Epoxy Polymerization Initiated by BF₃–Amine Complexes. I. Synthesis and Characterization of BF₃–Amine Complexes and BF₃–Amine Complexes Dissolved in γ-Butyrolactone

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SYNOPSIS

With the aim of identifying the species responsible for initiating epoxy homopolymerization, several BF₃–amine complexes were synthesized. Their characterization was accomplished by several spectroscopic techniques, notably by ¹¹B-NMR. In these polymerizations, the active species appears to be the R—NH₃⁺BF₄⁻ salt and not the BF₃–amine complex. The interactions between BF₃–amine complexes and the γ-butyrolactone were also studied by FTIR. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Boron trifluoride forms many complexes with Lewis bases. The stability of these complexes depends on the chemical nature of the ligand, the presence of polar substituents in the donor molecule, and steric effects. Primary and secondary aliphatic or aromatic amines readily form 1 : 1 complexes with boron trifluoride.[1] Some of them are widely used in the polymerization of vinyl or oxirane monomers. However, the mechanism for the initiation of this polymerization has proved difficult to determine.

Although a large number of boron trifluoride complexes has been described in the literature,[2] only the boron trifluoride monoethylamine (BF₃–MEA) complex has found widespread use as a latent "catalyst" for chain polymerization of epoxides and as an accelerator for the addition of aromatic amines to epoxide groups. However, this complex has a low reactivity. For example, the chain polymerization of the glycidyl ether of bisphenol A (DGEBA) begins only above 100°C, and the glass transition temperature, T_g, of the final network is low: 110°C.[3] In-

dustrial processes for liquid reactive systems such as epoxy resins (e.g., RIM, RTM, pultrusion, and prepregging) require increasingly shorter polymerization times and a range of polymerization temperatures from 90 to 120°C. A recent study[4] of different BF₃–amine complexes, derived from aromatic or aliphatic primary amines for initiating epoxy homopolymerizations, has shown that their reactivity depends on the basicity of the amine. With certain complexes, the reaction begins at room temperature; for others, it is in the range of 30–100°C. As with BF₃–MEA, these complexes are solid at room temperature. Thus, their use gives some problems as their solubility in epoxy prepolymers is low and homogeneous mixtures are difficult to obtain.

To overcome these difficulties, a solvent must be used. Liquid poly(ethylene oxide) (PEO) of low molecular weight is often employed and, indeed, some of BF₃–amine complexes dissolved in PEO are commercially available.

Nevertheless, the presence of PEO leads to other problems such as transfer reactions that cause an induction period and a decrease in the glass transition temperature of the final networks. The detailed mechanism of the polymerization of mono- and diepoxide initiated by BF₃–amine complexes predissolved in PEO and the thermal, mechanical

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properties of formed networks have previously been described.[4-6]

With the aim of suppressing the induction period, increasing the reactivity, and improving the thermal properties of the final network, we have replaced the liquid PEO by a lactone.[7] The γ-butyrolactone (γ-BL) has been chosen because of its opening by cationic initiators such as BF_3–amine complexes that are used for epoxides. Moreover, γ-BL cannot homopolymerize.[8-12] Thus, in the presence of epoxy monomers, we expect to have a copolymerization.[9-11,13]

The aim of this work was to study the structure of the BF_3–amine and the interactions between BF_3–amine and γ-BL. The reaction mechanism with epoxy monomers will be described in future publications.

EXPERIMENTAL

Classical Syntheses of Complexes in CH_2Cl_2

The BF_3–amine complexes have been synthesized by the interchange reaction between BF_3–etherate and amine in dichloromethane (CH_2Cl_2) according to a method proposed in the literature.[14,15] The reaction was carried out at room temperature and under nitrogen sweeping:

$$RNH_2 + BF_3 : O(C_2H_5)_2 \xrightarrow{CH_2Cl_2}$$

$$BF_3 : H_2NR + (C_2H_5)_2O$$
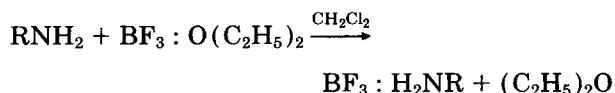
The precipitated complex was filtered, repeatedly washed with CH_2Cl_2, and dried under vacuum at 80°C for 24 h. Amines and BF_3–etherate were purchased from Aldrich.
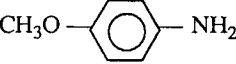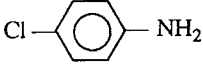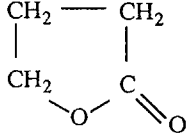
Although various BF_3–amine complexes could be used, this report will deal mainly with the BF_3–4-methoxyaniline (BF_3–4MA) complex, since its relatively low reactivity allows sufficient time to study the epoxy polymerization kinetics. For comparison, results obtained with the two other complexes, BF_3–monoethylamine (BF_3–MEA) and BF_3–4-chloroaniline (BF_3–4CA), are also presented. The characteristics of these amines are given in Table I.

Syntheses of Complexes in the Absence of Solvents

For comparison with the complexes synthesized in CH_2Cl_2, some syntheses were carried out in the absence of solvent. All manipulations were performed under argon atmosphere in a glove box (vacuum atmosphere type). The gas was continuously dried by bubbling through a sodium amalgam trap. The reagents were purified as follows. 4-Methoxyaniline (4MA) (Aldrich) was sublimated under high vacuum, monoethylamine (MEA) (Carlo Erba) was distilled at low temperature, and BF_3–etherate [$BF_3(Et_2O)$] (Aldrich) was distilled under vacuum before use.

The BF_3–4MA complex was prepared by direct addition of 4MA to an excess of pure $BF_3(Et_2O)$.

Table I Products from Aldrich Used in This Work

Name	Formula	pK_a[a]
(Mono)ethylamine (MEA)	$CH_3 — CH_2 — NH_2$	10.8
4-Methoxyaniline (4MA)	$CH_3O —\langle\bigcirc\rangle— NH_2$	4.52
4-Chloroaniline (4CA)	$Cl —\langle\bigcirc\rangle— NH_2$	3.98
Poly(ethylene oxide) (PEO) $\overline{M_n} = 400$	$HO —(CH_2 — CH_2 — O —)_nH$	
γ-Butyrolactone (γ-BL)		

[a] cf. Ref. 16.

The excess of $BF_3(Et_2O)$ was removed from the crude product under high vacuum. Dry white BF_3–4MA complex was obtained with a quantitative yield. A similar procedure was used to obtain BF_3–MEA.

Solvents for BF₃–Amine Complexes

Poly(ethylene oxide) of number-average molecular weight 400 (PEO 400) and γ-butyrolactone (γ-BL) were used. Moreover, in this study, the γ-BL was dried on $MgSO_4$ and distilled under vacuum before use (Table I).

Techniques

The ^1H- and ^{19}F-NMR spectra were recorded with a Bruker AC200 at 200 and 188 MHz, respectively. In every case, deuterated solvents were used and the field locked on the deuterium signal. The ^1H-NMR chemical shifts are reported with tetramethylsilane (TMS) as the reference (0 ppm). For ^{19}F-NMR, $CFCl_3$ was used as the reference. The ^{11}B-NMR spectra were performed with a Bruker AM300 at 96.26 MHz and were externally referenced to $BF_3(Et_2O)$ (positive values downfield).

Fourier transform infrared (FTIR) studies were performed with a Nicolet MX-1 equipped with a thermostatted sample holder to allow isothermal analysis. Products were placed between two KBr disks or two KBr pellets. The samples were then secured in the sample holder that had been preheated to the desired temperature.

The differential scanning calorimetry (DSC) thermograms were obtained under argon in a Mettler TA3000 apparatus. Samples of 10–20 mg were tested in crimped aluminum pans. Indium was used as the standard. The heating rate was 7.5 K min^{-1}.

RESULTS AND DISCUSSION

Characterization of BF₃–Amine Complexes Synthesized in CH₂Cl₂

The ^1H-NMR spectra of 4MA and BF_3–4MA in d_6-acetone are given in Figure 1(A) and (B), respectively. All resonance peaks are shifted downfield due to the complexation. Of note is that the NH_2 peak is not seen in Figure 1(B). The chemical shifts are reported in Table II.

