Monoepoxy Polymerization Initiated by BF_3-Amine Complexes in Bulk. III. Influence of γ-Butyrolactone on Polymer Formation

PHILIPPE CHABANNE, LAN TIGHZERT,* and JEAN-PIERRE PASCAULT

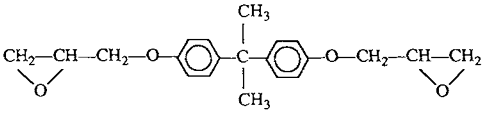
Laboratoire des Matériaux Macromoléculaires, URA CNRS No. 507, Institut National des Sciences Appliquées de Lyon, 20, Avenue A. Einstein, 69621 Villeurbanne Cedex, France

SYNOPSIS

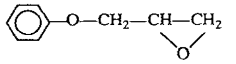
The influence of γ-butyrolactone (γ-BL), used as solvent of BF_3-amine complexes, on the polymerization of monoepoxides was studied. Different intermediate reaction products of PGE initiated by BF_3-4-methoxyaniline (BF_3-4MA) previously solubilized in γ-BL (55% by weight), were separated and analyzed by ^1H-NMR. It is shown that there is the opening of both epoxy and γ-BL. The latter does not homopolymerize, but copolymerizes well with epoxy groups. The use of a large quantity of γ-BL leads to a decreasing molar mass of the formed polymer. The kinetic study allowed to propose the mechanism of the cationic polymerization of epoxy initiated by BF_3-amine complex in the presence of γ-BL. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In two previous articles,[1,2] results concerning epoxy polymerization initiated by BF_3-amine complexes have been presented. In the first one,[1] the behavior of BF_3-amine complexes in γ-butyrolactone was accurately described. The tetrafluoroborate ammonium salt resulting from the BF_3-amine complex dissociation was identified by ^{11}B, ^{19}F-NMR analyses. It acts as the active cationic initiator for epoxy polymerization. In the second article,[2] the kinetics of the cationic polymerization of a monoepoxy monomer initiated by BF_3-4-methoxyaniline (BF_3-4MA) in bulk was studied. From these results a polymerization mechanism was proposed. The phenylglycidyl ether (PGE) was chosen as monomer because it is a suitable model compound for the diglycidyl ether of bisphenol A (DGEBA), as shown by their structural formulae:



DGEBA



PGE

Contrary to DGEBA, PGE is a good solvent of BF_3-amine complexes. This fact allows the characterization of the PGE polymerization without the use of a solvent for BF_3-amine complexes.[2]

Generally, the BF_3-amine complexes pose a problem to the users. Indeed, because of their solid state at room temperature, a good mix with epoxy prepolymers, like DGEBA or epoxy Novolak, is difficult to obtain. To overcome this drawback, the complexes are necessarily predissolved in solvents. The first solvent earlier used and accurately studied was the liquid polyethylene oxide (PEO).[3-5] The aim of this work is to replace PEO by a lactone as solvent of BF_3-amine complexes to get a suitable initiator mixture for epoxy systems. The γ-butyrolactone (γ-BL) has been chosen because it is a better solvent of BF_3-amine complexes than PEO.[1] Further, γ-BL is less viscous than PEO; thus, its incorporation in epoxy prepolymers is easier. Finally, γ-BL ring can be opened by an acid catalyst,[6] but it cannot homopolymerize.[7-11] So, in the presence of epoxy monomers, the literature[8-10,12-21] reported that BF_3-etherate can initiate a copolymerization. Indeed, interesting results[22] such as an increase in reactivity and increasing thermal properties of the fully cured epoxy network have been obtained in previous experiments with the introduction of γ-BL in epoxy system. These results have been confirmed by others in the literature.[23] They are consistent with the

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 53, 787–806 (1994)

CCC 0021-8995/94/060787-20

industrial requirements in processes of liquid reactive systems like Reaction Injection Moulding (RIM), Reaction Transfer Moulding (RTM), pultrusion, . . .

In the present article, the influence of γ-BL in the epoxy polymerization was studied. With the aim of clarifying the polymerization mechanism, we also used large quantities of γ-BL to determine accurately its effect on the polymerization of PGE.

The study of the network formation from diepoxy prepolymer initiated by BF_3-amine complexes predissolved in γ-BL will be described in a future paper.

EXPERIMENTAL PART

Commercial 1,2-epoxy-3-phenoxypropane (phenylglycidylether-PGE) and γ-butyrolactone (γ-BL) were supplied by Aldrich and used without further purification. Among various complexes that could be used,[3] the BF_3-4-methoxyaniline (BF_3-4MA) was chosen to initiate the PGE polymerization. Its low reactivity allowed us sufficient time to study the polymerization kinetics. The BF_3-4MA was synthesized according to the procedure described in the literature[1,24,25] from commercial 4-methoxyaniline (4MA) and boron trifluoride etherate (BF_3-Et_2O) (Aldrich). The structure of all products used is shown in Table I.

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/γ-BL/BF_3-4MA system. Number- and mass-average molar masses were calculated using a calibration with polystyrene standards (PS). The reaction was achieved in glass tubes containing accurate weights of about 50 mg of the samples. Glass tubes were plunged into 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% wt solution that was injected into the chromatograph.

The ^1H-NMR spectra were recorded with a Brucker AC200 at 200 MHz. Deuterated solvent was used for field lock. The ^1H-NMR chemical shifts are reported with tetramethylsilane (TMS) as the reference (0 ppm). The deuterated acetone was used as solvent for all samples.

Fourier Transform Infra-Red (FT-IR) studies were performed with a Nicolet MX-1. Products were placed between two KBr disks.

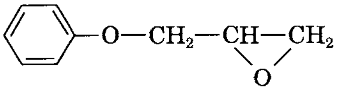
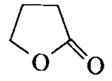
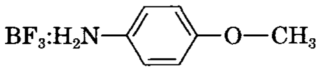
RESULTS AND DISCUSSION

Influence of High Concentration of the γ-Butyrolactone on the Epoxy Polymerization

With the aim of determining if the γ-butyrolactone (γ-BL) undergoes only side reactions or if it effectively copolymerizes with epoxy groups, three high concentrations of γ-BL equal to 0.25, 0.5, and 1 mol per mol of PGE were used for polymerization at 60°C.

Figure 1 illustrates various SEC chromatograms obtained from the reactive mixture 1 mol of γ-BL for 1 mol of PGE initiated by BF_3-4MA (1.8×10^{-2} mol per mol of PGE). The SEC chromatogram at t

Table I Structure of Products Used

Formula	Name	State at Room Temperature
	1,2-epoxy-3-phenoxypropane or Phenylglycidylether (PGE)	Liquid
	γ-butyrolactone (γ-BL)	Liquid
	BF_3-4-methoxyaniline (BF_3-4MA)	Solid

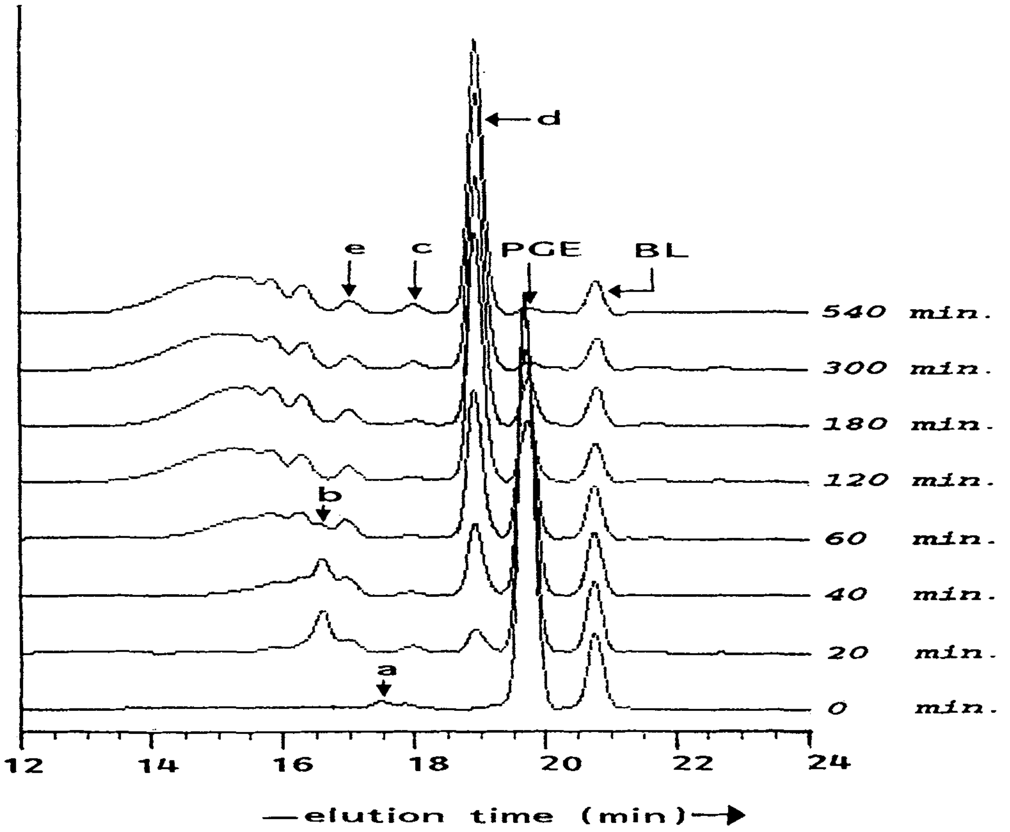
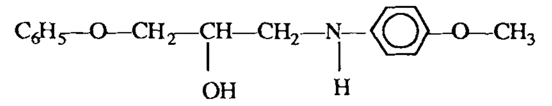
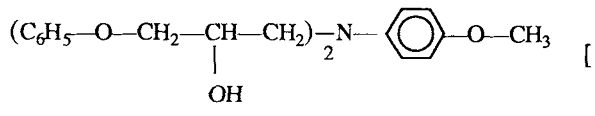


Figure 1 Chromatograms of PGE : γ-BL (1 mol : 1 mol). Polymerization at 60°C, initiated by $[BF_3\text{-}4MA] = 1.8 \times 10^{-2}$ mol per mol of epoxide (PGE).

= 0 shows, beside the peaks of PGE and γ-BL, the presence of peak a. It is no longer seen on the chromatogram at 20 min, but simultaneously the appearance of peak b is noticed. We have already seen these two peaks on SEC chromatograms attached to the polymerization in bulk of PGE initiated by the BF_3-4-methoxyaniline (BF_3-4MA) without γ-BL.[2] These two products were assigned to the following structures:



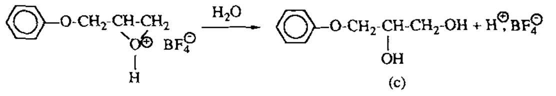
[a]



[b]

They result from the two successive addition reactions between the PGE and the 4-methoxyaniline (4MA) released during the initiation of growth chain polymerization.

