction shown in Scheme 6.

If the rates of both reactions are equal one to another, the equality shown in Scheme 7 holds, allowing the determination of the ratio of both rate constants.

The phosphine ion trapping method gives the overall concentrations of the tertiary and the secondary oxonium ions. For the tertiary oxonium ions, the determined concentration corresponds indeed to the concentration of species appearing in Scheme 4, because all of the tertiary oxonium ions may react according to Scheme 6. This does not apply for the secondary oxonium ions. Protons are exchanging fast and protonate any nucleophile present in the system, thus not only EO groups but also THF and HO$^-$ groups and, in the later stages, also chain ether groups. The ion trapping method gives thus the overall concentration of all these species, while only protonated EO participates in reaction by which secondary oxonium ions are converted into the tertiary ones (cf. Scheme 5).

Thus, to determine the ratio of the rate constants of interconversion, it is necessary to know not only the overall concentration of the secondary oxonium ions but also the concentration of this fraction of the secondary oxonium ions which exists as protonated EO.

The distribution of protons between all of the nucleophiles (bases) present in the system is governed by their relative basicities. Using values of pK_B known from the literature, the concentration of protonated EO can be expressed as a fraction of the overall concentration of the secondary oxonium ions.[14−16] Then, the final equation, allowing calculation of k_6/k_2 ratio may be derived (Scheme 8).

The ratios of rate constants, calculated for two experiments shown in Table 1, are equal to $k_6/k_2 = 6.2 \times 10^{-3}$ and 1.1×10^{-2}. Ratios of the rate constants, calculated from two independent experiments, differ by almost two

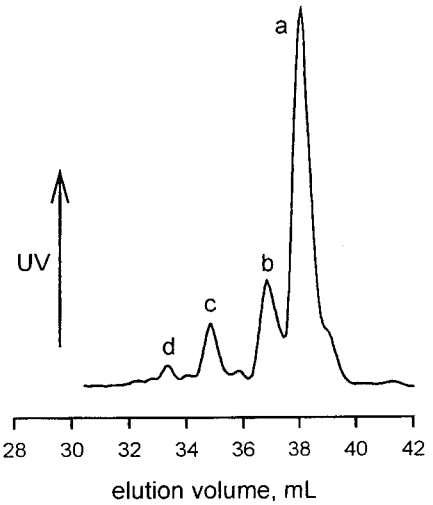


Figure 2. HPLC chromatogram (UV detection) of the reaction mixture: $[THF]_0 = 4.8$ mol/L; $[EO]_0 = 1.2$ mol/L; $[C_6H_5CH_2CH_2OH]_0 = 4.8$ mol/L; $[HBF_4{\cdot}Et_2O] = 0.1$ mol/L; 25 °C; CH_2Cl_2 solvent; 2 h. Assignments of signals: (a) unreacted $C_6H_5CH_2CH_2OH$ (R−OH); (b) $C_6H_5CH_2CH_2O(CH_2)_2OH$ (R−EO−OH); (c) $C_6H_5CH_2CH_2O(CH_2)_4O(CH_2)_2OH$ (R−THF−EO−OH), (d) $C_6H_5CH_2CH_2O(CH_2)_4O(CH_2)_4O(CH_2)_2OH$ (R−THF−THF−EO−OH).

times, which is most probably due to the limited reliability of the pK_B values. The results indicate, nevertheless, that reaction of protonated EO with THF is $(1-2) \times 10^2$ faster than the reaction of alkylated THF with HO^- groups. This difference reflects the much higher reactivity of the protonated three-membered ring as compared to that of the alkylated five-membered ring due to different ring strains in corresponding ions.

Reactions of the Protonated EO. The first reaction, starting the sequence of reactions leading to formation of a copolymer, involves reaction of the protonated EO with a THF molecule (reaction 3.2 in Scheme 3). Protonated EO may, however, also react with other bases present in the system, namely EO and HO^- groups (reactions 3.1 and 3.3 in Scheme 3).