In a similar manner, changes due to the complexation were observed in the IR spectra of 4MA and BF_3–4MA [Fig. 2(A) and (B)]. According to the literature,[16–19] an ionic form, attributed to the ammonium salt, $-NH_3^\oplus$, is observed at 1550 and 2600 cm^{-1}.

These results present us with some questions: How is the structure of the synthesized complexes? What is the proportion of the salt, $-NH_3^\oplus$, and how many chemical species are present? Hence, the complexes were analyzed in two solvents of different polarities such as benzene and acetone. We expected to solubilize all chemical species, polar and nonpolar.

BF_3–MEA is the only complex synthesized from the primary amines that could be both dissolved in both polar and nonpolar solvents. However, the BF_3–MEA is only slightly soluble in benzene. The ^{11}B-NMR spectrum recorded in benzene [Fig. 3(A)] has only one quartet at -0.704 ppm due to the spin-spin coupling between ^{11}B–^{19}F. This quartet, $J_{(^{11}B-^{19}F)} = 14.5$ Hz, was attributed to the BF_3 form of the complex BF_3–MEA (neutral or molecular form), since other ionic forms would be insoluble in benzene.

The spectrum recorded in acetone [Fig. 3(B)] is completely different. It shows a solvent effect on the number of species and on their chemical shift. Very likely, these results were due to the presence of moisture in polar solvents. The quartet due to the BF_3 form [$J_{(^{11}B-^{19}F)} = 14.5$ Hz] is found at 0.220 ppm. The second quartet [$J_{(^{11}B-^{19}F)} = 17$ Hz] and the singlet at 0.956 and -0.532 ppm were attributed to the ionic forms $BF_3OH^\ominus$ and $BF_4^\ominus$, respectively. The $BF_4^\ominus$ ion appears as a pseudosinglet in this spectrum due to the small value of the ^{19}F—^{11}B coupling constant. In fact, in the literature,[20–23] the coupling constant $J_{(^{11}B-^{19}F)}$ of $NaBF_4$ is equal to 4.6 Hz.[21] Meanwhile, it is difficult to differentiate the BF_3 form the $BF_3OH^\ominus$ ionic form by only taking into account the value of the ^{11}B—^{19}F coupling constant. In fact, the values found in the literature[20–23] are rather different, depending on the complexing base (ligand) and the solvents used. For example, the coupling constants $J_{(^{11}B-^{19}F)}$ in BF_3–N(C_2H_5)$_3$, BF_3–N(CH_3)$_3$, BF_3–NH(CH_3)$_2$, BF_3–NH_2CH_3, and BF_3–NH_3 are 16.4, 13.8, 15.1, 16, and 13.9 Hz, respectively. They are consistent with our measured value of 14.5 Hz attributed to the BF_3 form. For $BF_3OH^\ominus$, very few results have been reported concerning only alkaline earth compounds studied in water. According to the results in the literature,[20–23] the $BF_3OH^\ominus$ anion resonance should appear at lowest field, then the molecular complex BF_3 resonance, and at highest field, the $BF_4^\ominus$ anion resonance. Thus, our conclusions involving the ^{11}B chemical shifts agree with the literature.

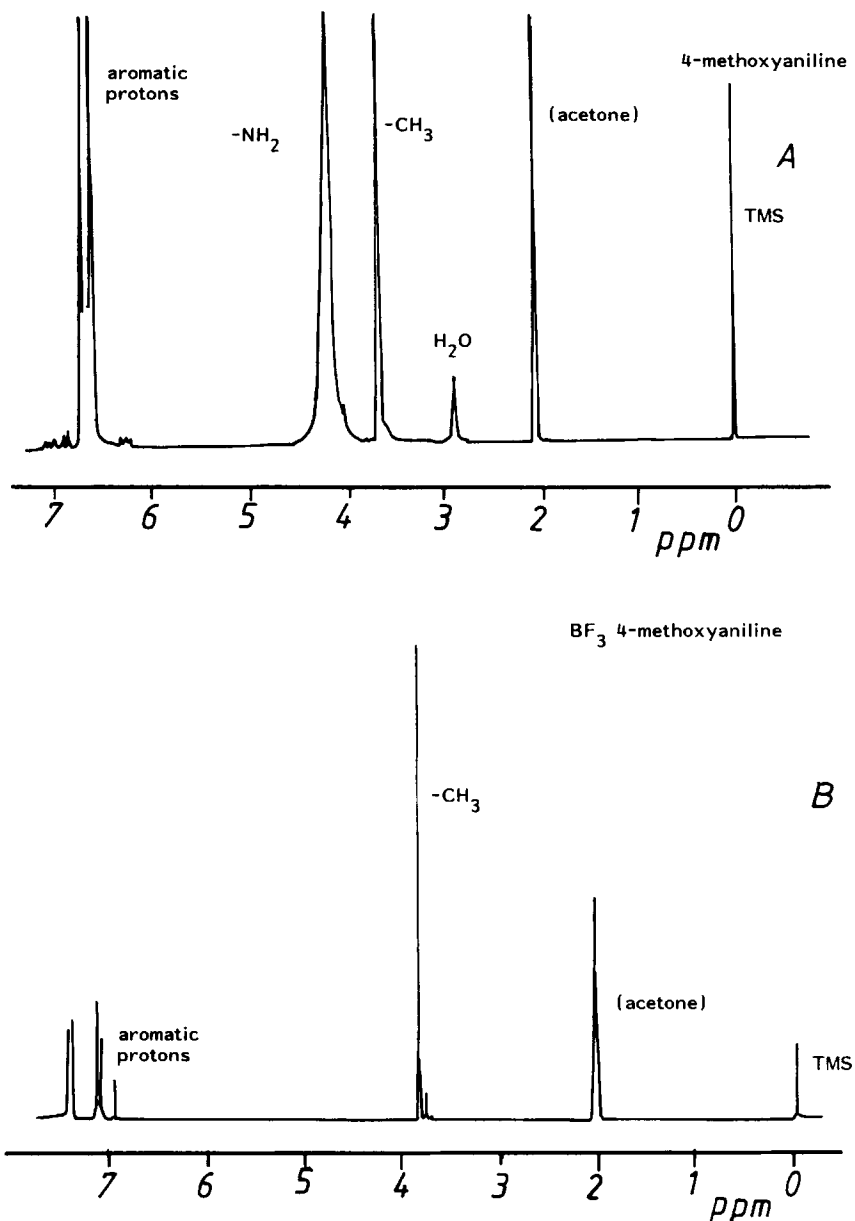Table III summarizes the quantity of each boron species present in benzene and in acetone solutions

Figure 1 ^{1}H-NMR spectra in acetone-d_6: (A) 4MA; (B) BF$_3$-4MA.

as determined by the ^{11}B-NMR study. In benzene, the solubility of the BF$_3$–MEA complex is low. It is possible that the BF$_3$–MEA complex also contains, in the solid state, other ionic forms insoluble in benzene. Thus, they are not seen in the spectrum.
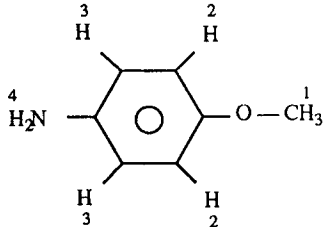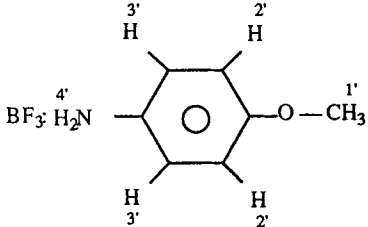
Similar results were also obtained in the cases of ^{11}B-NMR analyses of BF$_3$-4MA and BF$_3$-4CA in acetone. Presently, we believe that the complexes synthesized in CH$_2$Cl$_2$ without particular precautions could be rapidly hydrolyzed, giving BF$_3$OH$^\ominus$ and BF$_4^\ominus$ forms. Thus, for comparison, the syntheses of the complexes were carried out in a glove box.

Characterization of BF$_3$–Amine Complexes Synthesized in the Absence of Solvents

All used products, either complexes or solvents used for ^{11}B-NMR analyses, were stored under argon before studies. In spite of precautions, as in previous results, the BF$_3$–MEA shows the presence of the neutral form BF$_3$ in benzene and two ionic forms, BF$_3$OH$^\ominus$ and BF$_4^\ominus$, in acetone. The corresponding ^{11}B-NMR spectra are not given here.

