Progress in Activated Monomer Polymerization. Kinetics of AM Polymerization.

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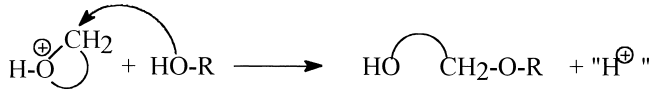
SUMMARY: Understanding of the kinetics of polymerization process is essential for exploiting the synthetic possibilities offered by different polymerization mechanisms. Cationic polymerization of cyclic ethers proceeding by Activated Monomer (AM) mechanism allows preparation of linear polyethers free of cyclic fraction. According to this polymerization mechanism, only activated form of monomer may participate in propagation, which should be considered when analyzing kinetics of AM polymerization. Approaches allowing analysis of the kinetics of AM polymerization of oxiranes and formally similar polyaddition of activated oxiranes to derivatives of phosphoric acids (P-OH acids), are discussed.

Introduction

Propagation in cationic polymerization of cyclic ethers in the majority of instances proceeds by Active Chain End (ACE) mechanism as the reaction between monomer and active center: tertiary oxonium ion, located at the growing chain end. There is, however, an increasing number of systems known, in which propagation proceeds by different mechanism. It was shown, that if acid catalyzed polymerization of cyclic ethers was carried out in the presence of alcohols (more generally in the presence of HO- containing compounds), propagation proceeded as an attack of HO- terminal group on the α-carbon atom in the protonated monomer molecule [1].



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Such mechanism is therefore called: Activated Monomer (AM) mechanism, by analogy to the described earlier mechanism of anionic polymerization of lactams and NCA's [2].

Activated Monomer cationic polymerization of heterocyclic monomers has been reviewed [3, 4] and it has been stressed, that the major advantage of this polymerization mechanism is the elimination of major side-reaction typically accompanying ACE propagation i.e. back-biting. This is due to the absence of charged species at the end of the growing chain. Indeed, it was shown, that purely linear polymers can be prepared by AM polymerization from monomers which, when polymerizing by ACE mechanism, give a mixture of linear polymers and cyclic fraction [3].

When cyclic ether is polymerized with acid catalyst in the presence of HO- groups containing compounds, both ACE and AM mechanism can operate, competing with each other. To exploit fully the advantages of AM polymerization, the conditions should be chosen at which AM propagation is so much faster than ACE propagation, that the contribution of the later may be neglected. In other words AM propagation should be kinetically favored over ACE propagation. This requires the knowledge of the kinetics of polymerization proceeding by AM mechanism.

Kinetics of AM Polymerization of Cyclic Ethers

In the polymerization proceeding by ACE mechanism, the rate of polymerization is given by the following equation:

$$-d[M] / dt = k_p [-M^*] [M] \qquad \mathbf{2}$$

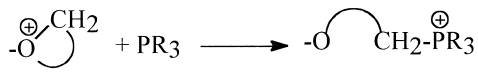
In order to determine the propagation rate constant, concentration of active species ($[-M^*]$) has to be known. In some systems it may be determined directly (e.g. by UV or NMR) but in many cases it is simply assumed to be equal to the concentration of initiator.

In AM polymerization of cyclic ethers, it is the activated monomer species and not monomer itself, which participates in propagation. The rate of polymerization is therefore given by equation:

$$-d[M] / dt = k_p [H\text{-}\overset{\oplus}{O}\bigcirc] [HO^-] \qquad \mathbf{3}$$

To determine the rate constant of propagation one should know the concentration of activated monomer species. It cannot be taken as equal to initial concentration of "protons" i.e. initial concentration of acid catalyst, because protons are exchanging fast between all bases present in the system and at any instant, only a part of protons participate in protonation (activation) of monomer. Therefore, there are different protonated species (secondary oxonium ions) present in the system, but only one type of species (protonated monomer) participate in propagation.

