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Ring-Opening Polymerization Processes Involving Activated Monomer Mechanism. Cationic Polymerization of Cyclic Ethers Containing Hydroxyl Groups.

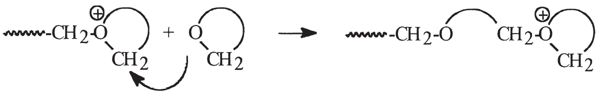
M. Bednarek, T. Biedroń, K. Kałużyński, P. Kubisa*, J. Pretula, S. Penczek

Center of Molecular and Macromolecular Studies
Sienkiewicza 112, 90-363 Łódź, Poland

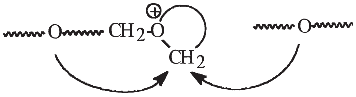
SUMMARY: Cationic polymerization of cyclic ethers containing hydroxyl groups as substituents is discussed in terms of contribution of Active Chain End (ACE) and Activated Monomer (AM) polymerization mechanisms.

Introduction

In the cationic polymerization of cyclic ethers proceeding by Active Chain End (ACE) mechanism, propagation involves nucleophilic attack of oxygen atom of monomer molecule on carbon atom in α- position to the oxygen bearing the positive charge in growing species - tertiary oxonium ions.


(1)

Because linear ether units in polymer are also relatively strong nucleophiles, back-biting and/or transeterification processes involving an attack of oxygen atom of linear unit of the own (cyclization) or foreign chain (so called scrambling) on growing species, cannot generally be avoided.


(2)

If other nucleophiles are present in the system in sufficient concentration, they may successfully compete with cyclic ether monomer in the reaction with initiating species. This provides a base for Activated Monomer (AM) mechanism of cyclic ethers polymerization [1-3]. AM polymerization is carried out in the presence of hydroxyl group containing compounds and is initiated by protonic acids introduced as such or formed in situ by reaction of e.g. Lewis acid with HO- group,

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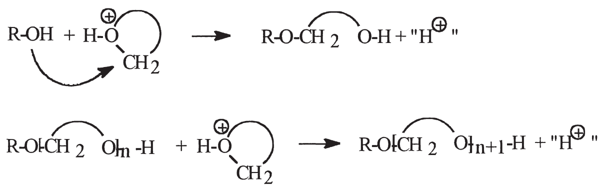
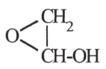
therefore, further in the text catalyst will be denoted as "H$^+$".



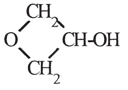
(3)

In the polymerization proceeding by AM mechanism, due to the absence of active species at the growing chain ends, back-biting is essentially eliminated and linear polymers free of cyclic fraction may be obtained 4,5). Kinetic studies of AM polymerization of cyclic ethers revealed, that in order to eliminate contribution of ACE mechanism, the instantaneous ratio: [HO-] / [monomer] should be kept above certain level, different for different monomers depending on their nucleophilicity, e.g. above 5 for epichlorohydrin [6].This may be achieved by carrying out polymerization at monomer starved conditions (i.e. by slow addition of monomer to polymerizing mixture).

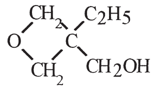
This raises an interesting question what is the mechanism of polymerization of cyclic monomers combining both functions i.e. cyclic ether function and hydroxyl function within the same molecule Several monomers of this class are easily available, examples are given below:



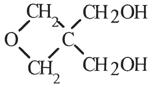
glycidol



3-hydroxymethyl-oxetane



3-ethyl-3-hydroxy-methyloxetane (EOX)



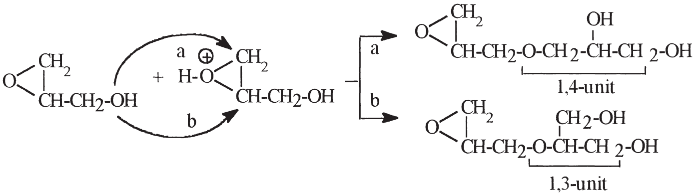
3,3-bis(hydroxymethyl) oxetane

(4)

The presence of HO- group inevitably leads to branching, therefore, in the past polymerization of this group of monomers was not extensively studied 7). In the recent years, however, an increasing interest in the preparation of highly branched macromolecules and increasing knowledge of AM polymerization mechanism led to renewed interest in the polymerization of this group of cyclic monomers. It may be argued, on the basis of schemes (1) and (2) that the structure of corresponding polymers (degree of branching) should depend on the relative contributions of ACE and AM polymerization mechanisms.