The BF$_3$-4MA complex was not soluble at all in C$_6$H$_6$ and only slightly soluble in CH$_2$Cl$_2$. The ^{11}B-

Table II Chemical Shifts of 4MA and BF$_3$–4MA in Acetone-d_6

Proton	Chemical Shift (ppm)	Proton	Chemical Shift (ppm)
H^1	3.66	H$^{1'}$	3.87
H^2	6.69	H$^{2'}$	7.43
H^3	6.58	H$^{3'}$	7.12
H^4	4.18	H$^{4'}$	Not seen

NMR spectrum of this solution shows a little quartet poorly resolved and a little singlet at high field; it could derive from the BF$_3$ form and BF$_4^{\ominus}$. On the contrary, in acetone, a good solubility was achieved and the presence of BF$_3$OH$^{\ominus}$ and BF$_4^{\ominus}$ is well noticed.

We can now formulate the two following hypotheses: First, in the glove box under an inert atmosphere the synthesized complexes are pure, i.e., there is only the neutral form of BF$_3$. In contact even with traces of water always present in the glove box, the complex obtained from an amine of low basicity, like 4MA, is instantaneously hydrolyzed. This hydrolysis is only partial. With a complex derived from an amine with high basicity, the hydrolysis does not take place. In fact, only the neutral form of BF$_3$ exists during the analysis. Second, the neutral form of BF$_3$ is difficult to obtain during synthesis in CH$_2$Cl$_2$ without particular precautions. The complexes prepared from low basic amines are entirely hydrolyzed and the complexes obtained contain only the ionic forms.
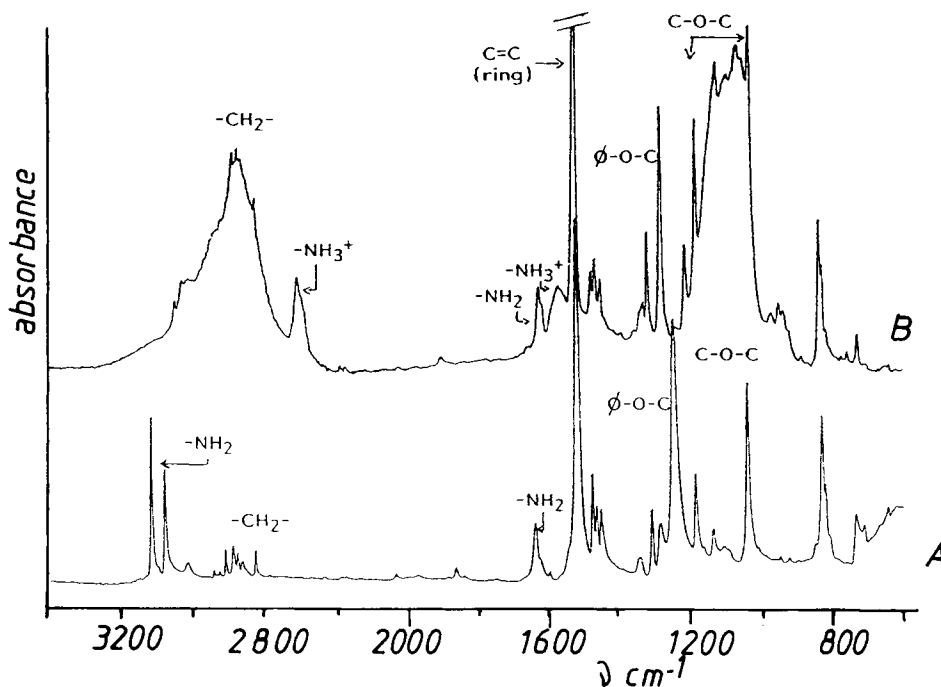
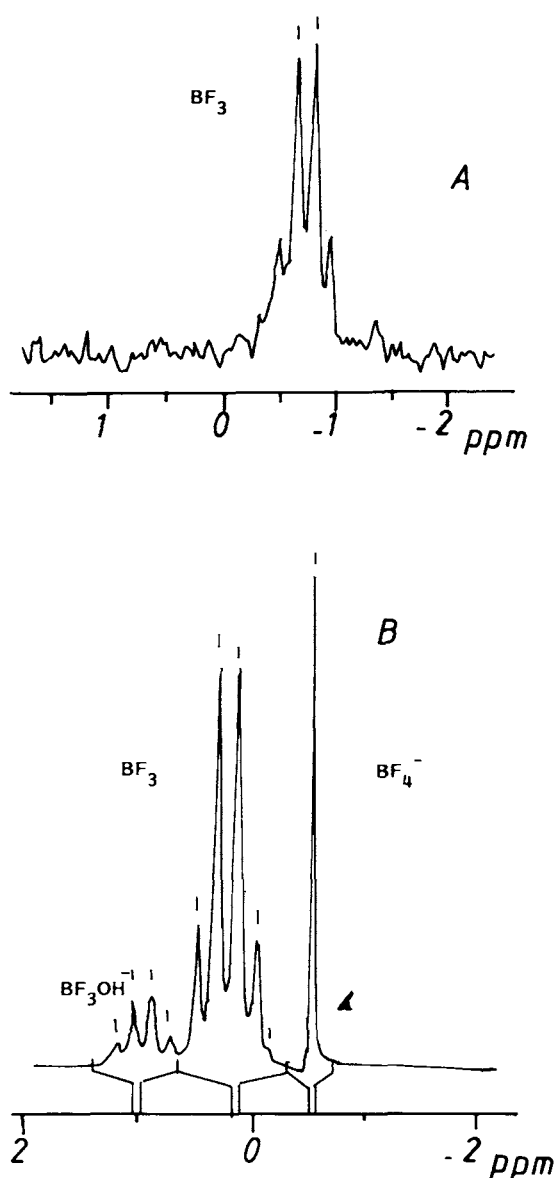**Figure 2** FTIR spectra of (A) 4MA and (B) BF$_3$–4MA.

Figure 3 ^{11}B-NMR spectrum of BF$_3$–MEA (approx. 10% b.w.) in (A) benzene and (B) acetone.

Effect of Poly(ethylene oxide) and γ-Butyrolactone Both Used as Solvents in Epoxy Polymerization

The ^{11}B-NMR spectrum of BF$_3$–4MA in γ-BL is given in Figure 4. Three species, BF$_3$, BF$_3$OH$^\ominus$, and BF$_4^\ominus$, are present. In addition, the H$_3$BO$_3$ and boric acid salt are seen at 20 and 23 ppm, respectively. In PEO, the presence of BF$_3$, BF$_3$OH$^\ominus$, and BF$_4^\ominus$ is also noticed.

The BF$_3$–MEA spectra in γ-BL and in PEO are presented in Figure 5(A) and (B), respectively. In γ-BL, the ionic form BF$_3$OH$^\ominus$ exists, but not in PEO.

The concentration of various boron species derived from BF$_3$–MEA dissolved in γ-BL and PEO is given in Table III. The concentration of the molecular species BF$_3$ is greater in PEO than in γ-BL (87.8% instead of 76.8%).

On the contrary, the ionic forms BF$_3$OH$^\ominus$ and BF$_4^\ominus$ are more important in γ-BL than in PEO. As will be shown later, these results partially explain the increasing reactivity of BF$_3$–amine dissolved in γ-BL with respect to the mixture BF$_3$–amine–PEO.

In Table IV, for three BF$_3$–amine complexes, the concentration of various species present in γ-BL is given. The concentration of BF$_4^\ominus$ increases with the decreasing basicity of amines. On the contrary, BF$_3$ concentration increases with the increasing basicity of amines. Experimentally, we observed that the BF$_3$–4MA was less reactive than was the BF$_3$–4CA in the epoxy polymerization. Once more, it is highly probable that the reactivity of BF$_3$–amine complexes in the cationic epoxy polymerization derives from the high acidity of the ammonium salt R—NH$_3^\ominus$BF$_4^\ominus$. The latter is formed easily from an amine of low basicity.

