Kinetics of the Polymerization of Ethyl Glycidil Ether and Allyl Glycidil Ether with BF_3OEt_2

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ABSTRACT

The kinetics of the polymerization of ethyl glycidyl ether and allyl glycidyl ether with BF₃OEt₂ as catalyst has been studied. Chain transfer to the monomer has been evidenced. It increased with the monomer concentration and decreased with the increase of the dielectric constant of the solvent used and decreased in the presence of a monomer more basic than glycidyl ethers, for example, 1,3-dioxepane.

INTRODUCTION

Investigation of the cationic copolymerization of some glycidyl ethers with tetrahydrofurane (THF) has shown a much greater activity of these monomers than expected based on their basicity [1]. The increased activity was ascribed to participation of the substituent oxygen atom in the copolymerization reaction. Some transfer reactions to the glycidyl ether substituent were also observed. This transfer has been demonstrated as follows:

Copolymers with epoxy end groups were formed.
The higher the glycidyl ether concentration in the system, the lower
the molecular mass of the copolymers obtained.
Allylic groups were identified in the material obtained by polymeri-
zation of THF in the presence of diallyl ether.

Consequently, it appeared interesting to investigate the influence
of the transfer to the monomer on the polymerization kinetics of
glycidyl ethers. Ethyl glycidyl ether (EGE) and allyl glycidyl ether
(AGE) as monomers and BF_3OEt_2 as catalyst were used. In these
systems only low molecular mass materials were reported [2, 3].

EXPERIMENTAL

Materials

AGE (bp 154 °C) was prepared by reaction of allylic alcohol with
epichlorohydrin. EGE (bp 65.5° C) was prepared from sodium ethoxide
and allyl chloride [4]. 1,3-Dioxepane (DH), epichlorohydrine (ECH),
and the solvents were conditioned as described previously [5].
BF_3OEt_2 was distilled at low pressure and used as a benzene solu-
tion.

Working Procedure

The experiments were carried out under the same conditions as
previously reported [5, 6]. The amount of monomers unreacted was
estimated by gas chromatography [6] using toulene as the internal
standard (0.94 mol/L). Column temperature was 100°C for EGE and
120°C for AGE. Hydrogen flow rate was 60 cc/min.

Analyses

The composition of the polymers obtained was determined by NMR
(60 MHz in CCl_4) [6]. The molecular mass of the polymers was deter-
mined by cryoscopy in benzene.

RESULTS AND DISCUSSION

Influence of the Monomer

The investigated monomers (EGE, AGE) have different substituents
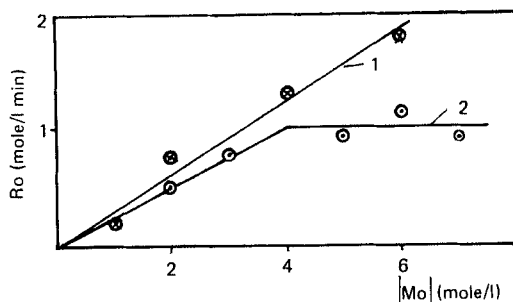(ethyl and allyl groups, respectively), but the basicity of the former

FIG. 1. Influence of initial concentrations of monomers on the initial consumption rate (R_0) ($|BF_3OEt_2|_0 = 1.5 \times 10^{-2}$ mol/L, (1) AGE, (2) EGE, t = 30°C).

is only slightly higher than that of the later ($pK_b(EGE) = 6.7$ and $pK_b(AGE) = 6.9$ [7]). However, as shown in Fig. 1, this difference in basicity does not increase the reactivity of EGE.

On the contrary, AGE exhibits a somewhat higher activity. The initial consumption rate of AGE is linearly dependent on its initial concentration, but the initial consumption rate of EGE depends on the initial concentration up to a certain value and remains constant after this concentration.

From the different behavior of these two monomers, it may be concluded that secondary process of different influence degrees occurs during their homopolymerization. This process is doubtless transfer to monomer. The effect of this transfer is more evident in the case of EGE because of the more enhanced interaction of this monomer with the cationic active center (higher basicity) and of higher mobility of the ethyl group as compared with that of the allyl group. These results are in good agreement with those reported by Ponomarenko et al. [1] regarding the copolymerization of methyl glycidyl ether (MGE) and AGE with THF. For these monomers, transfer to MGE is higher.

