

Monoepoxy Polymerization Initiated by BF_3 -Amine Complexes in Bulk. II. Influence of Water and By-Products on Polymer Formation

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SYNOPSIS

The polymerization of a monoepoxy, phenylglycidylether (PGE), initiated by BF_3 -4-methoxyaniline (BF_3 -4MA) was studied at 60°C. The polymerization rate was found to be $R_p = k_p [\text{BF}_3\text{-4MA}]^{0.53} [\text{PGE}]$. The improper fraction of BF_3 -4MA shows the complexity of the polymerization mechanism. Moreover, the influence of water, temperature, by-products formed during the polymerization, on the kinetics of PGE was also examined. Furthermore, two other monoepoxy monomers, glycidylmethacrylate (GMA) and α -naphthylglycidylether (NGE), were studied for the comparison with PGE. Finally, an overall mechanism of the cationic polymerization of epoxy by BF_3 -amine complex was proposed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins as high performance polymers have increasingly received interest as composite materials, protective coatings, or encapsulation materials for many electronic components. Excellent thermomechanical properties and resistance against environmental influences are usually achieved by thermal crosslinking of epoxy prepolymers with multifunctional amines, anhydrides, or phenols as hardeners. But with these classical epoxy systems, the cure reaction is not very fast. At the present time, the industrial processes of liquid reactive systems (RIM, RTM, pultrusion, . . .) need increasingly short polymerization times in a range of polymerization temperatures of 90–120°C. Recent studies^{1–5} have shown that the cationic chain-growth polymerization could give to epoxides the potential for development in the above-named industrial processes. In these studies, among all possible cationic initiators well described in the literature,⁶ Lewis acids are the most commonly used. The boron trifluo-

ride (BF_3) is the most typical one. It is generally used through different complex forms with Lewis bases, e.g., ether, alcohol, amine. The BF_3 -amine complexes lead to initiators that can be applied in industrial applications. Indeed, the reactivity of these complexes depends on the basicity of the amines.^{1,7} With certain complexes the reaction begins at room temperature; for others, it is in the range of 40–100°C. Moreover, depending on the chemical structure of epoxy prepolymers, the glass transition temperature, T_g , of the final networks can reach a value of 165°C.⁴ In spite of the qualities such as high reactivity, high T_g , the BF_3 -amine complexes pose a problem to the users: a good mix in epoxy prepolymers is difficult to obtain due to their solid state at room temperature. With the aim of overcoming this drawback, the complexes are predissolved in solvents such as liquid polyethylene oxide^{1–3} or γ -butyrolactone (γ -BL).^{4,8} But the introduction of the former induces a certain latency period due to many transfer reactions. Moreover, transfer reactions cause a decreasing T_g of the final networks. Meanwhile, transfer reactions are reduced with the use of γ -butyrolactone.^{4,8}

In the literature, results concerning the mechanism of epoxy homopolymerization initiated by BF_3 -

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amine complexes are not abundant.^{7,10} Authors have compared the curing temperature of an epoxy prepolymer initiated by BF₃-amine complexes with that by their tetrafluoroborate ammonium salt and have considered different possible behaviors of BF₃-amine complexes in the curing of epoxy monomers. Finally, they have suggested a curing mechanism initiated by a labile hydrogen of dissociated complex acid. This complex acid resulting from the equilibrium distribution between boron trifluoride-amine complex and a cocatalyst-like protolytic compounds containing hydroxyl, alcohols, or traces of water normally present in these polar prepolymers.

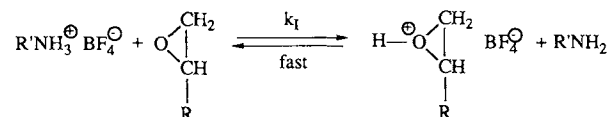
Furthermore, other authors¹¹ have proposed for the cationic polymerization of epoxy prepolymers initiated by the BF₃-etherate in the presence of ethylene glycol, a propagation reaction occurs with two competitive mechanisms: Activated Chain End mechanism (ACE) and Activated Monomer mechanism (AM). The same authors have assumed the formation of secondary cyclic oxonium ions as initial active species in the growing chain, involving a rapid nucleophilic attack of epoxy molecules to labile hydrogen atoms. These labile hydrogen atoms result from the Brønsted acid obtained from the dissociation of BF₃ etherate in the presence of a cocatalyst.¹²

In a previous article,⁸ we presented our results concerning the structure of BF₃-amine complexes and the interactions between BF₃-amine complexes and solvents. The behavior of BF₃-amine complexes in γ -butyrolactone was accurately described. We identified by ¹¹B-NMR, the tetrafluoroborate ammonium salt resulting from the BF₃-amine complex dissociation, as the species active for the cationic polymerization.

From previous results^{8,11} we have assumed that the polymerization of an epoxide monomer initiated

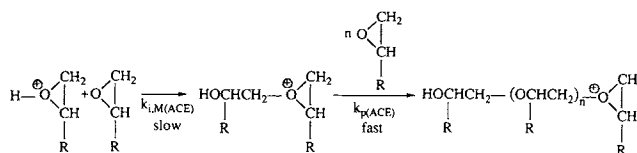
by a BF₃-amine complex could be expressed in a simplified form by the following scheme.

Preinitiation

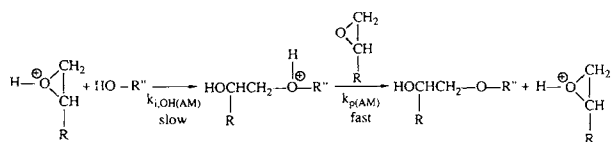


Homopolymerization

ACE Mechanism (Polymerization Through Tertiary Cyclic Oxonium Ion)



AM Mechanism (Addition of Monomer and Rapid Formation of a New Protonated Monomer Molecule)



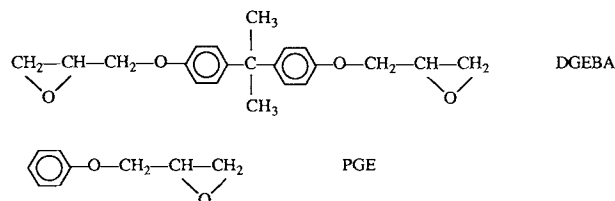
The aim of the present paper is to determine the global kinetic parameters attached to the cationic polymerization of epoxy monomers, initiated by a BF₃-amine complex. So to achieve it, we have chosen a model system. Indeed, we have used the phenyl-

Table I Monoepoxide Monomers Used

Epoxy Monomers	Structure	Supplier	Characteristics
1,2-epoxy-3-phenoxypropane Glycidylphenylether (PGE)		Aldrich	Molar weight 150.18 purity 99%
α -naphthylglycidylether (NGE)		Shell	Molar weight 202.43 epoxy 4.94 mEq/g purity 99.5%
2,3-epoxypropyl methacrylate Glycidylmethacrylate (GMA)		Aldrich	Molar weight 142.15 purity 97%

glycidylether (PGE) as monomer for the following three main reasons.

First, it is a suitable model compound for the diglycidyl ether of bisphenol A (DGEBA) as shown by their structural formulae:



Second, the BF_3 -amine complexes are directly soluble in PGE. Thus, we can make studies without the use of γ -butyrolactone.

Finally, PGE contains only one epoxy group per molecule; consequently, its polymerization gives linear soluble products that are easily analyzed by Size Exclusion Chromatography or other techniques.

Two other monomers, α -naphthylglycidylether (NGE) and 2,3-epoxypropyl methacrylate (glycidylmethacrylate-GMA), were also examined for the comparison with PGE.

In the two future articles the effect of γ -butyrolactone, used as solvent of BF_3 -amine complexes, on the cationic polymerization of PGE will be described.

A polymerization mechanism will be proposed in both cases of PGE and DGEBA.

EXPERIMENTAL PART

Three commercial epoxy monomers used in this study were employed without further purification. Their formulae are presented in Table I.

Among various BF_3 -amine complexes, the BF_3 -4-methoxyaniline (BF_3 -4MA) was chosen to initiate the polymerization. Its low reactivity allowed us sufficient time to study the polymerization kinetics. The BF_3 -4MA was synthesized, from the 4-methoxyaniline (4MA) and the boron trifluoride etherate ($\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$), in our laboratory according to the procedure described in the literature.^{7,13}

Size exclusion chromatography (SEC) was performed with a Waters device, model 6000A pump (Waters Associated), equipped with a U6K injector, a R401 refractive index detector, and an ultraviolet detector set at 254 nm. The mobile phase was tetrahydrofuran (THF) at 1 mL/min flow rate. Two columns Shodex 801, 803 were used. SEC was employed to determine the reaction kinetics for the PGE/ BF_3 -4MA system. Number- and mass-average molar masses were calculated using a calibration with polystyrene standards (PS).