To confirm the results obtained from ^{11}B-NMR analysis, we have performed ^{1}H- and ^{19}F-NMR measurements on the mixture of BF$_3$–4MA and γ-

Table III Quantitative ^{11}B-NMR Analysis of Borofluorine Species from the BF$_3$–MEA Complex Dissociation in Different Solvents

Solvents	μ (Debye)	ε	BF$_3$ (%)	BF$_3$OH$^\ominus$ (%)	BF$_4^\ominus$ (%)
Benzene	0.00	2.27	100.0	—	—
Acetone	2.69	20.56	70.6	15.0	14.4
γ-BL	4.12	39.00	76.8	8.6	14.6
PEO	—	—	87.8	0.0	12.2
Triethylene oxide	5.58	23.69			

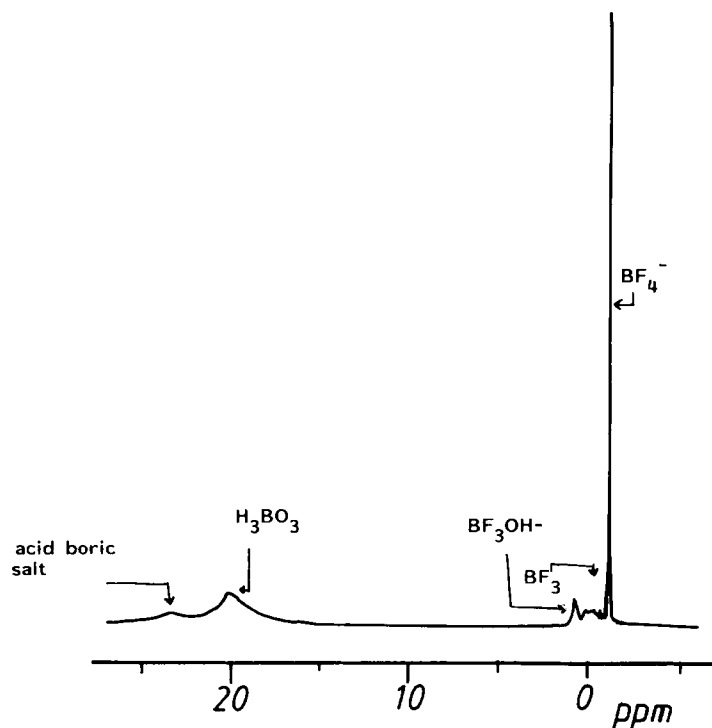μ and ε are the dipolar moment and dielectric constants, respectively.

Figure 4 ^{11}B-NMR spectrum of BF$_3$–4MA (approx. 10% b.w.) in γ-BL.

BL (30% by weight). Acetone was the solvent used for these analyses. These spectra are presented in Figures 6 and 7. Figure 6 shows that all the resonances of the BF$_3$–4MA complex are not perturbed by the presence of γ-BL; the same chemical shifts were found again, as in Figure 1(B). In addition, we clearly see the resonances of three methylene groups of γ-BL. The protons —NH$_2$ of the initial free amine (4MA) are not seen; this fact allows us to conclude that the complex dissociation cannot occur by the scission of the dative bond giving the free molecules of BF$_3$ and amine.

Concerning the two peaks at −149.85 and −149.50 ppm on the ^{19}F-NMR spectrum (Fig. 7), we do not agree with the literature,[17,18] using DMSO as solvent, which attributes the large peak (high field) to the covalent form

$$BF_3 \cdot H_2N \; -\!\!\langle\!\bigcirc\!\rangle\!-\, O-CH_3$$
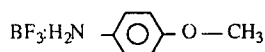
and the small peak (downfield) to the ionic form

$$BF_4^{\ominus}, H_3N \; ^{\oplus} -\!\!\langle\!\bigcirc\!\rangle\!-\, O-CH_3$$
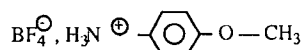
These attributions seem to be incorrect because only ionic forms have been characterized in polar solvents.

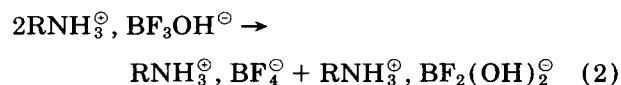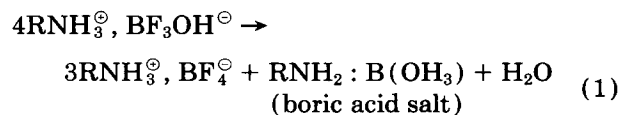Our results and explanation agree closely with explanations found in a general book about boron

chemistry. The authors[2] assign, from the ^{19}F-NMR spectrum of BF$_4^{\ominus}$, the two quartets to the coupling between ^{11}B—^{19}F (high field) and ^{10}B—^{19}F (downfield) (Fig. 7). As in the case of the ^{11}B-NMR spectrum and for the same reasons, the BF$_4^{\ominus}$ appears as a pseudosinglet. The two other forms, BF$_3$ and BF$_3$OH$^{\ominus}$, that agree closely with our previous results are not seen, perhaps because they exist only in small quantity (Table IV). Moreover, it is also possible that the peaks of these species are superimposed on the two peaks of BF$_4^{\ominus}$.

In agreement with all obtained results and basing this on the literature,[2,15,17] a mechanism of complex dissociation can be proposed as follows:

In the presence of water in solvents or humidity:

$$BF_3 : H_2NR + H_2O \rightarrow RNH_3^{\oplus}, BF_3OH^{\ominus}$$
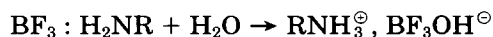
Then, the disproportionation occurs according to eqs. (1) and (2):

$$4RNH_3^{\oplus}, BF_3OH^{\ominus} \rightarrow$$

$$3RNH_3^{\oplus}, BF_4^{\ominus} + RNH_2 : B(OH_3) + H_2O \atop \text{(boric acid salt)} \quad (1)$$

$$2RNH_3^{\oplus}, BF_3OH^{\ominus} \rightarrow$$

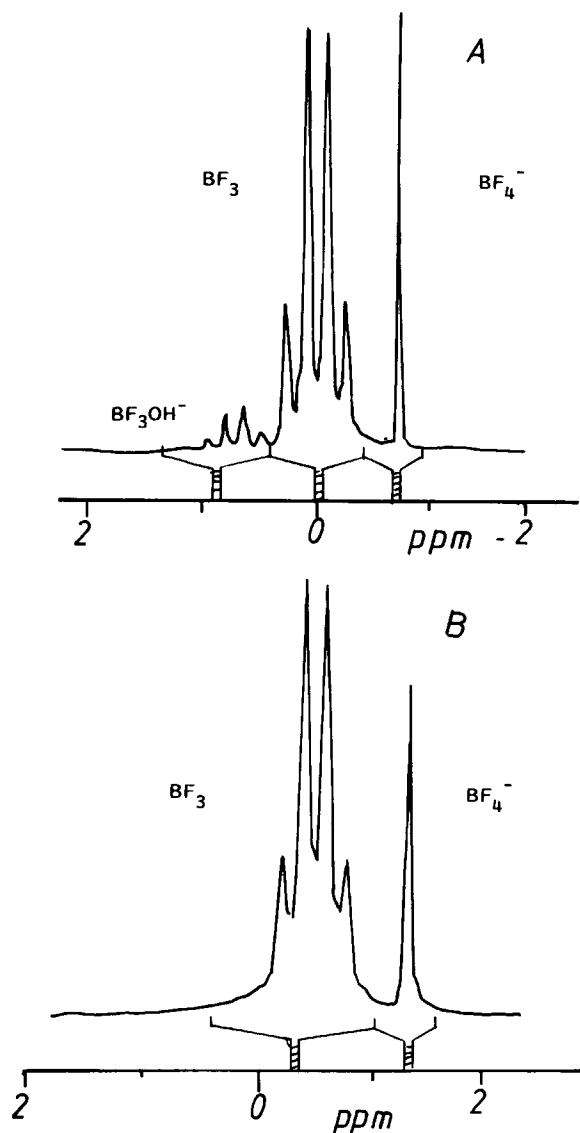$$RNH_3^{\oplus}, BF_4^{\ominus} + RNH_3^{\oplus}, BF_2(OH)_2^{\ominus} \quad (2)$$
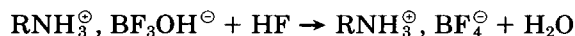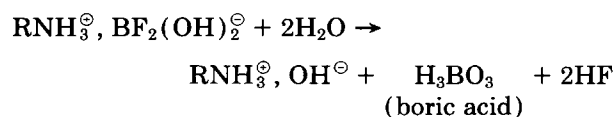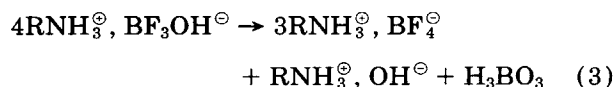
Figure 5 ^{11}B-NMR spectrum of BF$_3$-MEA in (A) γ-BL (approx. 10% b.w.) and (B) in PEO (approx. 10% b.w.).