Furthermore, in Figure 1, three other peaks, c, d, and e can be seen after 20 min of reaction. Peak c has already been characterized in our earlier paper[2] and is attributed to the following structure:



[c]

resulting from the reaction between water and a promoted molecule of PGE.

The two peaks d and e were not been seen on SEC chromatograms from the polymerization of PGE initiated by BF_3-4MA without γ-BL.[2] The behavior of peaks d and e during the reaction and their respective structure will be discussed further in this article.

The PGE conversion vs. time is plotted in Figure 2. Comparatively, the PGE conversion corresponding to the reaction without γ-BL[2] is also reported in the same figure. The curves show a rapid increase and it is as large as the γ-BL concentration increases. So the PGE conversion is clearly slower without γ-BL. This increase in the PGE conversion may be due to the presence of peak d (Fig. 1) which arises simultaneously with the broad peak of polymer (t_e = 13.5–16.6 min). We can assume now, from earlier works in the literature[4,26] and from our results on the cationic polymerization of PGE without γ-BL,[2] that the rate of PGE conversion is an apparent first order with respect to the concentration of PGE.

From the simplified and integrated equation of the polymerization rate, we have plotted in Figure 3 the $\ln\left(\frac{h_o}{h_t}\right)$ vs. reaction time for the three above systems with γ-BL and for comparison also the system without γ-BL. h_o and h_t are the initial peak height and the peak height at the reaction time t measured on SEC chromatograms, respectively. For each system we obtained straight lines with a change in slope. The linear regions fit to first-order kinetics with respect to overall conversion. Consequently, the previous hypothesis, which is the polymerization of PGE initiated by a BF_3-amine, is an apparent first order with respect to the concentration of PGE is still verified even in presence of large amount of γ-BL (Fig. 3).

In Figure 4, the γ-BL conversion is very fast initially. As previously with the PGE, the initial rate of disappearance of γ-BL is calculated from the slope in the one part of curves plotted in Figure 4. As with the PGE, the assumption to have an apparent first order with respect to the concentration of γ-BL is still verified only at the beginning of the reaction (Fig. 5). Furthermore, rate constants and ratios of rate constants $k_{PGE}/k_{\gamma\text{-BL}}$ reported in Table II show that the PGE is consumed more rapidly when the initial concentration of γ-BL increases. On the other hand, the $\overline{M_n}$, $\overline{M_w}$, and I_p calculated only from the broad peak of polymer formed (elution time from 13.5 to 16.6 min) decrease at full conversion of PGE. This last result means that γ-BL limits the polymer chain formation.

Now we can discuss the behavior of peaks d and e during the reaction. The intensity of peak d still increases until 540 min of reaction, but that of peak e remains almost constant. Furthermore, we have to note that peak c retains roughly a constant intensity. The evolution of peak d height, h_t, at the reaction time t measured on SEC chromatograms, reported to a constant weight of sample injected in SEC, is plotted in Figure 6 for three concentrations of γ-BL. It rapidly increases with increasing the γ-BL concentration, but a ceiling value is reached at about 180 min of reaction for all three concentrations of γ-BL.

The results obtained so far prompt the following questions. If all the disappeared quantity of γ-BL is used to form peak d, does the formed polymer contain γ-BL? Therefore, the intensity h_t of peak d is plotted vs. the decrease ($h_o - h_t$) of the γ-BL peak in Figure 7. h_o and h_t are still the initial peak height

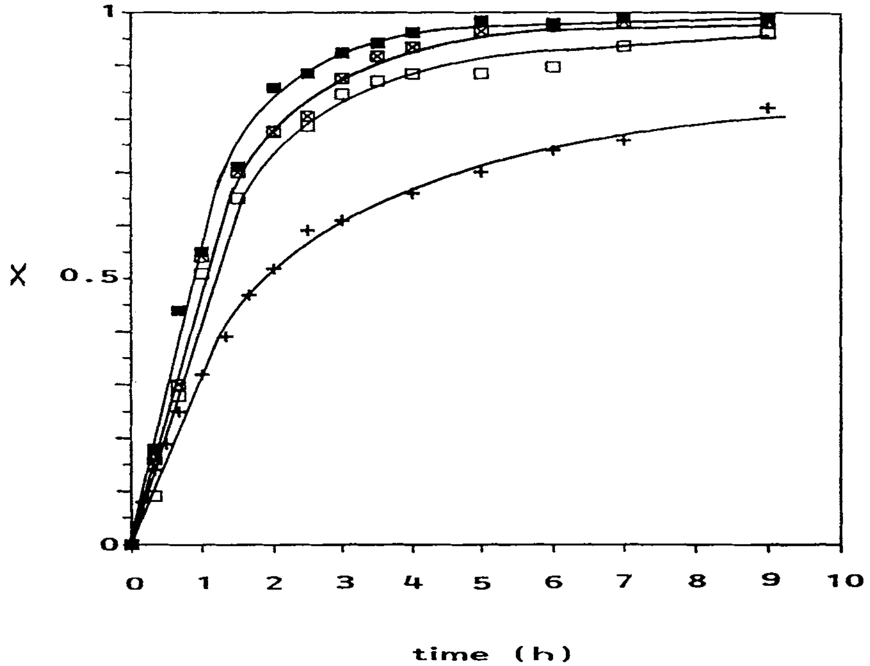


Figure 2 Conversion of PGE vs. time. 1 mol of PGE for: (■) 1 mol of γ-BL; (☒) 0.5 mol of γ-BL; (☐) 0.25 mol of γ-BL; (+) without γ-BL.

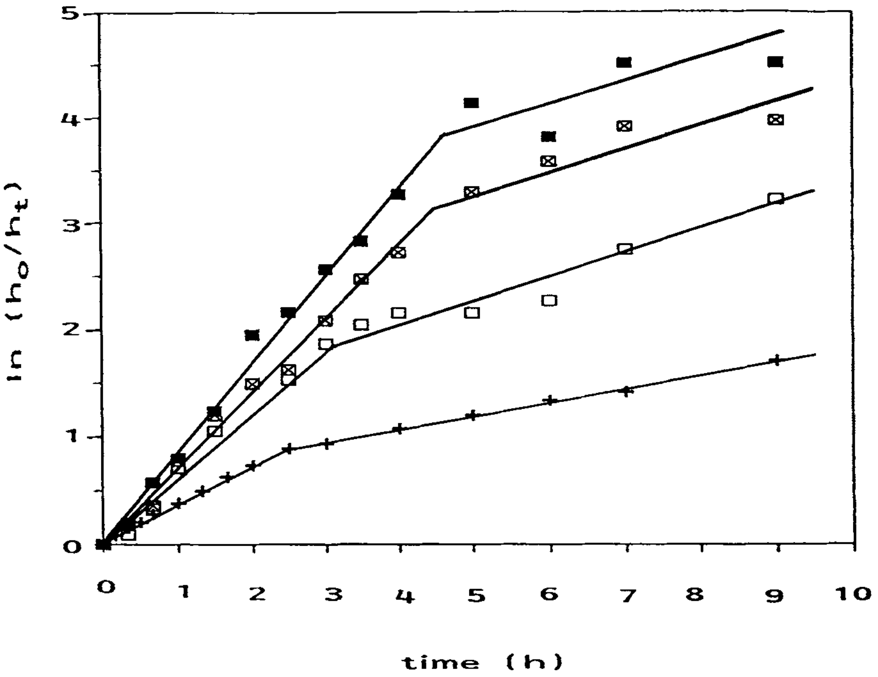


Figure 3 In $\left(\frac{h_o}{h_t}\right)$ vs. time. 1 mol of PGE for: (■) 1 mol of γ-BL; (☒) 0.5 mol of γ-BL; (□) 0.25 mol of γ-BL; (+) without γ-BL.

and the peak height at the reaction time *t* measured on SEC chromatograms, respectively. Three straight lines are obtained with a slope slightly inferior to 0.5. We can note that the higher the γ-BL concentration, the more the slope of these straight lines increases. In light of these observations, we can as-

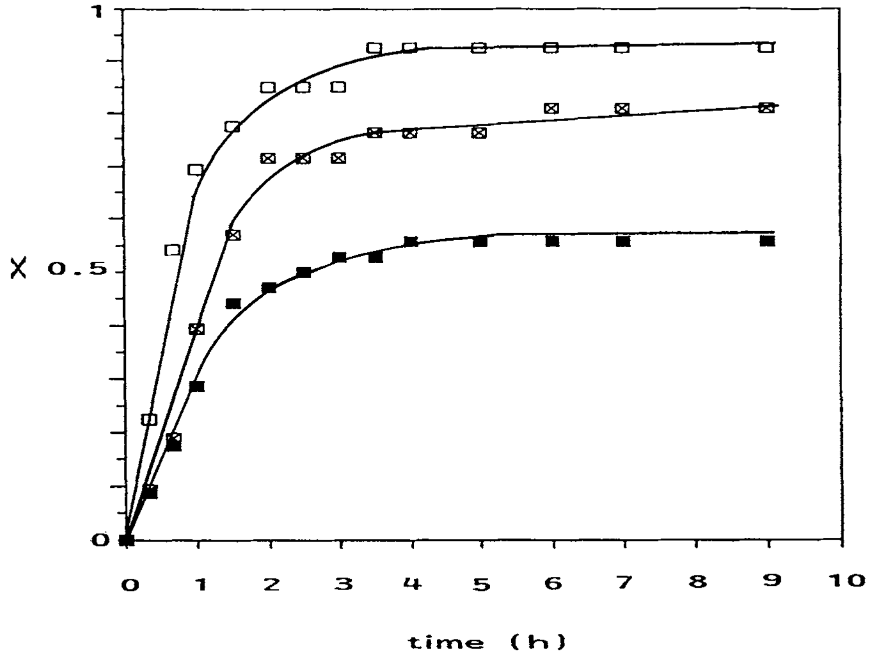


Figure 4 Conversion of γ-BL vs. time. 1 mol of PGE for: (■) 1 mol of γ-BL; (☒) 0.5 mol of γ-BL; (□) 0.25 mol of γ-BL.

