Cationic Ring-Opening Polymerization (CROP) Major Mechanistic Phenomena

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ABSTRACT: A number of today’s accepted basic viewpoints related to cationic ring-opening polymerizations (CROP) were a matter of vivid disagreements between various research groups in the past. These controversies are described in this article and reasons of some differences in opinions are explained. It is shown in which way we learned that polyacetals are not exclusively cyclic (as it was assumed), why CROP ions and ion pairs have similar reactivities, and why it was necessary to propose that CROP proceeds at certain conditions by Activated Monomer Mechanism. Among other subtle kinetic problems, application of the dynamic NMR and “temperature jump” techniques in determining rate constants of active species interconversions are discussed. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 1919–1933, 2000

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INTRODUCTION

General Importance of the Ring-Opening Polymerization

Ring-opening polymerization contributed to the macromolecular science and polymer technology in a number of ways. The most important was the work of Staudinger establishing the existence of the covalently bonded macromolecules, and using as models poly(ethylene oxide) and polyformaldehyde.\(^1\)

Preparation of thermally stable polyformaldehyde failed however at that time. A few decades later the discovery of "self stabilization" in the cationic copolymerization of 1,3,5-trioxane (TR) with ethylene oxide or 1,3-dioxolane solved this problem. Polyformaldehyde (polyacetal) has become since then one of the largest scale industrial polymers made by cationic polymerization comparable only (in terms of the value of production) with polyisobutylene.\(^2\)

Another important polymer prepared by cationic ring opening polymerization, namely polytetrahydrofuran (polyTHF), has also a rather long history. Polymerization of THF was studied first by Meerwein.\(^3\) If Meerwein would have studied polymerization after 1956, that is, after the famous article by Szwarc appeared on living polymerization,\(^4\) he could have used the expression "living" for the polymerization of THF, since he and his group had all of the kinetic elements at hands. Later, all of the features of livingness of CROP of THF became apparent in works of four research groups that came to this conclusion independently of each other and working in Russia, Great Britain, and the United States.\(^5\)

PolyTHF has become an important technical product, since the \(\alpha,\omega\)-dihydroxy oligomers with \(M_n 1000\div 3000\) constitute the soft-elastic segments in thermoplastic elastomers: polyurethanes (Lycra), polyesters (Hytrel), and, more recently, polyamides.

Besides, CROP has been applied in technical polymerization of cyclic siloxanes, imines, oxazolines, and phosphazenes.\(^6\)

On the other hand, basic research in academia became enhanced by the fact that both polymerization of 1,3-dioxolane (DXL) and of THF provided excellent models to study chemistry of elementary reactions in cationic polymerization. Moreover, just at that time, studies of living anionic polymerization provided intellectual and technical tools and had shown how to attack similar problems arising in CROP. It was in this atmosphere that several research groups had undertaken basic research that has eventually led to the description of CROP in the way having no equivalent in the cationic vinyl polymerization and approaching the level of understanding of these few vinyl anionic systems, which established the background of the modern polymerization kinetics, including new wave of radical polymerizations.

Major Controversies of the Past

Our present understanding of the CROP is based on several fundamental pillars coming from studies of model monomers, mostly DXL and THF. These phenomena were often established and finally accepted as results of resolving controversies arising between various research groups. Our laboratory was involved in almost all of these discussions. Thus, a certain part of this article is devoted to the description of these different viewpoints.

One of the basic early controversy was related to the mechanism of polymerization of cyclic acetals and the structure of related polymers. It was proposed that polyacetals (e.g., polyDXL) are exclusively cyclic and are formed by "ring expansion". The Keele and Mainz groups were involved in discussing this theory. We shall briefly repeat here our article, published after a decade of painstaking studies in this area, and showing how the ion-trapping method allowed determination of the simultaneous presence of linear and cyclic macromolecules fitted with ions and coexisting during propagation.\(^7\)

Studies of the living THF polymerization, particularly polymerization with interconverting covalent and ionic
active species, allowed measuring of all of the involved rate constants of elementary reactions. Our contribution will also be covered in this short review. The most striking at the time of those studies (late sixties) was the result showing the identity of reactivities of ions and ion pairs, since it was in disagreement with a dominating paradigm of higher reactivity of ions, and based on the studies of anionic polymerization of dienes and styrenes.

The established in our works kinetic features of the ionic and covalent propagations will also be reviewed, as well as the kinetics and mechanism of interconversion of propagating ions and dormant (practically not contributing to propagation) macroesters. Today, it became apparent that in both vinyl cationic and radical polymerizations, particularly nitroxy mediated and ATRP, similar kinetic phenomena exist.

Finally, this article will describe another general contribution of our group, namely the Activated Monomer Mechanism (AMM) in CROP. This mechanism resembles the better known AMM in anionic polymerization of NCA and lactams, where the propagation step is based on the addition of the ionized monomer molecule to the nonionic growing chain end.

Basic Mechanistic Principles of the Cationic Ring-Opening Polymerization

I have chosen only a few examples of our contributions that on my judgement are related to the most basic phenomena of CROP.