In the copolymerization of cyclic ethers of various ring size, proceeding by ACE mechanism, it was possible to distinguish between different active species using phosphine ion trapping method [5]. The principle of this method is outlined below:



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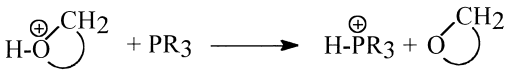

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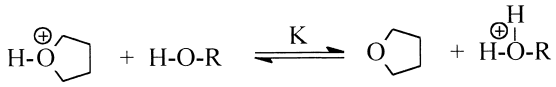
Chemical shifts of quaternary phosphonium ions derived from tertiary oxonium ions of different ring size are sufficiently different, to allow observation of individual signals corresponding to all species present. Secondary oxonium ions, however, behave differently, instead of ring opening, there is a simple transfer of proton from cyclic (or linear) ether to phosphine, giving the tertiary phosphonium ion.

Thus, different secondary oxonium ions lead to the same tertiary phosphonium ions. In the systems where there are simultaneously tertiary and secondary oxonium ion species present, the method allows therefore to determine the concentration of each tertiary oxonium ion and the sum of concentrations of all of secondary oxonium present. This approach was successfully applied to analyze the kinetics of cationic copolymerization of tetrahydrofuran (THF) with ethylene oxide (EO) initiated by low molecular weight diols and catalyzed by acids where two types of species participate in propagation : 5-membered tertiary oxonium ions (alkylated THF) and 3-membered secondary oxonium ions (protonated EO) [6].

Phosphine ion trapping method, giving only the over-all concentration of secondary oxonium ions, cannot therefore be applied for determination of the concentration of protonated monomer in the systems where there are other protonated bases present.

The distribution of protons among bases present in the system can in principle be estimated from the known pK_B values. Different authors report, however, different values, depending on the method of pK_B determination. Thus, the attempt was undertaken to measure the position of proton exchange equilibria between cyclic ethers and hydroxyl groups by ^1H NMR directly at the conditions of kinetic experiments [7].

In the system containing cyclic ether (tetrahydrofuran taken as example), alcohol and fully ionized protic acid such as $H^+BF_4^-$ or $H^+PF_6^-$ (in form of its complexes with e.g. ethers) the following equilibrium takes place:



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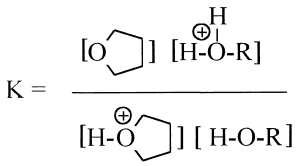

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Due to the fast exchange, only one averaged signal is observed for each group in both protonated and free cyclic ether, the same is true for each group in alcohol. Knowing the chemical shifts of corresponding groups in free form and in fully protonated form (this may be determined from ^1H NMR spectra of cyclic ether or alcohol recorded in the presence of sufficient excess of acid), one may calculate the concentrations of both protonated and non-protonated forms. Thus, by recording ^1H NMR spectra of solutions containing different concentrations of cyclic ether and alcohol in the presence of protic acid, one should be able to determine the equilibrium constant according to equation **7**.

The dependence of molar fractions of protonated bases on the ratio of concentrations of both bases, determined by ^1H NMR, is shown in Fig. 1 while the plot corresponding to equation **7** is shown in Fig. 2 [7].

Instead of being linear, according to equation **7** the plot shows a curvature indicating, that due to the e.g. hydrogen bonding, the simplified treatment based on equation **7** is not applicable over the broader range of concentration.

The applied approach allowed therefore to calculate the relative concentration of both types of secondary oxonium ions at the conditions of NMR experiments, it was not possible, however, to extrapolate these results to the conditions of kinetic experiments, where different concentrations of cyclic ether and alcohol had to be used.