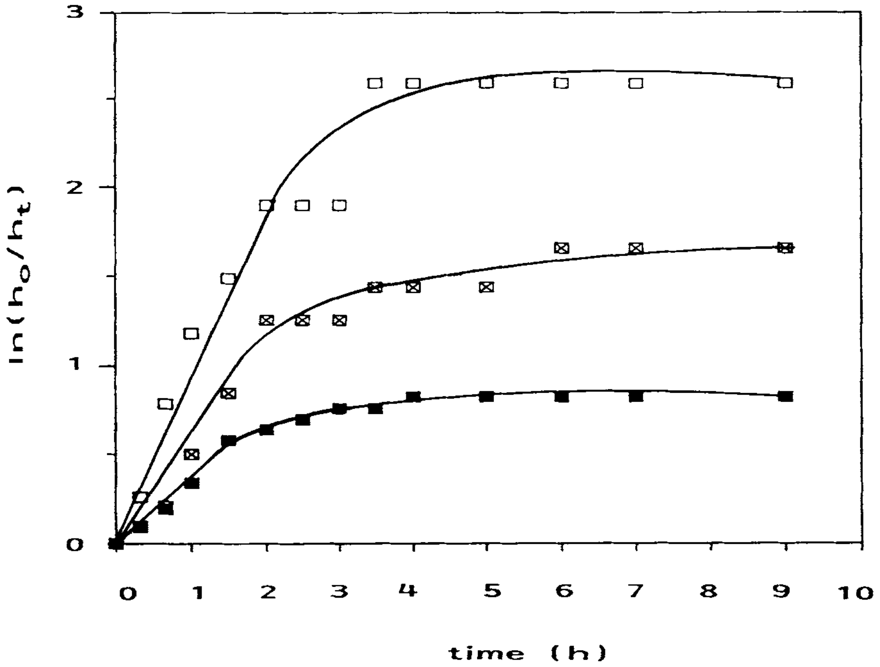


Figure 5 $\ln\left(\frac{h_o}{h_t}\right)$ vs. time. 1 mol of PGE for: (■) 1 mol of γ-BL; (☒) 0.5 mol of γ-BL; (□) 0.25 mol of γ-BL.

sume that a major disappeared quantity of γ-BL serves to give peak d and the rest may be found in the broad peak of polymer arising at low elution times on SEC chromatograms.

In the literature, many authors,[8-10,12-21] agree with the cationic copolymerization between the γ-BL and epoxy monomers occurring by a ring-opening reaction. But only some of these authors[12-21] have given an accurate mechanism for the copolymerization. They have suggested the formation of an intermediate spiro structure (spiroorthoester—SOE) resulting from an addition reaction between one epoxy ring and one lactone ring. This spiroorthoester (SOE) structure is relatively stable and acts as a monomer that can copolymerize with epoxy group by a cationic initiation.[12-21]

In other respects, for the confirmation of the ring opening copolymerization of the γ-BL with epoxy monomers, we have recorded a FT-IR spectrum of the initial reactive mixture (1 mol of γ-BL for 1 mol of PGE initiated by BF_3-4MA). On this spectrum, Figure 8a, the carbonyl group (C═O) of the γ-BL ring is a single peak at 1771 cm^{-1} (peak 4). After 4 h of reaction in a glass tube at 60°C in an oven, a new FT-IR spectrum is recorded (Fig. 8b). Several peaks attributed to characteristic bands of the reactive system are reported in Table III. An arising peak at 1734 cm^{-1} (peak 4') characteristic of an ali-

Table II Results of the PGE Polymerization in the Presence of a High Concentration of γ-BL

[γ-BL] mol/mol of PGE	k_{PGE} min^{-1}	k_{BL} min^{-1}	k_{PGE}/k_{BL}	$\overline{M_n}$[a] t = 540 min	$\overline{M_w}$[a] t = 540 min	I_p t = 540 min
0	0.60 × 10^{-2}	/	/	1190	1940	1.40
0.25	1.10 × 10^{-2}	1.70 × 10^{-2}	0.65	1020	1940	1.90
0.5	1.20 × 10^{-2}	1.10 × 10^{-2}	1.10	850	1290	1.50
1	1.50 × 10^{-2}	0.70 × 10^{-2}	2.10	660	920	1.40

The concentration of BF_3-4MA was 1.8 × 10^{-2} mol per mol of PGE. Data obtained without γ-BL is reported for comparison.

[a] $\overline{M_n}$ and $\overline{M_w}$ were calculated only from the large peak of the formed polymer (elution time from 13.5 to 16.6 min) at 540 min of reaction time.

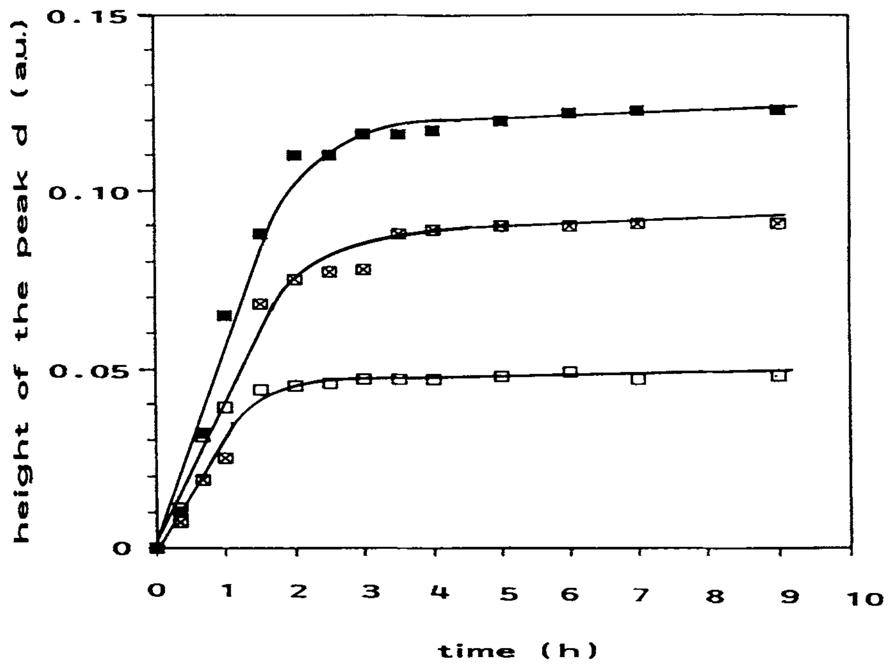


Figure 6 Intensity of peak d vs. time, measured by SEC. (■) 1 mol of γ-BL; (☒) 0.5 mol of γ-BL; (☐) 0.25 mol of γ-BL.

phatic carbonyl ester is noticed. This result confirms that there is the opening of the γ-BL ring during the reaction with epoxy monomer.

Until now, all results obtained reveal that a fractionation is necessary to clarify the kinetic mechanism. Before the fractionation procedures, we have

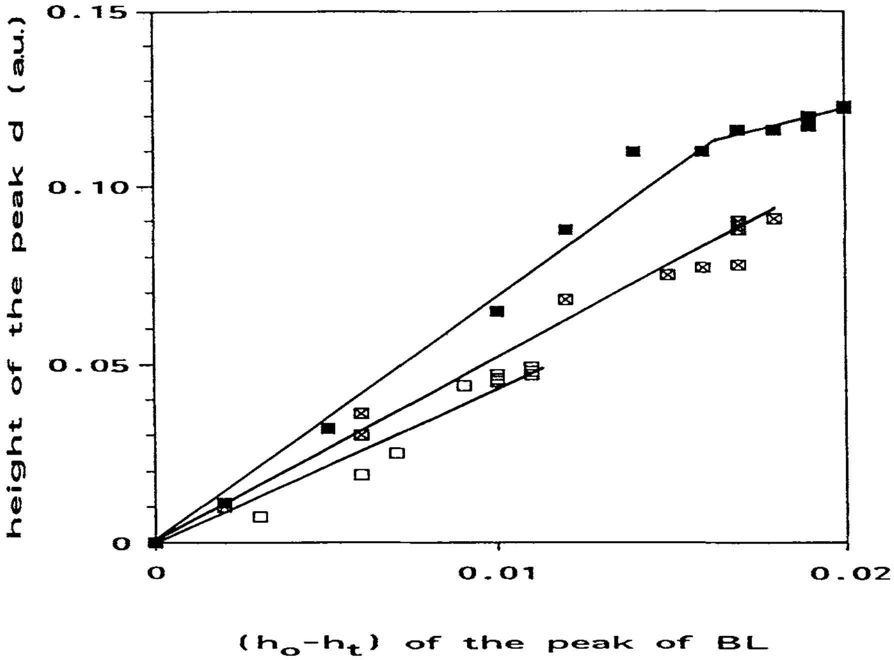


Figure 7 Intensity of peak d vs. $(h_o - h_t)$. h_o and h_t are the initial intensity and intensity of γ-BL at time t, respectively. (■) 1 mol of γ-BL; (☒) 0.5 mol of γ-BL; (☐) 0.25 mol of γ-BL.

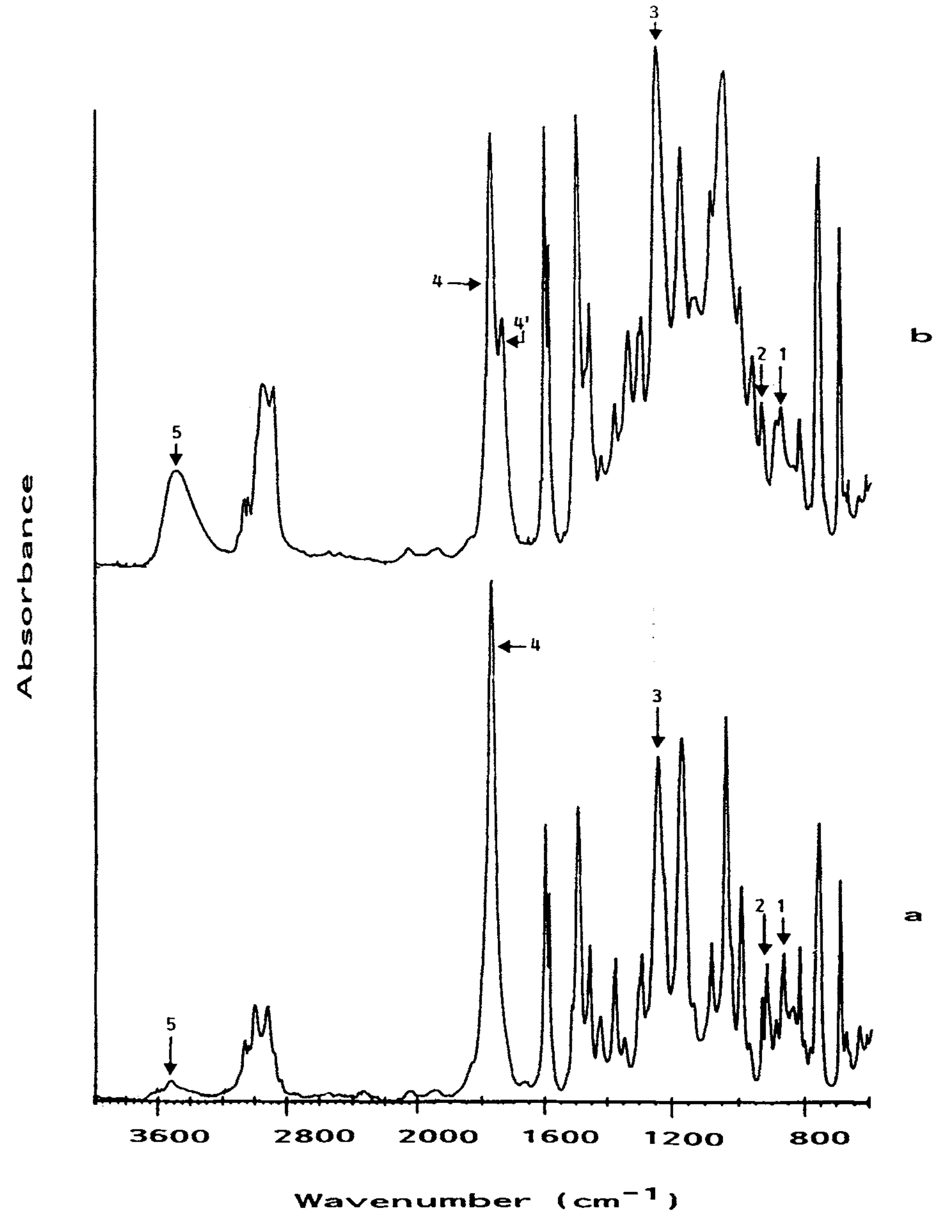


Figure 8 FT-IR spectra of the mixture 1 mol of γ-BL for 1 mol of PGE initiated by BF_3-4MA. a) initial mixture; b) after 4 h at 60°C.