Structure of Polyacetal Chains and the Mechanism of Cyclic Acetals Polymerization

In the late 1960s the idea of the ring-expansion polymerization was formulated in Keele when attempts failed to find the end groups in the poly-1,3-dioxolane, prepared with HClO₄ initiator. Thus, it was proposed that polymerization proceeds by subsequent additions of the monomer molecules to the protonated (activated) rings, enlarging in every next step of propagation (Scheme 1).

A given proton was, of course, assumed to travel to any nucleophilic center in the system—oxygen atom in monomer or macrocyclic molecule.

Meanwhile, in Mainz, Volker Jaacks, working on a similar system but at higher monomer concentrations did observe end groups, and there was no doubt that both laboratories were careful enough with their analytical techniques and in formulating their final conclusions.

After the untimely passing away of our friend Jaacks during his journey to Himalaya, we decided to enter into this not finished at that time of discussion. We assumed that not only the back-biting should take place in such a system, but also the end-to-end biting, and that the extent of end-biting should depend on the chain length (given below by n) (Scheme 2).

Thus, in order to show that active linear and cyclic macromolecules do coexist during the chain growth we used our method of ion-trapping with phosphines, assuming that the secondary oxonium ions (cyclic active species that could be formed by end-biting) would give a protonated phosphine by fast proton transfer (tertiary phosphonium salt), whereas the oxocarbenium (and oxonium) ions should give quaternary phosphonium ions. Thus, if the rate of exchange between these two species is not higher than the rate of trapping, then the proportions of linear and cyclic active species should be related to the proportions of two phosphoryl ions: quaternary and tertiary, respectively. Their chemical shifts are known and several ppm apart (Scheme 3).

Below, in Figure 1, two ³¹P{¹H} NMR spectra are given, for a system with [M]₀/[I]₀ = 20 and [M]₀/[I]₀ = 7·10¹. These ratios are not far from the determined experimentally DPₙ (slightly higher).

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There are two major conclusions following from these experiments:
1. Both oxocarbenium (and/or tertiary oxonium) ions, and secondary oxonium ions (i.e., “protons”) are present in the system, therefore propagation can take place on the linear active macromolecules (this is not excluding propagation on the cyclic ones).

2. The proportion of the linear macromolecules fitted with oxocarbenium (tertiary oxonium) ions is higher for longer chains, as it could be expected.

Actually, if the rate of exchange were much higher than the rate of trapping, then only one kind of species would have been observed.

In the next series of experiments with triethyl oxonium ion as initiator and 1,3-dioxolane-\textsubscript{d} \textsubscript{6} as monomer, it was possible to show by \textsuperscript{1}H NMR that after initiation one ethyl group is transferred from the oxonium ion to the noncharged chain end. \textsuperscript{1}H NMR allowed observation of these end groups in the growing macromolecules with $M_n$ up to 10\textsuperscript{4}.\textsuperscript{17} (Scheme 4).

Comparison of the chemical shifts of the corresponding models clearly indicated that also in this instance there are linear active macromolecules, since the chemical shift of CH\textsubscript{2}CH\textsubscript{2}OC\textsubscript{2}CD\textsubscript{2}CD\textsubscript{2} . . . differed substantially from the chemical shift of CH\textsubscript{2}CH\textsubscript{2} $^{\oplus}$ O $^{\ominus}$ < 17. These experiments did show that indeed growth proceeds on the linear macromolecules. Thus the assumption of the growth by ring expansion could not be dismissed but could be considered as redundant.

Further analysis of the work of the Keele and Mainz groups revealed, that in Keele much lower [M]/[I] ratio was used than in Mainz. Therefore, in agreement with results of Figure 1, mostly cyclics could be observed in Keele and high proportion of linear molecules could be observed in Mainz. Thus, both groups were correct in describing their own results and not quite right in criticizing of the work of the other group.

Nevertheless, the “ring-expansion” has been an ingenious enlargement of our vision of the way polymerization could have proceeded, and it was shown more recently that, for example, $\beta$-propiolactone, initiated with cyclic tin dialkyldialkoxide grows by ring-expansion.\textsuperscript{18} More recent work confirmed this general possibility in the polymerization of other lactones, although final preparation of the entirely cyclic population of macrocyclic macromolecules by a direct polymerization is not yet achieved.\textsuperscript{19,20}

Thus, still the most general way of preparing macrocycles in polymerization is by thermodynamic control.

Remembering that the concentration of macrocycles of a given size at equilibrium is equal to $\left[\frac{[m_n]}{([m]_0)}\right]_n = A \cdot n^{-5/2}$,\textsuperscript{21,22} the total concentration of all of the cyclic macromolecules (of all sizes) is given by:

$$\sum \left[\frac{[m_n]}{([m]_0)}\right] = A \cdot \sum n^{-5/2}$$
Therefore, if the starting concentration of a given monomer (e.g., DXL) is equal to this sum, thus, is then practically all of the macromolecules should be cyclic. This relationship, based on the Jacobson–Stockmayer equation, is valid for thermodynamically ideal systems (“no interactions”), in practice some shorter linear oligomers can also be present.

Attempts to prepare exclusively cyclic polymers is important, since there is a difference of various properties including the higher stability of the cyclic macromolecules devoid of the chain ends. Besides, breaking once the cyclic macromolecule does not change its polymerization degree.