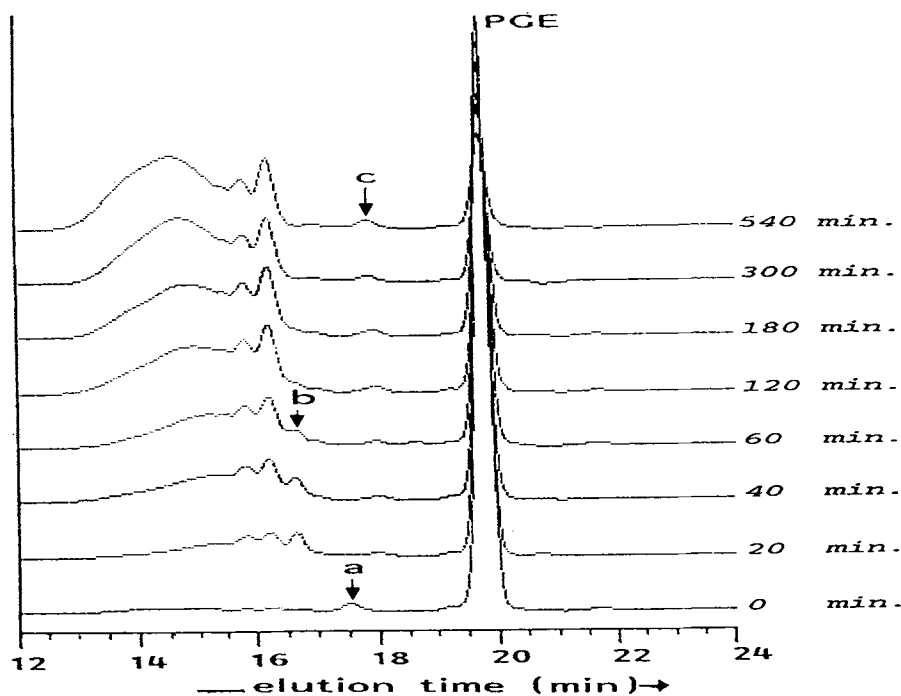


Figure 1 SEC Chromatograms of PGE initiated by BF_3 -4MA at 60°C recorded at different reaction times.

The reaction was achieved in glass tubes containing accurate weights, about 50 mg of the sample. Tubes were plunged in a thermoregulated oil bath at a selected temperature and were removed at different reaction times. The reaction was quenched by rapid cooling in an ice bath. THF was then added to get a 1% (by weight) solution, which was injected into the chromatograph.

RESULTS AND DISCUSSION

Polymerization of PGE in Bulk at 60°C Initiated by Different Concentrations of BF₃-4MA

The polymerization of PGE initiated by several concentrations of BF₃-4MA was studied at 60°C. Figure 1 shows the size exclusion chromatograms obtained at different reaction times. These chromatograms show the rapid appearance of the broad peak of the formed polymer at elution time between 13.5 and 16.6 min. Meanwhile, the narrow peak of PGE at 19.75 min decreases. Furthermore, other small arising peaks, a, b, and c are seen at 17.5, 16.5, and 18 min, respectively. They are assigned as by-products formed during the different steps of the cationic polymerization. Their structures and their influence on the kinetics of polymerization will be discussed further in this article.

The conversion of PGE calculated from the height of peak versus time for different initial concentrations of the initiator is presented in Figure 2. The monomer conversion increases rapidly and no latency period is observed at the beginning of the reaction, whereas a latency period has been observed when the liquid polyethylene oxide has been used as solvent for BF₃-amine complexes.¹⁻³ So, in the simplified system of epoxy monomer/BF₃-amine complex, according to the above observation, the initiation step of this cationic polymerization could be assumed as a fast reaction. Figure 3 shows the number-average molar mass (\overline{M}_n) vs. time. Initially, a strong increase in \overline{M}_n is noticed; this result is characteristic of chain polymerization whose rate constant of the initiation reaction is much lower than that of the propagation reaction ($k_i \ll k_p$). In the present case, according to the literature,¹¹ we assume that the polymerization can occur with both ACE and AM mechanisms. The rate constant of the initiation step that leads to growing polymer chains from initial protonated monomer molecules is lower than the rate constant of propagation of these polymer chains.¹¹ However, beyond 60 min, \overline{M}_n increases very slightly.

Table II summarizes the data obtained from Figures 2 and 3. The initial consumption rates of PGE with respect to the influence of the amount of ini-

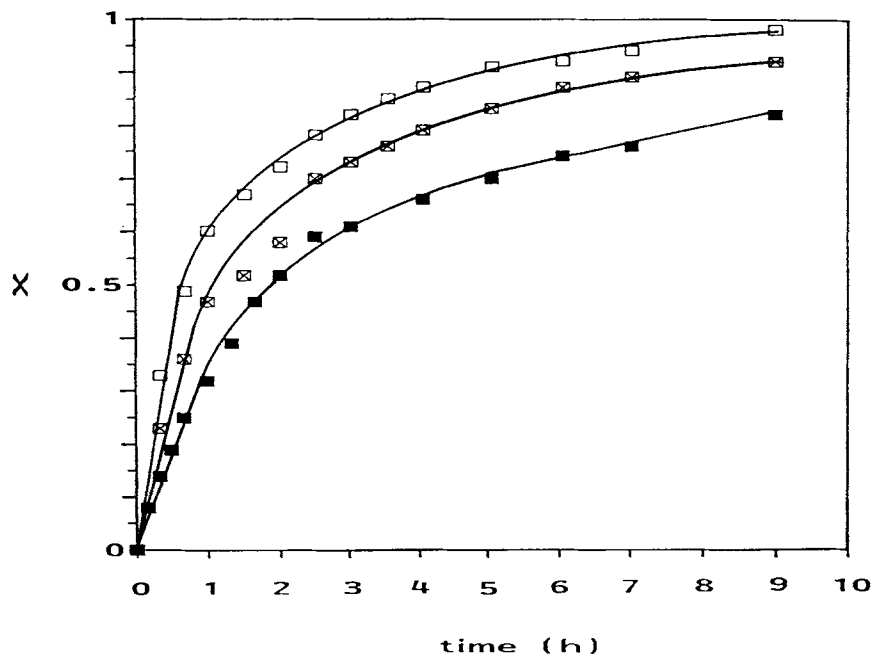


Figure 2 The PGE conversion at 60°C calculated by SEC vs. reaction time. [BF₃-4MA]: (■) 1.8×10^{-2} mol/mol of PGE; (⊗) 4.37×10^{-2} mol/mol of PGE; (□) 8.47×10^{-2} mol/mol of PGE.

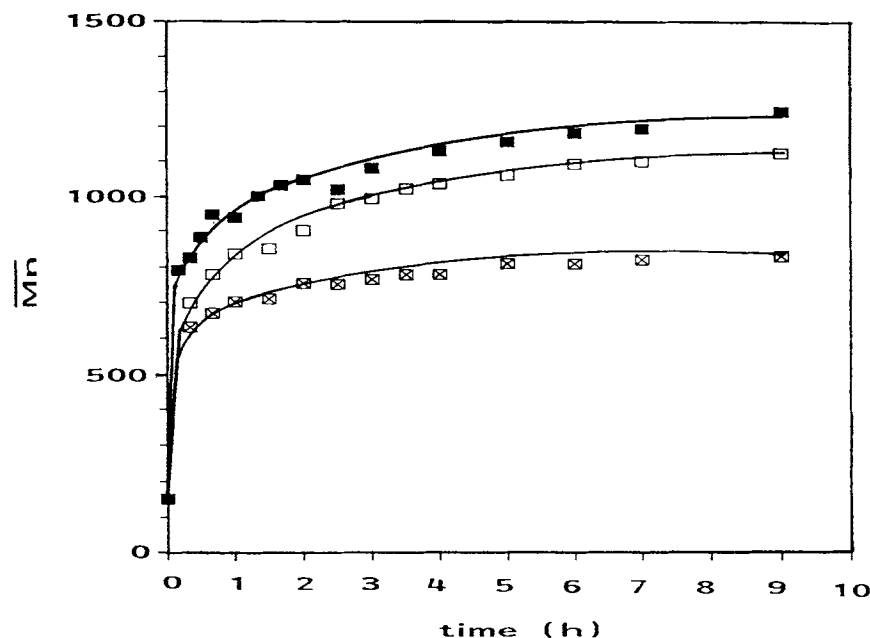


Figure 3 Number average molar mass \overline{M}_n vs. reaction time. \overline{M}_n value calculated by SEC from PS standards. $[\text{BF}_3\text{-4MA}]$: (■) 1.8×10^{-2} mol/mol of PGE; (□) 4.37×10^{-2} mol/mol of PGE; (⊗) 8.47×10^{-2} mol/mol of PGE.