achieved a scouting experiment. The aim of this experiment was to stop the reaction by addition of water and to check the behavior of the reactive mixture in the presence of water. Figure 9 illustrates the chromatograms obtained before (Fig. 9a) and after adding water (Fig. 9b). In Figure 9a, the PGE has completely reacted after 24 h of reaction. The presence of products c, d, e, the formed polymer, and the residual γ-BL can clearly be seen. After adding water (Fig. 9b) the chromatogram feature changes completely, product d decreases, leading to the increase in product e. This change means that product d is hydrolyzed into product e. Simultaneously, we can also note a small increase in product c.

Owing to this previous experiment, we had to take care during the fractionation to avoid the hydrolysis of product d and to succeed in its collection. So we have prepared different reactive mixtures to achieve the following fractionation procedures.

Table III Infrared Absorption Assignments for Several Characteristic Bands of the Reactive System (PGE : γ-BL, 1 : 1)

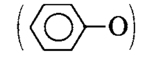
Band	Wave Number ν (cm^{-1})	Band Assignment
1	863	epoxy bending
2	915	epoxy bending
3	1220	aromatic CH bending aromatic ether (C—O) stretching
4	1771	carbonyl (C=O) stretching cyclic ester (γ-BL)
4'	1734	carbonyl (C=O) stretching aliphatic ester
5	3600–3200	free and linked hydroxy bending (OH)

Fractionations and Fraction Analyses

Different fractionations were carried out with the reactive mixture (1 mol of γ-BL for 1 mol of PGE initiated by BF_3-4MA) reacted 24 h in a glass tube at 60°C in an oven. The polymer, products c, d, and e were collected and analyzed by ^{1}H-NMR.

Separation of the formed polymer from the bulk

After precipitation of the bulk reactive mixture in water, an insoluble part was collected. This insoluble part was then washed with isobutanol, an insoluble part was still obtained. The latter is effectively the formed polymer (Fig. 10). Its SEC chromatogram given in Figure 11b, compared with Figure 11a of the whole initial mixture, shows the presence of polymer and the disappearance of molecules having low molar masses.

The infrared spectrum of the polymer is given in Figure 12. From the assignment of all characteristic bands summarized in Table III, we can confirm the presence of a copolymer between epoxy and γ-BL. Indeed, the band 1734 cm^{-1} is characteristic of a carbonyl (C=O) stretching in an aliphatic ester molecule. This band can only result from the ring opening reaction of the γ-BL. The band 1320 cm^{-1} is characteristic of an aromatic ether  stretching. This band belongs to the PGE structure. The large peak at 3500 cm^{-1} is due to hydroxyl chain ends and in part due also to the humidity in KBr disk. Furthermore, we cannot see the bands at 863, 915, and 1771 cm^{-1} which are attached to unreacted PGE and γ-BL, respectively.

The copolymer structure is more accurately confirmed by the ^{1}H-NMR spectrum in Figure 13. The peak assignment is reported in Table IV. It confirms the copolymer structure. The peak integration gives a calculated average molar ratio PGE:γ-BL equal to 3.25 : 1.

Separation of product c from the bulk

From the bulk reactive system the precipitation in water was realized. A soluble part (1) was obtained;

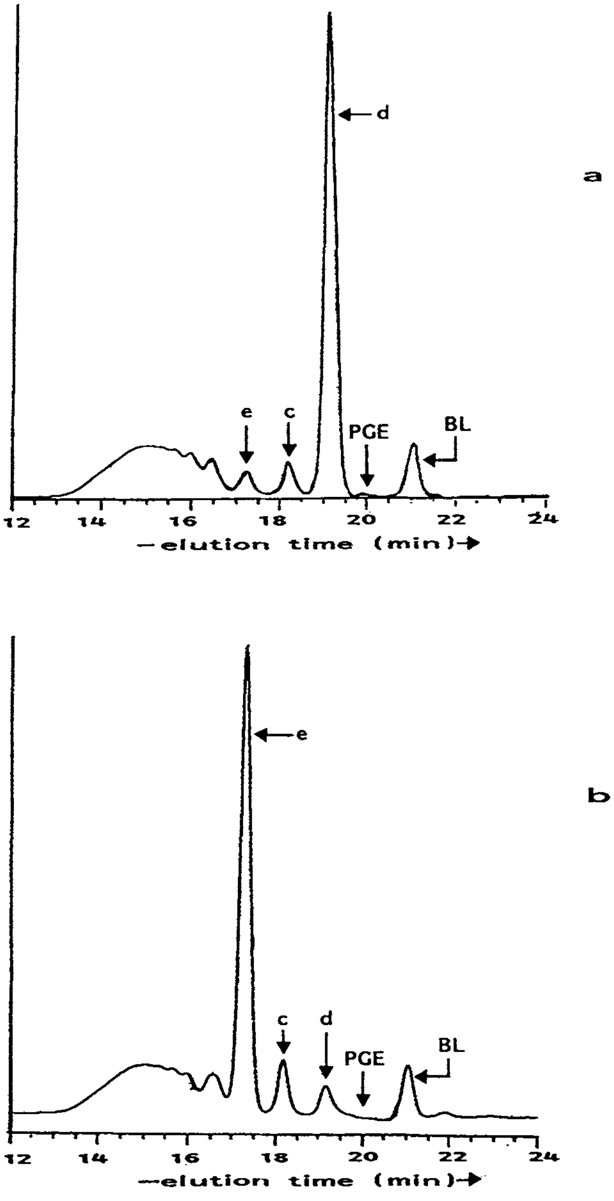


Figure 9 SEC chromatograms. a) before addition of water; b) after addition of water.

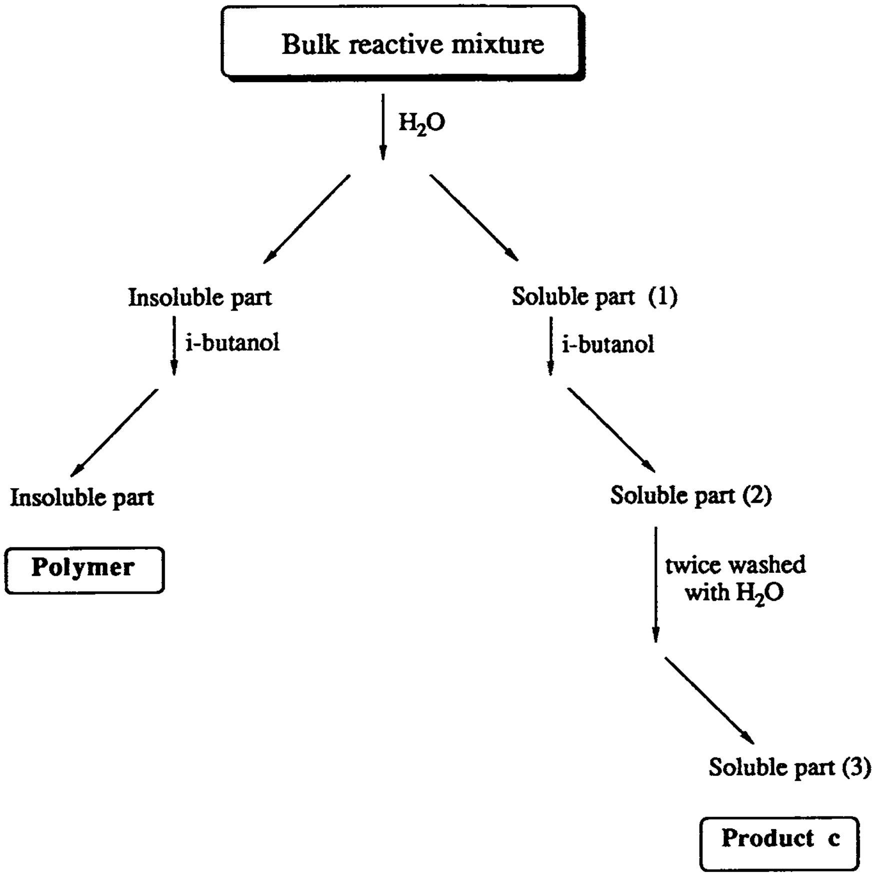
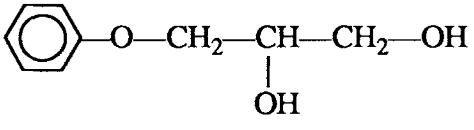


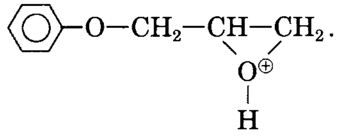
Figure 10 Scheme of fractionation routes to obtain the formed polymer and product c.

it was then washed with isobutanol. Another soluble part (2) was obtained and was washed twice with water and filtered. Finally, the third soluble part (3) was the product c (Fig. 10). In fact, its chromatogram (Fig. 14b) compared with the chromatogram of the initial reactive mixture (Fig. 14a), shows the fractionation efficiency and the purety of product c.

The ^{1}H-NMR spectrum of the product c (Fig. 15, Table V) shows that its structure is the following:



The confirmation of the structure of product c corresponds with its characterization reported in our earlier article[2] (Part II). Indeed, product c was already seen in the reactive system, cationic polymerization of PGE initiated by BF_3-4MA. It results from the transfer reaction between water and a first active molecule of PGE initiated by BF_3-4MA,



Separation of product d

To avoid the unwanted hydrolysis of product d, the precipitation of the bulk mixture was achieved in petroleum ether. The soluble part (1) obtained was then washed twice with a mixture of petroleum ether: i-butanol (95 : 5 by volume). Owing to these purifications, another soluble part (2) was obtained and it was still washed twice with petroleum ether and filtered. The final soluble part (3) gives product d (Fig. 16). The chromatograms in Figure 17 confirm the efficiency of this fractionation.