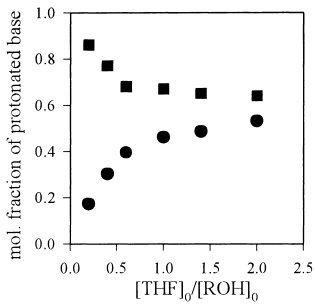


Fig.1. The dependence of mol. fraction of: protonated THF (circles) and protonated ROH (squares) on $[THF]_0/[ROH]_0$ ratio

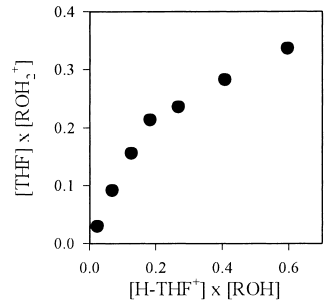


Fig.2. Plot in coordinates of equation (7)

Analysis of the kinetic equations shows, however, that by combining equation for the rate of AM polymerization and equation for the proton exchange equilibrium, the final equation may be derived in the form allowing determination of proton exchange equilibrium constant and therefore also propagation rate constant, from the kinetic data [8-10].

At the early stage of AM polymerization of cyclic ethers, when the concentration of the polymer (linear polyether) is still sufficiently low to be neglected, the only two bases present in the systems are: cyclic ether (monomer) and hydroxyl groups. If protic acid, which may exists only in fully ionized form, such as $H^+BF_4^-$ or $H^+PF_6^-$ is used as catalysts (in form of its complexes with e.g. ethers) , then the following dependencies hold:

$$[H^{\oplus}]_0 = [H\text{-}O^{\oplus}\text{◯}] + [\,H\text{-}\overset{\oplus}{O}\text{-}R\,] \qquad \mathbf{8}$$

$$H\text{-}O^{\oplus}\text{◯} + H\text{-}O\text{-}R \underset{}{\overset{K}{\rightleftharpoons}} O\text{◯} + H\text{-}\overset{\oplus}{O}\text{-}R \qquad \mathbf{9}$$

$$[H\text{-}O^{\oplus}\text{◯}] = [H^{\oplus}]_0 / \left(1 + K\,\frac{[H\text{-}O\text{-}R]}{[O\text{◯}]}\right) \qquad \mathbf{10}$$

In this way concentration of activated monomer may be related to the over-all concentration of acid catalyst. After substituting equation **10** into equation **3** one obtains the following equation for the rate of AM polymerization:

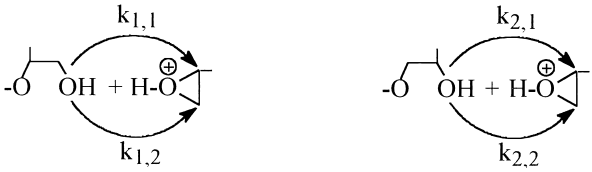
$$R_p = -d \ln [ROH] / dt = k_p \cdot [H^{\oplus}]_0 / (1 + K \frac{[H\text{-}O\text{-}R]}{[O\bigcirc]}) \qquad \textbf{11}$$

$$\frac{[H^{\oplus}]_0}{R_p} = \frac{1}{k_p} + \frac{K}{k_p} \frac{[H\text{-}O\text{-}R]}{[O\bigcirc]} \qquad \textbf{12}$$

If the rate of monomer consumption for known $[H^+]_0$ concentration (equal to concentration of acid catalyst) and different $[HO\text{-}]_0/[M]_0$ ratios is measured and the results are plotted in coordinates of equation **12**, the linear plots allowing determination of both k_p and K values should be obtained. Indeed, as shown for the AM polymerization of two substituted oxiranes: propylene oxide (PO) and epichlorohydrin (ECH), the corresponding plots are linear and the values of apparent propagation rate constants are equal to [9]:

k_p app (PO) = 0.29 mol^{-1} L s^{-1} and k_p app (ECH) = 0.135 mol^{-1} L s^{-1}

These values are only apparent ones, because in the AM polymerization of substitutes oxiranes, there are four possible propagation reactions:



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By analyzing the rate of consumption and the rate of formation of primary and secondary hydroxyl groups in the model systems (e.g. reactions of $ROCH(CH_3)CH_2OH$ and $ROCH_2CH(CH_3)OH$ with propylene oxide or $ROCH(CH_2Cl)CH_2OH$ and $ROCH_2(CH_2Cl)CHOH$ with epichlorohydrin in the presence of acid) these apparent values were separated into rate constant of individual reactions. The knowledge of the values of rate constants of four possible propagation reactions, leading to formation of different diads, allows calculation of the regioisomeric diad contents in resulting polymers. These calculated values were in good agreement with the content of h-h, h-t (t-h) and t-t diads, determined from ^{13}C NMR spectra of polymers [10].