tiator are calculated from the slope in the first linear part of the variation of the concentration of PGE vs. time. The molar masses \overline{M}_n and \overline{M}_w corresponding to the reaction time 540 min are calculated from the SEC measurements and polystyrene standard calibration. From Table II, the consumption rate of PGE increases with increasing concentration of the initiator $\text{BF}_3\text{-4MA}$. On the contrary, the molar masses \overline{M}_n and \overline{M}_w decrease with the increasing concentration of $\text{BF}_3\text{-4MA}$. Indeed, the higher the concentration of initiator, the higher the number of active centers; consequently, the higher the number of initiated polymer chains, so it is logical to find a decrease in the molar masses. However, the polydispersity index I_p is roughly constant around 1.3. This broadening of the molar mass distribution is

due to both transfer and termination reactions. This result is already a sufficient proof of deviation from the living nature of cationic polymerization.¹⁴

The number average degree of polymerization vs. PGE conversion is plotted in Figure 4. In the case of a cationic chain-growth polymerization where $k_t > K$, k_t and K are the rate constants of the monomer initiation and consumption reactions, respectively; we have $[P^+] = [I]_0$, i.e., the concentration of initial growing chain initiated is equal to the initial concentration of initiator. Thus, for a living process, the evolution of the number average degree of polymerization \overline{DP}_n is:

$$\overline{DP}_n = \frac{[M]_0 - [M]_t}{[P^+]} = \frac{[M]_0 - [M]_t}{[I]_0}$$

Table II Results of the Polymerization of PGE at 60°C, with Three Different Concentrations of $\text{BF}_3\text{-4MA}$

$[\text{BF}_3\text{-4MA}] \times 10^2$ mol/mol of PGE	$R_M = \frac{-d(\text{PGE})}{dt}$ mol · kg ⁻¹ · min ⁻¹	\overline{M}_n^a $t = 540$ min	\overline{M}_w^a $t = 540$ min	I_p
1.80	3.91×10^{-2}	1190	1640	1.40
4.37	6.31×10^{-2}	1100	1470	1.35
8.47	8.79×10^{-2}	820	1050	1.30

^a \overline{M}_n and \overline{M}_w were calculated from PS standards by SEC only for the large peak of the formed polymer (elution time from 13.5 to 16.6 min).

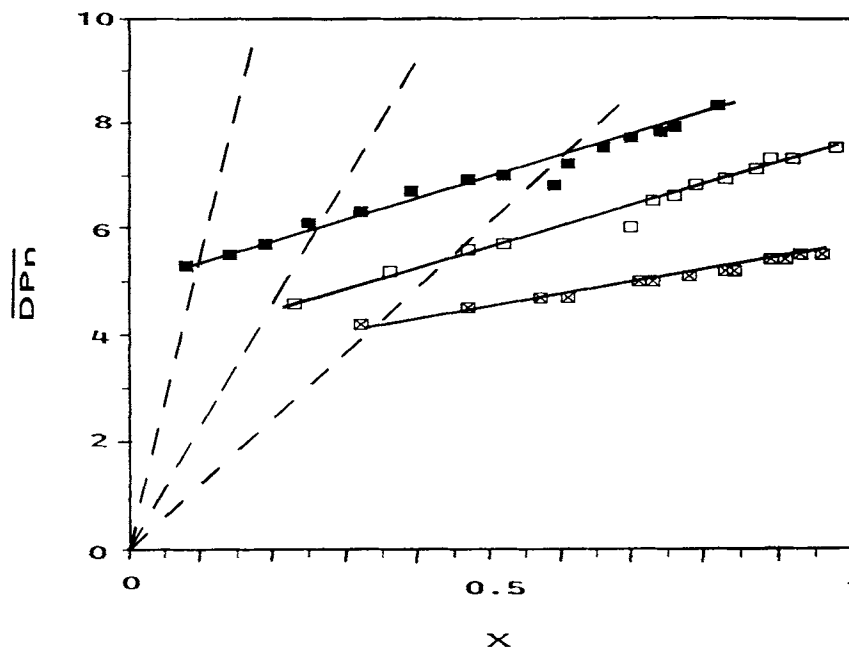
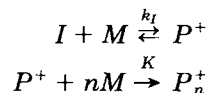


Figure 4 Number average degree of polymerization \overline{DP}_n versus PGE conversion. [BF₃-4MA]: (■) 1.8×10^{-2} mol/mol of PGE; (□) 4.37×10^{-2} mol/mol of PGE; (⊠) 8.47×10^{-2} mol/mol of PGE. (----) theory; (—) experimental.

where $[M]_0$ and $[M]_t$ are the initial concentration and concentration of monomer at reaction time t , respectively. So the theoretical evolution of \overline{DP}_n vs. monomer conversion is a straight line whose slope is $1/[I]_0$. For each concentration of BF₃-4MA, we have obtained from experiments, lines with a straight slope lower than that expected (Fig. 4). This difference with the expected slope still means that transfers and/or terminations occur. From all the previous data, we can consider the system PGE, initiated by BF₃-4MA, is a deviation from the living cationic chain-growth polymerization system.

From the following scheme:



with $k_t > K$, we have initially a rapid formation of protonated monomer molecule

$$[P^+] = [I]_0 \quad (\text{Eq. 1})$$

The rate of consumption of monomer (R_M) is expressed as:

$$R_M = -\frac{d[M]}{dt} = K[P^+]^a[M]_t^b \quad (\text{Eq. 2})$$

Thus, after substitution of $[P^+]$ from eq. 1 into eq. 2 we have:

$$R_M = -\frac{d[M]}{dt} = K[I]_0^a[M]_t^b, \quad (\text{Eq. 3})$$

where $[M]_t$ is the concentration of monomer (PGE) at the reaction time t and a, b are the orders with respect to the concentration of initiator and the concentration of PGE, respectively.

Now, we supposed, from earlier works found in the literature,^{2,15} that the rate of disappearance of PGE is first order with respect to the concentration of PGE.

Thus, we can simplify and integrate the eq. 3, so we have:

$$\ln\left(\frac{[\text{PGE}]_0}{[\text{PGE}]_t}\right) = K[I]_0^a t = \ln\left(\frac{h_0}{h_t}\right) \quad (\text{Eq. 4})$$

where h_0 and h_t are the peak heights initially and at the reaction time t measured on SEC chromatograms.

In Figure 5, the plots of the equation, eq. 4, concerning the three above kinetics of PGE initiated by different amounts of initiator, lead to three straight lines with a change in the slope. These

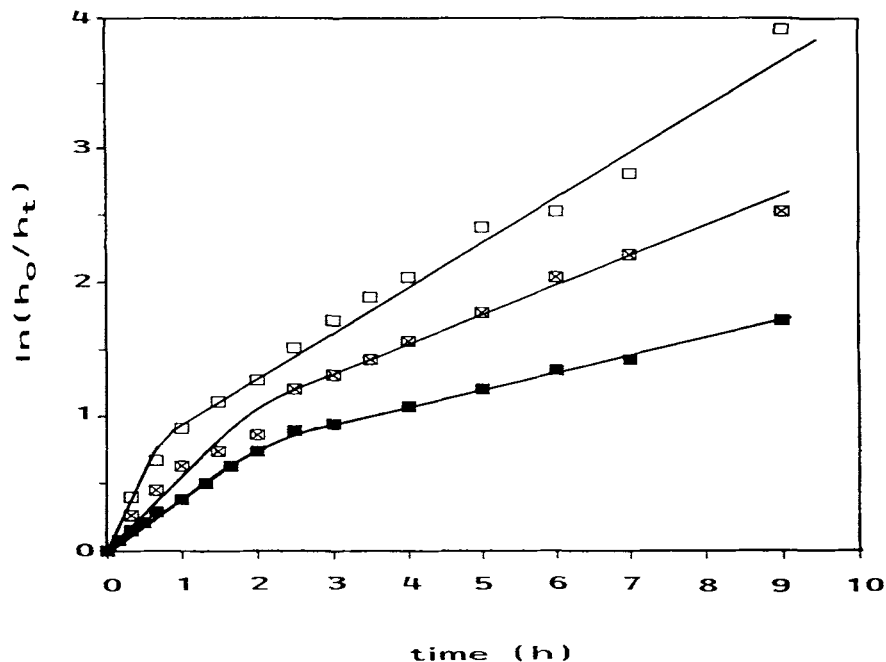


Figure 5 Experimental results showing that the reaction is first order with respect to the PGE. $[\text{BF}_3\text{-4MA}]$: (■) 1.8×10^{-2} mol/mol of PGE; (⊠) 4.37×10^{-2} mol/mol of PGE; (□) 8.47×10^{-2} mol/mol of PGE.

