Stopped-Flow and ^{1}H NMR Study of the Ionization of Cumyl Chloride by Boron Trichloride.

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Received December 30, 1997; Revised Manuscript Received March 2, 1998

ABSTRACT: Study of the ionization of cumyl chloride by boron trichloride was carried out using stopped-flow UV−visible and ^{1}H NMR spectroscopy in methylene chloride. Cumyl chloride is very weakly ionized to form the cumyl cation (λ_{max} = 330 nm) which is stable at low temperature (<−60 °C) with tetrachloroborate anion since no elimination could be observed. At that temperature, owing to the presence of traces of α-methylstyrene in the cumyl chloride solutions, the ionization step was immediately followed by the addition of this monomer, resulting in the formation of the dimeric (or oligomeric) cation (λ_{max} = 348 nm), which slowly cyclized into the corresponding indanic derivatives. At −65 °C, the equilibrium constant of ionization of cumyl chloride is much smaller than that of the chlorinated dimeric (or oligomeric) species. At room temperature, dehydrochlorination of the cumyl cation leading to α-methylstyrene was evidenced and the indanic dimer was the only final product.

Introduction

Controlled cationic polymerization could be achieved by a dynamic equilibrium between propagating carbenium ions and corresponding inactive covalent halides.[1,2] The initiating system is usually composed of an alkyl halide, ether, or ester precursor which is reversibly ionized by a Lewis acid, and initiation proceeds via addition of the resulting carbocation to the monomer. The initiation step is of major importance and should be at least as fast as propagation to ensure a priori control of molecular weight as well as narrow molecular weight distribution. Such a requirement implies both the efficient ionization of the covalent precursor and sufficient reactivity of the formed cation. These are two opposite trends, but a compromise can be found when using initiators leading to cations with a structure similar to that of the propagating species. For instance, it was shown that 2-chloro-2,4,4-trimethylpentane (i.e. the hydrochlorinated dimer of isobutene) ionized with $TiCl_4$ was an efficient initiator in the cationic polymerization of isobutene.[3,4] The extent of ionization, i.e., the concentration of the initiating cation, depends also on the respective natures of Lewis acid and of the leaving group.

Among aralkyl precursors, cumyl derivatives activated by BCl_3 or $TiCl_4$ have been extensively used.[1,2] For instance, the cationic polymerization of isobutene initiated by the cumyl chloride/BCl_3 system was described as one of the first "living" carbocationic systems,[5] and in this polymerization, the cumyl chloride was considered as an initiator as well as a transfer agent (a so-called inifer[6,7]). The first controlled carbocationic polymerization of α-methylstyrene was achieved using the same initiating system.[8] However, initiator efficiency was relatively low for batch polymerizations which was considerably improved when the monomer was continuously fed into the reactor. For this monomer, a low initiating efficiency was reported with an initiating system consisting of cumyl chloride/tin tetrabromide.[9] Both results indicated that propagation was faster than initiation.

The ionization of various alkyl halides by Lewis acids has been studied, especially for tertiary and secondary species with stabilizing aryl and alkoxy groups. The corresponding carbenium ions were directly observed by various spectroscopic techniques.[10] For alkyl halides substituted with aryl groups, the equilibrium constants were measured by UV since even small amounts of the carbocations could be detected due to their large extinction coefficients. Relatively large equilibrium constants of ionization were reported for benzhydryl cations ascribed to the stabilization by resonance by two aromatic rings. For example, $K_i = 64$ L·mol^{-1} for diphenylmethyl chlorides with two p-CH_3 susbtituents, and $K_i = 0.17$ L·mol^{-1} with one p-CH_3, when ionized with BCl_3 in dichloromethane at −70 °C.[10]

There is no data on the rate constants and equilibrium constants of the ionization of cumyl chloride by Lewis acids, due to their respectively high and low values. However, kinetics of these rapid reactions could be investigated by the stopped-flow technique with fast real-time UV−visible detection. This technique, applicable to species absorbing in the UV−visible range, seems to be the most suitable tool to study ionization of cumyl chloride since it allows one to follow kinetics of reactions with half-lifetimes longer than 10 ms and to measure concentrations of cations as low as 10^{-5} mol·L^{-1}. The apparatus which has been designed in our laboratory is compatible with high-vacuum purification, and the temperature can be controlled down to −65 °C.[11] It has been successfully used for the kinetic study of the polymerization of styrene and its derivatives initiated by protonic acids.[12,13]

The aim of this work has been to use NMR spectroscopy and the stopped-flow technique to investigate the ionization of cumyl chloride by boron trichloride at

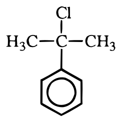
S0024-9297(97)01883-4 CCC: $15.00

Table 1. Stopped-Flow Experiments of the Ionization of Cumyl Chloride (CumCl) by Boron Trichloride (BCl_3) in Dichloromethane and the Influence of CumCl Initial Concentration on the Evolution with Time of the Peak at 348 nm

expt no.	$[CumCl]_0$ ($mol{\cdot}L^{-1}$)	$[BCl_3]_0$ ($mol{\cdot}L^{-1}$)	T (°C)	initial slope (OD unit/s)	ΔOD_{max} at 348 nm	$[D^+]_{max}/[CumCl]_0{}^a$	t_{max} (s)	apparent rate const of decrease of species absorbing at 348 nm (s^{-1})
1	0.0076	0.56	−65	12	0.52	0.013	0.3−0.4	0.0072
2	0.0086	0.56	−65	8	0.45	0.010	0.13	0.0096
3	0.0113	0.53	−62	≈7	0.31	0.005	0.15	0.0090
4	0.0173	0.56	−65	17	0.77	0.008	0.12	0.0079
5	0.0225	0.56	−65	34	1.20	0.010	0.20	0.0078
6	0.0236	0.55	−65	17	0.53	0.004	0.15	0.0071
7	0.0345	0.56	−65	22	0.87	0.005	0.10	0.0079

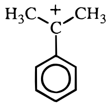
[a] $[D^+]_{max}$: maximum concentration of the dimeric cation of α-methylstyrene calculated with ϵ at 348 nm = 26 300 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$.