Cationic polymerization of glycidol

Three membered cyclic ether - glycidol is a convenient model for studying the polymerization mechanism because its AM polymerization may lead to isomerized 1-4 units and not only to regular 1-3 units, as in ACE polymerization mechanism [8,9]. 1-3 units contain primary hydroxyl groups while 1-4 units contain secondary hydroxyls. The presence of secondary hydroxyl groups in polymers of glycidol with molecular weights up to 10000 ($DP_n = 140$) was shown by analysis of ^{29}Si NMR spectra of silylated samples. Two signals at 16.35 and 15.70 ppm δ corresponding to silylated primary and secondary hydroxyl groups respectively were observed in nearly equal intensity, showing that contribution of AM mechanism is significant.



(5)

Dworak et al. estimated the contribution of AM mechanism on the basis of analysis of ^{13}C NMR spectra of polyglycidol, assuming that isomerized 1-4 units and branched units are formed by AM mechanism while linear 1-3 units are formed by ACE mechanism [10]. The results are collected in Table 1.

Table 1. Estimated contribution of AM mechanism in the polymerization of glycidol initiated with different initiators.

Initiator (catalyst)	Contribution of AM, %	DP_n
$SnCl_4$	80	65
$BF_3 \cdot Et_2O$	60	93
$HOSO_2CF_3$, $HPF_6 \cdot Et_2O$	50	142

Results shown in Table 1 indicate, that there seems to be a correlation between the contribution of AM mechanism and DP_n of the resulting polymers. The values of DP_n correspond to polymers prepared in bulk with concentration of catalyst (protonic acid or Lewis acid) close to 10^{-2} mol/L. The ratio of initial concentrations: $[M]_0$ / $[catalyst]_0$ was therefore above 10^3. The observed polymerization degrees were much lower, and apparently the higher was the contribution of AM mechanism the lower was DP_n.

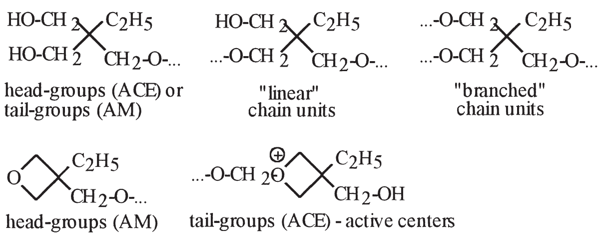
This raises an interesting question what should be the DP_n values if polymerization proceeded exclusively by AM mechanism. In such a system protonic or Lewis acid would act merely as catalyst (not as initiator) while part of the monomer molecules would act as initiator through their hydroxyl group functions. The degree of polymerization would then be related to relative rates of the competing reactions and not to concentrations of reactants. Assuming, that the terminal oxirane groups can further participate in reaction, the degree of polymerization should in principle increase continuously. This was not observed and the possible explanation is, that oxirane rings may be consumed also in intramolecular reaction with hydroxyl group of the same macromolecule. In such a process the cyclic structure would be formed and the macromolecule would be no longer able to grow after all oxirane rings were consumed. In qualitative terms, such explanation is consistent with the observation, that the higher the contribution of AM mechanism (i.e. mechanism involving the reaction of activated oxirane ring with HO- group) the lower the observed DP_n.

Cationic polymerization of hydroxymethyloxetanes

Vandenberg et al. studied the cationic polymerization of 3-hydroxyoxetane 11). This monomer gives medium molecular weight polymers (M_n up to 2200) containing both primary (at the ends) and secondary (along the chain) hydroxyl groups and about 5 branching points per chain. From the point of view of the uniformity of structure, more interesting are oxetane derivatives substituted at 3-position with hydroxymethyl groups, because independently on the polymerization mechanism, HO- groups may appear only in $HO-CH_2-C$ units. Until recently, there was essentially no information in the literature on the cationic polymerization of these monomers, except for a brief information in Vandenberg's paper that 3,3-bis(hydroxymethyl)oxetane can be polymerized to low molecular weight oligomers, which were not fully characterized 12).