Kinetics of Self-catalyzed Polyaddition of Oxiranes to P-OH Acids

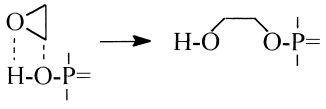
It has been shown recently, that relatively high molecular weight (M_n up to 10^4) linear polyphosphates can be prepared by polyaddition of diepoxides to derivatives of phosphoric acid in the absence of intentionally added catalyst [11].

In order to get more insight into the mechanism of this process, the kinetics of model reactions between simple epoxides (ethylene oxide and its substituted derivatives) and acids of phosphorus, was studied [12, 13]. This reaction resembles discussed earlier propagation in AM polymerization in this respect, that it requires activation of oxirane molecule. In the absence of intentionally added acid catalyst, oxirane is activated by acidic P-OH group, acting thus both as an reactant and as catalyst.

In contrast to described earlier systems, in which protic acid catalysts (e.g. $H^+BF_4^-$) were fully ionized even in relatively low polarity medium (bulk monomer or its solution in e.g. CH_2Cl_2), P-OH acids are not fully ionized in e.g. 1,4-dioxane (one of a few solvents in which phosphoric acid and its derivatives are soluble).

The degree of ionization of model monofunctional acid: diethylphosphoric acid (DEPA - diethyl ester of phosphoric acid) was determined as equal to $5 \cdot 10^{-4}$ at the conditions used for kinetic experiments [12]. Analysis of the kinetics of the reaction led to the conclusion, that concentration of ionized forms is much too small (about one order of magnitude) to account for the observed rates of reaction. Therefore, reaction proceeds mainly with participation of oxirane molecule activated by non-ionized form of acid, through hydrogen bonding.

Two possible mechanisms can be envisaged; either reaction proceeds by rearrangement of bonds within oxirane - P-OH complex or one molecule of acid activate the oxirane molecule for the reaction with another P-OH group:



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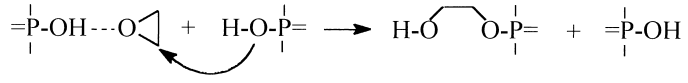

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In principle, these two possibilities could be distinguished on the basis of the kinetic data;

in the first case reaction should be of the first order with respect to P-OH group while the second order should be observed for the later case.

The situation is however complicated by the fact, that P-OH acids exist in solution mainly in forms of dimers. If only monomeric form of acid were active, than dissociation of dimer would introduce factor 1/2 into the exponent in kinetic equation. Therefore, if the reaction were second order with respect to concentration of monomeric acid, it would be of the first order ($1/2 \cdot 2$) with respect to over-all acid concentration. Experimentally determined reaction order with respect to acid concentration is indeed close to one, which indicates that one of the two possible mechanisms operates but does not permit the conclusion which of them actually takes place [12].

From the kinetic data, the apparent rate constant of reaction between oxirane and P-OH group may be determined as equal to $2.6 \cdot 10^{-4}\ mol^{-1} \cdot L \cdot s^{-1}$ [12].