Chart 1



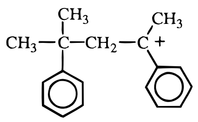
Cumyl chloride, **CumCl**

(2-Chloro-2-phenylpropane)



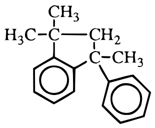
Cumyl cation, **Cum⁺**

(2-phenyl-2-propylium)



Dimeric cation of α-methylstyrene , **D⁺**

(4-methyl-2,4-diphenyl-2-pentylium)



Cyclic dimer of α-methylstyrene, **I**

(1,1,3-trimethyl-3-phenylindan)

various temperatures in dichloromethane solvent to better understand the first initiation steps in the "living" cationic polymerizations using this system. In addition, in the presence of α-methylstyrene (α-MeSt), this system can be considered as a model of carbocationic polymerization of α-MeSt. The four major species present in this system are shown in Chart 1.

Experimental Section

Materials. Dichloromethane (CH_2Cl_2 from SDS, stabilized with amylene; CD_2Cl_2 from SDS) was used as a solvent and purified under high-vacuum conditions according to the methodology used in our laboratory.[14] Boron trichloride (BCl_3, from Aldrich) was purified by successive high-vacuum distillations and stored under vacuum on 3 Å molecular sieves. Cumyl chloride (CumCl; 2-chloro-2-phenylpropane) was prepared by bubbling gazeous HCl (produced by the reaction of sulfuric acid with ammonium chloride) into bulk α-methylstyrene at room temperature. After distillation under reduced pressure (T = 36 °C, P = 1 mmHg), the main fraction was degassed by high vacuum freeze−thaw cycles and stored under vacuum. Purity estimated by ^1H NMR was approximately 96%; CumCl contained less than 4 mol % of α-methylstyrene. Chemical shifts of CumCl are as follows: ^1H NMR, δ (ppm) = 1.97 (s, CH_3, 6H), 7.2−7.6 (m, aromatic CH, 5H); ^{13}C NMR, δ (ppm) = 34.23 (CH_3), 69.54 (C−Cl), 125.38, 127.48, 128.17 (aromatic CH), 146.19 (aromatic C).

The respective dichloromethane solutions of BCl_3 and cumyl chloride were prepared under vacuum before use and stored in 60 mL ampules equipped with high-vacuum taps (from Young). Concentrations of solutions were calculated at room temperature and were corrected for the adequate reaction temperature using 0.00137 K^{-1} for the CH_2Cl_2 volume contraction coefficient.

Sealed Tubes ^1H NMR Procedure. The ionization of CumCl was directly studied in purified CD_2Cl_2 using ^1H NMR spectroscopy (FT AC200 Bruker spectrometer at 200 MHz for ^1H). Experiments were carried out under vacuum in 5 mm diameter sealed tubes using the following procedure. A CD_2Cl_2 solution of CumCl (0.3 mL) was first introduced in the NMR tube and frozen in liquid nitrogen. Then, CD_2Cl_2 (0.3 mL) and a given amount of BCl_3 were successively added by distillation and immediately frozen. The tube was sealed off and kept in liquid nitrogen. Just before analysis, the three layers were melted and rapidly mixed at −78 °C. The first spectrum was recorded within 30 s after mixing.

Stopped-Flow Procedure. A complete description of the stopped-flow apparatus has been reported previously.[11] In this study the reactor was equipped with a 2 mm optical path quartz cell. For each experiment, 100 spectra of 118 points were recorded between 270 and 540 nm ($\Delta\lambda$ = 2.30 nm) and time interval between spectra was varied between 5 ms (with total duration of experiment of 0.5 s) and 2 or 5 s (total duration of 200 or 500 s). From crude results expressed in arbitrary units of intensity, optical density (OD) was calculated using a standard intensity spectrum of the solvent. First spectrum corresponded to time zero of the reaction, but the first 5 ms of the reaction could not be used due to incomplete mixing. The results of various experiments are summarized in Tables 1 and 2. To determine accurate optical densities, subtraction of the baseline was necessary and values are then expressed as ΔOD in the tables.

Results and Discussion

^1H NMR Study. Chemical shifts have been previously reported for the cumyl cation (Cum^+, 2-phenyl-2-propylium) formed by the ionization of CumCl in superacidic media at −30 °C[15−17] and by the ionization of CumCl by SbF_5 in CD_2Cl_2 at −70 °C.[18] In the latter case, it had been observed that cumyl chloride was almost quantitatively converted into the Cum^+ cation; the indanic dimer of α-methylstyrene (I, 1,1,3-trimethyl-3-phenylindan) and some oligomeric species were also identified as byproducts.

In this work, the ionization of CumCl with BCl_3 was first studied at −60 °C and −78 °C with the following respective concentrations: $[CumCl]_0 = 0.045\ mol{\cdot}L^{-1}$ and $[BCl_3]_0 = 0.53\ mol{\cdot}L^{-1}$; $[CumCl]_0 = 0.060\ mol{\cdot}L^{-1}$ and $[BCl_3]_0 = 2.3\ mol{\cdot}L^{-1}$. For both experiments the cumyl cation Cum^+ could not be detected indicating its very low concentration and therefore very weak ionization, even in the presence of a large excess of Lewis acid. This contrasts with the strong ionization with SbF_5 and is in agreement with respective strength of both Lewis acids.[19] At low temperatures in the presence of BCl_3, cumyl chloride was stable during several hours.

In the second experiment, temperature was raised from −78 to +13 °C. It was observed that cumyl chloride was slowly consumed and quantitatively converted into I (peaks at 1.71, 1.37, and 1.06 ppm for the methyl groups in ^1H NMR spectra) with simultaneous formation of HCl (1.30 ppm). This reaction is slow at 13 °C as illustrated in Figure 1 where $\ln([CumCl]_0/[CumCl])$ is plotted vs time: 80% cumyl chloride conversion is reached only after 1 h. Neither α-methylstyrene (α-MeSt) nor the monomeric (Cum^+) and dimeric (D^+,

Table 2. Stopped-Flow Experiments of the Ionization of Cumyl Chloride (CumCl) by Boron Trichloride (BCl_3) in Dichloromethane and Influence of Temperature on the Evolution with Time of the Peak at 348 nm

expt no.	$[CumCl]_0$ ($mol{\cdot}L^{-1}$)	$[BCl_3]_0$ ($mol{\cdot}L^{-1}$)	T (°C)	ΔOD_{max} at 348 nm	$[D^+]_{max}/[CumCl]_0$	t_{max} (s)	apparent rate const of decrease of species absorbing at 348 nm (s^{-1})
7	0.0345	0.56	−65	0.87	0.0048	0.10	0.0079
8	0.0223	0.53	−60	0.43	0.0037	0.10	0.0141
9	0.0111	0.52	−51	0.18	0.0031	0.05	0.0441
10	0.0440	0.52	−50	0.46	0.0020	0.04	0.0405
11	0.0434	0.52	−40	0.21	0.0009		0.0795

