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Polymerization of Hydroxymethyloxetanes - Synthesis of Branched Polyethers with Primary Hydroxyl Groups

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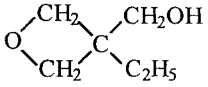
Summary: Oxetanes containing hydroxyl groups can conveniently be prepared using commercially available trimethylolpropane or penthaerithritol. The corresponding monomers, such as 3-ethyl-3-hydroxymethyloxetane (EOX) have been polymerized cationically and it has been shown, that resulting polymers are branched. These polymers are of particular interest, since in contrast to some other polyhydroxyethers (like polyglycidol) all of the hydroxyl groups are primary ones. Moreover, all of the -CH_2OH groups are attached to the quaternary carbon atoms. These features are rather unique and may be advantageous from the point of view of possible applications.

Introduction

3-Ethyl-3-hydroxymethyloxetane (EOX) is a monomer combining within one molecule two nucleophilic sites: cyclic ether function and hydroxyl group:



Several years ago we have studied cationic polymerization of cyclic ethers in the presence of hydroxyl groups containing compounds (alcohols, diols) and we found, that the mechanism of polymerization differs from conventional mechanism of cationic polymerization of cyclic ethers involving successive addition of monomer molecules

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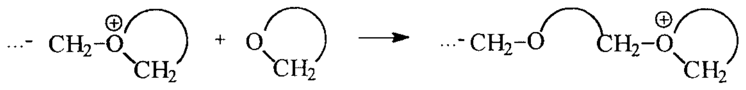
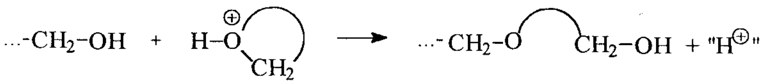
to the tertiary oxonium ion active centers (Active Chain End Mechanism - ACE).



In the presence of sufficiently high concentration of hydroxyl groups containing compounds another mechanism, involving addition of protonated (thus activated) monomer to the terminal hydroxyl groups of the growing macromolecule, is becoming dominating:



The basic features of cationic polymerization of cyclic ethers by Activated Monomer (AM) mechanism have been described in series of papers and reviewed [1-3].

The concept of cationic Activated Monomer polymerization of cyclic ethers has been extended to the system containing both functions (i.e. cyclic ether and hydroxyl group) in the same molecule and it was found, that in the cationic polymerization of glycidol both mechanism compete with each other, leading to branched polymers, having however both primary and secondary hydroxyl groups at the chain termini [4], similar as in anionic glycidol polymerization [5].

More recently we have turned our attention to the group of monomers studied earlier by Vandenberg et al. namely 3-hydroxymethyloxetanes. Vandenberg has already noted that the cationic polymerization of these monomers leads to low molar mass branched polymers [6,7].

In the present contribution, results of our studies of cationic polymerization of 3-ethyl-3-hydroxymethyloxetane (EOX) are discussed. Preliminary results have recently been published [8], almost at the same time results of studies of similar system were published bu Hult et al. [9].

Results and Discussion

Structure of propagating species in the polymerization of EOX

In the previously studied cationic polymerization of glycidol participation of secondary oxonium ions (corresponding to propagation by AM mechanism) and tertiary oxonium ions (corresponding to ACE mechanism) was shown indirectly, by analysing the content of isomerised 1-4-units, which could be formed only by AM propagation step [4]. For four membered rings such an approach is not possible because structure of repeating unit does not depend on the mechanism of propagation step due to the fact that both -CH_2-O- bonds are equivalent. Therefore, the method allowing direct observation of secondary and tertiary oxonium ion active centers, namely phosphine ion trapping method, developed earlier in our group, was applied. This method is based on the transformation of oxonium ions into corresponding phosphonium ions by fast, quantitative and irreversible reaction with tertiary phosphines and determination of resulting tertiary and quaternary phosphonium ions formed respectively from secondary and tertiary oxonium ions by ^{31}P NMR [10].

Using this method it was shown that in the cationic polymerization of EOX oxonium ion active centers are mainly (~90%-mol) secondary oxonium ions although tertiary oxonium ion active species are also present (~10%-mol). The rate constants of reactions involving both types of active centers are not known and therefore their contribution to the chain growth cannot be exactly determined. It may be concluded, however, that suitable conditions for significant participation of secondary oxonium ions in the chain growth do exist in the system.