changes in the slope correspond to the end of first part of the curves in Figure 2, PGE conversion vs. time. Let us neglect the reason for this change in the slope for a moment. The first linear regions in Figure 5 correspond to first-order kinetics with respect to the overall conversion of epoxy groups. Consequently, the previous hypothesis is verified, the polymerization of PGE initiated by a BF_3 -amine complex is an apparent first order with respect to the concentration of PGE. Recently in the literature,^{2,15,16} the same result was found with different experimental techniques. Authors in the literature^{2,11,17} have established that the cationic chain-growth polymerization of epoxy monomer occurs with successive nucleophilic attacks of monomer molecules on electrophilic active species on growth polymer chain. Some of the authors^{2,11} have studied the cationic polymerization of an epoxy monomer initiated by a Lewis acid complex, i.e., BF_3 -etherate or BF_3 -amine, in the presence of a diol. They have assigned to the above systems, a main cationic chain growth polymerization mechanism occurring by AM mechanism. The AM mechanism is favored over the ACE mechanism in the presence of alcohol because of its higher nucleophilic affinity with active cyclic oxonium ions compared to epoxy monomer. On the other hand, authors¹⁷ have as-

sumed that cationic chain growth polymerization of a system containing only epoxy monomers initiated by BF_3 -etherate without a diol, is achieved by ACE mechanism. Thus, in this type of cationic polymerization two ring-opening mechanisms are possible. So it means that linear and cyclic oxonium ions should coexist, through AM and ACE mechanisms, respectively. Of these two growing species, cyclic oxonium ions are usually assumed to be more reactive than linear ones.¹¹

Now, from all these above conclusions in the literature, we can propose a possible explanation for the change in the slope of straight lines plotted in Figure 5. Indeed, the first linear region, the cationic ring-opening chain growth polymerization is mainly influenced by the ACE mechanism. It involves rapid successive additions of PGE molecules to polymer growth chains terminated by active cyclic tertiary oxonium ions. The change in the slope in the second linear part is ascribed to a decrease in active growing species in the ACE mechanism because of termination reactions. So the lead effect of the ACE mechanism in the general polymerization mechanism decreases. Thus, in the second linear region of plots, the influence of the AM mechanism, occurring through less reactive linear secondary oxonium ions, involves attacks of hydroxyl end chains onto cyclic

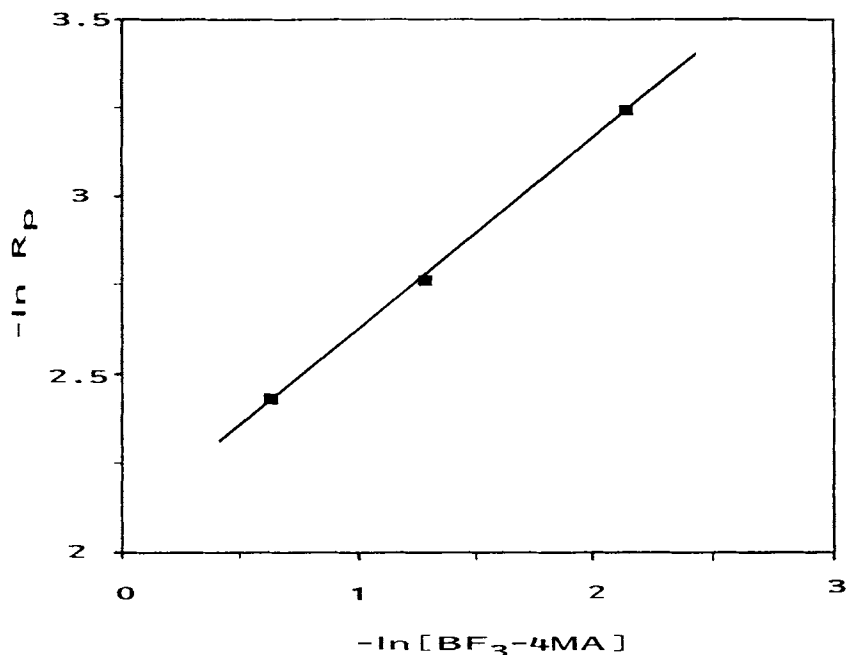


Figure 6 Determination of the reaction order with respect to the initiator (BF_3-4MA). Plot of \ln of the polymerization rate vs. \ln of initiator concentration.

oxonium ions of protonated monomer molecules. The amount of hydroxyl functions in the system results from the first ring-opening reaction of epoxy monomer in the ACE mechanism.

To determine the reaction order of initiator, BF_3-4MA , R_M vs. $[BF_3-4MA]$ is plotted in Figure 6 in a \ln - \ln scale. The slope of this straight line is equal to 0.53. Therefore, the polymerization of PGE is of 0.53 order with respect to BF_3-4MA in the initiation reaction and in the polymerization process. Hence, the general equation of the consumption rate of PGE initiated by BF_3-4MA is:

$$R_M = K[BF_3-4MA]_0^{0.53}[PGE]_t$$

Effect of the Temperature on the Behavior of the Polymerization. Determination of the Apparent Activation Energy

The PGE polymerization was investigated in the range of 50 to 80°C only for the system with the BF_3-4MA concentration equal to 1.8×10^{-2} mol/ee. The increase in reaction temperature leads to an increase in the PGE conversion vs. time (Fig. 7). From data collected in Table III, we can note that the rate of monomer consumption increases, whereas the number- and mass-average molar masses \overline{M}_n and \overline{M}_w measured by SEC after 540 min of reaction remain roughly constant. The disap-

Table III Results of the Polymerization of PGE Achieved at Different Isothermal Temperatures

Isotherm Temperature of Kinetics (°C)	$R_M = \frac{-d(PGE)}{dt}$	\overline{M}_n^a	\overline{M}_w^a	I_p
	mol · kg ⁻¹ · min ⁻¹	$t = 540$ min	$t = 540$ min	
50	2.60×10^{-2}	1110	1940	1.75
60	3.91×10^{-2}	1190	1640	1.40
70	12.37×10^{-2}	1250	1890	1.50
80	22.46×10^{-2}	1200	1800	1.50

Reaction initiated by a constant concentration in BF_3-4MA (1.8×10^{-2} mol/mol of PGE).

^a \overline{M}_n and \overline{M}_w were calculated from PS standards by SEC only for the large peak of the formed polymer (elution time from 13.5 to 16.6 min).

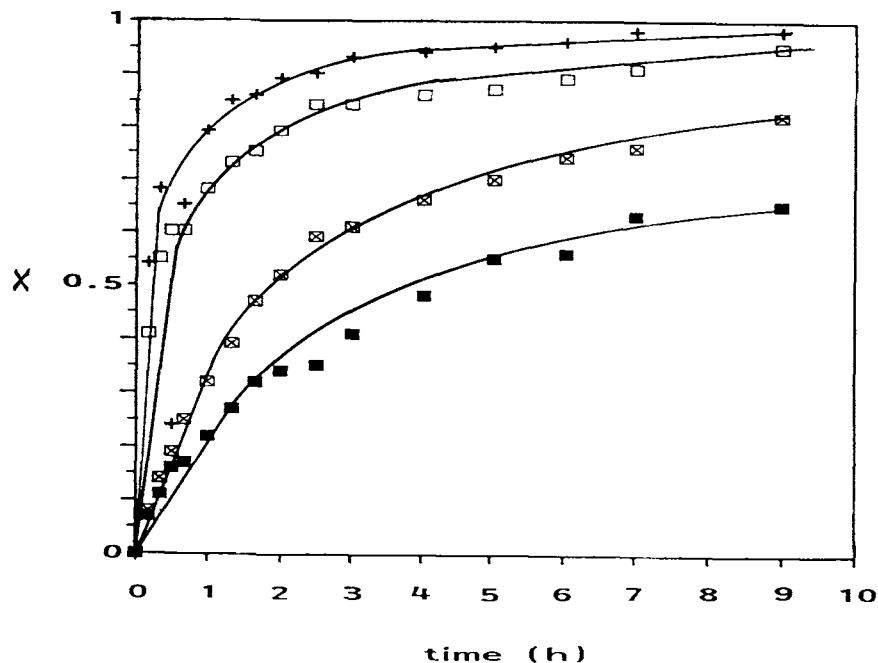


Figure 7 PGE conversion vs. reaction time at various isothermal temperatures. (+) 80°C; (□) 70°C; (⊠) 60°C; (■) 50°C.