The instability of the ionic form RNH$_3^{\oplus}$, BF$_2$(OH)$_2^{\ominus}$ leads to the following formula:

$$RNH_3^{\oplus}, BF_2(OH)_2^{\ominus} + 2H_2O \rightarrow$$

$$RNH_3^{\oplus}, OH^{\ominus} + \underset{(boric\ acid)}{H_3BO_3} + 2HF$$

$$RNH_3^{\oplus}, BF_3OH^{\ominus} + HF \rightarrow RNH_3^{\oplus}, BF_4^{\ominus} + H_2O$$

The overall dissociation of the BF$_3$–amine complex is summarized by the general reaction

$$4RNH_3^{\oplus}, BF_3OH^{\ominus} \rightarrow 3RNH_3^{\oplus}, BF_4^{\ominus}$$

$$+ RNH_3^{\oplus}, OH^{\ominus} + H_3BO_3 \quad (3)$$

In any way, the HF formed reacts easily with BF$_3$: H$_2$NR, giving the ionic species RNH$_3^{\oplus}$BF$_4^{\ominus}$.

It is important to note that from the above disproportion reactions (1) and (3), the expected ratios H$_3$BO$_3$: RNH$_3^{\oplus}$BF$_4^{\ominus}$ or RNH$_2$B(OH)$_2$: RNH$_3^{\oplus}$BF$_2^{\ominus}$ should be 1 : 3. But the ^{11}B-NMR results reported in Table IV are attached only to the quantitative analysis of the three following species: BF$_3$, BF$_3$OH$^{\ominus}$, and BF$_4^{\ominus}$. Indeed, accurate quantities of boric acid, H$_3$BO$_3$, or its salt form, RNH$_2$: B(OH)$_3$, could not be determined. The reason is that the quantitative analysis in ^{11}B-NMR spectroscopy can be achieved only on soluble species. Therefore, the low solubility of boric acid, H$_3$BO$_3$, in γ-BL, previously observed through the scouting test, has led, on ^{11}B-NMR spectra, to small broad peaks at around 20 ppm that could not be integrated.

Moreover, if HF is really formed, on the one hand, it is volatile; thus, its presence is difficult to detect. On the other hand, HF cannot be detected by ^{11}B-NMR. Gas chromatography must be used to confirm its presence.

Phase Transitions of BF$_3$–4MA Solutions in γ-BL

The literature[24] and the recent results of our laboratory[4] have shown that the glass transition temperature of PEO, usually used as a solvent of BF$_3$–amine complexes, depends on the concentration of the dissolved complex. The interaction between PEO and the complexes provokes physical cross-linking of the polyether chains. Thus, the glass transition temperature should increase with increasing number of physical cross-links, i.e., the hydrogen bond between the PEO and the BF$_3$–amine complex.

Following the same method as that of these previous studies, we have comparatively superimposed the DSC thermograms of γ-BL alone and various

Table IV   Quantitative ^{11}B-NMR Analysis of Borofluorine Species Coming from Different BF$_3$–Amine Complexes Solubilized in γ-BL

	Complexes		
	BF$_3$–4CA	BF$_3$–4MA	BF$_3$–MEA
% BF$_3$	5.2	2.7	76.8
% BF$_3$OH$^{\ominus}$	0.0	6.1	8.6
% BF$_4^{\ominus}$	94.8	91.2	14.6
H$_3$BO$_3$	Small broad peak		Very small broad peak
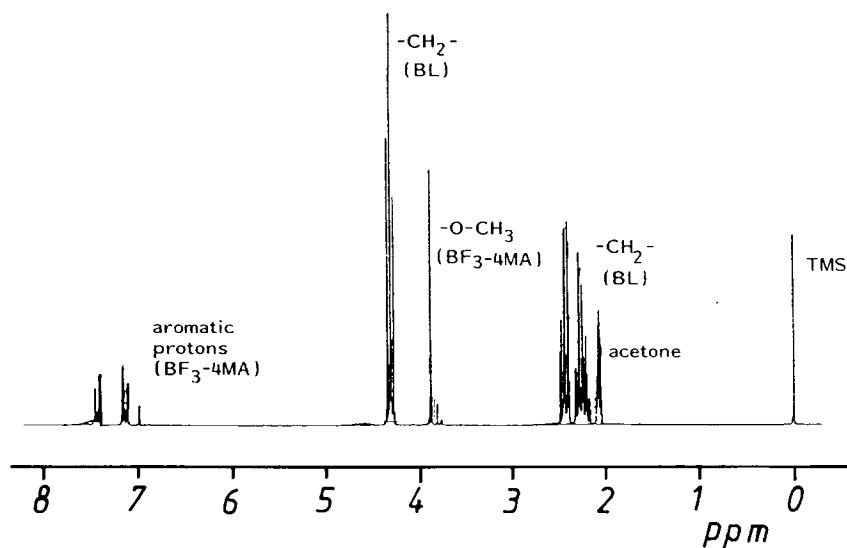
Figure 6 ^{1}H-NMR spectrum of BF$_3$–4MA (30% b.w.) in γ-BL in acetone-d_6.

mixtures of BF$_3$–4MA in γ-BL (Fig. 8). The melting peak of γ-BL takes place at $-40°$C. This peak shifts to a lower temperature by dissolving 20% by weight (10.1% by mole) of BF$_3$–4MA in γ-BL. In addition,

the crystallization peak is observed at $-87°$C. Beyond 30% by weight (16.2% by mole), the melting peak is no longer seen, but the glass transition temperature is still observed. This means that γ-BL be-
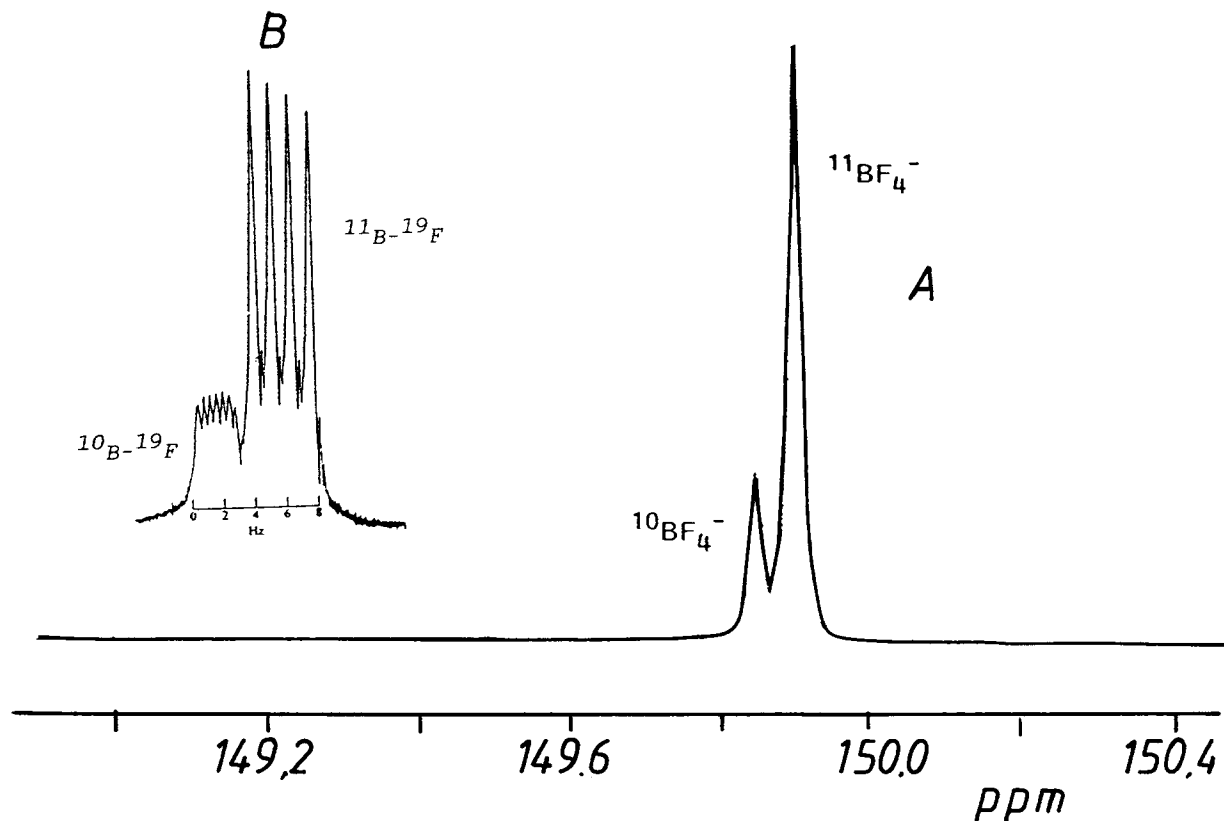