The next important problem in the ROP of cyclic acetals is related to the structure of active centers. In the polymerization of cyclic acetals, because of the stabilization of the carbenium ion by the oxygen atom in α-position, there in an enhanced possibility of the existence of carbenium ions (oxocarbenium) in spite of the highly nucleophilic environment of the oxygen atoms from monomers and the polymer units. Therefore it became of interest to establish whether indeed oxocarbenium ions do exist and how large is their proportion. Several groups were involved in this discussion, but the arguments produced were based mostly of the indirect evidences. We decided to study the model system, being as close as possible to the actual polymerizing system. Thus, we used the following systems (Scheme 5). Both systems were studied at equilibrium by dynamic 1H NMR. From the line broadening (shown in Fig. 2) the rate constants were determined.

The rate constants of reactions of carbenium ions with nucleophiles were found to be close to the values typical for the diffusion controlled processes (above 30 °C). Further analysis of this system allowed establishing contributions of the carbenium and oxonium ions to the chain growth, as well as the structure of active species bearing monomer molecules at their ends. 1H- and 13C NMR studies of the model system (Scheme 6), indicated, that after the first “cationation” of monomer (very fast) and subsequent ring opening, almost exclusively the seven-membered ring is formed, being in equilibrium with its open form (Scheme 7).

Similar, equilibrium with another monomer —seven-membered 1,3-dioxepane—looks differently: the enlargement to the nine-membered ring does not take place. This is because the seven-membered ring is less strained than five-membered ring but also less strained than the nine-membered one.

Structure of Active Species in the Polymerization of Cyclic Ethers and Their Reactivities

Carbenium ions are very strong hydride ions (H\(^{\ominus}\)) acceptors. This reaction was observed in the polymerization of DXL; and respectively the—CH\(_2\)OCH\(_2\)OCH\(_2\) end groups were detected, resulting from the chain transfer to the—CH\(_2\)OCH\(_2\)OCH\(_2\) active species. The absence of the H\(^{\ominus}\) transfer products in the polymerization of cyclic ethers was used as one of the arguments for the unique-
ness of the chemical structures of active species, namely the tertiary oxonium ions that by themselves are not abstracting H\(_2\) anions.

These ions were first observed by \(^1\)H NMR in polymerization of THF in our group \(^{29,30}\) (later an improved spectrum was published). Protons in the endo- and oxo-methylene groups were separately observed as two superimposed triplets.\(^{30}\) There is only one kind of chemical species (in contrast to cyclic acetals), because of the much higher nucleophilicity of ethers when compared with acetals of the similar ring sizes.

In the first articles published on the determination of \(k^+\) (on ions) and \(k^\pm\) (on ion pairs) the \(k^+\) in CH\(_2\)Cl\(_2\) solvent was found to be several times larger than \(k^\pm\).\(^{31,32}\) We reexamined this system and then studied polymerization of THF and oxepane in a number of other conditions, changing counterions and solvents. In all of these systems we observed \(k^+ \approx k^\pm\), within an experimental error. The dependence of the observed rate constant \(k^{app}\) (proportional to the rate) on the degree of dissociation \(\alpha\) is for oxepane shown in Figure 3. The independence of the rate on the proportion of a given kind of ions clearly indicated that both ions and ion pairs propagate with identical rate constants.\(^{33}\)

Further work has shown, that \(k^\pm\) does not depend on the anion structure; this result complements the earlier observation of \(k^+ \approx k^\pm\).

Thus, the similar reactivity of ions and ion pairs as well as indepence of \(k^\pm\) on the structure of anion is the most general feature of the CROP.\(^6\)

Two interlinked explanations have been given to these facts. The first is related to the size of active species; tertiary oxiranium ion has structure and dimensions as shown in Figure 4; anions are large and Coulombic attractions with cations are relatively weak (distances are given in Å). The second explanation is based on the assumed mechanism of the propagation step. The picture in Figure 4 shows a counterion as a “large ball under the relatively steep roof” and it can be further visualized that this ball (counterion) flows to the new position when the monomer adds to the oxonium ion, in which over 90% of the positive charge is located on the CH\(_2\) groups. This is an additional argument that the counterion does not have to be removed far away from its position in the ground state during the propagation step, and there is no reason for the activation energies for the propagation step on ions or ion pairs to differ substantially.

Thus, \(k^+ \approx k^\pm\), as found experimentally, is not surprising for these systems.

In the anionic ring-opening propagation the negative charge is concentrated on the anion (e.g., alkoxide anion), and the stereochemistry of the monomer addition requires an extensive charge separation in the ion pairs. Therefore, in the propagation on the ion pairs, the path from the ground state to transition state requires additional energy to counteract the Coulombic attraction when monomer is added to the carbanion.
Propagation on Active Covalent Bonds and Macroion Pairs and Their Interconversions

There are two groups of anions (counterions) used in CROP. The complex anions, like AsF$_6^-$, BF$_4^-$, SbF$_6^-$ that are not able to form covalent bonds, since their coordination sphere cannot be further enlarged, and the non-complex ones, like CH$_3$SO$_3^-$, CF$_3$SO$_3^-$, ClO$_4^-$, that form covalent bonds, using two electrons of the central oxygen atom to form a sigma bond.