disappearance rates of PGE have been calculated from the slope of the first part of the curves (Fig. 7). Moreover, the disappearance rate is directly proportional to the rate constant of reaction. Hence,

we can apply the Arrhenius relation to calculate the apparent activation energy (Fig. 8). The linearity of the plot demonstrates the conformity with Arrhenius' equation. The apparent activation energy

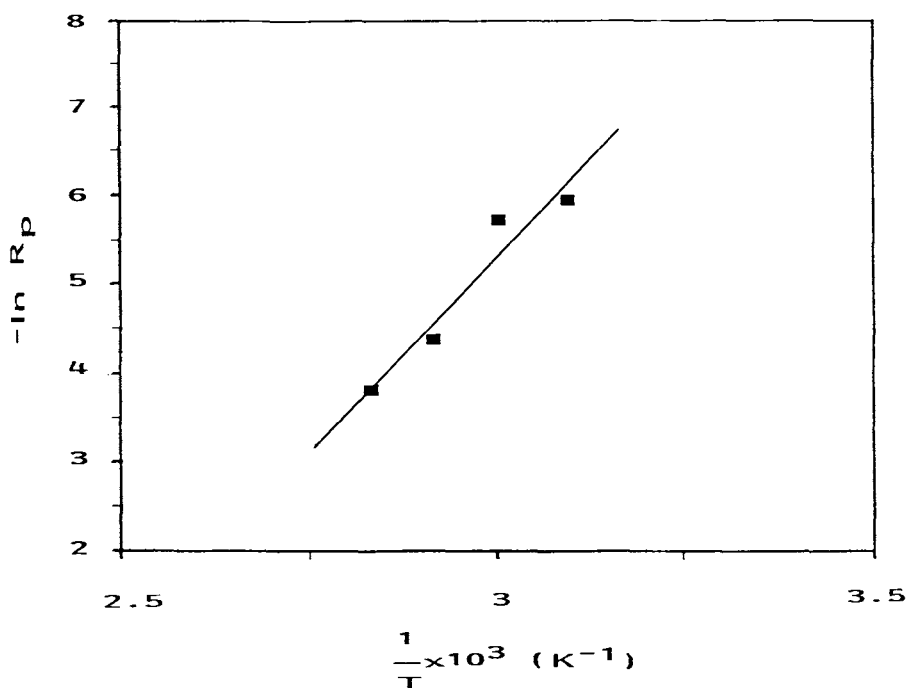


Figure 8 Application of the Arrhenius relation to calculate the activation energy of the polymerization.

determined from the slope is of 70 kJ/mol. This result agrees with the literature^{2,18} where $E_a = 64$ kJ/mol was found for a cationic copolymerization of trioxane and PGE in nitrobenzene initiated by BF_3 -etherate and $E_a = 77$ kJ/mol was obtained for an epoxy monomer initiated by a BF_3 -amine complex solubilized in liquid polyethylene oxide.

Influence of Water on the Cationic Polymerization Mechanism

At the starting state without any precaution, the PGE contains $\epsilon = 0.04\%$ (by weight) of water, due to its hygroscopic character. The measure of the quantity of H_2O was achieved by the Karl Fischer method in our laboratory. The kinetics with adjunction of $1 + \epsilon$ and $2 + \epsilon\%$ by weight of water with respect to PGE have been achieved at 60°C with our standard system with the BF_3 -4MA concentration equal to 1.8×10^{-2} mol/ee. The SEC chromatograms recorded after 540 min of reaction are reported in Figure 9. We can see that there is a great difference between the two chromatograms with ϵ and $2 + \epsilon\%$ of water (Fig. 9a and d). In Figure 9d the appearance of several peaks in the broad peak

of high molar mass oligomers is detected. We have supposed that these arising peaks could be due to an increase in number of oligomer chains that have reacted with water by transfer reaction, through a ring-opening hydrolysis of their active tertiary oxonium. So we have assumed that each peak is an oligomer chain terminated by a hydroxyl function whose molar mass is $150n + 18$, where n is the degree of polymerization number, 150 and 18 are the molar mass of PGE and water, respectively. Thus, we have plotted the log of the estimate molar mass of oligomers $M_{150n+18}$ attached to each peak vs. their elution time (Fig. 10). The accurate value of the elution time of peaks has been attributed, as the minimum of peaks in the second derivated chromatogram, from our SEC computer program. The straight line obtained in Figure 10 confirms our previous hypothesis assuming that the growing oligomer chains can be killed by transfer reactions with water. Furthermore, this result is similar with a part of work reported in the literature¹⁹ whose aim was the use of SEC and HPLC as a method to calibre the oligomers from a cationic system, i.e., polymerization of PGE initiated by hydrolyzed boron trifluoride ($\text{H}^+, \text{BF}_3\text{OH}^-$) in presence of polyethylene oxide 300.

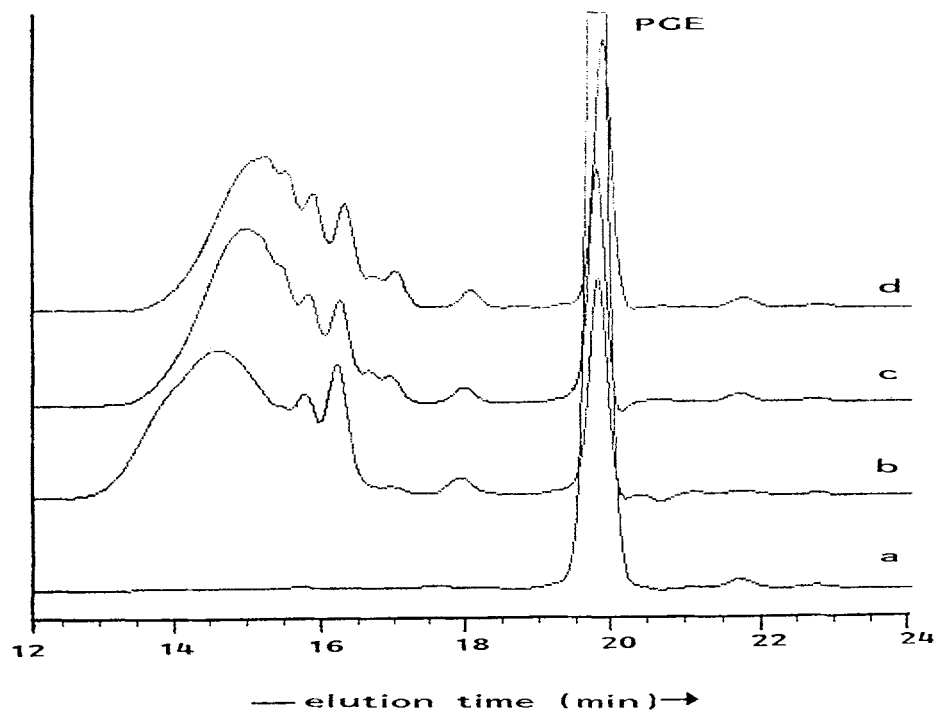


Figure 9 Influence of presence of water on the polymerization. SEC chromatograms of PGE polymerization recorded after 540 min of reaction. a) $\epsilon = 0.04\%$ wt of water, before the polymerization; b) $\epsilon\%$ wt of water; c) $1 + \epsilon\%$ wt of water; d) $2 + \epsilon\%$ wt of water.