Figure 7 (A) ^{19}F-NMR spectrum of BF$_3$–4MA predissolved in γ-BL (30% b.w.), in acetone-d_6. (B) ^{19}F-NMR spectrum from the Ref. 2. The two quartets are due to the coupling between ^{10}B—^{19}F (downfield) and ^{11}B—^{19}F (high field).
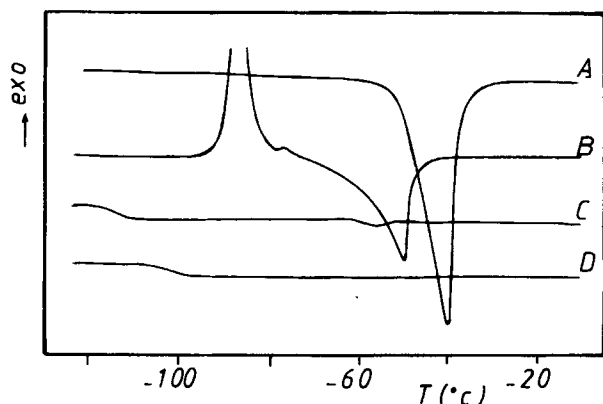
Figure 8 DSC thermograms of γ-BL with different weight concentrations of BF₃-4MA: (A) γ-BL alone; (B) 20%; (C) 30%; (D) 40% by weight (67.7% by mole) of BF₃-4MA in γ-BL.

comes completely amorphous. There is no measured value for the T_g of the γ-BL alone because it was impossible to quench the γ-BL quickly enough in its expected amorphous state without leading systematically to its crystalline state.

Moreover, the glass transition temperature (T_g) increases with the BF₃-amine complex concentration due to the increasing interactions between the BF₃-amine and γ-BL (Fig. 9). The T_g strongly increases from 20% (10.1% by mole) to 50% by weight (31% by mole) of BF₃-4MA in γ-BL, but after that,

it slightly increases and a saturation limit is reached at 70%, which corresponds to a molar ratio of BF₃-4MA/γ-BL, equal to 1.

For comparison, we have reported in the same figure (Fig. 9) the evolution of the T_g of BF₃-4MA dissolved in PEO 400. The limit of dissolution of BF₃-4MA in PEO 400 is in a range of 40% (58.3% by mole) to 50% by weight (67.7% by mole). This value corresponds approximately to a molar ratio BF₃-4MA/PEO 400 equal to 2. Thus, we can conclude that the increase in T_g attributed by the previous authors[4,20] to the formation of hydrogen bonds between hydrogen atoms of the BF₃-amine complex and ether linkage of PEO 400 is not completely correct. In fact, through the results reported until now, we have shown that only ionic forms of BF₃-amine exist ($BF_3OH^{\ominus}$ and $BF_4^{\ominus}$). Therefore, it seems reasonable to consider these interactions as one type of hydrogen bond between salts having acid character and basic functions. The result is that these bonds must be stronger with the ester function of the γ-BL than with ether groups of PEO 400, since the basicity of the former is higher.

To achieve these conclusions, we intend to investigate more precisely the nature of the interactions between the BF₃-4MA complex and γ-BL. We have examined the behavior of the carbonyl group and ether linkage in the γ-BL molecule by FTIR spectroscopy.
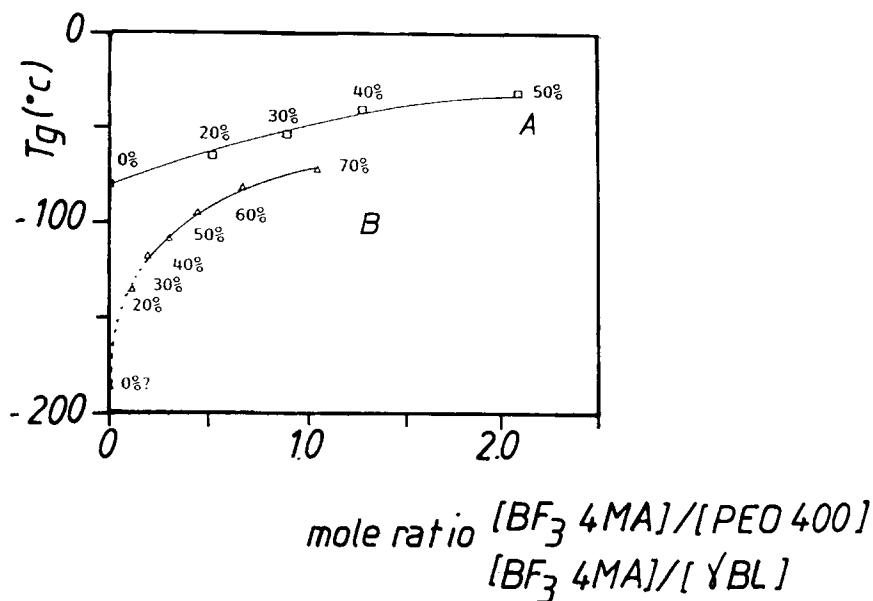

Figure 9 Comparative evolution of glass transition temperature of the initiator mixtures with an increasing quantity of BF₃-4MA predissolved in a poly(ethylene oxide) (PEO 400) or in γ-BL: (A) 0-50% by weight of BF₃-4MA in PEO 400; (B) 0-70% by weight of BF₃-4MA in γ-BL.
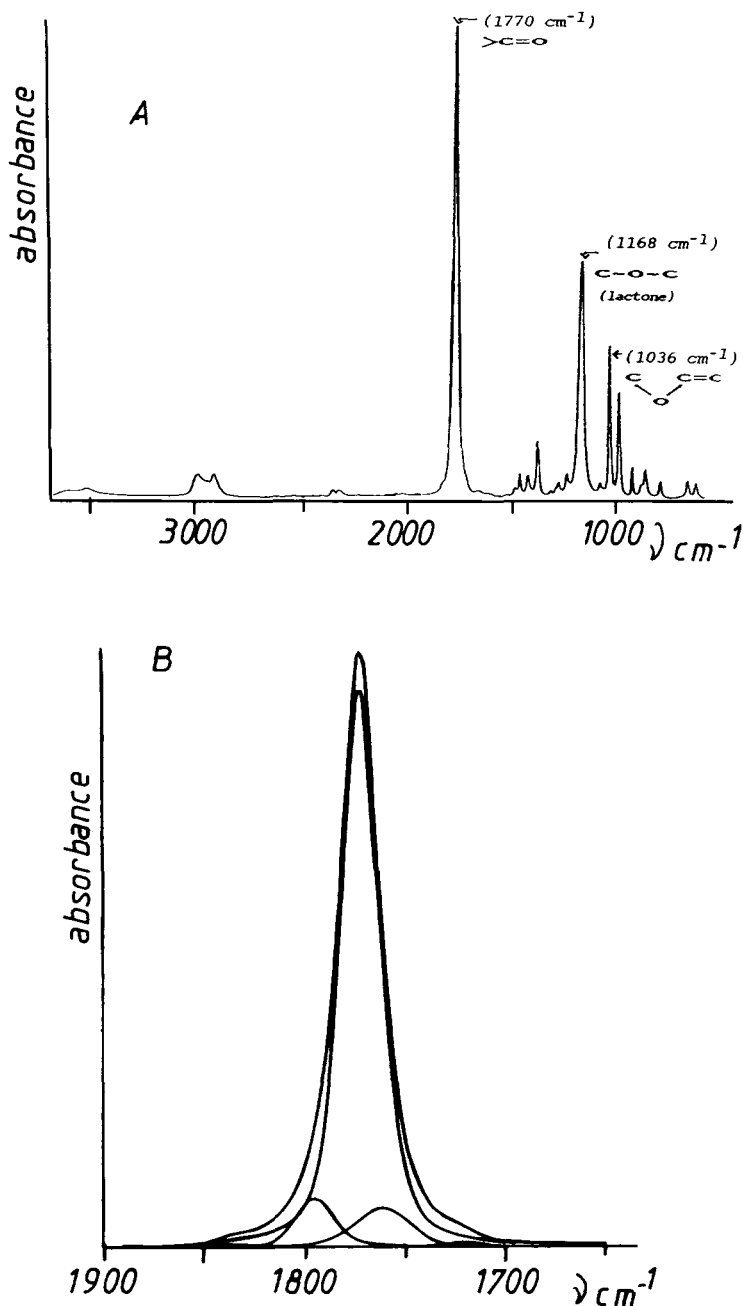
Figure 10 FTIR spectrum of (A) γ-BL and (B) magnificated carbonyl absorption peak.

