Cationic Polymerization of Glycidol: Coexistence of the Activated Monomer and Active Chain End Mechanism

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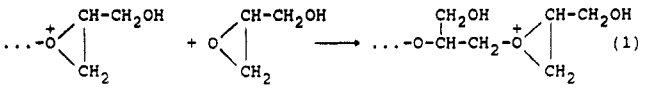
ABSTRACT: Cationic polymerization of glycidol ((hydroxymethyl)oxirane) may involve two competing propagation mechanisms: active chain end (ACE) mechanism (nucleophilic attack of the monomer on the tertiary oxonium ion active species) and activated monomer (AM) mechanism (an attack of the hydroxyl group of the polymer on the protonated monomer). The first mechanism should lead to polymers containing exclusively primary hydroxyl groups. Propagation by the AM mechanism leads on the other hand to polymers containing both primary and secondary (mostly) hydroxyl groups, depending on the direction of the opening of the protonated oxirane ring. Analysis of the microstructure of polymers of glycidol of relatively high molecular weights ($\bar{M}_n$ = 10^3–10^4) by ^{13}C NMR spectroscopy as well as by ^{29}Si NMR spectroscopy of the silylated samples shows the presence of the secondary hydroxyl groups. The significant fraction (up to 50%) of the secondary hydroxyl groups in the polymer indicates the important contribution of the AM mechanism of propagation.

Introduction

Glycidol, having in the molecule two functions, namely the oxirane ring and hydroxyl group, is very well suited for studying the competition between the active chain end (ACE) and activated monomer (AM) mechanism of propagation.[1-3] Surprisingly, there were no attempts to polymerize glycidol directly by the cationic mechanism. Only recently, Goethals reported on the cationic polymerization of glycidol, leading to branched polyols.[4]

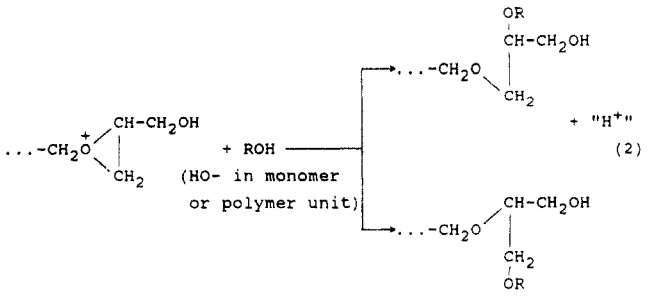
Polymerization of glycidol proceeding by the ACE mechanism would lead to the backbone composed exclusively of $-CH_2-CH(CH_2OH)-O-$ repeating units; thus only primary hydroxyl ($-CH_2OH$) groups should be present as substituents of the polyether chain:



(1)

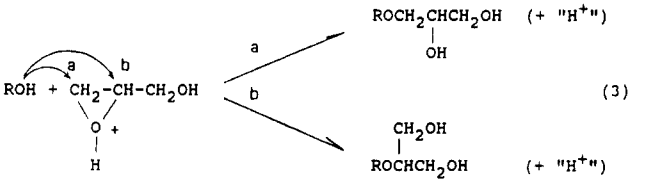
α- or β-ring opening may lead to h-h, h-t, or t-t sequences, but in any case the CH_2OH substituent is preserved.

The same is true for chain transfer involving the hydroxyl groups from polymer or monomer.



(2)

On the other hand, propagation by the AM mechanism may lead to two types of repeating units, namely

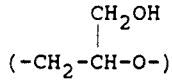


(3)

(ROH is the chain end or the side group; in the latter case branching occurs).

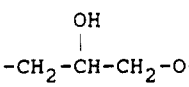
The scheme above shows the way the secondary hydroxyls occur. There is no other way (neither by ACE nor by AM) by which the secondary hydroxyl groups, other than these present as the end groups, could be formed.

The aim of the present work was to prepare reasonably high molecular weight polymers of glycidol and to investigate their structure and, more specifically, the proportions of the primary and secondary hydroxyl groups present in the polymer chain. These are to be present in the "three atom" (1-3) polymer units formed by the ACE mechanism



(4)

and in the "four atom units" (1-4 units), formed by the AM mechanism,



(5)

Experimental Section

Glycidol (Fluka) was distilled under reduced pressure prior to use.