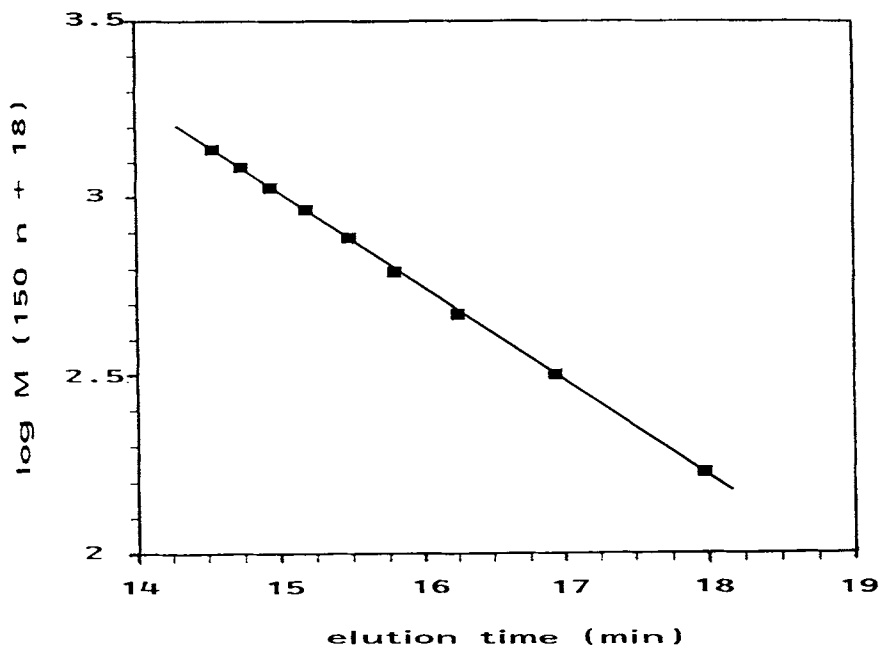


Figure 10 Evolution of the molar mass of the oligomers formed during the polymerization of PGE with an initial addition of 2% wt of water ($2 + \epsilon$ % wt). Plot of log M vs. elution time of oligomer peaks.

Still, in the case of the addition of water, the PGE conversion vs. time is presented in Figure 11. The PGE conversion decreases with increasing water

concentration. Nevertheless, no latency period has been observed at the beginning of the reaction. Table IV summarizes all data obtained from these kinetic

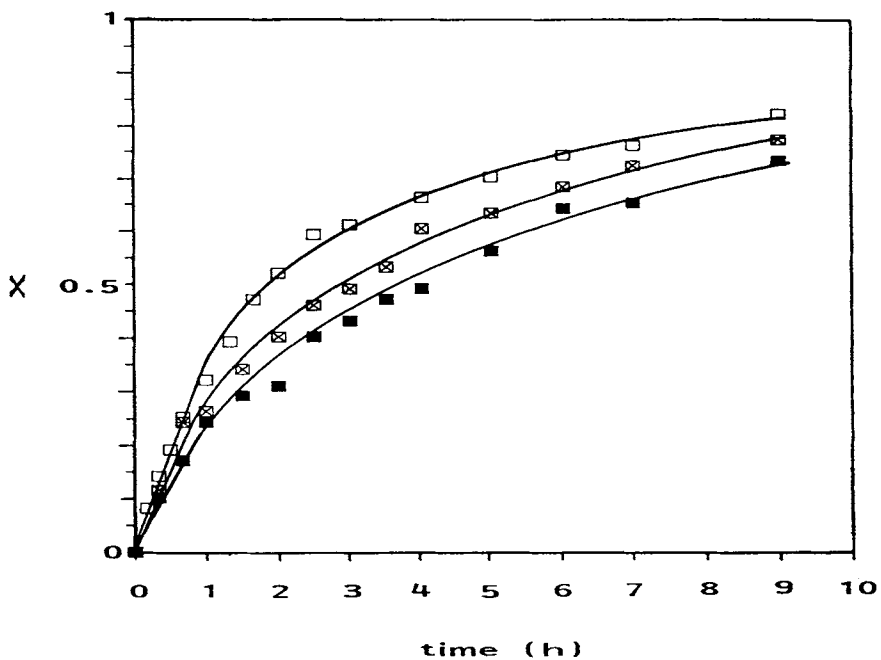


Figure 11 Influence of the presence of water on the polymerization. Plot of the PGE conversion vs. reaction time. (■) ϵ % wt of H_2O ; (⊠) $1 + \epsilon$ % wt of H_2O ; (□) $2 + \epsilon$ % wt of H_2O .

Table IV Influence of Water in the PGE Polymerization at 60°C

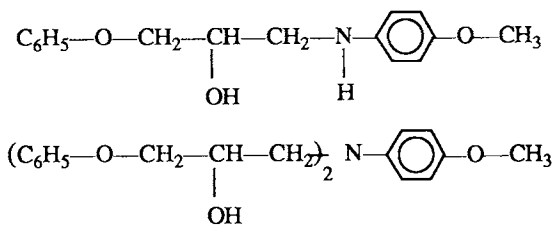
[H ₂ O] in the Reactive System % wt	$R_M = \frac{-d(\text{PGE})}{dt}$ mol · kg ⁻¹ · min ⁻¹	\overline{M}_n^a t = 540 min	\overline{M}_w^a t = 540 min	I_p
$\epsilon = 0.04$	3.91×10^{-2}	1190	1640	1.40
1 + ϵ	3.05×10^{-2}	1040	1260	1.20
2 + ϵ	2.23×10^{-2}	930	1120	1.20

Reaction initiated by a constant concentration in BF₃-4MA (1.8×10^{-2} mol/mol of PGE).
^a \overline{M}_n and \overline{M}_w were calculated from PS standards by SEC only for the large peak of the formed polymer (elution time from 13.5 to 16.6 min).

studies. The number and mass average molar masses \overline{M}_n and \overline{M}_w measured by SEC after 540 min of reaction decrease with increasing concentration of H₂O. The same observation is made for the rate of the monomer disappearance, R_M . The latter is still measured in the initial linear part of the PGE conversion vs. time. We can think that H₂O acts as a transfer agent and competes with the PGE polymerization.

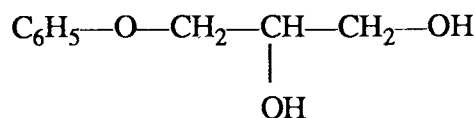
Influence of By-Products of Reaction on the Kinetics of Polymerization

We have seen earlier in Figure 1 that by-products are formed during the polymerization. So we have identified three products named a,b,c. The latter arises on the chromatograms at the beginning of the polymerization. According to our above proposal mechanism where the initial amine releases during the initiation step, we have assumed first that product a and b result from the two successive addition reactions between the 4-methoxyaniline (4MA) and initial active molecules of PGE (secondary oxonium ion). Products a and b are attributed to the structures:



Furthermore, the structure of these products has been confirmed by the direct reaction of PGE with 4MA with a molar ratio 2 : 1 and during 1 h at 90°C. The two peaks seen have had exactly the same elution time as products named a and b in Figure 1. At the end of the reaction, as the molar ratio is 2 : 1,

one single narrow peak whose elution time is equivalent to the product b was observed. This last result is still confirmed by the calibration curve obtained in Figure 10. The elution time of the products a and b leads to the molar masses of 250 g/mol instead of 273 g/mol and 417 g/mol instead of 423 g/mol, respectively, for the above proposal structures of the products a and b. So we can conclude that our first assumption about the structure of the products a and b has been confirmed. Moreover, the molar mass of the product c has still been evaluated from its elution time by the calibration curve in Figure 10. We have determined a molar mass of 168 that is consistent with the structure of the product resulting from the transfer reaction between water and active molecules of PGE. This structure corresponds to the following formula:



We have also confirmed this structure by the injection in SEC of the same commercial product purchased from Aldrich (3-phenoxy 1,2-propanediol).

Finally, to complete the knowledge of this cationic chain growth polymerization, we have studied the influence of products b and c on the reaction kinetics. In order to examine the effect of by-products, a large amount of them was added in the initial standard system. Two formulations (PGE/BF₃-4MA/by-product b) and (PGE/BF₃-4MA/by-product c) through a single molar composition ($1/1.8 \times 10^{-2}/0.1$) were studied. Figure 12 shows their respective influence on the PGE conversion vs. time, the PGE conversion of the standard (PGE/BF₃-4MA) is still plotted as reference. Hence, we can note a real decrease in the rate of the PGE conversion during the reaction in the presence of the by-products b and c.