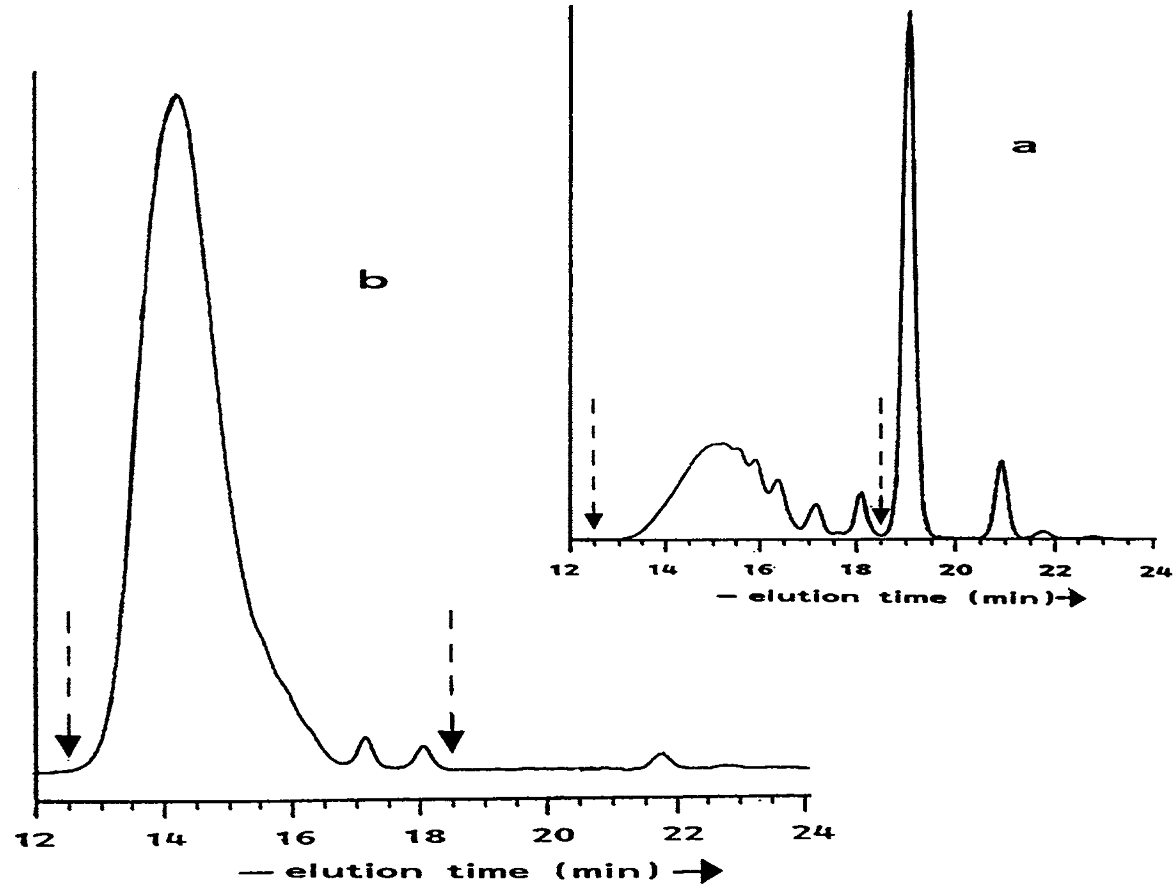
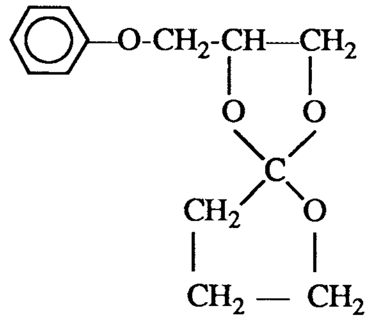


Figure 11 SEC chromatograms. a) initial mixture; b) polymer obtained after precipitation in H_2O, and then in i-butanol.

The ^{1}H-NMR spectrum of product d is shown in Figure 18. It suggests that its structure is the following cyclic molecule.



The peak assignment attached to this structure is reported in Table VI.

This structure is the expected spiroorthoester (2-phenoxymethyl-1,4,6-trioxaspiro [4,4] nonane) also cited in the literature[12–21] as the intermediate species in the cationic polymerization between γ-BL and PGE initiated by the BF_3-etherate. The spiroorthoester has a hygroscopic character and is highly sensible to the hydrolysis. So, owing to this sensitivity, we can note on the ^{1}H-NMR spectrum in Figure 18, traces of hydrolyzed product d (product e) corresponding to the small arising peaks at around 5.2, 3.5, and 2.9 ppm. The former is attached to —CH(PGE) and the latter are attached to —OH (PGE, γ-BL) resulting in ring-opening hydrolysis of the spiroorthoester.

Discussion on the Mechanism

From the results obtained and from our earlier published work,[1,2] we are able to propose an accurate cationic polymerization mechanism of PGE initiated by BF_3-4MA in the presence of γ-BL according to Scheme 1.

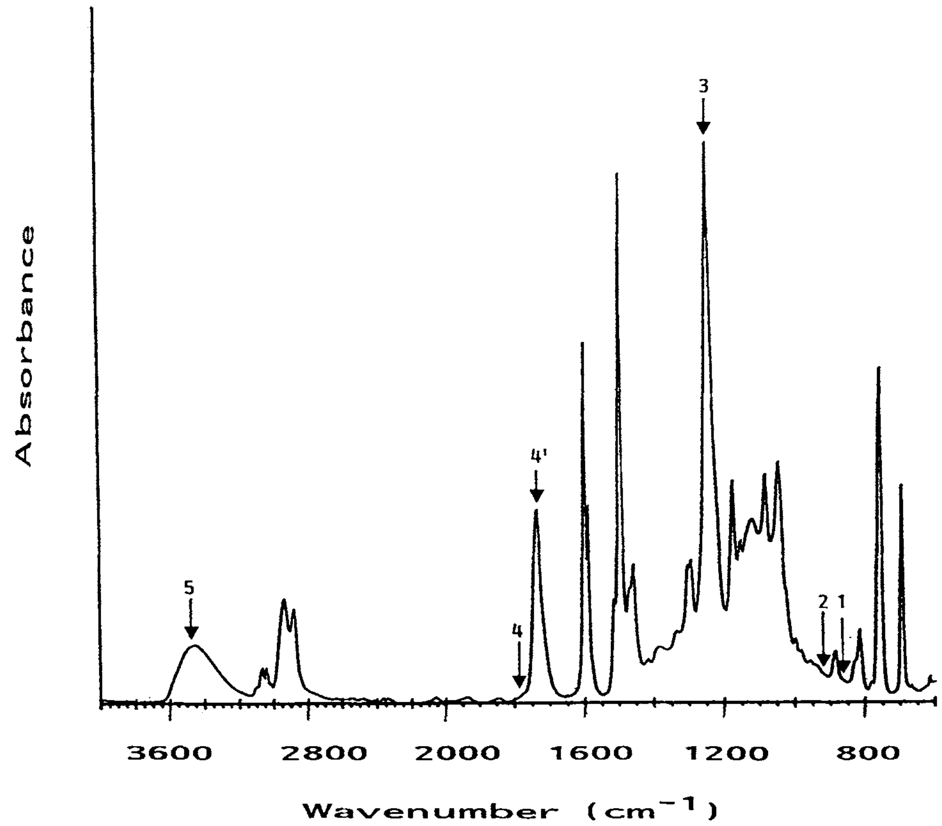


Figure 12 FT-IR spectrum of the polymer obtained after precipitation of the initial reactive mixture in H_2O and then in i-butanol.

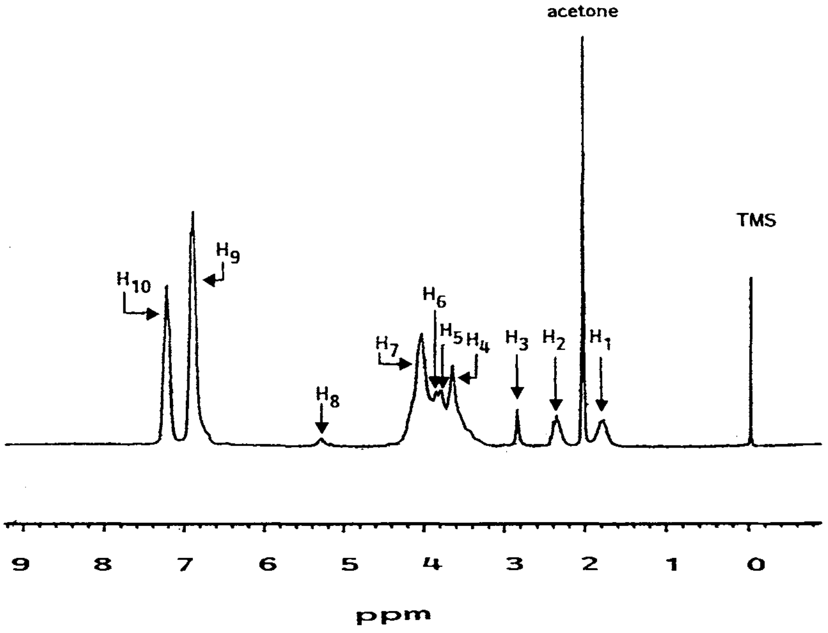
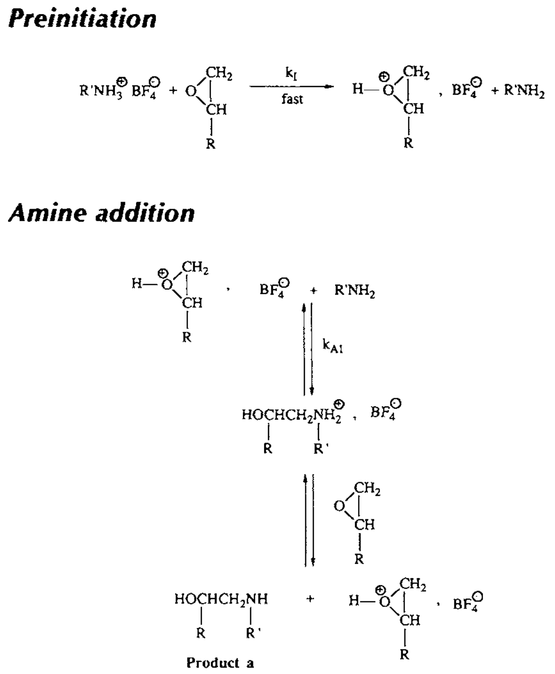


Figure 13 ^1H-NMR spectrum of the copolymer PGE/γ-BL.

Table IV ^{1}H-NMR Peak Assignment of the Formed Polymer

Proton	Chemical Shift δ (ppm)	Peak Assignment
H_1	1.76	CH_2 (γ-BL)
H_2	2.35	CH_2 (γ-BL)
H_3	2.83	OH (end chain)
H_4 H_5 H_6 H_7	3.63 3.78 4.02	OH (end chain) CH_2 (PGE) CH_2 (PGE) CH (PGE) CH_2 (γ-BL)
H_8	5.29	CH (PGE)
H_9	6.86	CH ring (PGE)
H_{10}	7.21	CH ring (PGE)

Analysis was performed in acetone-d_6.