Reaction of protonated EOX molecule (secondary oxonium ion) with HO- group of growing macromolecule is a source of branching. On the other hand, reaction of tertiary oxonium ion active centers with monomer should in principle lead to linear macromolecules. Thus, high fraction of secondary oxonium ion active species provide a favourable conditions for the formation of highly branched macromolecules.

Molar masses of EOX polymers

Molar masses of poly-EOX were determined by GPC using polystyrene calibration. Because the standard calibration method may be not applicable for determination of correct values of M_n for branched polyethers, the determined values may differ from real M_n values. Thus, M_n's determined by GPC should be rather treated as approximations allowing only relative comparisons.

With this reservation, results of M_n determination for polymers prepared at different polymerization conditions (bulk or solution polymerization at 25°C), point out to two conclusions:

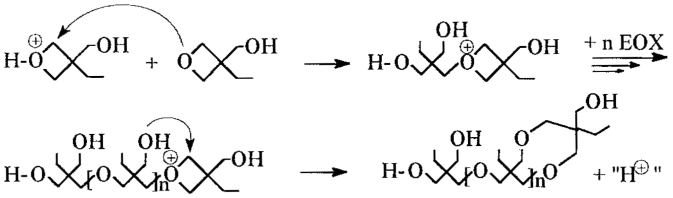
- M_n is essentially constant throughout polymerization (it does not significantly increase with conversion)
- M_n is considerably lower than it would be expected for polymerization at applied monomer and initiator concentrations if polymerization proceeded without transfer.

M_n's irrespectively of polymerization conditions were in the range from 10^3 to $2 \cdot 10^3$. Polymers isolated at different stages of polymerization (between 20 and 95% conversion) were analysed by MALDI TOF mass spectrometry. The only signals observed in MALDI TOF spectra were the signals of series of macromolecules with molar mass being the multiplicity of molar mass of monomeric units. Results of MALDI TOF analysis, coupled with results of analysis of ^1H NMR spectra indicating the absence of oxetanyl end-groups, led to conclusion that macromolecules do not contain any groups incorporated in initiation and termination. This may occur only if cyclic fragment is formed by intramolecular chain transfer to polymer.

Intramolecular chain transfer to polymer leads to the same structure of cyclic macromolecule irrespectively of mechanism of chain growth as shown in the scheme below. Therefore, structure of isolated polymer does not provide any information on the mechanism of chain growth (AM vs ACE). It explains, however, relatively low molar masses of polymers. and their insensitivity to polymerization conditions. Apparently at the certain stage of the growth of macromolecule (approximately 15 monomeric units), some hydroxyl groups have to appear in so close vicinity of propagating center, that intramolecular chain transfer reaction is becoming inevitable, leading to termination of growth of this particular macromolecule and initiation of growth of another macromolecule.

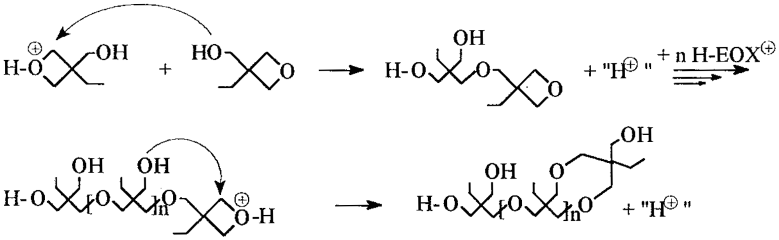
Below, reactions leading to chain growth and chain transfer, are shown schematically:

Polymerization according to ACE mechanism

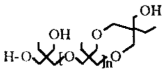


any HO- group of the macromolecule

Polymerization according to AM mechanism



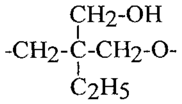
any HO- group of the macromolecule



This is only a schematic representation of branched macromolecule containing cyclic fragment formed in reaction between "chain end" and one of the CH_2OH groups.