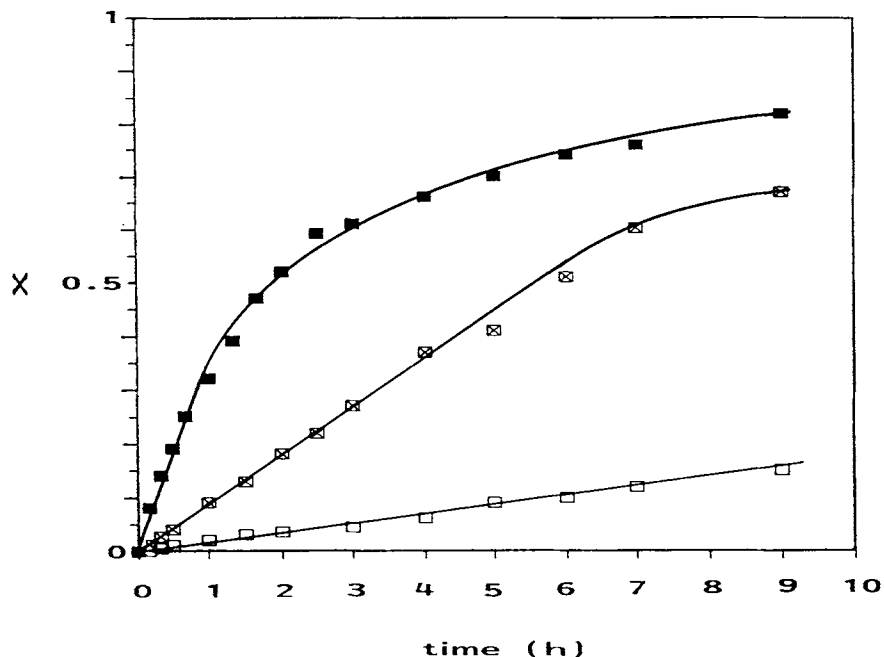


Figure 12 Influence of by-products of reaction on the polymerization of PGE. (■) standard system PGE + $\text{BF}_3\text{-4MA}$; (⊠) kinetics with adding of $\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH(OH)-CH}_2\text{-OH}$ (0.10 mol/mol of PGE) in the standard system; (□) kinetics with adding of $(\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH(OH)-CH}_2)_2\text{-N-C}_6\text{H}_4\text{-O-CH}_3$ (0.10 mol/mol of PGE) in the standard system. All kinetics initiated by $\text{BF}_3\text{-4MA}$ (1.8×10^{-2} mol/mol of PGE).

So we can think that the polymerization mechanism is modified. Indeed, previously we have seen that the cationic polymerization proceeds via two possible mechanisms. At the beginning of the polymerization, the Activated Chain End mechanism (ACE) is the lead mechanism. But during the reaction, the Activated Monomer mechanism (AM) occurring

through secondary aliphatic oxonium ions is favored by a decrease in the number of reactive tertiary cyclic oxonium ions in the ACE mechanism because of termination reactions. Thus, this change in the whole polymerization mechanism leads to a decrease in the rate of the PGE consumption due to the change in the reactivity of the active species. In the

Table V Influence of By-Products on the PGE Polymerization Kinetics Achieved at 60°C

By-Products	$R_M = \frac{-d(\text{PGE})}{dt}$ mol · kg ⁻¹ · min ⁻¹	\overline{M}_n^a $t = 540$ min	\overline{M}_w^a $t = 540$ min	I_p
/	3.91×10^{-2}	1190	1640	1.40
product b	1.54×10^{-2}	960	5280	5.50
product c	8.41×10^{-2}	930	1510	1.60

Reaction initiated by a constant amount of $\text{BF}_3\text{-4MA}$ (1.8×10^{-2} mol/mol of PGE) and with 0.10 mol/mol of PGE of by-product b and c, respectively.

^a \overline{M}_n and \overline{M}_w were calculated from PS standards by SEC only for the large peak of the formed polymer (elution time from 13.5 to 16.6 min).

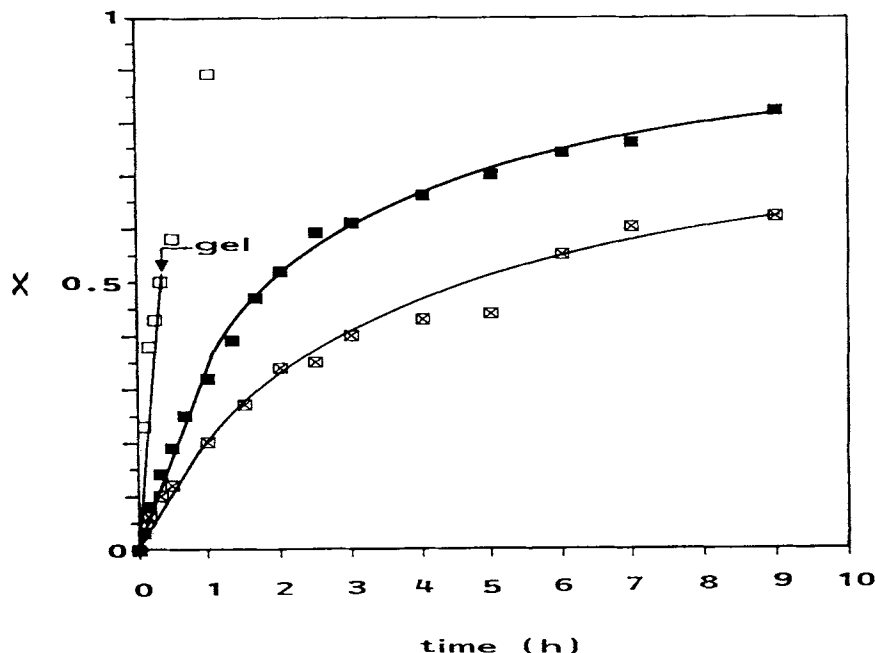


Figure 13 Kinetics of cationic polymerization of different epoxy monomer initiated by $\text{BF}_3\text{-4MA}$ achieved at 60°C . (\square) GMA; (\blacksquare) PGE; (\boxtimes) NGE. All kinetics initiated by 1.8×10^{-2} mol of $\text{BF}_3\text{-4MA}$ /mol of epoxy functions.

presence of by-products we have initially increased the amount of hydroxyl functions in the system. So we can suppose we will obtain principally the influence of the Activated Monomer mechanism (AM) during the whole reaction. This assumption is confirmed by the slow variation of PGE conversion vs. time during the polymerization (Fig. 12). All the data obtained from these two reactions in the presence of by-products is summarized in Table V.

Influence of the Chemical Structure of the Monomer

The SEC kinetics were studied at 60°C with three kinds of monomers: glycidylmethacrylate (GMA),

phenylglycidylether (PGE), and α -naphthylglycidylether (NGE). For all cases the concentration of $\text{BF}_3\text{-4MA}$ was 1.8×10^{-2} mol per epoxy equivalent. The epoxy conversion vs. time is shown in Figure 13. We can see that the conversions of GMA and NGE are higher and lower than that of PGE, respectively. The rates of the monomer disappearance and molar masses \overline{M}_n , \overline{M}_w are reported in Table VI. From these results, we can see that the polymerization rate R_M of GMA is 10 times superior to $R_{M(\text{PGE})}$ and this latter is twice $R_{M(\text{NGE})}$. The same remark can be made with the molar masses \overline{M}_n and \overline{M}_w .

The three monomers do not have the same kinetics because of their different chemical structures.

Table VI Influence of the Structure of the Monomer on the Cationic Polymerization Achieved at 60°C Initiated by a Constant Concentration in $\text{BF}_3\text{-4MA}$ (1.8×10^{-2} mol/mol of Monomer)

Monomers (M)	$R_M = \frac{-d(\text{PGE})}{dt}$ mol \cdot kg $^{-1}$ \cdot min $^{-1}$	\overline{M}_n^a $t = 20$ min	\overline{M}_w^a $t = 20$ min	\overline{M}_n^a $t = 540$ min	\overline{M}_w^a $t = 540$ min
PGE	3.91×10^{-2}	825	1045	1190	1640
NGE	1.82×10^{-2}	725	864	1045	1336
GMA	17.17×10^{-2}	1547 (gel)	15820 (gel)	/	/

^a \overline{M}_n and \overline{M}_w were calculated from PS standards by SEC only for the large peak of the formed polymer (elution time from 13.5 to 16.6 min).

The literature²⁰ assumes that no direct correlation exists between the size of substituents and the polymerizability. Nevertheless, it is reported that the reactivity may be affected by substituents. Indeed, the decrease in basicity of the monomer owing to the inductive effect of substituents leads to a decrease of nucleophilic character of epoxy groups. Therefore, their polymerizability in cationic polymerization decreases. Very likely, the drawing inductive effect of methacrylate group is weaker than that of phenoxy group. Moreover, the drawing inductive effect of the phenoxy group is weaker than that of the naphthalene group. Thus, in the case of GMA, the lone electron pairs of the oxygen in oxirane cycle are more available to react with H^{\oplus} than in the cases of PGE and NGE.