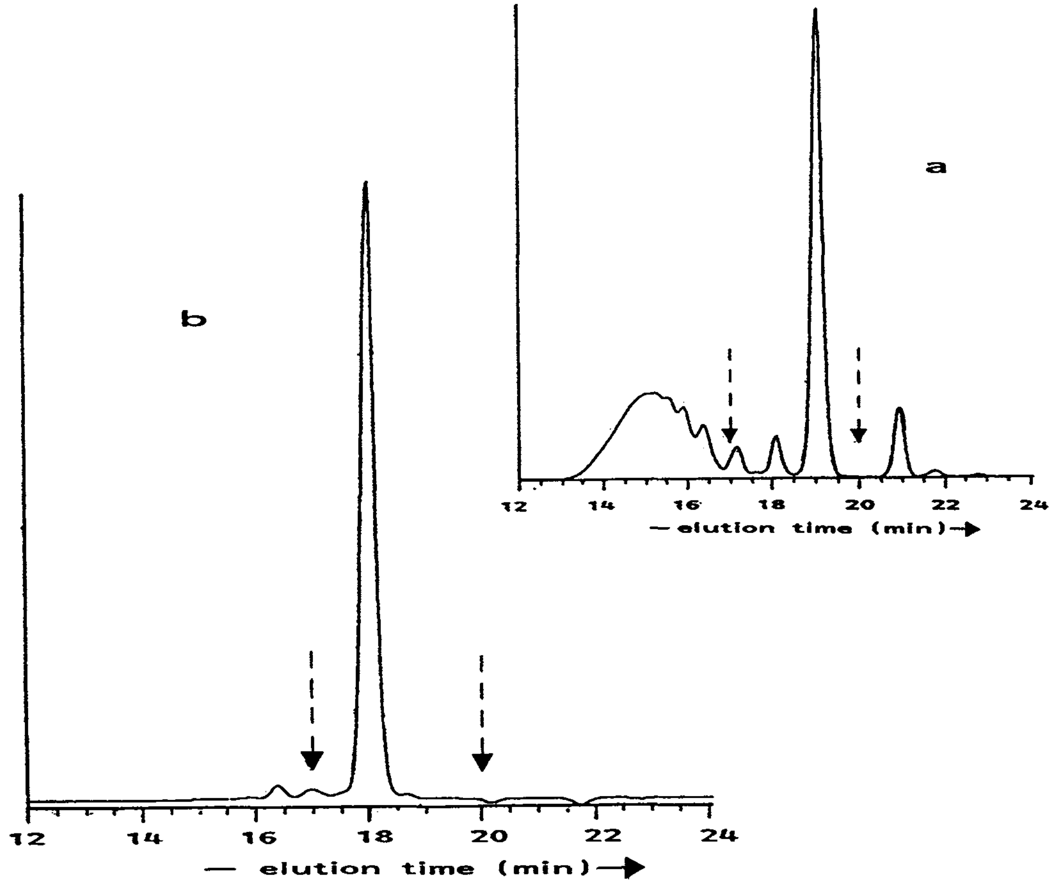


Figure 14 SEC chromatograms. a) the whole initial mixture; b) after fractionation, product c.

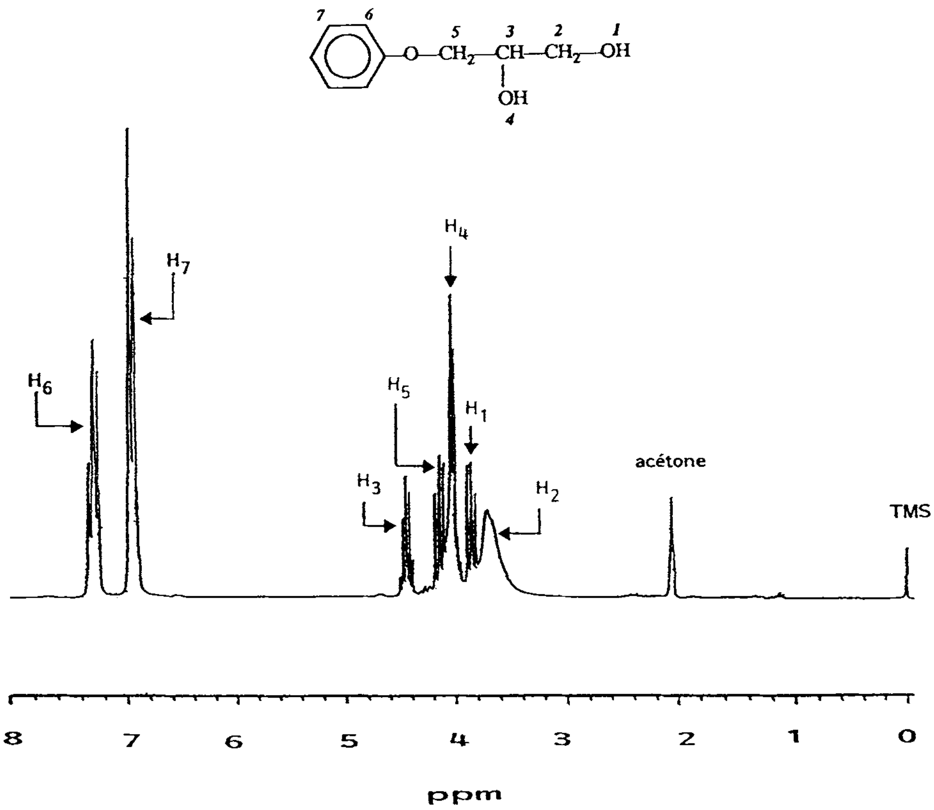
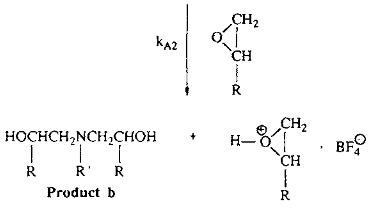
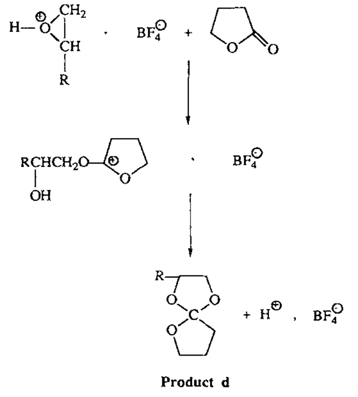


Figure 15 ^{1}H-NMR spectrum of product c.

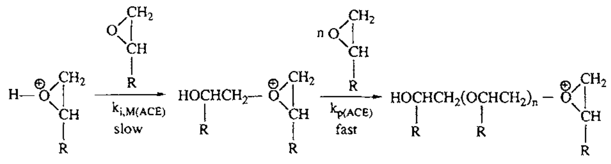


Spiroorthoester formation

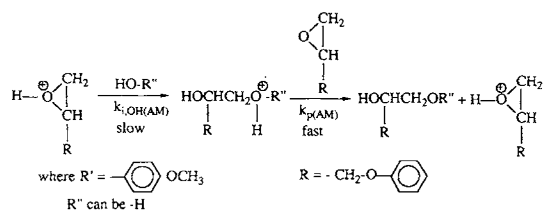


Propagation

Activated Chain End Mechanism (ACE).



Activated Monomer Mechanism (AM).



Scheme 1 Mechanism of initiation and propagation.

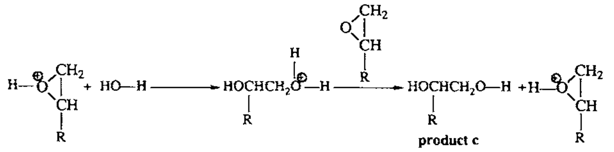
In the presence of water the Activated Monomer mechanism (AM) is equivalent to a transfer reaction to the monomer. The transfer reaction to the first

Table V ^{1}**H-NMR Peak Assignment Corresponding to Product c**

nProton	Chemical Shift δ (ppm)	Peak Assignment
H_1	3.84	OH
H_2	3.71	OH
H_3	4.44	CH
H_4	4.02	OH
H_5	4.13	CH_2
H_6	7.28	CH ring
H_7	6.94	CH ring

Analysis was performed in acetone-d_6.

active molecule of PGE leads to the product c (Scheme 2).



Scheme 2 Product c formation.

Moreover, in the presence of water, the spiroorthoester (product d) can be hydrolyzed into product e.

During the polymerization of the spiroorthoester (product d), we have assumed a double ring-opening reaction. All of the authors[16–21] who have reported the acid initiated cationic copolymerization of the spiroorthoester structures that cannot homopolymerize, have also proposed a double ring-opening process. Nevertheless, some of them[17,19,20] have suggested two competitive copolymerization mechanisms that depend on the temperature of the reaction. Indeed, they have suggested that cationic polymerization at low temperature affords single ring-opened poly(cyclic orthoester), while tandem double ring-opening polymerization takes place at a temperature above 40°C to give poly(ether-ester). Furthermore, they have observed the formation of poly(ether-ester) from poly(cyclic ortho-ester) occurring by intermolecular isomerization at 60°C. Owing to these results, the above authors[19,20] have attributed the typical aliphatic carbonyl absorption (1736 cm^{-1}) in the case of a polymer obtained above 40°C, to the carbonyl of the poly(ether-ester)

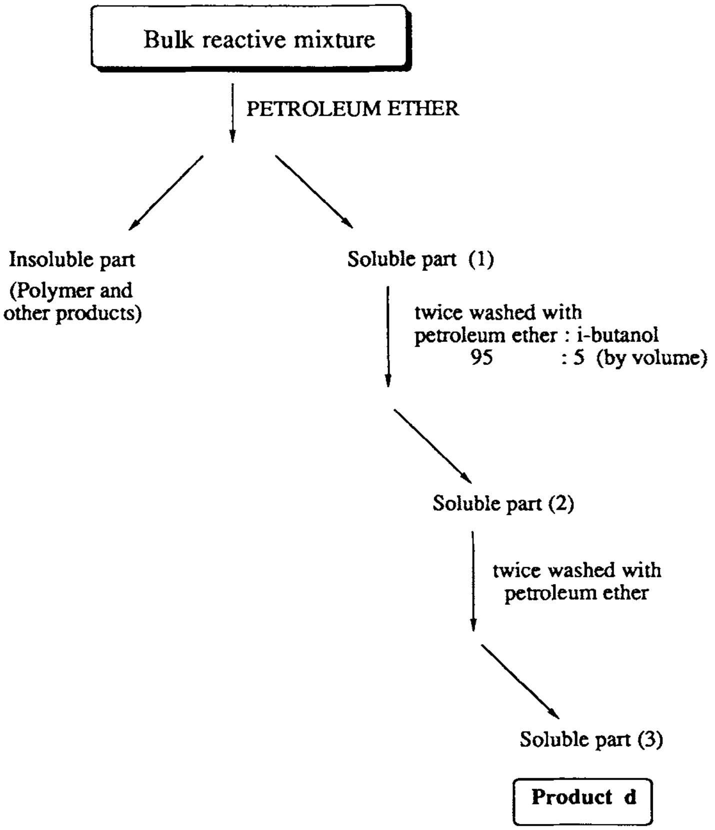


Figure 16 Scheme of fractionation routes to obtain product d.