Therefore, whenever polymerization proceeds with these non-complex anions reversible ester formation takes place (e.g., for polyTHF and CF$_3$SO$_3^-$) (Scheme 8). This particular process was studied in our group extensively, reactivities of covalent and ionic species were determined and the rate constants of interconversion were measured.

Soon after the first article by Smith and Hubin on the polymerization of THF with HSO$_3$CF$_3$ (thus, CF$_3$SO$_3^-$ counterion) was published we proposed a general scheme of this kind of polymerization.

Surprisingly, as it will be shown later in this paragraph, although this scheme was solved in details, it has not fully been comprehended by research groups working with other cyclic monomers. Not to mention vinyl cationic polymerization, like polymerization of styrene and (particularly) vinyl ethers where reversible formation of macroester was also postulated.

The following questions were asked, and finally answered:

1. How to determine concentrations of esters and ions? What does it mean “covalent propagation”? Could the monomer addition proceed by a direct inclusion across the covalent bond, omitting the ion formation? (e.g., for CF$_3$SO$_3$-ester, the simultaneous rupture of two bonds and formation of two new bonds in the four center concerted mechanism). Or, does it proceed, on the contrary, exclusively by nucleophilic attack of the monomer molecule on the CH$_2$ group adjacent to the ester bond, followed by oxonium ion formation (external ionization: $k_{ei}$)

2. Whatever is the covalent propagation, is it faster or slower than ionic propagation and why?

3. If covalent propagation proceeds exclusively by “external ionization”, that is, by the bi-molecular attack of monomer molecules, then another ionization process has also to be taken into account, namely the “internal ionization” (Scheme 9) where, due to the anchimeric assistance mostly the five-membered oxonium ion is formed. Then the question arises: is the external or internal ionization faster?

4. How fast is the dominating ionization? If it mostly proceeds (as it was shown and will be discussed below) by an intramolecular process, is it fast enough to assume an equilibrium taking place between the ionic and covalent species throughout the complete polymerization?

5. How to determine contribution of covalent and ionic species to the building of the macromolecules?

Finally all of these questions were answered, and because some of these answers are of general importance, the way these answers were found is discussed below.

Direct Observation of Macroesters and Macroions

One of the important early observations was related to the NMR spectra of the covalent and ionic species. Some early articles disregarded the presence of esters and/or gave incorrectly assigned chemical shifts. Finally, correctly understood $^1$H NMR and $^{13}$C NMR spectra allowed estimation of concentrations of both species. This is illustrated in Figure 5, where $^1$H NMR spectra are given for both ions and esters in three different solvents.

The relative concentrations of macroesters and macroion pairs in CCl$_4$, CH$_2$Cl$_2$, and CH$_3$NO$_2$ vary dramatically. There are almost no ions in CCl$_4$, and almost no covalent species in CH$_3$NO$_2$ (the sum of concentrations of both species was kept constant). The controversy that arose already in 1976 was rather of quantitative character, since various groups were not observing the same proportions of covalent and ionic species in the same solvents. Then, we have shown that the proportion of ions increases with a total concentration of active species. Apparently ion pairs form higher ionic aggregates, increasing this way the concentration of ionic species observed at $^1$H NMR. Thus, in order to properly determine the thermodynamic equilibrium constant covalent species $\rightleftharpoons$ ion-pair, measurements have to be done at sufficiently low total concentration of active species. Otherwise there is more than this one equilibrium involved.

Concerning the second part of the first question, and related to the covalent propagation (the four-center addition), we proposed a direct experimental proof.
Let us imagine reaction of methyl triflate with THF proceeding in two ways. Either by direct inclusion or by cationation–ion-collapse. In both ways eventually the ester-ion equilibrium will be reached. However, if equilibration is established slower than the actual reaction takes place, then overshooting over the equilibrium concentration should be observed of these species that are formed first, at least at the very beginning of reaction. Thus, at these conditions the concentration of the species formed first should be higher (overshooting) than their concentration at equilibrium.

The preliminary results have shown that indeed, at the early stage of reaction concentration of ions is higher than their concentration at the established equilibrium. This overshooting indicates that reaction proceeds rather by “cationation” of the monomer by ester and not by a direct insertion, as shown below is Scheme 10.

The Relative Rates of Propagation: Covalent Versus Ionic

As it has already been shown, the most basic feature of the cationic ring-opening polymerization is the equality of $k^+_p$ and $k^-_p$, that is, the equal reactivities of the macroion pairs (independently of the anion structure) and macroions. Therefore, it was justified to assume, that $k^-_p$ for macroion pairs with noncomplex anions (like $\text{ClO}_4^-$ or $\text{CF}_3\text{SO}_3^-$) are the same as for the complex anions ($\text{BF}_4^-$, $\text{SbF}_6^-$ etc.). Then, determination of $k^\text{cov}_{cov}$ is straightforward and simple, since the rate of monomer consumption is given by the following relationship:

$$-d[M]/dt = k^-_p[P^-_i][M] + k^\text{cov}_{cov}[P^\text{cov}_i][M]$$

Since the rate is determined experimentally, concentrations of both kinds of active species, [$P^\text{cov}_i$] and [$P^-_i$], are known from $^1\text{H}$ NMR and $k^-_p (= k^+_p$) is also known, then from any kinetic run $k^\text{cov}_{cov}$ could directly be calculated. Moreover, thus determined rate constant of reaction of the macroester with monomer, namely $k^\text{cov}_{cov}$ (in another notation $k_{ei}$ was used for $k^\text{cov}_{cov}$) could directly be compared with the rate constant of reaction of a low molar mass ester with THF. Indeed, within the accuracy of kinetic measurements $k_{m}$ was found to be practically equal to $k^\text{cov}_{cov}$, at the otherwise similar conditions. Of course, $k_{m}$ had to be measured at the early stages of reaction, before the first ion pair starts to participate in the reverse and forward reactions.