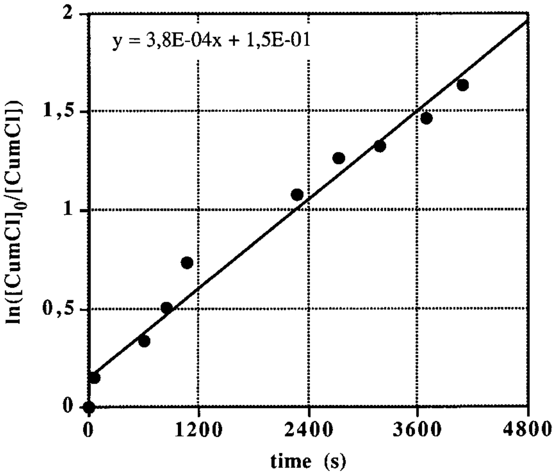
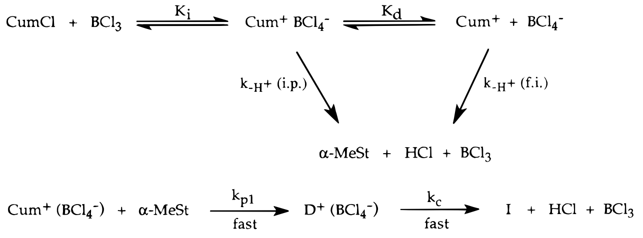


Figure 1. ^1H NMR analysis for the reaction of cumyl chloride with BCl_3. Consumption of cumyl chloride vs time: $[CumCl]_0 = 0.06\ mol{\cdot}L^{-1}$; $[BCl_3]_0 = 2.3\ mol{\cdot}L^{-1}$; $T = +13$ °C.

Scheme 1. Reactions at 13 °C



with :

K_i : ionization equilibrium constant

K_d : dissociation equilibrium constant

k_{-H^+} (i.p.) : rate constant of β-proton elimination from $Cum^+BCl_4^-$ (ion-pairs)

k_{-H^+} (f.i.) : rate constant of β-proton elimination from Cum^+ (free ions)

k_{p1} : rate constant of addition of $Cum^+(BCl_4^-)$ to α-MeSt

k_c : rate constant of Friedel-Crafts cyclization of D^+

4-methyl-2,4-diphenyl-2-pentylium) cations could be observed during the reaction although formation of dimers implies the existence of all of the three species. Formation of dimers can be explained by a slow deprotonation of the cumyl cation into α-methylstyrene followed by fast dimerization to form the D^+ cation which is rapidly converted into the indanic dimer (see Scheme 1). Assuming that the equilibria of ionization and dissociation are rapidly established, the rate determining step would be the β-proton elimination from the cumyl cation. This reaction could be neglected at the lowest temperature since no consumption of cumyl chloride was detected.

Considering that the dynamics of ionization and dissociation are fast and that concentration of BCl_3 does not change significantly with time, the respective concentrations of ion-pairs and free-ions can be expressed as

$$[\mathrm{Cum^+BCl_4^-}] = K_i[\mathrm{CumCl}][\mathrm{BCl_3}]_0$$

$$[\mathrm{Cum^+}][\mathrm{BCl_4^-}] = K_dK_i[\mathrm{CumCl}][\mathrm{BCl_3}]_0$$

Since the rate determining step for the consumption of CumCl and formation of the indanic dimer is the β-proton elimination from Cum^+, it can be written

$$\begin{aligned}\frac{d[I]}{dt} &= k_{-H^+(i.p.)}[\mathrm{Cum^+BCl_4^-}] + k_{-H^+(f.i.)}[\mathrm{Cum^+}][\mathrm{BCl_4^-}] \\ &= (k_{-H^+(i.p.)} + K_d k_{-H^+(f.i.)})K_i[\mathrm{CumCl}][\mathrm{BCl_3}]_0 \\ &= k_{-H^+(apparent)}K_i[\mathrm{CumCl}][\mathrm{BCl_3}]_0\end{aligned}$$

$$\frac{d[\mathrm{CumCl}]}{dt} = -2\frac{d[I]}{dt} = -2k_{-H^+(apparent)}K_i[\mathrm{CumCl}][\mathrm{BCl_3}]_0$$

$$\ln\left(\frac{[\mathrm{CumCl}]_0}{[\mathrm{CumCl}]}\right) = 2k_{-H^+(apparent)}K_i[\mathrm{BCl_3}]_0 t$$

The consumption rate of CumCl has been measured and $\ln([CumCl]_0/[CumCl])$ vs time is linear with slope $= 3.8 \times 10^{-4}\ s^{-1}$ (Figure 1). With $[BCl_3]_0 = 2.3\ mol{\cdot}L^{-1}$, it gives

$$k_{-H^+(apparent)}K_i = 8.3 \times 10^{-5}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$$

Unfortunately, the two constants cannot be calculated separately. The slow conversion of cumyl chloride into the indanic dimer of α-methylstyrene at +13 °C proceeds via intermediate carbocations which are formed through weak ionization of CumCl (low value of K_i) followed by β-proton elimination.

Stopped-Flow Spectroscopic Study. At −65 °C, with large excess BCl_3 ($[CumCl]_0 = 0.008-0.035\ mol{\cdot}L^{-1}$; $[BCl_3]_0 = 0.53-0.56\ mol{\cdot}L^{-1}$; see Table 1) two transient absorption bands were observed. The more intense one had its maximum (λ_1) between 340 and 350 nm, and the second one had its maximum at $\lambda_2 = 468$ nm (Figure 2).

In the first spectrum, recorded 5 ms after mixing, both peaks were already visible, indicating very fast appearance. These two peaks reached their maximum intensity (OD_{max}) within about 0.1−0.3 s (t_{max}) (Figure 3A). Subsequent decrease was comparatively slow and peaks had completely disappeared after a few hundreds of seconds (Figure 3B). Both absorption bands had the same kinetic behavior (Figure 3) with a constant ratio OD_1 to OD_2 (approximately 7), and for that reason, they could be considered as belonging to the same species.