Proposition for the Structure of the Complexes

Figure 10(A) shows the FTIR spectrum of pure γ-BL. The magnification of the carbonyl absorption peak of pure γ-BL is given in Figure 10(B). The single peak at 1770 cm^{-1} characterizes the stretching of free γ-BL carbonyl groups. The deconvolution analysis of this peak confirms that only one carbonyl peak exists.

With the same varied mixtures of BF$_3$-4MA in γ-BL used during analysis by ^{11}B-NMR spectros-

copy and DSC, we have registered different infrared spectra. Comparing these spectra to the initial spectrum of pure γ-BL, two influences appear:

First, the initial absorption of the group C — O — C in the γ-BL ring (1168 cm^{-1}) is modified by the BF$_3$-4MA concentration, as shown in Table V. The absorption frequency of this peak increases with increasing amount of BF$_3$-4MA. This increase is less significant than that observed when we have compared pure diethyl ether (Et$_2$O) and the com-

Table V **Behavior of C—O—C Absorption with the BF₃–4MA Concentration; Comparison with Et₂O and BF₃(Et₂O)**

Experimental Conditions	ν_{C-O-C} (cm^{-1})
100% γ-BL	1168
γ-BL + 20% (b.w.) of BF₃–4MA	1170
γ-BL + 30% (b.w.) of BF₃–4MA	1172
γ-BL + 40% (b.w.) of BF₃–4MA	1179
γ-BL + 50% (b.w.) of BF₃–4MA	1180
γ-BL + 70% (b.w.) of BF₃–4MA	1181
100% diethyl ether	1126
Commercial BF₃ diethyl ether, two peaks are visible	1207–1167

mercial BF₃–diethyl ether [BF₃(Et₂O)], both used to model this interaction.

We can therefore conclude that no covalent complex exists between the BF₃ form and ether linkage of the γ-BL cycle. This conclusion was foreseeable because according to our first ^{11}B-NMR analysis no significant BF₃ form existed.

Second, the deconvolution analysis of the peak of the carbonyl group (> C=O) (Fig. 11) from the different spectra reveals peaks that shape it. Two new peaks appear at lower frequencies, respectively, around 1754 and 1738 cm^{-1}. The initial peak is always present at around 1770 cm^{-1}. It is near another new peak picked at a higher frequency: 1794 cm^{-1}. Without deconvolution, these additional peaks could not be perfectly defined; only a feature change of global peak could be seen.

Following this deconvolution analysis, Table VI summarizes the change in the area percentage of each peak shaping the carbonyl peak absorption with different BF₃–4MA concentration by weight. The three peaks at 1835, 1812, and 1718 cm^{-1} do not have a physical sense. Their contribution is only to improve the peak deconvolution.

From the position of the absorption frequency, it is possible to extract a considerable amount of information about the environment of the carbonyl group in the molecule. As a reference, the absorption of the free carbonyl group of γ-BL at 1770 cm^{-1} is regarded as the "normal" frequency. The shift from this position may be correlated with the influence of polar, electronic, and steric effects, which arise from the nature of substituents attached to the carbonyl group or of the entities that surround it.

One generally assumes that inductive and mesomeric effects can cause changes in the frequency of absorption of the carbonyl group. Indeed, the in-

ductive effects from an electron-attracting group lead to a shorter carbonyl–oxygen bond. Thus, there will be an increase in the frequency of absorption. Moreover, concerning the mesomeric effect, when an electron-attracting group that can effectively conjugate with the carbonyl group, either by virtue of lone electron pairs or π-electrons, a decrease in the frequency of absorption is observed. Also, it is well known that ring structures can be formed by hydrogen bonding between acid or aldehyde functions with themselves. Ring structure can also be formed by alcohols or molecules having hydrogen
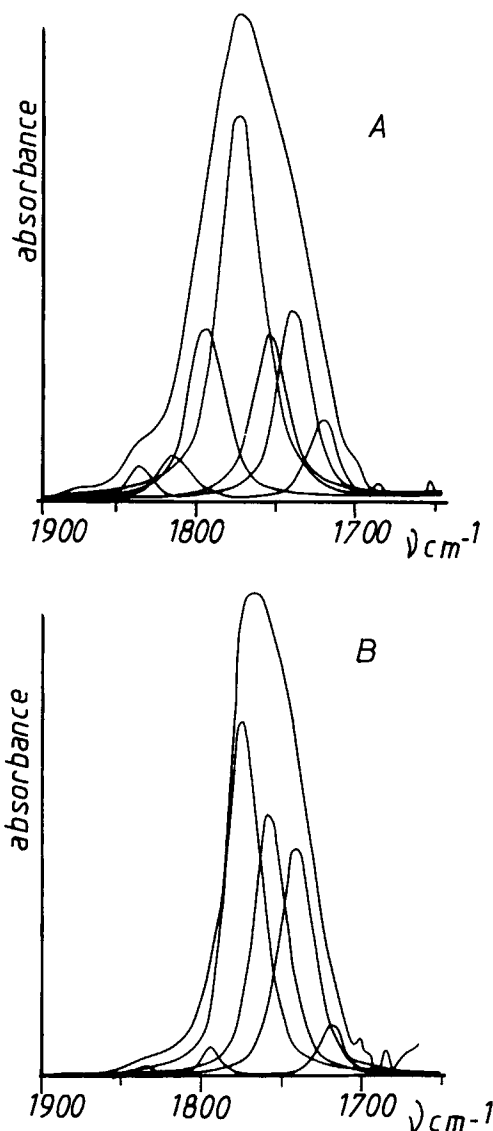

Figure 11 Deconvolution analysis of FTIR spectra showing the evolution of different associated carbonyl groups with the BF₃–4MA weight concentration: (A) 20% by weight of BF₃–4MA in γ-BL; (B) 70% by weight of BF₃–4MA in γ-BL.

Table VI **Evolution of the Percentage of Different Associated Carbonyl Groups ($\diagdown$ C = O) with the BF₃-4MA Concentration by Weight**

	ν_{CO} (cm^{-1})						
	1835	1812	1794	1770	1754	1738	1718
BF₃-4MA 20%	1.8	3.3	15.6	43.2	14.1	16.0	6.0
BF₃-4MA 30%	2.1	2.3	6.1	48.8	15.9	20.8	3.9
BF₃-4MA 40%	1.1	1.0	4.4	44.2	28.3	17.8	3.1
BF₃-4MA 50%	1.1	1.0	4.9	44.7	18.5	25.5	4.3
BF₃-4MA 70%	0.7	0.6	1.5	39.2	28.8	25.4	3.8

atoms susceptible to establish hydrogen bonds. Powerful hydrogen bonding between these molecules and the strength of these bonds has been accounted for on the basis of a large contribution of an ionic resonance structure.