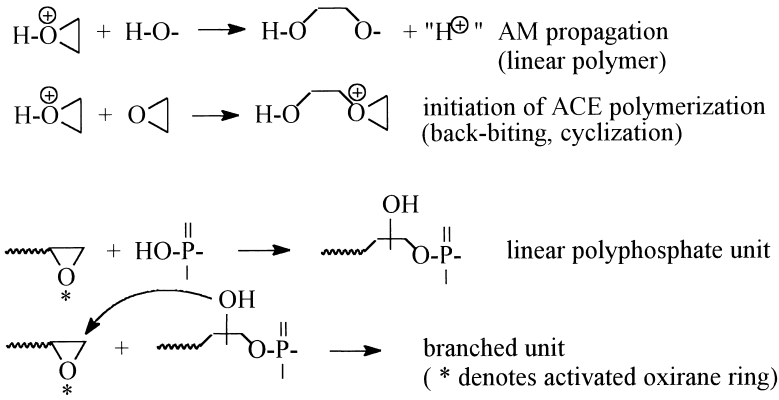
Analysis of the kinetics of addition of activated oxirane to P-OH groups in terms of elementary reactions is much more difficult, than in the case of AM propagation of oxiranes described in the previous section. First of all, in contrast to well defined species: secondary oxonium ion (protonated monomer) in AM propagation, in analyzing addition of activated oxirane to P-OH group one deals with not so well defined hydrogen bonded species. Even if it is assumed that only one type of hydrogen bonded species exists, the questions remains (as in analysis of kinetics of AM propagation of oxiranes) what is the actual concentration of activated oxirane. It cannot be taken as equal to the over-all concentration of P-OH groups, because some of these groups are involved in formation of hydrogen bonded species with solvent (1,4-dioxane) and C-OH groups appearing in reaction products.

Because the approach outlined by scheme **12** cannot be applied for analyzing the kinetics of addition of activated oxirane to P-OH group, only the values of apparent rate constant was determined for this and related systems [12, 13].

Synthetic Applications of Polymerization Processes Involving Activated Monomers

AM polymerization of oxiranes offers a convenient synthetic route to linear, telechelic polyethers while addition of activated oxiranes to P-OH acids may be applied for synthesis

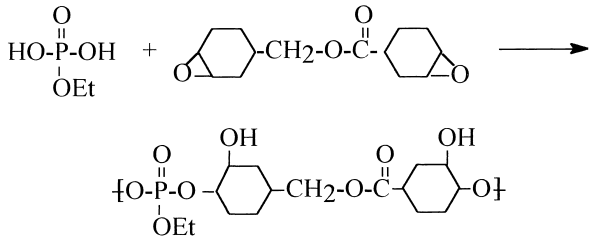
of linear polyphosphates. In both cases, however, competing reactions may proceed, leading to undesired side-products or undesired structures. This is illustrated by the scheme below:



The contribution of side-reactions is governed by the kinetics of the process i.e., as in the case of AM polymerization, by the ratio of rates of AM polymerization to the rate of initiation of ACE polymerization, leading to formation of cyclic fraction. Understanding of the kinetics of polymerization processes involving activated monomers helps to adjust the polymerization conditions in such a way, that the contribution of side-reactions is minimized.

The most important factor is the concentration of "free" monomer in the system. It has been shown, that in order to eliminate side-reactions in both types of processes described in this paper, i.e. AM polymerization of oxiranes and addition of activated oxiranes to P-OH acids, polymerization should be carried out at monomer starved conditions, at low instantaneous concentration of the monomer. This is practically achieved by slow addition of the monomer to reaction mixture, with a rate corresponding to the rate of monomer consumption.

Using this approach, telechelic polymers and macromonomers, essentially free of cyclic fraction were prepared by the cationic AM polymerization of epichlorohydrin (with M_n up to $3 \cdot 10^3$) [14] and propylene oxide (with M_n up to 10^3) [4]. On the other hand, almost perfectly linear polyphosphates with M_n up to 10^4 were obtained by polyaddition of diepoxides (e.g. 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate) to ethylphosphoric acid [11]:



1,4-cyclohexyl or isomeric 1,3-cyclohexyl units

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Several other examples of successful application of cationic Activated Monomer polymerization principle for the synthesis of telechelic polymers from heterocyclic monomers indicate, that if proper kinetic conditions are chosen, this mechanism of polymerization offers interesting synthetic possibilities [3, 4].

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