Some variation with time of the wavelength at the maximum of the first peak was observed. In the first spectrum, the value of λ_1 was 343−345 nm and in-

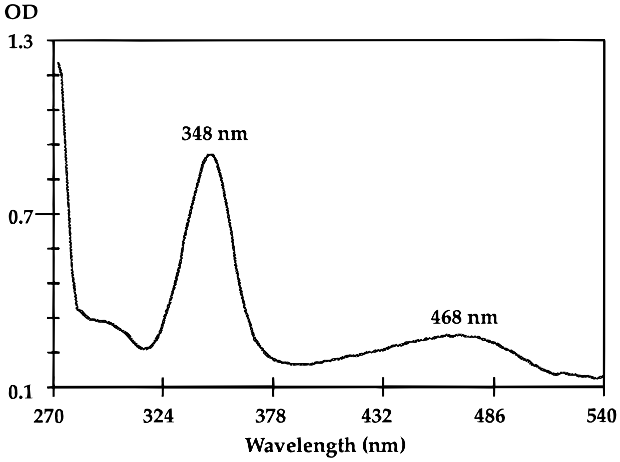


Figure 2. Stopped-flow study: UV−visible spectrum at t = 0.095 s. Conditions: $[\mathrm{CumCl}]_0 = 0.0236$ mol·L^{-1}; $[\mathrm{BCl_3}]_0 = 0.55$ mol·L^{-1}; $T = -65$ °C.

creased with time to reach 348 nm in less than 50 ms. As long as absorbance was near its maximum value, λ_1 did not change. However, simultaneous with the decrease of the peak intensity, it subsequently reached 329−332 nm value (Figure 4). This peak at 329−332 nm was very stable and it could be observed for times longer than 15 min (Figure 5). Such a shift of the maxima can be explained by the existence of two superimposed peaks with respective maximum at 348 nm and around 330 nm which have different kinetic behaviors. From the observed evolution of λ_1 with time, it can be supposed that a weak stable peak at 330 nm, with a low OD value, appears very rapidly in the reaction. Simultaneously, a strong transient peak at 348 nm is formed, increases progressively to higher intensity, and then slowly disappears to allow the 330 nm peak to be visible again.

At temperatures between −65 and −30 °C, peaks at 348 and 468 nm were both observed and their maximal intensities decreased with the temperature increase. At temperatures higher than −30 °C, no peak ascribed to carbocations could be detected.

The various peaks observed at wavelengths higher than 300 nm are characteristic of carbocationic species with an aryl substituent. The 330 nm absorption band should be assigned to the cumyl cation Cum$^+$. This assignment is based on values reported for systems in which only the monomeric cumyl cation was formed without any oligomeric species. For example, Olah reported $\lambda_{\max} = 326$ nm in superacid medium[20] and MacClelland reported $\lambda_{\max} = 325$ nm for Cum$^+$ formed by laser flash photolysis in trifluoroethanol.[21] A similar wavelength ($\lambda_{\max} = 333$ nm) was previously reported in our laboratory[18] for Cum$^+$ formed by the ionization of CumCl with $\mathrm{SbF_5}$ in dichloromethane, the molar extinction coefficient being $\epsilon_{333\ \mathrm{nm}} = 26\,300$ L·mol^{-1}·cm^{-1}. The behavior of the 330 nm peak, observed by the stopped-flow technique, indicates that the cumyl cation is rapidly formed when cumyl chloride is mixed with $\mathrm{BCl_3}$ and that its concentration remains relatively low, suggesting that cumyl chloride is only weakly ionized by $\mathrm{BCl_3}$. This is in perfect agreement with the low-temperature NMR results.

The 348 nm peak associated with the one at 468 nm should correspond to higher molecular weight cations (α-methylstyrene dimer, D$^+$, and oligomers, P$^+$, although formation of high polymer is not possible at a α-MeSt concentration below its equilibrium value, $[\alpha\text{-MeSt}]_{\mathrm{eq}} = 0.01$ mol·L^{-1} at −78 °C). This result correlates well with the first reported stopped-flow experiments where a peak at 350 nm was detected in the polymerization of α-methylstyrene initiated with perchloric acid in dichloromethane at −80 °C.[22] The evolution of the intensity of the 348 nm peak shows that the concentration of D$^+$ (and perhaps P$^+$) increases rapidly at the beginning of the reaction and then slowly decreases after reaching the maximum. This peak disappears after a few hundreds of seconds. This D$^+$ cation results from the reaction of Cum$^+$ with α-methylstyrene, and P$^+$ could be formed by the potential further oligomerization. According to the ^{1}H NMR results, the monomer cannot be formed in situ by β-proton elimination from Cum$^+$ since this reaction should be neglected, especially at very low temperatures. Thus, D$^+$ is most probably formed by the reaction of Cum$^+$ with the small amount of monomer initially present in the medium (<4 mol % of CumCl). Owing to reversibility of the ionization reaction, the corresponding Cl-terminated dimer and oligomers of α-methylstyrene (respectively DCl and PCl) should also exist in the medium and be in dynamic equilibrium with the respective carbocations. The complete disappearance of these cations can only be explained by an irreversible reaction which is supposed to be the indanic cyclization since the indanic dimer of α-methylstyrene, I, could be observed in the low-temperature NMR spectra. After complete consumption of α-methylstyrene and disappearance of the oligomeric cations, the only remaining reaction is the equilibration between CumCl/$\mathrm{BCl_3}$ and Cum$^+$. The cumyl cation is then the only carbocationic species absorbing in the UV range.

According to these experimental observations, a general scheme of the reactions occurring at low temperatures is proposed (Scheme 2).

Stopped-Flow Kinetic Study. We have concluded that the weak peak around 330 nm corresponded to the cumyl cation Cum$^+$. The total concentration of this cation, $[\mathrm{Cum^+}]_{\mathrm{total}}$, can be roughly estimated at −65 °C for the long time experiments (=500 s) after complete disappearance of the 348 nm peak (Figure 5). A value of $\epsilon = 26\,300$ L·mol^{-1}·cm^{-1} was used as previously reported.[18] For experiment no. 3, $\mathrm{OD}_{330\ \mathrm{nm}} \approx 0.1$ after 1000 s was reached ($[\mathrm{Cum^+}]_{\mathrm{total}} \approx 1.9 \times 10^{-5}$ mol·L^{-1}), and for experiment no. 5, $\mathrm{OD}_{330\ \mathrm{nm}} \approx 0.08$ after 500 s ($[\mathrm{Cum^+}]_{\mathrm{total}} \approx 1.5 \times 10^{-5}$ mol·L^{-1}).