Through our results reported in Tables V and VI, according to the well-known influence of inductive and mesomeric effects on the shift of carbonyl absorption, we can propose a general scheme of interaction between the ionic form of BF₃-amine complexes and γ-BL. As we indicated earlier, the peak at 1770 cm^{-1} is regarded as the "normal position" of absorption of the γ-BL carbonyl group without interaction. Further, the peak at higher frequency (1794 cm^{-1}) that decreases with the amount of BF₃-amine complex can be attributed to the inductive effect of the endocyclic oxygen atom following the molecular scheme:
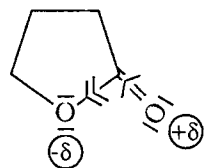
On the other hand, the two peaks observed at lower frequencies (1754 and 1738 cm^{-1}), which increase with the addition of the BF₃-amine complex, can be both assigned to two interactions: The first is the mesomeric hybrid of the polar forms of the carbonyl group of γ-BL due to hydrogen bonding, which becomes more powerful because of the ionic structure RNH₄⊕ BF₄⊖. This mesomeric effect can be symbolized by the following formula:
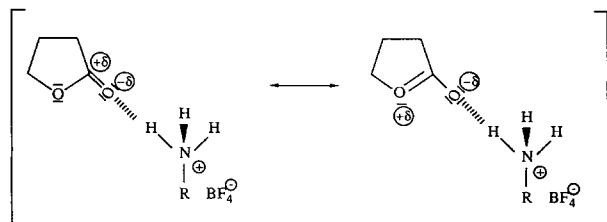
The second is the formation of a "pseudo" six-membered ring by "chelated" hydrogen bonding between one molecule of γ-BL and one molecule of ionic form RNH₃⊕, BF₄⊖. This following structure is confirmed, on the whole IR spectrum (Fig. 12), by a peak around 1600 cm^{-1}, which can characterize a chelated form of the carbonyl group:
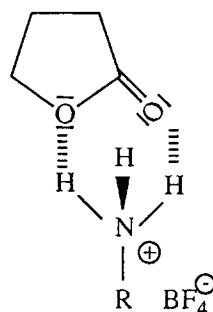
Many authors[9,25,26] involve the exocyclic oxygen atom of lactones (carbonyl group), like the more nucleophilic and basic site for complexing with an electrophilic compound. The authors[9] assign the shifting of the carbonyl absorption to around 1740 cm^{-1} to a protonated form of γ-BL obtained after the addition to γ-BL of a commercial aqueous perchloric acid containing 70% HClO₄. They proposed as an explanation the HClO₄ decomposition into the proton H⊕ and the counterion ClO₄⊖ leading to a mesomeric structure symbolized by the following formula:
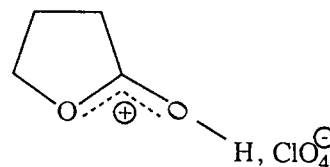
Through our experiments with the BF₃-4MA complex in γ-BL, we are in close agreement with this previous observation from the literature. But we have not exactly the same acid–basic interaction,
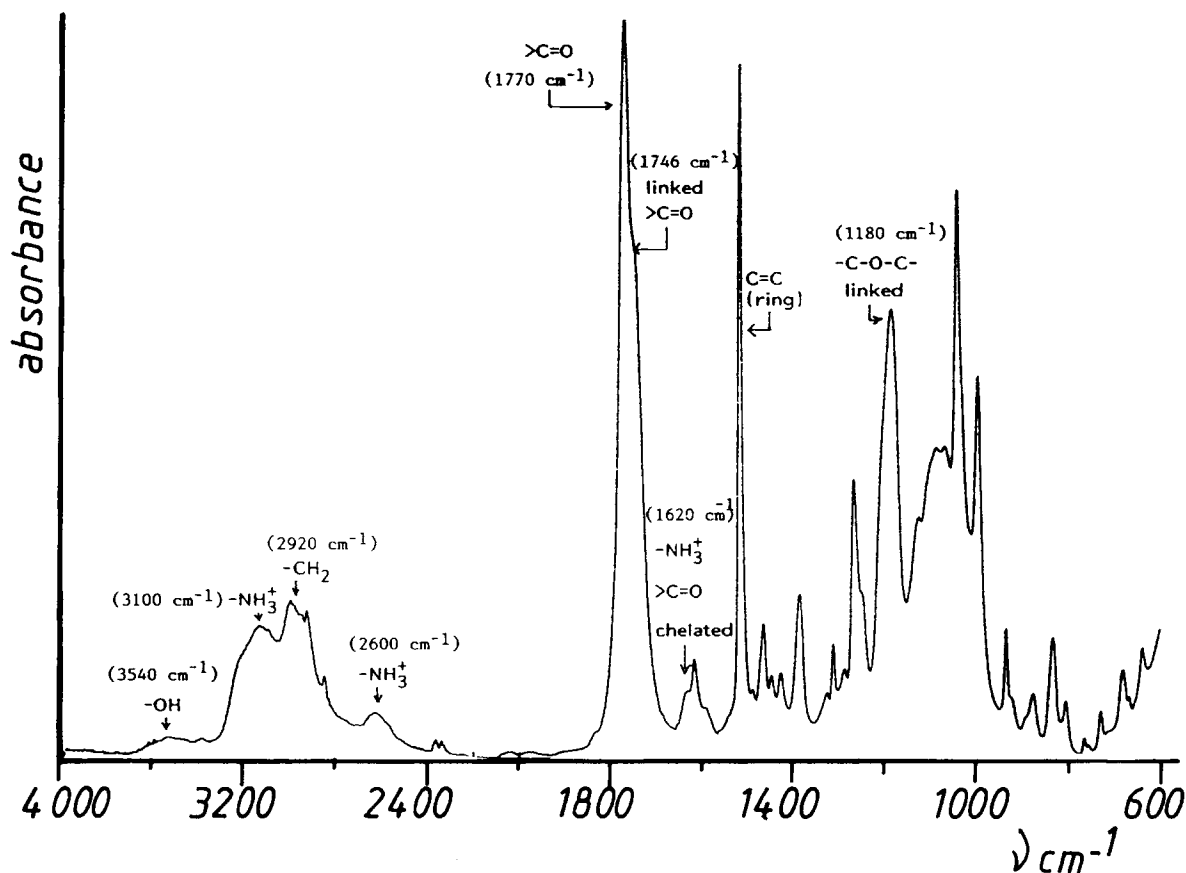
Figure 12   FTIR spectrum of mixture BF_3–4MA (50% by weight) in γ-BL.

i.e., formation of a covalent bond between the carbonyl group and the proton since no free amine was observed by ^{1}H-NMR. Therefore, we support completely our interpretations that a qualitative comparison of the ammonium salt acidity of the ionic form $RNH_3^\oplus$, $BF_4^\ominus$ with acid character of a protonic acid can be done.

CONCLUSION

According to FTIR and ^{1}H-NMR measurements, the synthesis of BF_3–amine complexes was complete. The obtained products do not contain the free amine. The study by ^{11}B-NMR has allowed us to characterize the stable species present when the BF_3–amine complexes are dissolved in γ-BL, PEO, or other solvents. These mixtures will be used to initiate the epoxy homopolymerization.

The $RNH_3^\oplus$, $BF_4^\ominus$ salt was identified as the active species that will act as cationic initiator for oxirane polymerization. These results will be presented in forthcoming reports.

Indeed, the complex is completely dissociated mainly as the ionic form $RNH_3^\oplus$, $BF_4^\ominus$ in polar solvents. The formation of this ionic form is due to a hydrolysis reaction. Small traces of water always exist in dry polar solvents having more or less hygroscopic character. The latter are still efficient to hydrolyze of the complex. Furthermore, we have shown by FTIR that the ionic form was even present in the bulk state of the complex, surely resulting from the wet surrounding.

Moreover, it appears that the dissociation of the complex in $RNH_3^\oplus$, $BF_4^\ominus$ is easier with amines having low basic character than with those having high basic character. In fact, the BF_3 neutral form was seen only in the case of BF_3–monoethylamine but not in the case of BF_3–4-chloroaniline or BF_3–4-methoxyaniline.

The BF_3–amine complexes are well soluble in γ-BL. This solubility is due to the solvatation of $RNH_3^\oplus$, $BF_4^\ominus$ by γ-BL. The solvatation is favored by many interactions like hydrogen bonding between the ionic form and γ-BL. Furthermore, for an amine of high basicity like BF_3–MEA, in γ-BL, the ion

forms $BF_3OH^{\ominus}$ and $BF_4^{\ominus}$ exist in greater quantity than in PEO. This fact leads to increasing reactivity in epoxy polymerization when γ-BL is used as a solvent for the BF_3–amine complex.

Finally, the glass transition temperature of the BF_3–amine/γ-BL mixtures is very low (from -140 to $-80°C$, depending to the BF_3–amine concentration); hence, they have a low viscosity that is a great advantage for the mixing in epoxy prepolymers.

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