BF_3·OEt_2 and HPF_6·OEt_2 (Aldrich) were used as received. $SnCl_4$ was distilled in the inert gas (Ar) atmosphere over Sn.

Polymerizations were carried out in the inert gas (Ar) atmosphere or in ampules sealed in vacuum. Resulting polymers were dissolved in methanol, neutralized with solid CaO, and filtered. Polymers were isolated by evaporation of the solvent or by precipitation into benzene or acetone. Thus prepared polyglycidol is a clear, glassy substance, soluble in water, lower alcohols, DMA (dimethylacetamide), DMF, and DMSO. It is

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Table 1. Polymerization of Glycidol (Monomer Conversion >80%, Other Conditions Given in Table)

no.	initiator	$[M]_0$, mol·L^{-1}	$[I]_0$, mol·L^{-1}	solvent	temp, °C	time, h	$\bar{M}_n$ (VPO) (solv)
1	BF_3·Et_2O	4.5	1.2×10^{-2}	CH_2Cl_2	−10	3	3050[a] ($CHCl_3$)
2	BF_3·Et_2O	4.5	1.2×10^{-2}	CH_2Cl_2	+10	3	1580[a] ($CHCl_3$)
3	BF_3·Et_2O	4.5	1.2×10^{-2}	CH_2Cl_2	+30	3	520[a] ($CHCl_3$)
4	BF_3·Et_2O	15.1 (bulk)	9.2×10^{-3}	-	−10	48	6800 (H_2O)
5	$SnCl_4$	15.1 (bulk)	1.6×10^{-2}	-	−20	8	4800[a] ($CHCl_3$)
6	$SnCl_4$	4.5	8.0×10^{-3}	CH_2Cl_2	−20	8	6500[a] ($CHCl_3$)
7	HPF_6·Et_2O	15.1 (bulk)	9.0×10^{-3}	-	−10	48	7600 (H_2O)
8	HPF_6·Et_2O	15.1 (bulk)	1.8×10^{-3}	-	−10	48	10500 (H_2O)

[a] $\bar{M}_n$ of corresponding urethane.

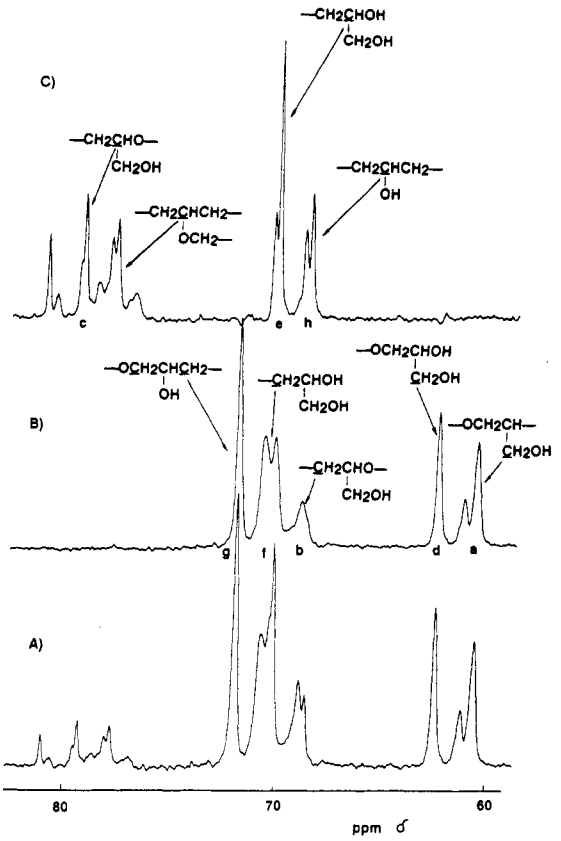


Figure 1. ^{13}C NMR spectra (D_2O, room temperature) of polyglycidol with $\bar{M}_n$ = 1600 obtained in the polymerization initiated with BF_3·OEt_2: (A) single pulse spectrum (2000 transients); (B) DEPT CH_2 subspectrum; (C) DEPT CH subspectrum.

insoluble in more common organic solvents, like hydrocarbons or chlorinated hydrocarbons.