At this stage, since the UV measurements provide a total concentration of ion-pairs and dissociated ions, we estimated an apparent constant K_1 (obviously linked to K_{i}, K_{d}, and concentrations)

$$K_1 = \frac{[\mathrm{Cum^+}]_{\mathrm{total}}}{[\mathrm{CumCl}]_0[\mathrm{BCl_3}]_0}$$

with

$$[\mathrm{Cum^+}]_{\mathrm{total}} = [\mathrm{Cum^+BCl_4^-}] + [\mathrm{Cum^+}] \approx K_{\mathrm{i}}[\mathrm{CumCl}]_0 [\mathrm{BCl_3}]_0 + \sqrt{K_{\mathrm{i}}K_{\mathrm{d}}[\mathrm{CumCl}]_0[\mathrm{BCl_3}]_0}$$

Thus

$$K_1 = K_{\mathrm{i}} + \sqrt{\frac{K_{\mathrm{i}}K_{\mathrm{d}}}{[\mathrm{CumCl}]_0[\mathrm{BCl_3}]_0}}$$

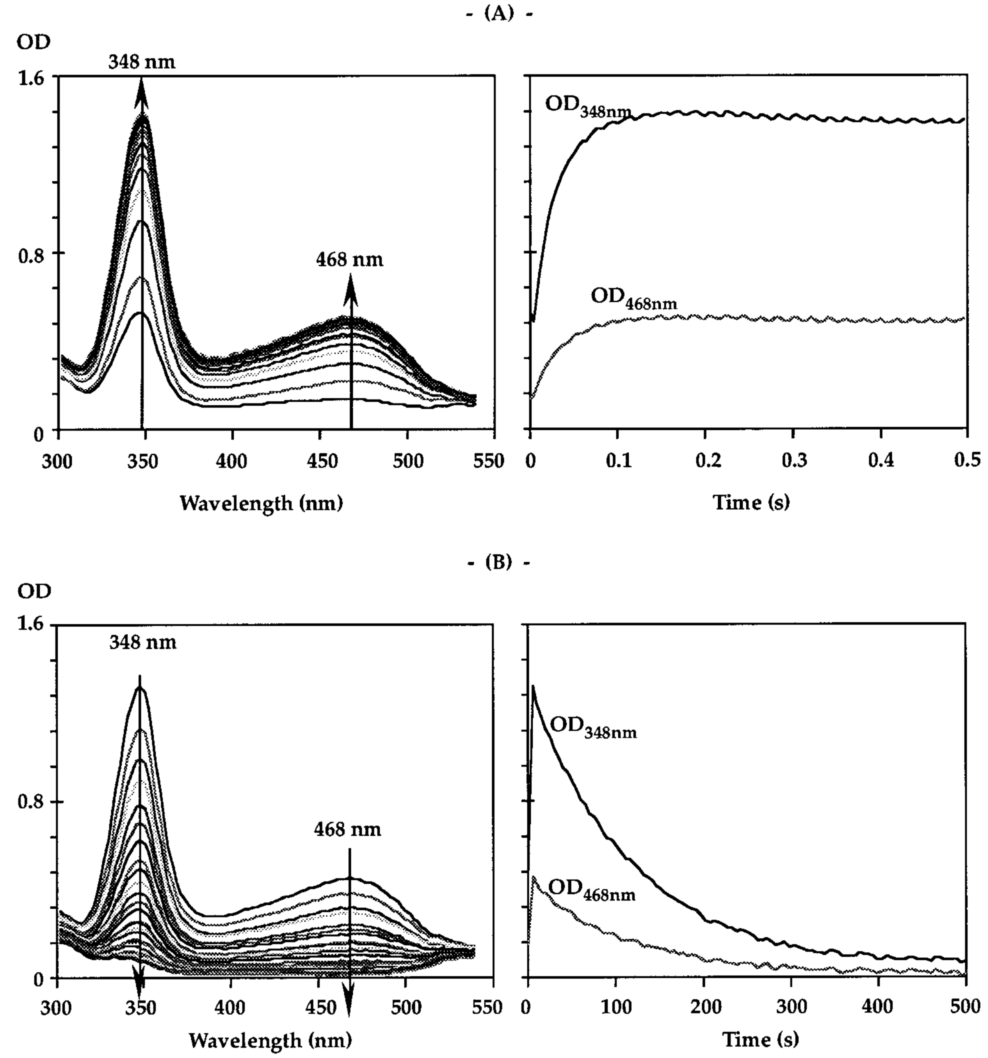


Figure 3. Stopped-flow study: $[\mathrm{CumCl}]_0 = 0.0225$ mol·L^{-1}; $[\mathrm{BCl_3}]_0 = 0.56$ mol·L^{-1}; $T = -65$ °C. Key: (A) evolution of spectra from 0 to 0.24 s, step 0.010 s; (B) evolution of spectra from 5 to 490 s, step 15 s.

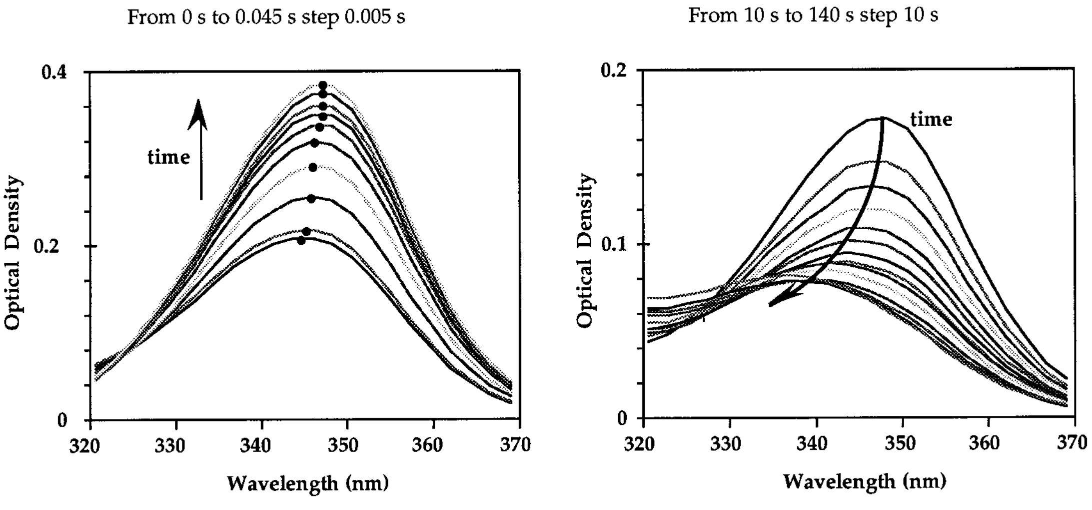


Figure 4. Stopped-flow study: evolution of the wavelength at the maximum of the peak at approximately 348 nm. Conditions: $[\mathrm{CumCl}]_0 = 0.0113$ mol·L^{-1}; $[\mathrm{BCl_3}]_0 = 0.53$ mol·L^{-1}; $T = -62$ °C.