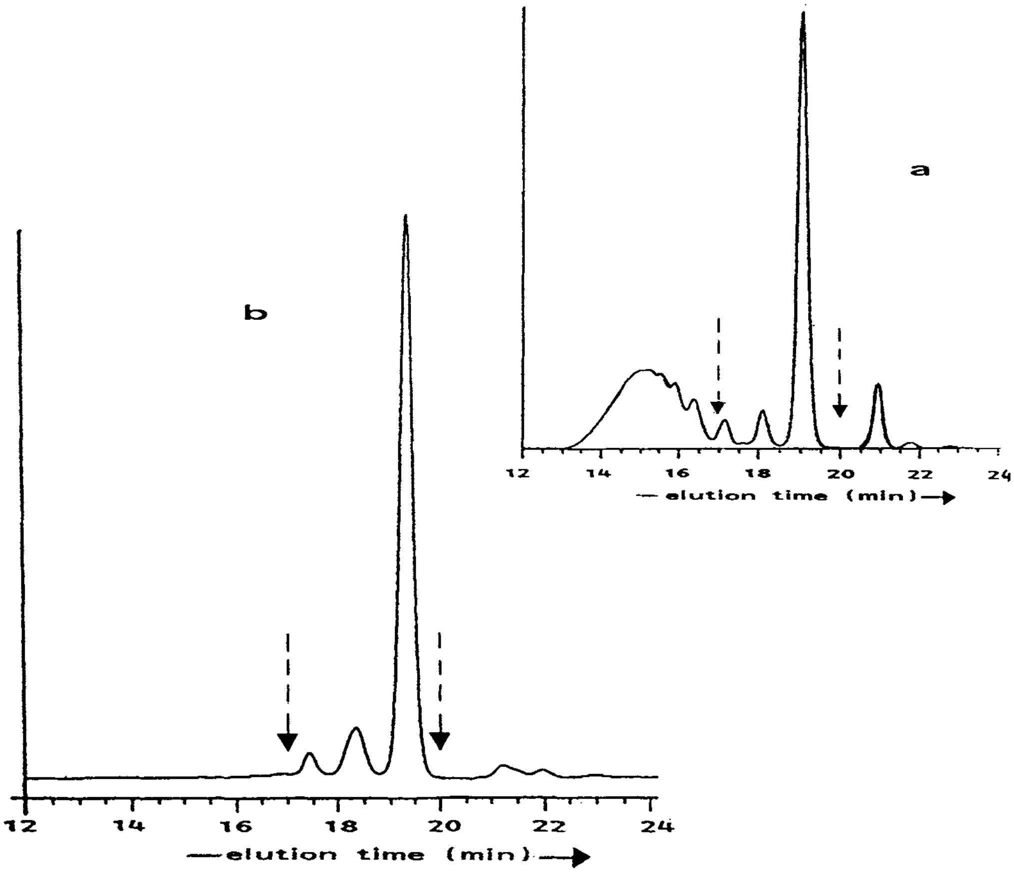


Figure 17 SEC chromatograms. a) the whole initial mixture; b) after fractionation, product d.

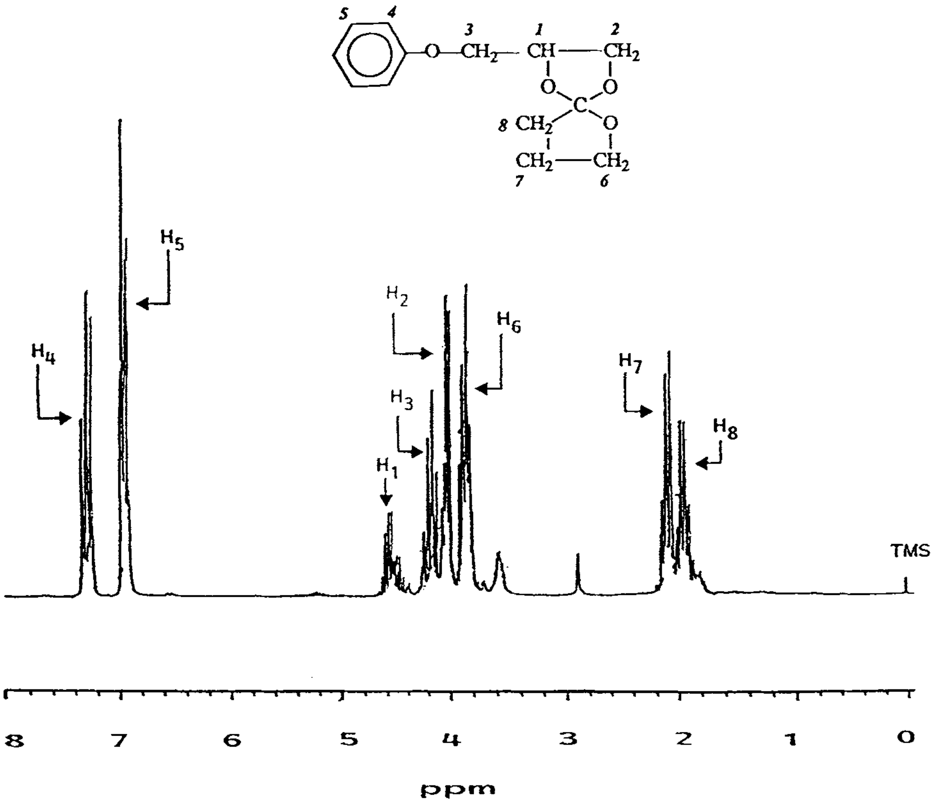
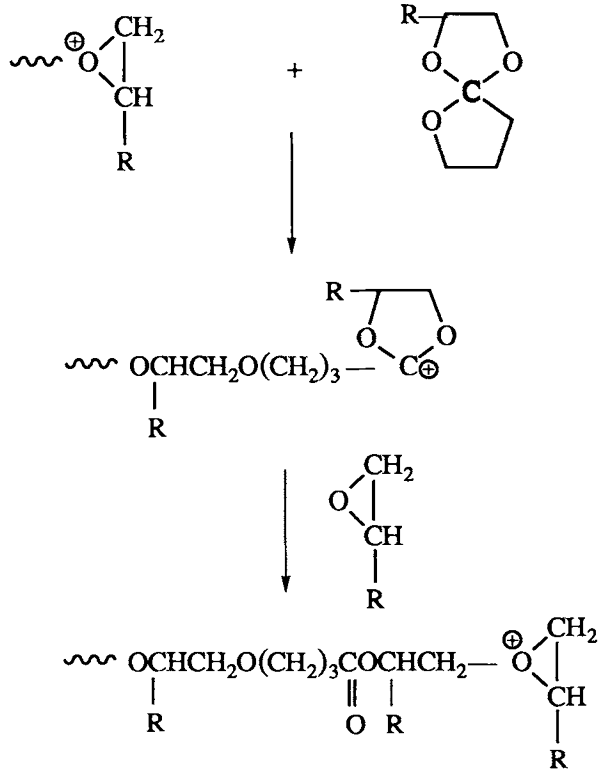


Figure 18 ^{1}H-NMR spectrum of product d.

structure. These results fit well with the rising peak at 1734 cm^{-1} in the FT-IR spectrum recorded after 4 h of reaction (Fig. 8). This rising peak confirms that the spiroorthoester structure obtained from the cationic copolymerization between the γ-butyrolactone (γ-BL) and an epoxy monomer (PGE) is able to copolymerize.

Thus, we can propose a copolymerization mechanism of the epoxy with the spiroorthoester, according to the literature[20] (Scheme 3).



Scheme 3 Copolymerization of the spiroorthoester with epoxy.

The mechanism proposed would not be complete if we did not mention transfer and termination reactions generally occurring in cationic polymerization and occurring with successive initiation and propagation steps. According to the literature,[27,28] these side reactions are inherent features of the cationic polymerization of heterocyclic monomers, and cannot be completely avoided. Transfer and termination reactions both occur by intra- or intermolecular nucleophilic attack on the exocyclic carbon atom of the cyclic tertiary oxonium ion in the growing chain of the polymer. Whichever transfer or termination reactions, they lead to either less reactive or nonreactive species or molecules.

Table VI ^{1}H-NMR Peak Assignment Corresponding to Product d

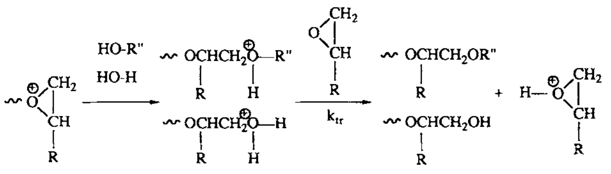
nProton	Chemical Shift δ (ppm)	Peak Assignment
H_1	4.57	CH (PGE)
H_2	4.03	CH_2 (PGE)
H_3	4.16	CH_2 (PGE)
H_4	7.27	CH ring (PGE)
H_5	6.93	CH ring (PGE)
H_6	3.88	CH_2 (γ-BL)
H_7	2.06	CH_2 (γ-BL)
H_8	1.97	CH_2 (γ-BL)

Analysis was performed in acetone-d_6.

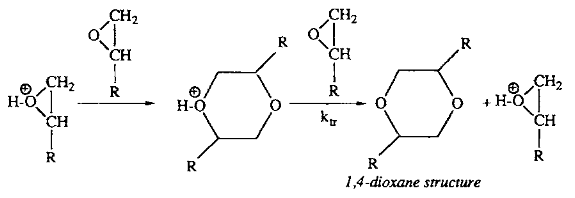
Indeed, the intermolecular chain transfer (termination) to polymer leads from reactive tertiary cyclic oxonium ion to less reactive "dormant species," which is a linear tertiary oxonium ion (Scheme 4).[27] Furthermore the intramolecular chain transfer to polymer leads from reactive tertiary cyclic oxonium ion to nonreactive cycles or macrocycles. These nonreactive cycles formed have a dioxane structure of which the smallest one is the 1,4-dioxane.

Transfer Reactions

Intermolecular.

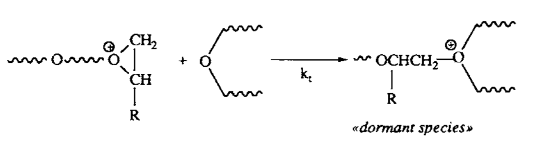


Intramolecular.