The Rate of Exchange Between Macroesters and the Macroion Pairs

Two ways of interconversions between the macroesters and the macroion pairs should be envisaged, namely the

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**Figure 5.** 300-MHz $^1\text{H}$ NMR spectra (the 4.5–5.0 $\delta$ region only) of living polyTHF with $\text{CF}_3\text{SO}_2\text{O}^-$ anion: (a) in CD$_3$NO$_2$, (b) in CH$_2$Cl$_2$, (c) in CCl$_4$ solvent (ref. 29).
intramolecular (unimolecular) and the intermolecular (bimolecular, involving monomer) (Scheme 11).

One may note that in the intramolecular reaction the back process involves attack on the endocyclic methylenic group whereas in the intermolecular reaction the exocyclic group is attacked.

The intramolecular process was found to be faster than the intermolecular one. If it is sufficiently faster, then the contribution of the bimolecular reaction is low enough and can be neglected. Then the relative proportions of macroesters and macroion pairs should be invariant during polymerization, since an equilibrium is practically established at the early stage of polymerization and is preserved throughout polymerization. This was indeed experimentally observed in the polymerization of THF: within the accuracy of the 1H NMR measurements the relative concentrations of macroesters and macroion pairs are constant during polymerization. Moreover, the internal kinetic order on monomer is equal to one, a feature only possible if the bimolecular interconversion is not important and therefore the proportions of both kinds of coexisting species do not depend on the monomer concentration. Therefore the proportion of macroion pairs does not decrease and the internal order on monomer does not deviate from the first order.

**Rate of the Macroester–Macroion Interconversion**

In order to measure these rates the “temperature jump” technique was used. The macroester–macroions interconversion was brought to equilibrium at a certain temperature in a reaction mixture contained in the NMR tube. Then, the temperature was abruptly changed and kinetics of interconversion, leading at this new temperature to the new equilibrium was measured. The rate of interconversion was relatively low in comparison with the rate of establishing the thermal equilibrium, that is, the new temperature in the NMR tube.37,38

In Figure 6 the change of the 1H NMR spectrum in the region in which macroesters and macroions are absorbing is given.38 Since in the previous paragraph we already established that the unimolecular ionization is faster, we know that this is the kinetics of the unimolecular opposed reaction that was measured (cf. also Scheme 11).

An expression “temporary termination” was used in order to stress that the macroesters add the monomer molecules much slower than the macroions do; today I would rather use an expression “temporary deactivation” or “reversible deactivation”.

Comparison of $k_i$ and $k_e$ ($= k_p$), that is, the rate constant of internal and external ionizations, led to the conclusion that in, for example, CH$_2$Cl$_2$ solvent, at 25 °C the external ionization would proceed with a rate comparable to the internal ionization provided, that THF concentration equals to 100 mol · L$^{-1}$ (so-called effective concentration). This is almost 10 times higher than the bulk concentration of THF (i.e., “THF in THF”). It follows, that in the polymerization of THF in solution, if one starts from 5.0 mol · L$^{-1}$ of THF the contribution of the external ionization to the total ionization processes is approximately 5%, falling down to approximately 2–3% when the living polymer–monomer equilibrium is reached. Therefore, indeed, at least in the polymerization of THF the contribution of the external ionization to the macroester–macroion pair interconversion can be neglected.

An interesting article has recently appeared, treating a similar problem in the polymerization of 2-methyl oxazoline.39 For the first time, in spite of a long history of studies of oxazolines the effective concentration was determined as be equal to 980 mol · L$^{-1}$, at 25°, in nitrobenzene solvent and for Br$^-\text{counterion.}$

**Contribution of Covalent and Ionic Species to the Chain Growth**

As it has already been discussed, it is interesting to establish contributions of each species to the building of the macromolecule in polymerizations involving simultaneously growing covalent and ionic species. The equation relating the contribution of polymer units introduced...
by covalent species (γ) with the propagation rate constants is given by the following expression:

\[
\gamma = \frac{\alpha k_{ei}}{(1 - \alpha)k_{pi} + \alpha k_{ei}}
\]

where \(\alpha\) is the proportion of covalent active species. In deriving of this equation it was assumed, that there is no direct insertion of a monomer into the covalent bond. Thus, the complete scheme of polymerization, involving ionic and covalent species reads (the meaning of the super- and subscripts are self-explanatory in this scheme) (Scheme 12).