The concentration of cumyl chloride at the equilibrium is supposed to be close to its initial concentration since its consumption is negligible as evidenced by NMR analysis. The initial concentration of BCl_3 has been used since the Lewis acid was always in excess. For experiments 3 and 5, $K_1 = 3.2 \times 10^{-3}$ L·mol^{-1} and $K_1 = 1.2 \times 10^{-3}$ L·mol^{-1} were respectively calculated. Only 0.1% of cumyl chloride is ionized when the initial concentration of boron trichloride is 0.5 mol·L^{-1} at −65 °C in CH_2Cl_2.

The value of K_1 is apparent and comprises the total concentration of cations including ion-pairs and free

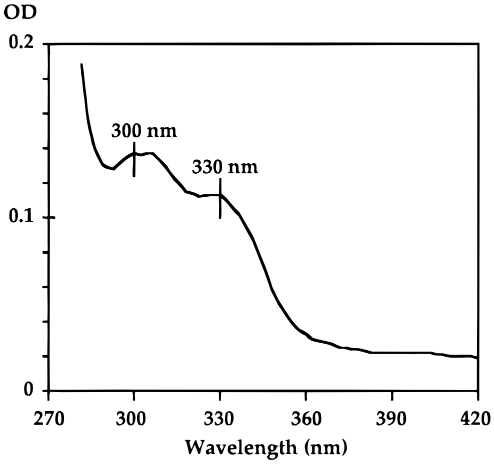
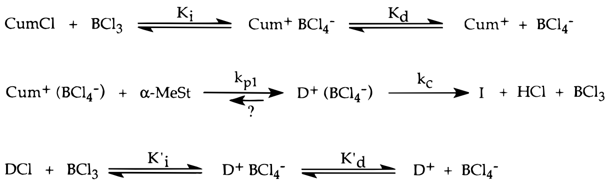


Figure 5. Stopped-flow study: spectrum at 1000 s. Conditions: $[\mathrm{CumCl}]_0 = 0.0113$ mol·L^{-1}; $[\mathrm{BCl_3}]_0 = 0.53$ mol·L^{-1}; $T = -62$ °C.

Scheme 2. Reactions at $T < -60$ °C



with :

K_i, K'_i :	ionization equilibrium constants (for CumCl and DCl respectively)
K_d, K'_d :	dissociation equilibrium constants (for $\mathrm{Cum^+BCl_4^-}$ and $\mathrm{D^+BCl_4^-}$ respectively)
k_c :	rate constant of irreversible termination of cations D^+
k_{p1} :	rate constants of propagation for $\mathrm{Cum^+}$

ions. At such a low concentration of cations, the dissociation equilibrium (equilibrium constant K_d) cannot be neglected, and the total concentration of cations depends on both equilibria of ionization (equilibrium constant K_i) and dissociation. For example, when using $K_d = 10^{-4}$ mol·L^{-1} (the dissociation constant for benzhydryl cations with $\mathrm{BCl_4^-}$ counteranion was determined to be $K_d = 2 \times 10^{-4}$ mol·L^{-1} in $\mathrm{CH_2Cl_2}$ solution at -70 °C,[10] and it should be lower for cumyl cation), at a total concentration of cumyl carbocationic species $[\mathrm{Cum^+}]_{\mathrm{total}} = 1.9 \times 10^{-5}$ mol·L^{-1} for experiment no. 3, it can be calculated that $K_i = 5 \times 10^{-4}$ L·mol^{-1} and that 90% of $\mathrm{Cum^+}$ should be in the form of free ions. However, this proportion is expected to be smaller in a polymerizing system owing to the common-ion effect in the presence of propagating cations with $\mathrm{BCl_4^-}$ counteranion. The estimated ionization constant K_i was found to be comparatively lower than the value of 0.02 L·mol^{-1} extrapolated (at -70 °C in $\mathrm{CH_2Cl_2}$ with $\mathrm{BCl_3}$ as a Lewis acid) from the ethanolysis rate constant of cumyl chloride at 25 °C[23] ($k = 3.94 \times 10^{-4}$ s^{-1}) using the correlation proposed by Schade and Mayr.[24]

The variation with time of $\mathrm{OD}_{348\ \mathrm{nm}}$ (corresponding to $\mathrm{D^+}$) has been examined and values are reported in Tables 1 and 2. The initial slopes of appearance of the peak at 348 nm were measured at -65 °C for various initial concentrations of CumCl and $\mathrm{BCl_3}$ and initial rates of formation of $\mathrm{D^+}$, $R_{\mathrm{i(D^+)}}$, could be calculated assuming that the extinction coefficient at 348 nm is similar to that of $\mathrm{Cum^+}$ at 330 nm ($\epsilon = 26\,300$ L·mol^{-1}·cm^{-1}). They ranged from 2×10^{-3} mol·L^{-1}·s^{-1} (experiment 3) to 6×10^{-3} mol·L^{-1}·s^{-1} (experiment 5). Formation of this peak corresponds to initiation, i.e., reaction of the cumyl cation $\mathrm{Cum^+}$ with α-methylstyrene. High initial rate values show that the initiation step is fast although ionization of CumCl is weak and the initial concentration of α-methylstyrene is very low (less than 4 mol % of CumCl as deduced from the ^{1}H NMR spectra). This suggests that the apparent rate constant of addition of $\mathrm{Cum^+}$, k_{p1}, is very high. From the initial rates $R_{\mathrm{i(D^+)}}$ for experiments 1–7 at -65 °C, the order of magnitude of k_{p1} could be estimated using $[\alpha\text{-MeSt}]_0 = 0.04[\mathrm{CumCl}]_0$ and $K_1 = 2 \times 10^{-3}$ L·mol^{-1}.

$$k_{p1} = \frac{R_{\mathrm{i(D^+)}}}{[\alpha\text{-MeSt}]_0[\mathrm{Cum^+}]_{\mathrm{total}}} = \frac{R_{\mathrm{i(D^+)}}}{[\alpha\text{-MeSt}]_0 K_1 [\mathrm{CumCl}]_0[\mathrm{BCl_3}]_0} \approx 3 \times 10^5\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$$

The calculated value of k_{p1} is about 10 times higher than the propagation rate constant previously reported by Villesange[25] for the polymerization of α-methylstyrene in $\mathrm{CH_2Cl_2}$ at -70 °C where $k_p = 22\,000$ L·mol^{-1}·s^{-1} was calculated assuming quantitative initiation. This may suggest that the value of k_p was underestimated and/or that the first-step addition rate constant k_{p1} is higher than the propagation rate constant k_p. It is possible that the rate constant of addition of low molar mass species is a few times larger than that of a polymeric species (i.e., propagation). This is for instance the case for phenylethyl radical which adds to styrene 15 times faster than it propagates.[26] High propagation rate constants in the range of 6×10^8 L·mol^{-1}·s^{-1} were also predicted by Mayr[27,28] for the oligomerization of isobutene, based on the behavior of monomeric species.