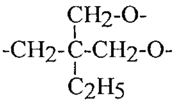
Microstructure of EOX polymers

Microstructure of EOX polymers may be studied conveniently by ^{13}C NMR. Differences in chemical shifts of quaternary carbon atoms in structural units shown below allowed determination of their fractions in polymers obtained at different experimental conditions:



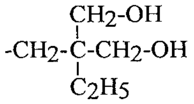
$-CH_2-\overset{CH_2-OH}{\underset{C_2H_5}{C}}-CH_2-O-$

"linear units"
42.67 ppm δ (^{13}C NMR)



$-CH_2-\overset{CH_2-O-}{\underset{C_2H_5}{C}}-CH_2-O-$

"branched" units
41.96 ppm δ (^{13}C NMR)



$-CH_2-\overset{CH_2-OH}{\underset{C_2H_5}{C}}-CH_2-OH$

terminal units
43.42 ppm δ (^{13}C NMR

Results of ^{13}C NMR analysis indicated, that fraction of "branched" and "linear" units depended only slightly on experimental conditions. The average proportion of "branched" to "linear" units was close to 1:2 indicating, that although macromolecules are indeed branched, macromolecules contain significant proportion of "linear" (not branched) units.

Conclusions

Results presented in this communication may be summarized as follows:

a. In the cationic polymerization of EOX both secondary and tertiary oxonium ion active centers participate in the chain growth, the former ones being much more abundant.

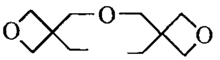
2. Chain growth is terminated after reaching certain stage of growth (in terms of number of monomeric units incorporated into macromolecule) due to intramolecular chain transfer to polymer.

3. Not each of the potential branching points is indeed forming one, on the average only one out of three HO- groups participate in formation of branching point.

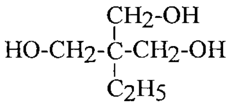
4. The fact, that macromolecules, after undergoing intramolecular chain transfer to polymer, do not grow any further by addition of protonated EOX to hydroxyl groups of the macromolecule, although this reaction has to occur at the earlier stage because it leads to formation of branching points, indicate that HO- groups are at certain stage becoming unaccessible for reaction. This is tentatively explained by strong aggregation of HO- groups due to hydrogen bonding, which may lead to particular conformation in which aggregated HO- groups are embedded inside the macromolecular coil.

Basing on these conclusions, in order to prepare polymers of EOX with higher M_n's and higher degree of branching, the following approaches may be envisaged:

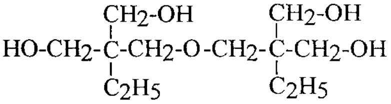
1. Increase M_n by copolymerizing EOX with small amount of difunctional monomer giving very similar structure of repeating unit e.g. with dioxetane shown below:



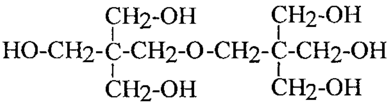
2. Increase the degree of branching by using easily available multihydroxyl initiators/chain transfer agents, such as those shown below:



$$\begin{array}{r@{}c@{}l} & CH_2\text{-}OH & \\ & | & \\ HO\text{-}CH_2\text{-} & C & \text{-}CH_2\text{-}OH \\ & | & \\ & C_2H_5 & \end{array}$$



$$\begin{array}{r@{}c@{}c@{}c@{}l} & CH_2\text{-}OH & & CH_2\text{-}OH & \\ & | & & | & \\ HO\text{-}CH_2\text{-} & C & \text{-}CH_2\text{-}O\text{-}CH_2\text{-} & C & \text{-}CH_2\text{-}OH \\ & | & & | & \\ & C_2H_5 & & C_2H_5 & \end{array}$$



$$\begin{array}{r@{}c@{}c@{}c@{}l} & CH_2\text{-}OH & & CH_2\text{-}OH & \\ & | & & | & \\ HO\text{-}CH_2\text{-} & C & \text{-}CH_2\text{-}O\text{-}CH_2\text{-} & C & \text{-}CH_2\text{-}OH \\ & | & & | & \\ & CH_2\text{-}OH & & CH_2\text{-}OH & \end{array}$$

3. Increase the degree of branching by reducing the possibility of aggregation of HO-groups i.e. by using solvent or additive known to reduce the extent of intramolecular hydrogen bonding.

All of these approaches are presently under investigation.

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