The equation for \(\gamma\) was first derived neglecting the depopagation.\(^{40,41}\) The complete treatment, including depopagation, is given in our article, published a few years ago.\(^{42}\) Introduction of reversibility did not change the final expression. Apparently, insensitivity of \(\gamma\) to depopagation is related to the uniformity of the polymer chains, that is, the equal probabilities of finding at any chain position a polymer unit introduced by one or another species.

Reversible Deactivation: Its Influence on the Overall Kinetics

In a process with reversible deactivation, like in the polymerization of THF with triflates or perchlorates, a given macromolecule propagates on its ionic species for a certain time, adding a certain number of monomer molecules, then the ion pair collapses into the covalent species. If these are much less reactive than ionic species (\(k_{p}^{cov} \ll k_{p}^{i}\)) then this reaction is equivalent to the temporary deactivation. A macromolecule spends some time as an inactive one, until, as a result of internal ionization (\(k_{ii} \gg k_{ei}[M]\)) it reconverts into the active ionic form. This record of life can be visualized as segments of the line. The lengths of these segments, shown below, are equivalent to the time spent in a given state, and not to the length of the macromolecule (Scheme 13). Below it is shown how these periods oscillate in the polymerization of THF, conducted in two solvents, namely in CCl\(_4\) and in CH\(_3\)NO\(_2\) ([THF]\(_0\) = 8.0 mol · L\(^{-1}\), 25 °C) (Scheme 14).

The illustrated life records give the following information: \(\tau^\pm\) and \(\tau^E\) are the corresponding lifetimes of the ion pair and an ester, \(X_p^\pm\) and \(X_p^E\) are equal to the number of monomer molecules added to the ionic and ester active species, \(X_d^\pm\) is a number of monomer molecules that depopagate from ionic active species. The lifetimes are given by intramolecular exchange processes.

This picture is a general one and applies equally well to any other polymerization with a temporary deactivation. It would differ, however, for vinyl polymerizations, where the intramolecular interconversion cannot proceed.

The real life records of polymer chains are more complex; lengths of segments corresponding to times of being in the given state, ionic or covalent, are not identical, not only for different chains in the given polymerization, but for the same chain as well. Distribution of lengths is approximately the most probable one.

Activated Monomer Mechanism

During the early 1980s a striking phenomenon was observed: addition of alcohols to the polymerization of some oxiranes reduced proportion of cyclics, known to be formed by back-biting. Moreover, the lower the instantaneous monomer concentration (i.e., the higher the...
[alcohol]/[monomer] ratio)—the lower proportion of cyclics. Some typical results are given below in Table I.43–45

Back-biting is the unimolecular reaction, therefore any external factor, like addition of an alcohol, is not able to influence its rate, and consequently the proportion of cyclics formed. Therefore, we proposed that in the presence of alcohols there is a mechanism of propagation in which formation of cyclics is either hampered or eliminated. The best candidate for such a mechanism is polymerization in which chain ends in the growing macromolecules are devoid of ions. Then, ions should be located in the monomer molecules, and this kind of polymerization is called “Activated Monomer Polymerization” (AM). What we proposed for the cationic process has already been introduced, for a different reason in anionic polymerization.

Thus, the AM mechanism, in its simplest form, can be described by an equation, in which the nucleophilic attack of the hydroxyl end group from the macromolecule on the carbon atom, adjacent to the oxonium ion, provides the propagation step (Scheme 15). (H+) denotes a proton, located on one of the nucleophilic sites in the system, that is, —OH, monomer molecule, or repeating unit.)

The AM mechanism may operate effectively, providing that the concentration of the nucleophilic end groups (reproduced in each propagation step) is high enough to make this route competitive with respect to the ACE mechanism. This may be illustrated by the scheme given below (Scheme 16).

Both ACE and AM mechanisms can contribute in building of the macromolecules, since both mechanisms can operate simultaneously.

The proof of the AM polymerization to proceed was obtained in several ways. The most direct one came from our studies of polymerization of glycidol. In this polymerization the polymer formed contains both primary and secondary hydroxyl groups. In the ACE polymerization ring opening should lead to the repeating units with pendant —CH₂OH groups (Scheme 17). Thus, for both α- and β-ring openings (presumably, the α opening should prevail) polymer units contain three atoms (—O—C—C—) with CH₂OH pendant group. Chain transfer involving hydroxyl groups would not change this structure, because any opening of the tertiary oxonium ion (attack on CH₂ or CH) would generate primary hydroxyl group. Secondary hydroxyl groups can, however, be observed only if the AMM operates. Indeed, as it is shown below, in one mode of attack, namely in α opening, the corresponding repeating units are formed (Scheme 18). Thus, concentration of the secondary hydroxyls in the polymer units provides the lowest contribution of the AMM in the chain growth.29 Si-NMR was applied after silylation of the polymer and both primary and secondary —OH were detected.