Molecular weights were determined by VPO either in water (polyglycidol) or in $CHCl_3$ (polyglycidol converted into the corresponding urethane by reaction with trichloromethyl isocyanate).

^1H and ^{13}C NMR spectra were recorded in D_2O solutions using a Varian VXR 300 NMR spectrometer, operating at 300 MHz for ^1H and 75 MHz for ^{13}C.

Silylation of the polymers was carried out by adding a 2–4-fold excess of bis(trimethylsilyl)acetamide (BSA) to the solution of polyglycidol in DMA, directly in NMR tubes. ^{29}Si NMR spectra were recorded at 56.6 MHz.

Results and Discussion

Glycidol was polymerized in bulk or in solution with typical protic or Lewis acid initiators. Some representative results are given in Table 1.

The molecular weights of polymers clearly increase with decreasing temperature (cf. nos. 1–3 in Table 1). Even at −10 °C the observed $\overline{DP}_n$'s are considerably (at least 5 times) lower than the $[M]_0/[I]_0$ ratios. Polymers with $\overline{DP}_n$ up to ca. 150 can nevertheless be obtained, providing models for studying the structure of polymers not affected by the nature of the end groups formed in the initiation and termination.

The values of $\bar{M}_n$, measured in water and given in Table 1, cannot be considered as absolute values, due to possible association of polymer chains via hydrogen bonds, but they clearly indicate a degree of polymerization high enough to discuss the polymerization mechanism.

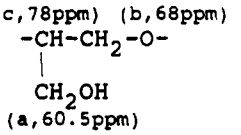
The ^{13}C NMR spectrum of polyglycidol in D_2O solution is given in Figure 1.

The assignment of signals in the ^{13}C NMR spectra of linear 1–3 polyglycidol was given by Vandenberg[5] and later by Spassky.[6] Vandenberg also proposed some assignments in much more complex ^{13}C NMR spectra of polyglycidol prepared by anionic polymerization of the silylated monomer, followed by hydrolysis.[7]

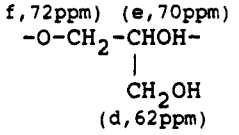
Not all lines could be assigned with the same degree of certainty. The above mentioned data, together with our study of $C_3H_7OCH_2CH(OH)CH_2OH$ and $C_2H_5OCH_2CH(OH)CH_2OH$ and DEPT experiments, in which a proper choice of two pulse sequences allows the separate registration of ^{13}C spectra of CH and CH_2 groups (for details, see ref 8), permit us to make well founded assignment of some lines and preliminary assignments of others.

The following structures have been identified:

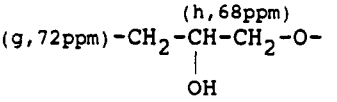
linear, nonbranched 1–3 units



(from spectra of 1–3 polyglycidol)
end groups



(from models $C_3H_7OCH_2CH(OH)CH_2OH$ and $C_2H_5OCH_2CH(OH)CH_2OH$)
1–4 units



(on the basis of assignments given by Vandenberg[9]

Other assignments in Figure 1 are less certain.

Groups, denoted d, e, f (end groups $-OCH_2-CHOH-CH_2OH$), could be present in linear molecules formed by ACE only at the chain ends. No. 1–4 units or chain branches should be observed. The analyzed polymer had $\overline{DP}_n$ = 23; consequently, the end groups should make less

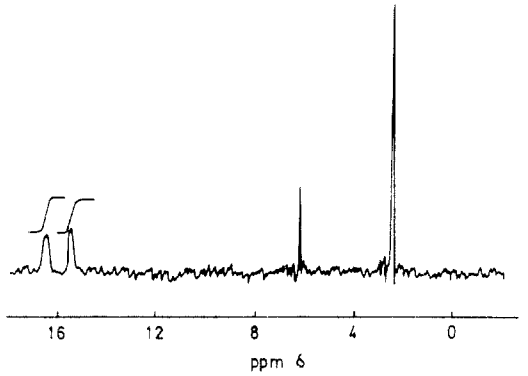
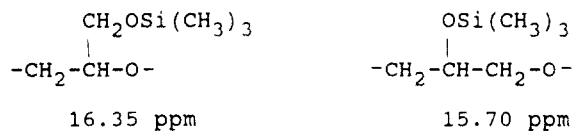


Figure 2. ^{29}Si NMR spectrum of polyglycidol with $\bar{M}_n$ = 7600 (no. 7 in Table 1) silylated with a 3-fold excess of bis-(trimethylsilyl)acetamide (BSA) in dimethylacetamide (DMA) solution. The NMR spectrum was recorded in DMA at room temperature.

than 10% of total signal intensity in the region 60–64 ppm. Although no attempt has been made to account for NOE or possible different relaxation times, it is obvious that the fraction of secondary hydroxyl groups in the analyzed polymers is much higher than 10%.