The real copolymerization process is carried out in such a way, that EO is introduced slowly to the bulk THF containing about 10 mol % of diol and 0.1 mol % of protic acid. Thus, instantaneous concentration of EO in the reaction mixture is low. It was determined by GLC that at the typical conditions used, the instantaneous concentration of EO is below 0.05 mol/L, i.e., is about 2 orders of magnitude lower than concentrations of THF and HO^- groups. It may be thus assumed that under real copolymerization conditions, the contribution of reaction 3.1 is negligible and protonated EO reacts almost exclusively with either THF or the HO^- groups.

To estimate the ratio of rate constants of these two reactions, the model system was studied. EO was added slowly to a solution of THF (4.8 mol/L) and $C_6H_5CH_2CH_2OH$ (4.8 mol/L) containing $HBF_4{\cdot}Et_2O$ (0.1 mol/L) in CH_2Cl_2. The amount of EO added corresponded to about 25 mol % of THF. The reaction mixture was then analyzed by GPC. A typical chromatogram is shown in Figure 2.

Two major products observed are oligomers resulting from reaction of the protonated EO with ROH and reaction of protonated EO with THF, followed by reaction with ROH. The final concentration of the latter one is equal to the concentration of alkylated THF formed by reaction 3.2 because this is the only product which

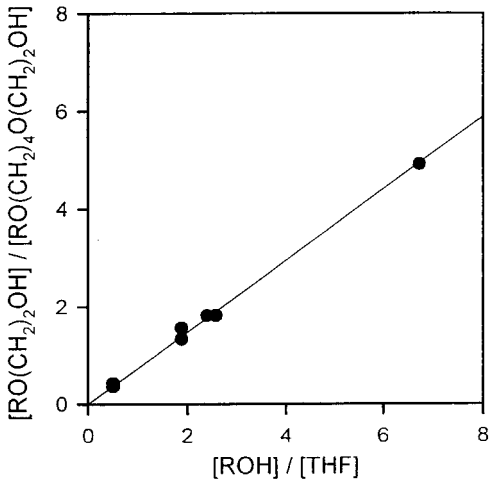


Figure 3. Plot of the left-hand side of the equation shown in Scheme 9 vs the $[HO^-]_0/[THF]_0$ ratio in CH_2Cl_2 at 25 °C.

Scheme 9

$$\frac{d\,[RO(CH)_2OH]}{d\,[RO(CH_2)_4O(CH_2)_2OH]} = \frac{k_3\,[ROH]\,[H\text{-}O^+\triangleleft]}{k_2\,[O\square]\,[H\text{-}O^+\triangleleft]}$$

at low conversion:

$$\frac{d\,[RO(CH)_2OH]}{d\,[RO(CH_2)_4O(CH_2)_2OH]} \cong \frac{[RO(CH)_2OH]}{[RO(CH_2)_4O(CH_2)_2OH]}$$

thus:

$$\frac{[RO(CH)_2OH]}{[RO(CH_2)_4O(CH_2)_2OH]} = \frac{k_3\,[ROH]}{k_2\,[O\square]}$$

is eventually formed from alkylated THF (no other oligomers were detected). It may be assumed, that at low conversion, the ratio of concentrations of both products is equal to the ratio of the rates of their formation (Scheme 9).

The plot of the left-hand side of equation shown in Scheme 9, as a function of $[HO^-]/[THF]$ ratio for a series of experiments performed at different $[HO^-]/[THF]$ ratios, is shown in Figure 3.

The slope gives the ratio of k_3/k_2 equal to 0.6. This result agrees with the similarity of nucleophilicities (expressed as pK_B) of THF and HO^- groups.

Reactions of the Alkylated THF. Alkylated THF, like protonated EO, may react with any nucleophile present in the system (cf. Scheme 3). Reaction 3.4 may be neglected, due to the low instantaneous concentration of EO. Reaction 3.5 is essentially THF homopropagation, for which the rate constant is known.[17] Thus, to estimate the contributions of reactions 3.5 and 3.6, it is sufficient to determine the rate constant of reaction 3.6.

The kinetics of reaction 3.6 was studied in the system, in which methoxyethanol ($CH_3OCH_2CH_2OH$) was added to the solution of living poly-THF obtained with $C_6H_5CO^+SbF_6^-$ as initiator in CH_2Cl_2 solution ($[THF]_0 = 5$ mol/L, $[C_6H_5CO^+SbF_6^-] = 0.1$ mol/L). Transformation of the tertiary into the secondary oxonium ions was followed either by recording the ^1H NMR spectra of a "living" reaction mixture or the ^{31}P NMR spectra of the reaction mixture after termination with an excess of an aliphatic tertiary phosphine.