After the period of increase, $\mathrm{OD}_{348\ \mathrm{nm}}$ reached a maximum value $\mathrm{OD_{max}}$ at a time t_{max} which was 0.1–0.3 s. The correlation with the initial concentration of cumyl chloride was relatively poor, presumably due to variations in the initial concentration of α-methylstyrene between experiments. Nevertheless, the maximum absorbance at 348 nm was always much higher than that at 330 nm. Since ϵ at 348 nm should be similar to ϵ at 330 nm, it may be concluded that concentration of the dimeric and plausible oligomeric cations is higher than concentration of $\mathrm{Cum^+}$. It is obviously the reverse for the corresponding covalent species since at low-temperature cumyl chloride concentration remains close to its initial value and the concentration of oligomeric species cannot be higher than that of the initial α-methylstyrene (<4 mol % of CumCl). This indicates much larger equilibrium constant of ionization for dimeric (and oligomeric) cations than for the monomeric cumyl cation. This trend can be explained by higher steric strain for the oligomeric covalent precursors as compared with cumyl chloride; this back strain is relieved after ionization owing to the planar structure of the carbocations (the so-called B-strain effect).[29] As reported in Table 1, the ratio of the maximum concentration of $\mathrm{D^+}$ to the initial concentration of CumCl is between 0.004 and 0.013. On the basis of the 4 mol % content of monomer in the CumCl solutions and considering that dimerization occurs with complete consumption of the monomer (i.e., no higher oligomeric cations are formed, $[\mathrm{D^+}] + [\mathrm{DCl}] = [\alpha\text{-MeSt}]_0 = 0.04[\mathrm{CumCl}]_0$), an apparent constant K_2 can be estimated at -65 °C, with $[\mathrm{BCl_3}]_0 = 0.56$ mol·L^{-1} (as was mentionned for K_1, K_2 is linked to K'_i, K'_d and concentra-

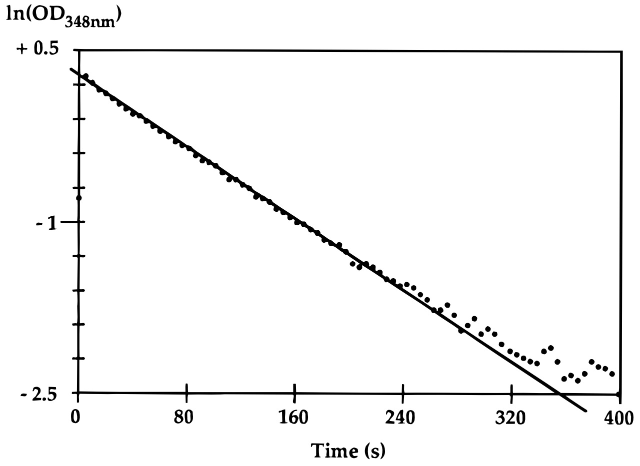


Figure 6. Stopped-flow study: Linear evolution of ln(OD_{348nm}) vs time after the maximum. Conditions: $[CumCl]_0 = 0.0225$ mol·L^{-1}; $[BCl_3]_0 = 0.55$ mol·L^{-1}; $T = -65$ °C.

tions).

$$K_2 = \frac{[D^+]_{max}}{[DCl][BCl_3]_0} = \frac{[D^+]_{max}}{([\alpha\text{-MeSt}]_0 - [D^+]_{max})[BCl_3]_0} = \frac{[D^+]_{max}/[CumCl]_0}{([\alpha\text{-MeSt}]_0/[CumCl]_0 - [D^+]_{max}/[CumCl]_0)[BCl_3]_0} = 0.5 \pm 0.3 \text{ L}\cdot\text{mol}^{-1}$$

This value would be higher for a lower initial concentration of α-methylstyrene and if either oligomerization occurred or if the monomer was not completely consumed. Therefore, ~25% of DCl is ionized when initial concentration of boron trichloride is 0.5 mol·L^{-1} at −65 °C in CH_2Cl_2.

The equilibrium constant of ionization of cumyl chloride is strongly lower than that of the higher oligomers. Although the rate constant of first addition k_{p1} is probably higher than the propagation rate constant k_p, this strong difference of ionization explains the experimentally observed low efficiency of cumyl chloride to initiate the cationic polymerization of α-methylstyrene.[8,9,30]

When temperature was raised from −65 to −40 °C, the ratio $[D^+]_{max}/[CumCl]_0$ was continuously decreased (Table 2), indicating the same trend for K_2. This decrease of K_2 with increasing temperature can be directly related to the apparently negative activation energy experimentally observed for the propagation of α-methylstyrene.[25,30,31]

The peak at 348 nm, after reaching its maximum, was followed by a first-order slow decrease until its complete disappearance (Figure 6). Values of the slope of ln($OD_{max}/OD_{348\ nm}$) vs time are reported in Table 1 for $T = -65$ °C and in Table 2 for different temperatures. At −65 °C, an average value of the first-order rate constant for the disappearance of the peak at 348 nm is 0.0081 s^{-1} (half-life time, $t_{1/2} = 86$ s). When temperature was raised from −65 to −40 °C, the apparent first order rate constant for the disappearance of the peak was significantly increased to reach 0.0795 s^{-1} at −40 °C ($t_{1/2} = 8.7$ s) (Table 2). Variation of the slope with temperature allows determination of an activation energy $E_a = 9$ kcal·mol^{-1} (Figure 7). Thus, the apparent first-order rate constant for the disappearance of the cation would be 3 s^{-1} at + 13 °C ($t_{1/2} = 0.23$ s), i.e., 370 times higher than at −65 °C. Such high value may explain why no trace of the dimeric cation D^+ could be seen in the NMR spectra at +13 °C but only the final indanic dimer of α-methylstyrene.