### Some Aspects of the Kinetics of AM Polymerization

When unsymmetrically substituted oxirane is polymerized, there are four propagation reactions possible, involving either primary or secondary hydroxyls at the polymer chain end and either α- or β-ring opening in the oxiranium cation in the actual propagation step. These four reactions are shown below (Scheme 19). The individual rate constants k₁₁, k₁₂, k₂₁, and k₂₂ are denoted in such a way that the first digit describes the attacking

![Scheme 15](image1)

![Scheme 16](image2)

### Table I. Polymerization of Propylene Oxide (PrOx): Influence of Instantaneous Monomer Concentration on the Proportion of Cyclic Oligomers Formed

<table>
<thead>
<tr>
<th>No.</th>
<th>Conditions</th>
<th>[PrOX]_{inat} mol · L⁻¹</th>
<th>Conversion of PrOx (wt)%</th>
<th>Tetramer Formed (wt)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PrOx introduced at once</td>
<td>2.0 (→0.0.)</td>
<td>Complete</td>
<td>~50</td>
</tr>
<tr>
<td>2</td>
<td>PrOx continuously charged faster</td>
<td>0.3</td>
<td>82</td>
<td>2.35</td>
</tr>
<tr>
<td>3</td>
<td>Slower</td>
<td>~0.05</td>
<td>Complete</td>
<td>0.95</td>
</tr>
</tbody>
</table>

[HBF₄-Et₂O] = 2.5 · 10⁻³ mol · L⁻¹; [PrOx]_{total} = 2.0 mol · L⁻¹; [—OH] = 4 · 10⁻¹ mol · L⁻¹, CH₂Cl₂, 25 °C.

* Complete polymerization in approximately 24 h.
hydroxyl and the second one the formed hydroxyl (1 stands for the primary and 2 for the secondary ones). Studies of the polymer end groups, at various stages of polymerization, revealed that after the first few additions to the initiator, the ratio of \(-\text{CH}_2\text{OH}/\text{CHOH}\) end groups becomes invariant. Thus, for \(X=\text{H}\) (propylene oxide) \([\text{CHOH}]/[\text{CHOH}] = 45 : 55\) and for \(X=\text{CL}\) (epichlorohydrin) \([\text{CH}_2\text{OH}]/[\text{CHOH}] = 5 : 95\). Thus, in the kinetic experiments initiator was composed from a mixture of alcohols modeling the growing chain ends in the proportion similar to that observed in polymerization.

The apparent (observed) rate constants of propagation, encompassing these four constants could be measured directly from the polymerization kinetics, but to determine the individual rate constants model studies had to be performed, allowing one to find the relationship between these constants; actually \(k_{p}^{\text{app}} = a k_{1,1} + (1-a) k_{1,2} + (1-a) k_{2,1} + k_{2,2}\) where \(a\) denotes molar fractions of the primary hydroxyl groups. Therefore, additional relationship between the constants had to be determined. This has been done in the following way for both monomers described in this section: first the corresponding primary and secondary alcohols were reacted separately with a monomer under study, and the rates of formation of products, due to \(\alpha\)- or \(\beta\)-ring openings, were measured by GLC in two separate sets of experiments: for the primary and for the secondary alcohol, both modeling the growing chain ends. These measurements gave the ratios \(k_{1,1}/k_{1,2}\) and \(k_{2,1}/k_{2,2}\). In the next step the relative reactivities of primary and secondary hydroxyl groups toward protonated monomer, that is, the ratio \(k_{1}/k_{2} = (k_{1,1}+k_{1,2})/(k_{2,1}+k_{2,2})\) were determined by reacting a mixture of two alcohols (primary and secondary) with a monomer and measuring by GLC the relative rates of disappearance of the used alcohols. The ratio of these relative rates is equal to \(k_{1}/k_{2}\). The apparent rate constant of propagation \(k_{p}^{\text{app}}\) is related, as discussed earlier, to \(k_1\) and \(k_2\) in the following way: \(k_{p}^{\text{app}} = a k_1 + (1-a) k_2\), where \(a\) denotes the proportion of the primary hydroxyls. Thus, for the four unknowns there are four equations relating them, allowing \(k_{1,1}, k_{1,2}\) and \(k_{2,2}\) to be independently determined once \(k_{p}^{\text{app}}\) is known. Then, e.g., \(k_{1}/k_{2} = a; k_{1,1}/k_{1,2} = b; k_{p}^{\text{app}} = a k_1 + (1-a) k_2\).

Solutions of these relationships gives, for instance, \(k_{1,1} = k_{p}^{\text{app}} b / [(\alpha(1-1/a) + 1/a)](1+b)\).

The ratios of rate constants are listed in Table II below.

The required apparent rate constant of propagation \(k_{p}^{\text{app}}\), needed for determination of the rate constants of elementary reactions, is related to the monomer consumption by the usual dependence:

\[-d[M]/dt = k_{p}^{\text{app}} [\text{H}^+ M] [-\text{OH}]\]

where \([-\text{OH}]\) is the sum of concentrations of the secondary and primary hydroxyl groups. The total concentration of the hydroxyl groups and their proportion are invariant (cf. preceding section). Thus, the knowledge of concentration of the activated monomer is required to determine \(k_{p}^{\text{app}}\).

At the very early stage of polymerization, the only two nucleophilic sites in the reaction mixture are the monomer molecule and hydroxyl chain ends. Then, we have Scheme 20. Combining the two equations given above, and remembering that \([\text{H}^+ M] + [-\text{OH}_2] = [\text{H}^+]_0\) \((\text{where } [\text{H}^+]_0 = [\text{catalyst}]_0)\), we finally have, after eliminating the unknown \([\text{H}^+ M]\), Scheme 21. \(-d[M]/dt\) denotes the monomer consumption at the very early
stage of polymerization (first additions), when the presence of polymer units can be neglected. At this stage this rate is approximately equal to the rate of initiator (alcohol) consumption. On this bases the individual rate constants have been determined. These constants are tabulated below for propylene oxide and epichlorohydrin polymerizations (Table III).