In the recently published paper, we investigated the cationic polymerization of 3-ethyl-3-hydroxymethyloxetane (EOX) and the structure of polymers in more detail [13)]. At the same time, the paper from another group, dealing with the same subject, was published [14)].

Below, all possible structures, which may appear in polymers of EOX, are shown:



(6)

Fig. 1 shows expanded region of ^{13}C NMR spectra in which signals of quaternary carbon atoms appear while Fig. 2 shows expanded region of ^{1}H NMR spectra of poly-EOX in which signals corresponding to $-OCH_2O-$ and $-OCH_2OH$ groups can be observed.

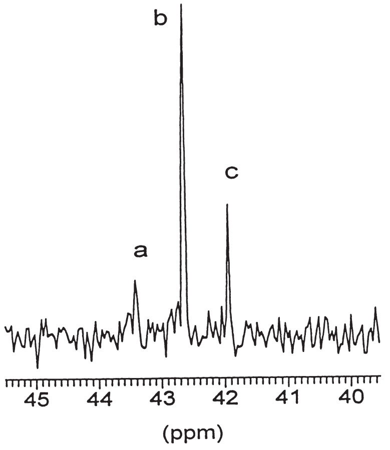


Fig. 1. ^{13}C NMR spectrum of poly-EOX (only the region of quaternary carbon signals shown).Assignments: a:$(-OCH_2)_3\underline{C}R$, b:$(-CH_2)_2\underline{C}RCH_2OH$, c: $-OCH_2\underline{C}R(CH_2OH)_2$.

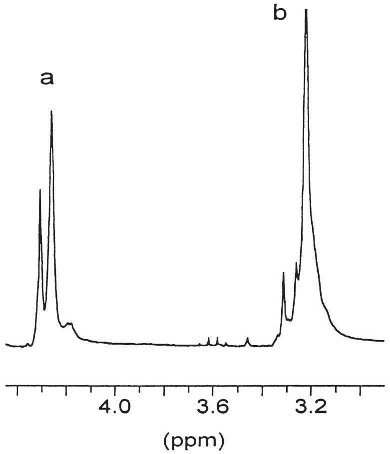


Fig. 2. ^{1}H NMR spectrum of poly-EOX (only the region of $-CH_2O-$ groups signals shown). Assignments: a: $-O\underline{CH_2}OH$, b: $-O\underline{CH_2}O-$

Signals corresponding to three types of units, namely to terminal units containing (except for C_2H_5- group) two HO-CH_2- groups and one -CH_2-O-CH_2- group bound to quaternary carbon atom, to linear chain units containing one HO-CH_2- group and two -CH_2-O-CH_2- groups bound to quaternary carbon atom and to branched chain units containing three -CH_2-O-CH_2 groups bound to quaternary carbon atom are clearly observed. In the isolated polymers (after work-up) neither the signals corresponding to terminal unit containing oxetane ring nor the signals corresponding to tertiary oxonium ion involving oxetane ring, could be detected. ^{13}C NMR spectra were recorded in Inverted Gate mode, allowing integration of the spectra. Therefore, the fractions of three observed chain units could be determined from the spectra.

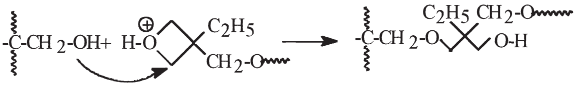
Typical results of the polymerization of EOX are collected in Table 2

Table 2. Cationic polymerization of EOX

Conditions	catalyst, mol%	Yield, precipitated polymer, %	M_n	M_w / M_n	DP_n	(linear + terminal)/ branched units
			gpc in THF			
bulk, -30^{0}C, 48 h	$BF_3 \cdot Et_2O$ 0,2	90	1430	1.70	13	4.0
4 mol/L in CH_2Cl_2 25^{0}C, 16 h	$BF_3 \cdot Et_2O$ 0,4	30 (0.5 h) 60 (5.5 h) 90 (48 h)	1140	1.35	10	4.7
bulk, 25^{0}C, 18 h	$HOSO_2CF_3$ 0.15	50	1270	1.30	11	high
+10 min. At 200^{0}C	"	100	1890	4,45	18	6.2
+20 min. At 200^{0}C	"	100	insoluble in THF			3.0
+30 min. At 200^{0}C	"	100	Insoluble in typical solvents			

Molecular weights were determined by GPC in THF solution for polymers in which hydroxyl groups were esterified with trifluoroacetic anhydride with standard polystyrene calibration. The results of the determination of molecular weights of branched polyethers, may therefore involve significant errors, they show, however, that independently on reaction conditions and the nature of catalyst, polymers with relatively low molecular weights are formed. Slightly higher (M_n about 3000) but also rather low values were reported by Hult et al. for polymers obtained at 120^0C in bulk with benzyltetramethylsulfonium hexafluoroantimonate as catalyst $^{14)}$.