Due to the fact that the transfer reactions take place from the beginning to the end of the polymerization process, leading to less active or even inactive products, the monomer is not always entirely consumed. Consequently, depending on the initial monomer concentration, the final conversions are different (Fig. 2).

The decrease of the final conversion of the monomers with the increase of their initial concentration is decisive proof demonstrating the effect of transfer reactions to the monomer on the polymerization of glycidyl ethers. Subsequently, the higher final conversion of AGE in comparison with that of EGE shows that the contribution of transfer reactions is less pronounced in AGE polymerization.

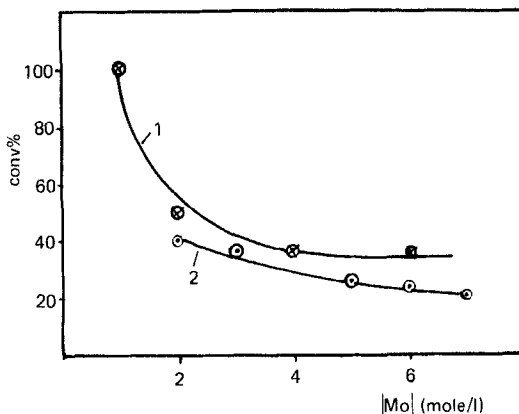The polymers obtained are syrupy materials of low molecular mass

FIG. 2. Correlation between initial concentrations of monomers and final conversions (reaction conditions as in Fig. 1).

(e.g., for an initial monomer concentration of 2 mol/L and 1.5×10^{-2} mol/L BF_3OEt_2 concentration, the molecular mass of AGE and EGE polymers was 540 and 450, respectively). The fact that the NMR spectra of AGE polymers exhibit allylic proton resonance proves that the epoxy groups were involved in the polymerization process. When the viscous polymers were exposed to an oxygenated atmosphere (i.e., air), the polymerization process continued although the allylic group and solid materials were formed.

Influence of the Catalyst

Regarding the influence of the catalyst concentration on the initial consumption rate of AGE and EGE, it again appears that the former monomer exhibits a higher reactivity than the latter (Fig. 3). In each case there is a linear dependence of both initial rate and final conversion vs initial catalyst concentration (Fig. 4).

For low catalyst concentration the final conversions are not complete, perhaps due to a stronger influence of transfer reactions.

Influence of the Solvents

In order to evaluate the influence of solvent on the reaction rate, three solvents of different dielectric constant values were used: hexane, toluene, and benzyl chloride. The initial consumption rate of EGE increases with solvent polarity (Fig. 5) in a manner similar to that encountered in other cationic polymerizations [8].
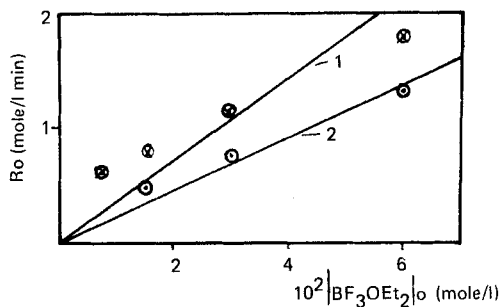
FIG. 3. Dependence of the initial consumption rate vs catalyst concentration ($|M|_0 = 2$ mol/L).
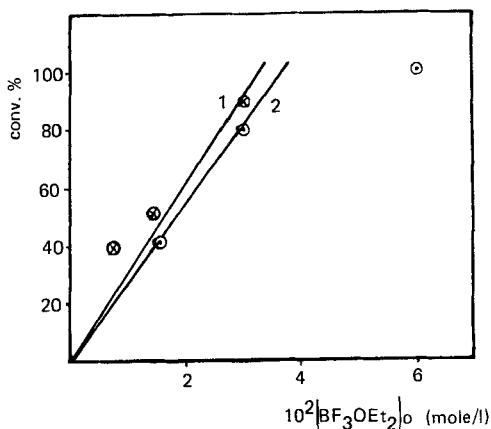

FIG. 4. Correlation between initial concentration of catalyst and final conversions (reaction conditions as in Fig. 2).