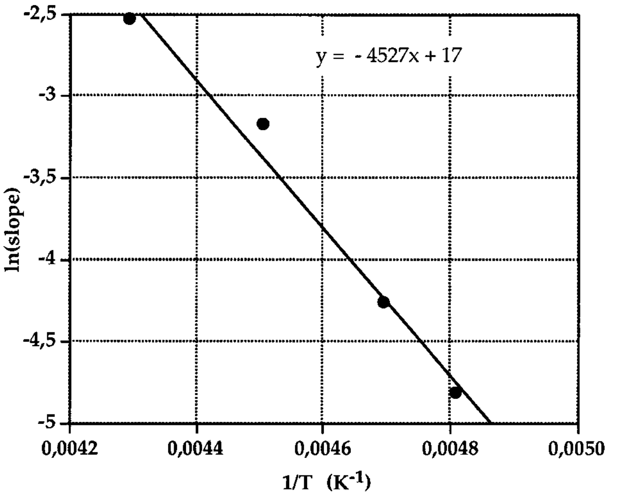


Figure 7. Arrhenius plot for the apparent rate constant of irreversible termination of cations absorbing at 348 nm.

The consumption of the dimeric cations is mainly attributed to indanic cyclization (and eventually to β-proton elimination from D^+, although not experimentally evidenced) with the rate constant k_c. If the equilibrium of interconversion of DCl and D^+ is rapidly established, the rate of decrease of $OD_{348\ nm}$ can be expressed with the first-order kinetics and gives a direct determination of k_c using the following equations:

$$\frac{d[D^+]}{dt} = -\frac{K_2[BCl_3]_0}{1 + K_2[BCl_3]_0}k_c[D^+]$$

$$\ln\left(\frac{[D^+]_{max}}{[D^+]}\right) = \frac{K_2[BCl_3]_0}{1 + K_2[BCl_3]_0}k_c t \quad \text{or} \quad \ln\left(\frac{OD_{max}}{OD_{348nm}}\right) = \frac{K_2[BCl_3]_0}{1 + K_2[BCl_3]_0}k_c t$$

At −65 °C, since $K_2 \approx 0.5$ L·mol^{-1} and $[BCl_3]_0 = 0.56$ mol·L^{-1}, the ratio $K_2[BCl_3]_0/(1 + K_2[BCl_3]_0) = 0.22$, and so the slope of ln($OD_{max}/OD_{348\ nm}$) vs time equals $0.22k_c$. Since the slope equals 0.0081 s^{-1}, it gives $k_c = 0.04$ s^{-1} at −65 °C.

This calculation is based on the assumption that no higher oligomeric cations were formed and that depropagation from dimeric to monomeric cations could be neglected. The latter assumption is reasonable, since the propagation−depropagation equilibrium constant is significantly higher for the dimeric than trimeric and polymeric species.[32,33]

Thus, with BCl_4^- as a counteranion, irreversible termination reactions are very slow as compared with propagation ($k_p = 22\,000$ L·mol^{-1}·s^{-1} at −70 °C[25]) in the low-temperature cationic polymerization of α-methylstyrene (neither elimination nor cyclization). The only termination event occurring during polymerization is reversible covalent C−Cl bond formation, and such a situation should lead to living polymerization. However, although slow with respect to propagation, irreversible indanic cyclization is not absent and leads to a decrease of concentration of the living chains of 50% in less than 100 s at −65 °C.

Conclusion

The first aim of this work was to measure the equilibrium constant of ionization of the cumyl chloride/BCl_3 system which was used as an initiator in many cationic polymerization systems. Study of the ionization of cumyl chloride by boron trichloride was carried out using stopped-flow UV−visible analysis and ^1H NMR spectroscopy in methylene chloride. A UV absorption band at 330 nm was assigned to the cumyl cation existing at very low concentrations even when excess Lewis acid was used. Only 0.1% of cumyl chloride was ionized with $[BCl_3]_0 = 0.5$ mol·L^{-1} at −65 °C which allowed one to estimate the equilibrium constant of ionization ($K_i \approx 5 \times 10^{-4}$ L·mol^{-1}). At that temperature the cumyl cation with BCl_4^- counteranion was stable since no elimination was observed and cumyl chloride was not consumed.

The system was however complicated by the presence of unavoidable traces of α-methylstyrene in the cumyl chloride solutions. Interestingly, this situation allowed one to consider this system as a good model for the cationic polymerization of α-methylstyrene initiated by cumyl chloride/BCl_3 in methylene chloride in which propagation was almost absent. Kinetics enables the study of the initiation step, ionization of Cl-terminated chains, and irreversible termination step of the cations. The ionization of cumyl chloride was immediately followed by the addition of the monomer to the cumyl cation which resulted in the formation of the dimeric cation with main absorption band at 348 nm. Appearance of this peak was very fast and the maximum concentration was reached in less than 0.3 s at −65 °C. The initial slopes allowed an estimation of the rate constant of initiation, i.e., of the reaction of the cumyl cation with α-methylstyrene: $k_{p1} = 3 \times 10^5$ L·mol^{-1}·s^{-1}. The maximum absorbance of the 348 nm peak was found to be much larger than that of the 330 nm peak, and assuming that the extinction coefficients are the same for both species, it was concluded that ionization is much stronger for the dimeric and oligomeric species as compared with the monomeric cumyl chloride, in agreement with the B-strain effect. This explains why cumyl chloride is not a good initiator for the cationic polymerization of α-methylstyrene whereas the hydrochlorinated dimer of α-methylstyrene is a good one.[30] After reaching its maximum concentration, the dimeric cation was slowly consumed and probably converted into the indanic dimer of α-methylstyrene, and the rate constant of irreversible termination could be estimated: $k_c = 0.04$ s^{-1} at −65 °C. When comparing the various rate constants, it was concluded that, at low temperature with BCl_4^- as a counteranion, the irreversible termination steps, i.e., β-proton elimination and indanic cyclization, are very slow as compared to propagation. Boron trichloride can be considered as an efficient Lewis acid for the living cationic polymerization of α-methylstyrene. At +13 °C, NMR analysis showed that cumyl chloride was slowly converted into the indanic dimer of α-methylstyrene with dehydrochlorination as the rate determining step.

The results reported in this paper give new quantitative information concerning both the ionization of cumyl chloride by BCl_3 as well as the cationic polymerization of α-methylstyrene. The calculated values highlight the previously reported experimental observations that cumyl chloride was not an efficient initiator whereas BCl_3 was a good Lewis acid leading to slow termination reactions and to "living" polymerization. Our conclusions are supported by the new findings concerning the efficient initiation with the hydrochlorinated dimer of α-methylstyrene ionized with BCl_3.[30]

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MA971883Q