As shown by the last two entries of Table 2, heating of the polymers after monomer had been consumed, results in further increase of the degree of branching but at the same time polymers are eventually becoming insoluble in typical organic solvent, which may indicate that cross-linking occurs. To some extent, the increase of the degree of branching may occur through the reaction of terminal oxetane groups, as indicated by the scheme below:

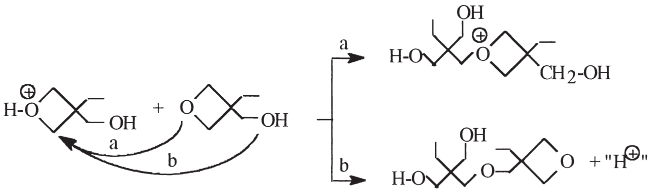


(7)

This process cannot, however, lead to cross-linking. The changes observed during heating of the polymer at relatively high temperature in the presence of acid catalysts may rather be related to condensation of the - CH_2-OH groups with elimination of water (it should be mentioned, however, that polymers after neutralization of acid catalysts, are stable at temperature 200^0C).

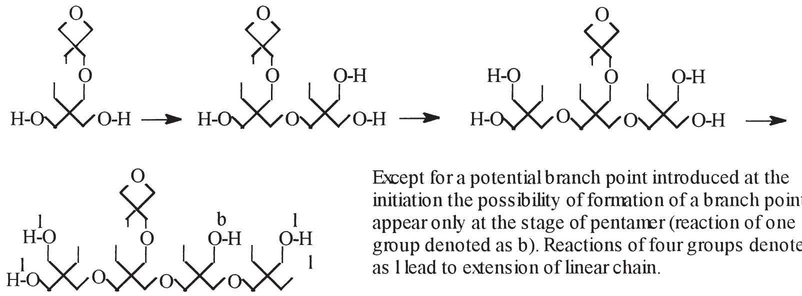
Mechanism of polymerization of 3-ethyl-3-hydroxymethyloxetane (EOX)

Polymerization of EOX catalyzed by protonic acid (added as such or formed from Lewis acid and HO- group) starts by reaction of protonated EOX:



(8)

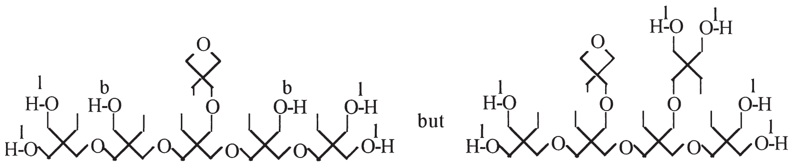
Reaction 8a, followed by subsequent propagation steps according to ACE mechanism leads to linear chain, although some branching may occur as a result of chain transfer to HO- group of the other macromolecule. Reaction 8b corresponds to AM propagation, but even if reaction proceeds exclusively by this route, branch points may be formed only after certain DP_n is reached, as shown schematically below:



Except for a potential branch point introduced at the initiation the possibility of formation of a branch point appear only at the stage of pentamer (reaction of one group denoted as b). Reactions of four groups denoted as l lead to extension of linear chain.

(9)

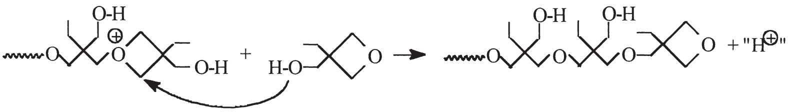
Only after reaching the stage of a pentamer, formation of branch point is possible, and even in this case the probability of forming branch point, assuming equal reactivities of all HO- groups is only 20% (one HO- group out of five). This probability increases with increasing DP_n but decreases with increasing degree of branching (as a result of a formation of branch point on $HO-CH_2$- group in linear unit is consumed and two $HO-CH_2$- end-groups are formed) as shown schematically below:



(10)