A typical ^1H NMR spectrum is shown in Figure 4.

In a series of experiments, in which a 2.5−10-fold excess of the $HO-CH_2-CH_2-$ groups with respect to

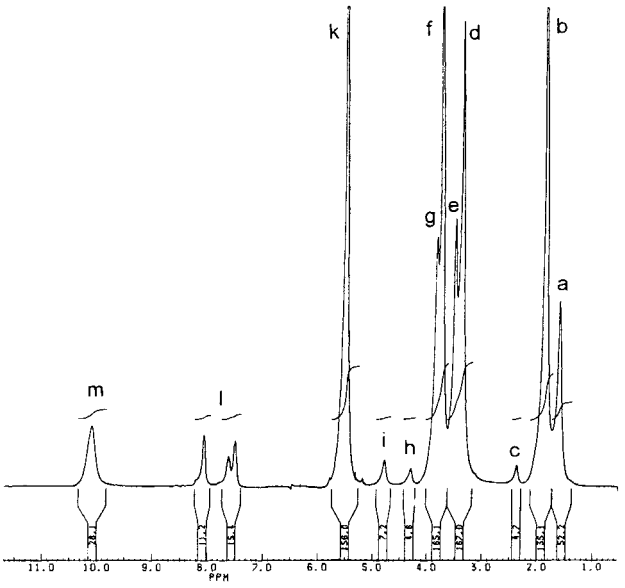


Figure 4. ^{1}H NMR spectrum of solution of living poly-THF after addition of an excess of $CH_3OCH_2CH_2OH$. Conditions: $[THF]_0 = 5.0$ mol/L; $[C_6H_5CO^+SbF_6^-]_0 = 0.1$ mol/L; $[CH_3OCH_2CH_2OH] = 0.2$ mol/L; CH_2Cl_2 solvent; −70 °C. Assignments of signals: see Scheme 11.

Scheme 10

$$(C_2H_5)_3O^+ + HOCH_2CH_2OCH_3 \longrightarrow$$

$$\longrightarrow C_2H_5OCH_2CH_2OCH_3 + (C_2H_5)_2O + \text{"}H^+\text{"}$$

the concentration of the tertiary oxonium ions was used, initially a fast reaction was observed, which stopped, however, at 20−60 mol % conversion of the tertiary oxonium ions (depending on the ratio $[HO^-]$/[tertiary oxonium ions]), in spite of the fact that there was still a large excess of the unreacted HO^- groups in the system. To confirm this observation, a model reaction was studied, in which living poly-THF was replaced with triethyloxonium ions (Scheme 10).

Also in this system, after the fast initial stage, reaction stopped at the limited conversion of the tertiary oxonium ions. Some typical conversion−time curves are shown in Figure 5.

One possible explanation could have been that reactions shown in Schemes 3.6 and 10 are not irreversible and stop at equilibrium. This possibility has been excluded; it was shown that no reaction occurs between two ethers appearing on the right-hand side of the equation shown in Scheme 10 in the presence of acid; i.e., the backward reaction does not proceed. The limited conversions of tertiary oxonium ions with an excess of HO^- groups must, therefore, be of kinetic origin.

To check the possibility that in the system containing a relatively high concentration of "protons", i.e., secondary oxonium ions, where the activity of the hydroxyl group in the $HO-CH_2-CH_2-O-$ moiety is considerably reduced due to the extensive hydrogen bonding, the reaction between tertiary oxonium ions and $HO-CH_2-$