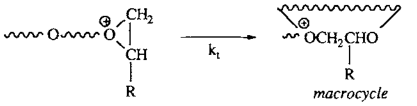


Termination-irreversible transfer to polymer

Intermolecular.



Intramolecular.



Scheme 4 Transfer and termination reactions.

Unfortunately, we have not checked the appearance of nonreactive dioxane ring structures, macrocycles, and tertiary linear oxonium ion ("dormant species") which are mentioned in the literature.[28]

So, according to the literature,[29] where the cationic polymerization of epichlorhydrin achieved in the presence of diol, initiated by Lewis or Bronsted acid, has led only to linear products at an early stage of reaction ($\overline{DP_n} \leq 5$). In the presence of large amounts of γ-BL, we can suppose we will obtain a small amount of cyclic oligomers. Indeed, we have seen in our previous work[2] that the cationic polymerization of PGE initiated by BF_3-4MA occurs initially with the ACE mechanism with terminations by cyclization reactions. Then the AM mechanism is favored and occurs from hydroxyl functions that are formed during the initiation of growing chains of polymer. In the presence of γ-BL, we have seen that the general mechanism of copolymerization can lead to an increase in hydroxyl functions because of the easy hydrolysis of the spiroorthoester. Furthermore, from these results, the termination reaction may be also attributed to the formation of less reactive tertiary linear oxonium ions ("dormant species").

Influence of Low Concentration of γ-BL in Epoxy Polymerization

In the last part of this article we have followed the PGE polymerization initiated by a constant amount of BF_3-4MA in the presence of a low concentration of γ-BL.

The aim of these experiments is to evaluate the real effect of the γ-BL as solvent of BF_3-amine complexes. Previous results[22] have shown that the best thermal properties of the final networks have been obtained with the following molar ratio of reactants in the reactive system: BF_3-amine/γ-BL/epoxy function = $1.8 \times 10^{-2}/3.3 \times 10^{-2}/1$. This formulation will be our standard condition in the study of the network formation from a diepoxy prepolymer. Thus, the effect of γ-BL, with a concentration about 3.3×10^{-2} mol per epoxy function (or mol of PGE) was accurately studied. Two kinetic studies of the PGE polymerization with 2×10^{-2} and 5.9×10^{-2}

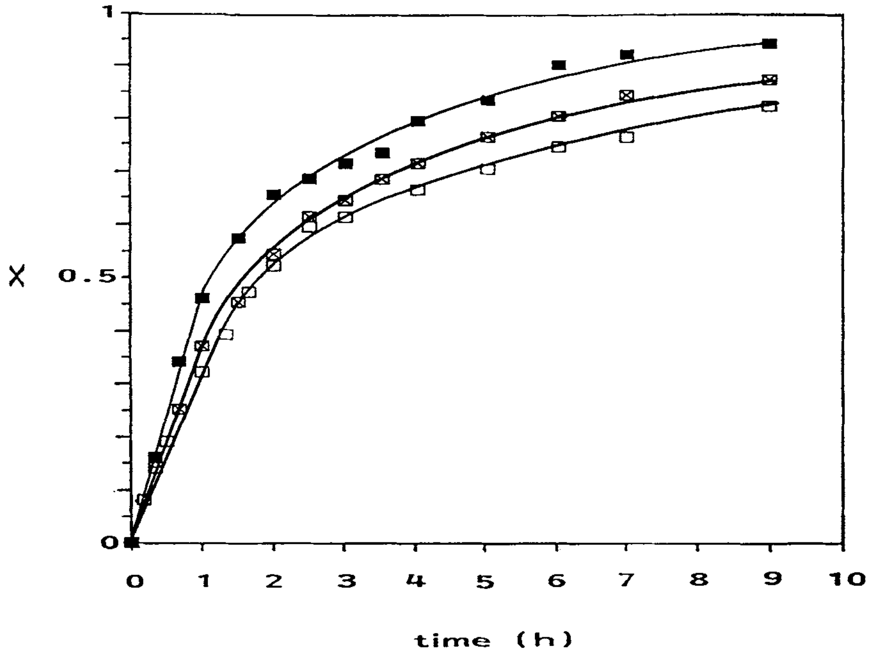


Figure 19 Conversion of PGE vs. time at 60°C with $[BF_3\text{-}4MA] = 1.8 \times 10^{-2}$ mol per mol of PGE. (■) 5.9×10^{-2} mol of γ-BL/mol of PGE; (☒) 2×10^{-2} mol of γ-BL/mol of PGE; (☐) without γ-BL.

Table VII Results of the PGE Polymerization in the Presence of a Low Concentration of γ-BL

[γ-BL] mol/mol of PGE	$R_{PGE} = \frac{-d(PGE)}{dt}$ mol·kg^{-1}·min^{-1}	$\overline{M_n}$[a] t = 540 min	$\overline{M_w}$[a] t = 540 min	I_p
0	3.91×10^{-2}	1190	1640	1.40
2×10^{-2}	4.02×10^{-2}	1094	1789	1.63
5.9×10^{-2}	5.20×10^{-2}	1145	2027	1.77

Concentration of BF_3-4MA was 1.8×10^{-2} mol/mol of PGE. Data obtianed without γ-BL is reported as reference.

[a] $\overline{M_n}$ and $\overline{M_w}$ were calculated only from the large peak of the formed polymer at 540 min of reaction time.

mol of γ-BL per mol of PGE were carried out. In these reactions, the concentration of BF_3-4MA was kept constant and equal to 1.8×10^{-2} mol per mol of PGE.

The PGE conversion vs. time for these kinetics achieved at 60°C is reported in Figure 19. Furthermore, we have plotted the PGE conversion attached to the system without γ-BL in the same figure, for comparison. The conversion of PGE increases more rapidly in the presence of γ-BL. This increase in PGE conversion must be attached to the formation of the spiroorthoester, as we have explained previously. The rates of PGE conversion, calculated from the slope in the first part of the curves, PGE conversion vs. time, are reported in Table VII. So we can note an increase in the rate of PGE disappearance with the increase in the amount of γ-BL, but at the same time, the number-average molecular weight obtained after 540 min of reaction decreases. Indeed, if we are sure that the γ-BL is able to copolymerize with an epoxy monomer through the formation of a spiroorthoester which, in turn, copolymerizes with the active growing chains by ring-opening reactions. The increase in the amount of γ-BL in the reaction mixture (Scheme 3) leads to a polymer with low molar mass.

CONCLUSION

In the cationic polymerization of epoxy initiated by BF_3-amine complexes, the use of γ-BL as solvent for BF_3-amines allows the suppression of the latency period observed when the PEO was used as solvent. The PGE polymerization shows a slight decrease in molar mass of the obtained polymer. However, the epoxy conversion is increased with increasing concentration of γ-BL. The latter does not homopolymerize but reacts with epoxy groups and leads to a spiroorthoester that is sensitive to the hydrolysis. Moreover, the spiroorthoester can copolymerize with epoxy groups giving the ether–ester polymer.

From the all results obtained, a mechanism of the formation of the spiroorthoester and its copolymerization with epoxy was proposed. Moreover, a general mechanism of the cationic polymerization of PGE in the presence of γ-BL was described.

The authors are gratefully indebted to Koninklijke/Shell-Laboratorium, Amsterdam, for the financial support of this research.

REFERENCES

1. P. Chabanne, L. Tighzert, J. P. Pascault, and B. Bonnetôt, *J. Appl. Polym. Sci.*, **49**, 685 (1993).
2. P. Chabanne, L. Tighzert, and J. P. Pascault, *J. Appl. Polym. Sci.*, **53**, 769 (1994).
3. N. Bouillon, J. P. Pascault, and L. Tighzert, *Makromol. Chem.*, **191**, 1403 (1990).
4. N. Bouillon, J. P. Pascault, and L. Tighzert, *Makromol. Chem.*, **191**, 1417 (1990).
5. N. Bouillon, J. P. Pascault, and L. Tighzert, *Makromol. Chem.*, **191**, 1435 (1990).
6. Chimie Organique 1-Généralités—Série Aliphatique, Biomolécules, M. Miocque, C. Combet Farroux, and H. Moskowitz, Masson, Paris, 1990, p. 223.
7. H. Cherdron, H. Oshe, and F. Korte, *Makromol. Chem.*, **56**, 179 (1962).
8. K. Ito, T. Inoue, and Y. Yamashita, *Makromol. Chem.*, **139**, 153 (1970).
9. H. Sekiguchi and C. Clarisse, *Makromol. Chem.*, **177**, 591 (1976).
10. A. Hamitou, T. Ouhaki, R. Jérome, and P. Teyssié, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 865 (1977).
11. B. V. Lebedev and A. A. Evstropov, *Soklady Phys. Chem.*, **263**, 334 (1982).

12. Y. Yamashita, T. Tsuda, M. Okada, and S. Iwatsuki, *J. Polym. Sci., Part A1,* **4,** 2121 (1966).
13. W. J. Bailley and R. L. Sun, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.,* **13**(1), 281 (1972).
14. W. J. Bailley, *J. Elastoplastics,* **5,** 142 (1973).
15. W. J. Bailley, *J. Macromol. Sci., Chem.,* **A9**(5), 819 (1975).
16. W. J. Bailley, R. L. Sun, H. Katsuki, T. Sægusa, and E. J. Gœthals, *ACS Symposium Series* **59,** 38 (1977).
17. K. Matyjaszewiski, *J. Polym. Sci., Polym. Chem. Ed.,* **22,** 29 (1984).
18. E. J. Gœthals, *Makromol. Chem., Macromol. Symp.,* **42/43,** 51 (1991).
19. S. Chikaoka, T. Takata, and T. Endo, *Macromolecules,* **24,** 25, 1991.
20. S. Chikaoka, T. Takata, and T. Endo, *Macromolecules,* **25,** 2, 1992.
21. R. F. Brady Jr., *J. Macromol. Sci., Rev. Macromol. Chem. Phys.,* **C32**(2), 135 (1992).
22. P. Chabanne, J. P. Pascault, and L. Tighzert, French Pat. 90.06608, May (1990).
23. S. Mortimer, A. J. Ryan, and J. L. Stanford, Congress *Fiber-Reinforced Composites '92,* UK, March (1992).
24. P. Novak and M. Saure, *Kunstsoffe,* **54, 9,** 557 (1964).
25. M. Tackie, G. C. Martin, *J. Appl. Polym. Sci.,* **48,** 793 (1993).
26. M. Tackie and J. C. Martin, *J. Appl. Polym. Sci.,* **48,** 793 (1993).
27. S. Penczek, P. Kubisa, and K. Matyjaszewski, *Adv. Polym. Sci.,* **37,** 60–100 (1980).
28. S. Penczek, P. Kubisa, and R. Szymanski, *Makromol. Chem., Macromol. Symp.,* **3,** 203 (1986).
29. T. Biedron, P. Kubisa, and S. Penczek, *J. Polym. Sci., Polym. Chem. Ed.,* **29,** 619 (1991).

Received June 10, 1993
Accepted February 7, 1994