The intensity of transfer reactions is dependent on the solvent nature or, in other words, on its dielectric constant. The correlation between the final conversion of EGE and the dielectric constant of the solvent is shown in Fig. 6. It can be seen that the amount of the reacted monomer increases with the polarity of the solvent. Consequently the intensity of the transfer reactions decreases with an increase of the solvent dielectric constant.

Influence of the Comonomers

It seemed interesting to study the influence of ethyl allyl ether (EAE) on the polymerization of glycidyl ethers. This derivative has
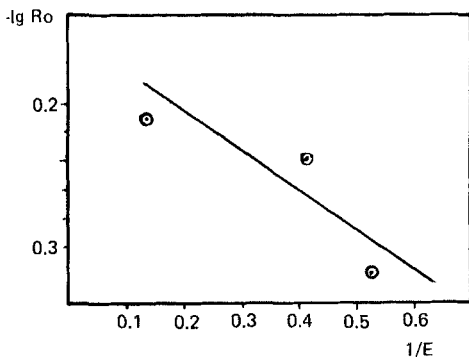
FIG. 5. Effect of dielectric constant of solvents on the initial consumption rate of EGE ($|EGE|_0 = 2$ mol/L, $|BF_3OEt_2|_0 = 1.5 \times 10^{-2}$ mol/L.
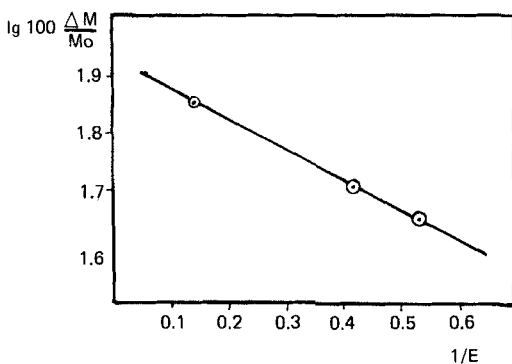
FIG. 6. Influence of dielectric constants of solvent on the final conversions ($\Delta M/M_0$) (reaction conditions as in Fig. 5).

both ethyl and allyl groups, each one common for EGE and AGE, linked by an etheric bond. Apparently EAE did not homopolymerize in the same conditions as used for glycidyl monomers in the present paper. For equimolar concentrations of EGE and EAE (i.e., $[EGE]_0 = [EAE]_0 = 2$ mol/L; $[BF_3OEt_2]_0 = 1.5 \times 10^{-2}$ mol/L), the reactivity of EGE is not affected by EAE. However, the NMR spectrum of the polymer exhibits peaks characteristic of allylic protons (1 allyl group for 22 EGE units) which could appear by transfer reactions with EAE only. This phenomenon was also observed for other epoxy monomers. Using ECH instead of EGE in the same conditions as above, methyl and allyl protons could be easily identified in the NMR

spectrum of the polymer obtained (1 allyl group for 10 ECH units). In each case the degree of participation of EAE to polymer formation could be related to the basicity of the monomer, i.e., ECH is less basic than EGE (pk_b(ECH) = 8.17 [9]), and consequently, EAE access to growing active centers is more likely.

In another experiment a monomer more basic than glycidyl ethers, DH (pk_b(DH) = 6.13 [9]), was used. We have previously shown that this monomer is very active when BF_3OEt_2 is used as the polymerization catalyst and that random copolymers are formed in the presence of ECH [10, 11]. For even a higher initial concentration of DH compared to that of EAE, i.e., $[DH]_0$ = 4 mol/L, $[EGE]_0$ = 2 mol/L (or $[AGE]_0$ = 2 mol/L) and $[BF_3OEt_2]_0$ = 3 × 10^{-2} mol/L, the glycidyl comonomers show a high reactivity. Complete conversions are achieved in a few minutes (without DH, the glycidyl monomers are not entirely consumed in the same conditions even after 24 h).

It may be concluded that by having an increased basicity, this monomer lowers the effectiveness of the transfer reactions. The materials obtained are true copolymers. Their NMR spectra present the same A-B-splitting of the acetal protons as does the NMR spectra of DH-ECH copolymers [11].

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