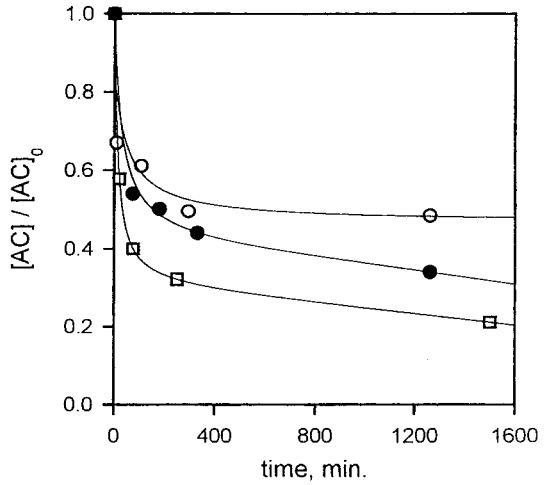


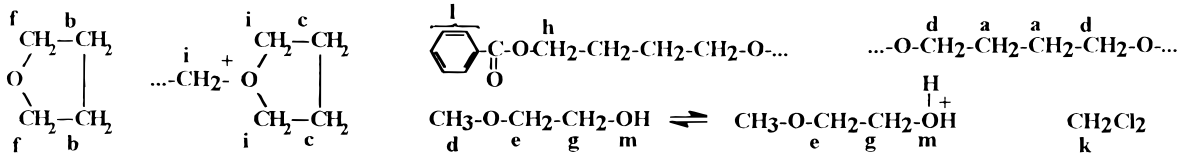
Figure 5. Conversion−time curves for the reaction of tertiary oxonium ions with $CH_3OCH_2CH_2OH$. Concentrations of tertiary oxonium ions were determined by ^{31}P NMR. Reaction conditions: (○) AC = tetrahydrofuranium cation (living poly-THF prepared with $C_6H_5CO^+SbF_6^-$ initiator; $[I]_0 = 0.10$ mol/L; $[THF]_0 = 5.0$ mol/L), $[CH_3OCH_2CH_2OH]_0 = 0.25$ mol/L, CH_2Cl_2, −78 °C; (●) AC = triethyloxonium cation, $[(C_2H_5)_3O^+BF_4^-]_0 = 0.10$ mol/L, $[CH_3OCH_2CH_2OH]_0 = 0.20$ mol/L, CH_2Cl_2, −25 °C; (□) AC = triethyloxonium cation, $[(C_2H_5)_3O^+BF_4^-]_0 = 0.10$ mol/L, $[CH_3OCH_2CH_2OH]_0 = 0.50$ mol/L, CH_2Cl_2, −25 °C.

CH_2-O- groups was studied in the presence of a proton trap. Indeed, in such a case, reaction proceeded to complete conversion of the tertiary oxonium ions, and in contrast to the system without proton trap, the logarithmic plots, in coordinates of the second-order kinetic equation, were linear, as shown in Figure 6.

This result shows clearly, that analysis of the kinetics of the cationic copolymerization of EO with THF in the presence of diols in terms of Scheme 3 is an oversimplification. At least some of the species appearing in this scheme may exist in the form of complex aggregates. In the presence of a proton trap, when "protons" are effectively removed from the system as soon as they are formed by reactions shown in Schemes 3.6 or 10, reaction proceeds to completion and obeys a second-order kinetic law, which indicates that all of the HO^- groups are available for reaction. In the absence of a proton trap, which corresponds to the real conditions of copolymerization, the reaction proceeds as if the concentrations of the HO^- groups were much lower than their real concentrations. Apparently, the activities of the HO^- groups involved in the complex equilibria through hydrogen bonds are much lower than the activities of the "free" HO^- groups.

Consequently, the kinetic constants presented in this paper should be treated not as a true absolute rate constants but instead as apparent values, allowing one nevertheless to estimate the relative reactivities of the involved species and to predict the contribution of the competitive reactions shown in Scheme 3 to the overall process, which was the major aim of this study.