Furthermore, in the case of GMA, the gelation was obtained after 20 min of reaction. Meanwhile, the gelation was not observed with PGE or NGE. This result means that the double bonds of GMA are opened by BF_3 -amine and/or temperature.

Discussion on the Mechanism

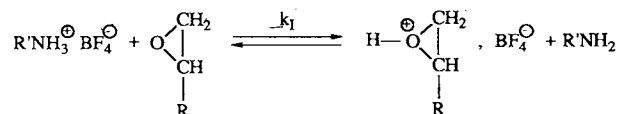
From all results obtained we can propose a mechanism for the cationic chain growth polymerization of epoxy monomer initiated by BF_3 -amine complex. Initially, the Activated Chain End mechanism (ACE) is predominant, but the presence of hydroxyl groups, i.e., water, polymer end chain, by-products b and c favors the Activated Monomer mechanism (AM). In the ACE mechanism, cyclic tertiary oxonium ions are predominantly formed and the polymerization will proceed on these growing species. On the other hand, the AM mechanism proceeds through active linear secondary oxonium ions that result from the addition of molecules containing hydroxyl groups to cyclic oxonium ions. Nevertheless, the AM mechanism is slower than the ACE mechanism because it is usually assumed that linear secondary oxonium ions are less reactive than cyclic tertiary ones. Thus, we can write for the rate constants of these mechanisms $k_{p(AM)} < k_{p(ACE)}$. This is in good agreement with our above results.

About the transfer and termination step we have assumed intra- and intermolecular transfer and termination reactions as proposed in the literature.^{11,21} The intermolecular transfer (termination) to polymer, occurring in ACE mechanism, leads from reactive tertiary cyclic oxonium ions to less reactive "dormant species" that are a linear tertiary oxonium ions.²¹ Furthermore, the intramolecular chain transfer to polymer still attached to the ACE mechanism, leads from reactive tertiary cyclic oxonium ions to nonreactive cycles or macrocycles. Nev-

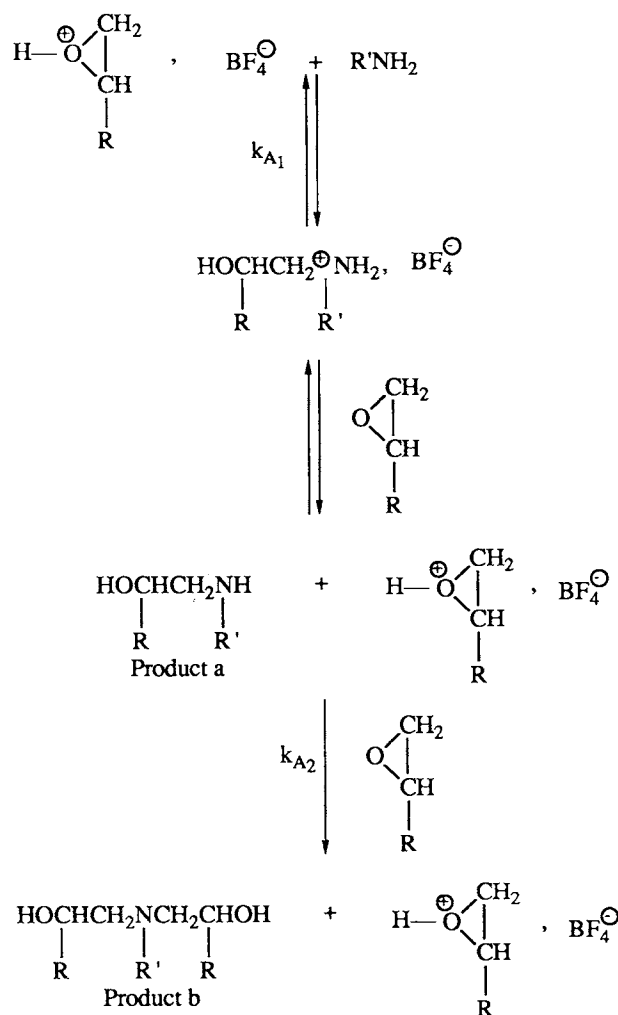
ertheless, the intramolecular transfer to polymer usually followed by a reinitiation step.

Till now, a general polymerization mechanism can be proposed according to the following scheme:

Preinitiation

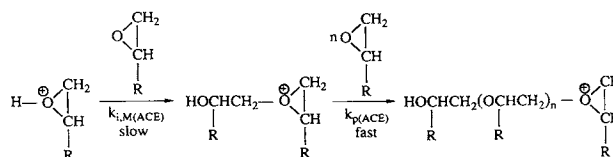


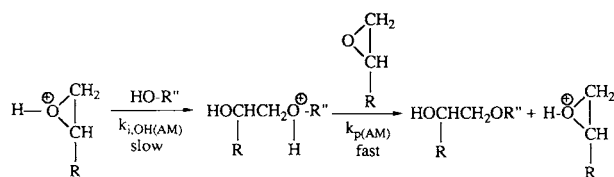
Amine Addition



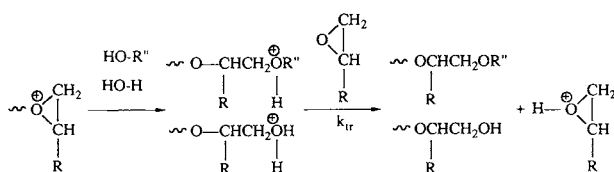
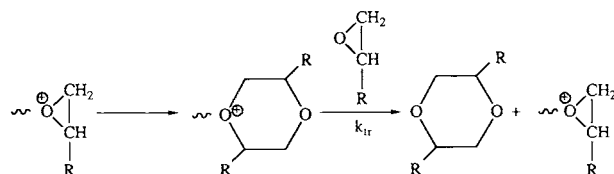
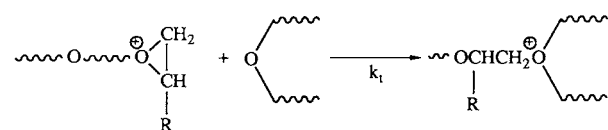
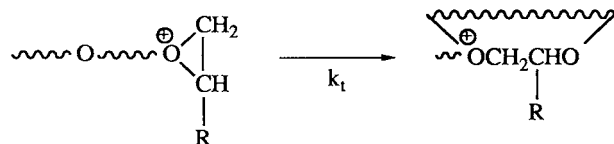
Homopolymerization

Activated chain end mechanism (ACE).



Activated monomer mechanism (AM).

$$\begin{array}{l}
 \text{with } k_{i,\text{M}(\text{ACE})} < k_{i,\text{OH}(\text{AM})} \\
 k_{\text{p}(\text{ACE})} > k_{\text{p}(\text{AM})}
 \end{array}$$

Transfer Reactions*Intermolecular.**Intramolecular.**Termination-irreversible transfer to polymer intermolecular.**Intramolecular.***CONCLUSION**

The polymerization kinetics of PGE initiated by $\text{BF}_3\text{-4MA}$ is first order with respect to PGE and 0.53 order with respect to $\text{BF}_3\text{-4MA}$. This improper frac-

tion shows the complexity of the action of $\text{BF}_3\text{-4MA}$ on the polymerization. $\text{BF}_3\text{-4MA}$ induces not only the initiation reaction but also the formation of by-products that can react during the polymerization with the epoxy group of PGE. The PGE polymerization has an activation energy equal to 70 kJ/mol which is in good agreement with the literature.

The presence of H_2O or products containing hydroxyl groups slows down the PGE polymerization. Water acts as transfer agent and competes through AM mechanism with the ACE mechanism in the PGE polymerization.

The amine released by the complex reacts with epoxy group giving the by-products containing the secondary hydroxyl groups. Their presence decreases the polymerization rate. These by-products have the same behavior as water.

From these results we can conclude that the main mechanism of PGE polymerization initiated by $\text{BF}_3\text{-4MA}$ is the Activated Chain End mechanism (ACE). In the presence of products containing hydroxyl groups, the Activated Monomer mechanism (AM) is favored.

Finally, in the monoepoxy monomer $\text{R}-\text{CH}-\text{CH}_2$, the chemical nature of R influences

the kinetics. If R is electron drawing, the cationic polymerization decreases. On the contrary, if R is electron repulsive the cationic polymerization increases. If the epoxy monomer contains double bonds, they can be opened during the polymerization and the gelation is obtained.

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