In the polymerization of propylene oxide the individual rate constants do not differ considerably from each other, indicating that there is no significant preference for any of the four growth reactions involved. The relatively small differences in the rate constants may be explained by the interplay of two factors, namely steric and electronic factors. Secondary hydroxyls in poly(propylene oxide) oligomers are more basic than the primary ones, but, on the other hand, there is considerably more steric hindrance for the reaction of the secondary groups. Thus, both effects are partly counterbalanced. The steric factors seem to be more important, because primary HO- groups are slightly more reactive than the secondary ones. Thus, the highest rate constant \( k_{1,2} \) is observed for an attack of the primary hydroxyl group on the unsubstituted carbon atom in the protonated monomer molecule, while the lowest \( k_{2,1} \) is for the attack of the more sterically hindered secondary group on the substituted carbon atom in the AM ring (Scheme 22).

In the polymerization of epichlorohydrin both primary and secondary hydroxyls react predominantly with the least substituted carbon atom. Thus, the electronic factor (the -CH\(_2\)Cl group has strong electron-withdrawing properties) is overshadowed by the steric factor. Indeed, from a purely charge distribution viewpoint the -CH(CH\(_2\)Cl) carbon atom should be (but is not) a preferred site of attack. The importance of the steric factor is much more pronounced for the polymerization of epichlorohydrin than for propylene oxide. The primary hydroxyl groups are a few times more reactive than the secondary ones, however, the effect of position of substituent is less important than the position of ring attack.

On the basis of the thus determined rate constants it was possible to calculate the polymers microstructures. It is remarkable, how well thus calculated microstructures agree with microstructures determined directly from the NMR data. This comparison is given below (Table IV). Cationic ring-opening polymerization involving activated monomer is the latest complex and comprehensive endeavor of our laboratory in the cationic field. For this reason our work in area is described in more detail.

### CONCLUSION

In the proceeding sections some contributions of our group to the understanding of the cationic ring-opening polymerization are reviewed. However, this is not a typical review, and Professor Percec, when asked me to prepare this article has also mentioned, that it may be more personal than usually. Therefore, I have taken a liberty in this last section to describe the contributions of my coworkers, that took part in this adventure, and quite often provided solutions by themselves.
We started our work on the CROP in the early seventies, the peak of our activity in this area was ten years later, but even now, after 25 years we are still involved in some related problems (activated monomer), although our major activity shifted to other areas of macromolecular science.

Structure of polyacetals, and the mechanism of polymerization of cyclic acetals were mostly established by Przemyslaw Kubisa in his Ph.D. (1970) and habilitation (1982). Studies of the reactivity of ions and ion pairs in CROP were started in Ph.D. of Stanislaw Slomkowski (H\(_2\) transfer, carbenium–oxonium equilibria) and in his subsequent work on THF ions and ion pairs. Then we were joined by Krzysztof Matyjaszewski, who in his Ph.D. (1976) and then in habilitation (1983) elaborated a more complete scheme of THF polymerization, including the ester ion pair equilibrium and kinetics of interexchange. The dynamic \(^1\)H NMR allowed Ryszard Szymanski establishing in his Ph.D. work (1981) the reactivities of carbenium and oxonium ions and the kinetics of their interchange. Then, in his habilitation (1989) a general theory of equilibrium copolymerization was developed. All those scientists are already for some time-independent researchers with their own research groups. Sometimes, however, we join our efforts in solving new problems. Like the kinetic theory of macrocyclization (with J. Chojnowski), the activated monomer polymerization (with P. Kubisa) or the kinetic theory of the chain transfer to polymer (with S. Slomkowski and R. Szymanski). K. Matyjaszewski has recently chosen a world of radical polymerization, and some of us are considering of joining him in this new endeavor where kinetics has some similarities with CROP, since it also involves reversibly formed dormant species.

There was also a larger number of gifted Ph.D. students and their names appear in the list of references.

**REFERENCES AND NOTES**


**Table IV.** Fractions of the h-t, h-h, and t-t Dyads in Polymerization of Propylene Oxide and Epichlorohydrin According to the AM Mechanism, Calculated from Kinetic Results (i.e., from the Values of \(k_{1,1}\), \(k_{1,2}\), \(k_{2,1}\), and \(k_{2,2}\)) and Found From \(^{13}\)C NMR

<table>
<thead>
<tr>
<th>Method of Determination</th>
<th>Propylene Oxide</th>
<th>Epichlorohydrin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>h-t</td>
<td>h-h</td>
</tr>
<tr>
<td>Kinetics</td>
<td>0.52</td>
<td>0.23</td>
</tr>
<tr>
<td>NMR</td>
<td>0.50</td>
<td>0.25</td>
</tr>
</tbody>
</table>
36. Matyjaszewski, K.; Sawamoto, M. In Cationic Polymerizations; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; Chapter 4, p 300.