Scheme 11



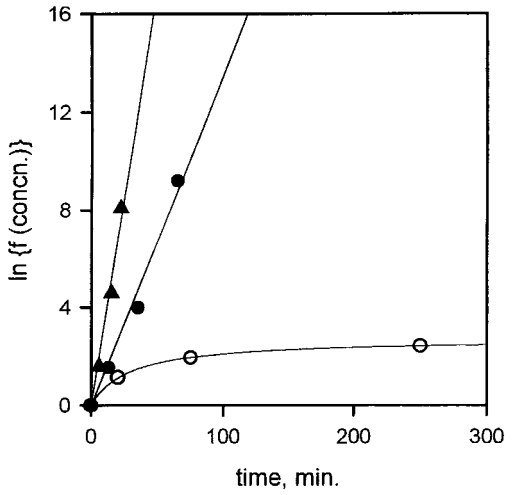


Figure 6. Kinetic plots, according to the second-order kinetic equation (semilogarithmic anamorphoses) for the reaction of tertiary oxonium ions (Et_3O^+) with $CH_3OCH_2CH_2OH$ (ROH) in the presence and in the absence of proton trap (2,6-di-*tert*-butylpyridine). $\ln\{f(\text{concn}) = \{1/([ROH]_0 - [Et_3O^+]_0)\} \times \ln([Et_3O^+]_0 \times ([ROH]_t/[ROH]_0)[Et_3O^+]_t)$ Reaction conditions: (▲) in the presence of proton trap (2,6-di-*tert*-butylpyridine, tBP), $[(C_2H_5)_3O^+BF_4^-]_0 = 0.20$ mol/L, $[CH_3OCH_2CH_2OH]_0 = 0.40$ mol/L, $[tBP]_0 = 0.40$ mol/L, CH_2Cl_2, 0 °C; (●) in the presence of proton trap (2,6-di-*tert*-butyl pyridine, tBP), $[(C_2H_5)_3O^+BF_4^-]_0 = 0.10$ mol/L, $[CH_3OCH_2CH_2OH]_0 = 0.50$ mol/L, $[tBP]_0 = 0.20$ mol/L, CH_2Cl_2, −25 °C; (○) in the absence of proton trap, $[(C_2H_5)_3O^+BF_4^-]_0 = 0.10$ mol/L, $[CH_3OCH_2CH_2OH]_0 = 0.50$ mol/L, CH_2Cl_2, −25 °C.

From the data shown in Figure 6, the apparent rate constant of the reaction of tertiary oxonium ions with HO^- groups as well as the temperature coefficient, can be obtained. The corresponding values are equal to $k_6 = 1.0 \times 10^{-3}$ mol^{-1}·L·s^{-1} (−25 °C), $E_a = 51$ kJ·mol^{-1}.

The value of the apparent rate constant corresponding to the reaction of the tertiary oxonium ion with the $HO-CH_2-CH_2-$ group may be compared with the value of the rate constant of THF homopropagation, corresponding to the reaction of tertiary oxonium ion with THF molecule, equal to $k_p = 8 \times 10^{-4}$ mol^{-1}·L·s^{-1} (−25 °C).[17] The small difference between both values agrees well with similar nucleophilicities of THF and primary HO^- groups.

Summary of the Kinetic Results. Results presented in this paper allowed the estimation of all of the apparent rate constants of the reactions appearing in Scheme 3, assuming that reactions 3.1 and 3.4 may be neglected, due to the discussed above reasons. The following parameters have experimentally been determined (all in CH_2Cl_2 solvent at 25 °C; when measurements were conducted at temperature other than 25 °C, the corresponding values for 25 °C were calculated using known activation energy values): $k_3/k_2 = 0.6$, $k_6/k_2 = 8 \times 10^{-3}$, and $k_6 = 6.35 \times 10^{-2}$ mol^{-1}·L·s^{-1}. Additionally, k_5 was assumed to be equal to k_p for THF $= 3.9 \times 10^{-2}$ mol^{-1}·L·s^{-1}.

This allows estimation of all of the involved rate constants: $k_2 = 8.0$, $k_3 = 4.8$, $k_5 = 3.9 \times 10^{-2}$, and $k_6 = 6.35 \times 10^{-2}$ (all values given in mol^{-1}·L·s^{-1}) (CH_2Cl_2, 25 °C).

Rate constants k_2 and k_3 correspond to reactions of the protonated EO (secondary oxonium ion) with THF and $HO-CH_2-CH_2-O-$ groups, respectively, and rate constants k_5 and k_6 correspond to the related reactions of the alkylated THF (tertiary oxonium ions). Protonated EO reacts with both nucleophiles with similar rate constants (k_2 vs k_3) and the same is true for reactions of the alkylated THF (k_5 vs k_6). This reflects the similar nucleophilicities of THF and the HO^- group.