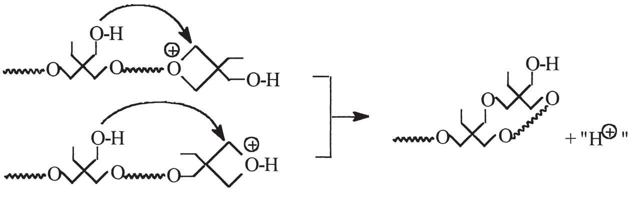
This reasoning is consistent with the experimental results presented in Table 2. The degree of branching is rather low and in macromolecules with DP_n between 10 and 13 there is no more than 2-3 branch points. From simple statistical considerations, it follows therefore, that in order to obtain polymers having the structure closer to dendritic structure (i.e. hyperbranched polymers), higher polymerization degrees, than these obtained until now, are needed.

What are the factors limiting the degree of polymerization in the studied systems? For ACE mechanism, chain transfer to HO- group of monomer may lead to termination of particular chain with formation of "proton" which may initiate a new chain. By this reaction, however, oxetane ring would be introduced at the chain end of the terminated macromolecule as shown in scheme below, and such macromonomer should be able to participate in further reaction:



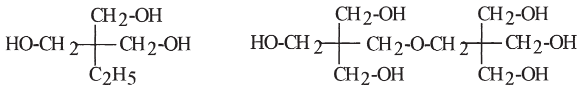
(11)

On the other hand, the same group should be present in all macromolecules growing by AM mechanism and also these macromolecules should undergo further polymerization even after complete consumption of monomer. The possible process by which the growth of macromolecules can be terminated, is the intramolecular reaction of either tertiary oxonium ion with HO- group of its own chain or intramolecular reaction of protonated oxetane end-group with HO- group of its own chain as shown schematically below:



(12)

One of a possible ways to avoid reactions shown in the scheme above, is to carry out the polymerization in the presence of multihydroxyl initiators at the monomer starved conditions. This should lead to increasing contribution of AM mechanism and growing macromolecules would not contain oxetane end-group. Two of the multihydroxyl initiators used in this work are shown in scheme:



$$\mathrm{HO\text{-}CH_2}\overset{\mathrm{CH_2\text{-}OH}}{\underset{\mathrm{C_2H_5}}{+}}\mathrm{CH_2\text{-}OH} \qquad \mathrm{HO\text{-}CH_2}\overset{\mathrm{CH_2\text{-}OH}}{\underset{\mathrm{CH_2\text{-}OH}}{+}}\mathrm{CH_2\text{-}O\text{-}CH_2}\overset{\mathrm{CH_2\text{-}OH}}{\underset{\mathrm{CH_2\text{-}OH}}{+}}\mathrm{CH_2\text{-}OH} \qquad (13)$$

As shown by model studies of AM polymerization of oxiranes, high contribution of AM mechanism, even at the monomer starved conditions, could be achieved only to certain limit of DP_n. Above this limit, the increasing participation of reaction of chain units was observed Essentially the same phenomenon was observed for polymerization of EOX with multihydroxy initiators. For [EOX] / [I] ratio equal to 10, the observed M_n = 1100 was still close to the calculated value of M_n = 1170 but for [EOX] / [I] ratio equal to 40 the observed value of M_n = 1970 was already much lower than calculated value of M_n = 4650. The degree of branching was not significantly higher than in the polymerization without added multihydroxyl initiator although increase of the degree of branching with increasing DP_n was clearly observed.

Table 3. The dependence of the degree of branching on $[\mathrm{EOX}]_{\mathrm{consumed}}$ / $[\mathrm{Trihydroxyl\ initiator}]_0$

$[\mathrm{EOX}]_{\mathrm{consumed}}$ / $[\mathrm{Trihydroxyl\ initiator}]_0$	4	6	8	10
Terminal + linear units / branched units	7.1	5.4	5.0	3.8

Conclusions

Cationic polymerization of 3-ethyl-3-hydroxymethyloxetane leads to medium molecular weight, branched polyethers containing $-\mathrm{CH_2}$-OH groups both at the chain ends and along the chain. The number of branch points is related to the degree of polymerization; up to now polymers with M_n up to 2000 were obtained and characterized. The extension of the available molecular weight range requires better understanding of polymerization kinetics, in particular the extend of participation of ACE and AM mechanism in the process.

References

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