The straightforward proof of the presence of the repeating units containing secondary hydroxyl groups (eq 3) comes from the studies of the ^{29}Si NMR spectra of the silylated polymers. A typical spectrum, recorded in $CDCl_3$ solution, is shown in Figure 2. In addition to the signal of the unreacted excess of BSA (δ 2.70 ppm) and a small signal at δ 6.40 ppm due to $(CH_3)_3Si-O-Si(CH_3)_3$ (side product of the reaction between BSA and adventitious water), two signals appear at δ 15.70 and 16.35 ppm, i.e. in the region characteristic for the $ROSi(CH_3)_3$ absorption.[10] Addition of the model alcohol, containing primary hydroxyl groups in the β position to the ether oxygen, i.e. $CH_3CH_2OCH_2CH_2OH$, leads to an increase of the intensity of the 16.35 ppm signal. This allows the following assignment:



Integration of the signals give 52% of primary and 48% of secondary hydroxyl groups.

This result still does not permit the quantitative determination of the mechanism participation, but it gives at least its lowest level. Had the AM mechanism operated exclusively, both types of units (eq 3) would still be formed in proportions depending on the relative rates of the reactions (3a) and (3b). These proportions are not known at present.

The only system for which the ratios of the rates of propagation proceeding according to (3a) and (3b) are known are the AM polymerizations of propylene oxide (PO) and epichlorohydrin (ECH).[3] Although the analogies cannot be extended too far because of the different inductive effects of the $-CH_3$, $-CH_2Cl$, and $-CH_2OH$ groups, it seems that route leading to the secondary hydroxyl groups should be preferred.

Further work should reveal the influence of the polymerization conditions on the ratio [sec-OH]/[pr-OH], proportional to the contribution of the AM to propagation. On the other hand, polyglycidol provides an interesting example of the highly branched, hydrophilic polymer. Studies of its cationic polymerization may lead to a better understanding of the conditions required to prepare higher molecular weight products with a desired macromolecular architecture (e.g. dendritic polymers).

References and Notes

(1) Penczek, S.; Kubisa, P.; Matyjaszewski, K.; Szymanski, R. Structure and Reactivities in the Ring Opening and Vinyl Cationic Polymerization. In *Cationic Polymerization and Related Processes*; Goethals, E. J., Ed.; Academic Press: New York, 1984; p 139.
(2) Brzezinska, K.; Szymanski, R.; Kubisa, P.; Penczek, S. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 1.
(3) Biedron, T.; Szymanski, R.; Kubisa, P.; Penczek, S. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 155.
(4) Goethals, E. J.; De Clercq, R. R.; De Clercq, H. C.; Hartmann, P. J. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 151.
(5) Vandenberg, E. J. In *Coordination Polymerization*; Price, C. C., Vandenberg, E. J., Eds.; Plenum Press: New York, 1981; pp 34, 36.
(6) Haouet, A.; Sepulchre, M.; Spassky, N. *Eur. Polym. J.* **1983**, *19*, 1089.
(7) Vandenberg, E. J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 915.
(8) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, New York, Beijing, Frankfurt, Sao Paulo, Sidney, Tokyo, Toronto, 1987; pp 97–128.
(9) Vandenberg, E. J.; Mullis, J. C.; Juvet, R. S., Jr.; Miller, T.; Nieman, R. A. *J. Polym. Sci., Part A* **1989**, *27*, 3113.
(10) Marsmann, H. In *NMR–Basic Principles and Progress*; Diehl, P.; Fluck, E., Kosfeld, R., Eds.; Springer Verlag: Berlin, Heidelberg, New York, 1981; p 170.