Reactivities of both types of oxonium ions in reaction with the same nucleophile are, however, considerably different, secondary oxonium (oxiranium) ion (protonated EO) reacts about 2 orders of magnitude faster than tertiary oxonium (oxolanium) ion (k_2 vs k_5 and k_3 vs k_6).

The secondary oxonium ion involves a highly strained three-membered ring (ring strain of EO molecule is equal to 114.3 kJ/mol) while the tertiary oxonium ion involves a five-membered ring for which the ring strain is much lower (ring strain of THF molecule is equal to 23.6 kJ/mol).[18] Thus, the much higher reactivity of the protonated EO results from the release of the considerable strain energy upon opening of the oxonium ion ring, which outweighs the inherently lower reactivity of the secondary oxonium ions.

The knowledge of the rate constants of the competing reactions gives an insight into copolymerization mechanism and allows the prediction of the dependence of composition and microstructure of copolymers on the reaction conditions.

Experimental Part

Reagents. Tetrahydrofuran (THF) (POCh, Poland) was kept for 48 h over KOH pellets to remove peroxides. After filtration, THF was heated over sodium for 12 h and distilled. Fraction boiling at 66 °C was collected and kept in a vacuum ampule over sodium−potassium alloy.

Ethylene oxide (EO) (Petrochemia Płock, Poland) was condensed (bp = 11 °C) on a vacuum line to the ampule containing CaH_2. This procedure was repeated three times, before use.

Ethylene glycol (EG) (POCh, Poland) was twice distilled (bp = 196−198 °C). 2-Phenylethanol (Aldrich) (bp = 215−217 °C), 2-methoxyethanol (Aldrich) (bp = 124−125 °C), and tributylphosphine (Aldrich) (bp = 100−101 °C/23 mmHg) were purified by distillation.

The ether complex of tetrafluoroboric acid, HBF_4·Et_2O (Aldrich), was used as supplied.

Benzoylium hexafluoroantimonate, $C_6H_5CO^+SbF_6^-$, was prepared from C_6H_5COF and SbF_5 according to the described procedure.[19]

Triethyloxonium tetrafluoroborate: $(C_2H_5)_3O^+BF_4^-$ was prepared from BF_3−etherate and epichlorohydrin, according to the described procedure.[20]

Methylene chloride was washed three times with concentrated sulfuric acid to remove unsaturated impurities and then washed several times with water, a 5% solution of $NaHCO_3$, and again with distilled water. After drying for 24 h over $CaCl_2$, methylene chloride was distilled over CaH_2 (bp = 39−40 °C) and kept in a vacuum ampule over fresh CaH_2.

Deuterated solvents ($CDCl_3$, CD_2Cl_2, C_6D_6) used for NMR analysis (Aldrich) were dried over CaH_2 before use.

Experimental Procedures. Kinetic experiments were carried out using vacuum line techniques. The applied procedures are illustrated as described below in detail by the experimental procedure for determination of concentrations of secondary and tertiary oxonium ions in copolymerization of THF with EO.

Required amounts of EG, THF, CH_2Cl_2, and EO were distilled (in this order) from the calibrated ampules into a reaction vessel on the vacuum line. The reaction vessel was an ampule with an attached NMR tube and four arms, each fitted with a breakseal containing tributylphosphine (distilled into each ampule before assembling the reaction vessel) and an attached NMR tube. After the solution was mixed, the phial containing the catalyst was broken at −78 °C and the solution was distributed into the four arms, which were sealed off. Part of the solution was transferred to the NMR tube, which was

sealed off. The progress of the reaction was followed by ^{1}H NMR. At different stages of reaction, the breakseals in the ampules were broken and tributylphosphine was introduced to the reaction mixture, terminating the reaction. Part of each solution was then transferred to NMR tube and, after each tube was sealed off, the ^{31}P NMR spectrum was recorded at −78 °C.

Measurements. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker MSL 300 MHz or Bruker AC 200 MHz instrument.

GPC measurements were performed with a LKB-2150 apparatus with UV detector (LKB 2238 UNICORD S II) equipped with a set of Waters Ultrastyragel columns, 100, 500, and 1000 Å. THF was used as the eluent.

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