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LIVING CARBOCATIONIC OLIGOMERIZATION OF ISOBUTYLENE BY TERTIARY ALCOHOL/BCl₃/1-METHYL-2-PYRROLIDINONE INITIATING SYSTEMS. KINETIC STUDY

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Key Words: Isobutylene, Tertiary Alcohol, Electron-Pair Donor, Living Carbocationic Polymerization, Kinetics

ABSTRACT

Low molar mass ($\overline{M}_n < 4000 \text{ g.mol}^{-1}$), narrow molar mass distribution ($M_w/M_n = 1.1-1.3$) linear α -(*tert*-butyl) ω -(*tert*-chloro) and α -cumyl ω -(*tert*-chloro) oligoisobutylenes (PIBs) were synthesized using two initiating systems: 2,4,4-trimethyl-pentan-2-ol (TMPOH)/BCl₃/-40°C and 2-phenylpropan-2-ol (CumOH)/BCl₃/-70°C in the presence of an efficient electron-pair donor (ED), 1-methyl-2-pyrrolidinone (NMP) in methyl chloride. The kinetics of oligomerization were investigated. In these two systems, similar polymerization mechanisms were observed with, nevertheless, a slight difference of growing species behavior in the early polymerization steps. The initiation and propagation rate constants were determined; their values are low showing that the addition of NMP to these initiating systems leads to controlled carbocationic polymerizations. Moreover, the living character of the polymerization was demonstrated.

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INTRODUCTION

Initiating systems associating BCl_3 with mono- and bifunctional *tert*-alcohols, e.g., cumyl alcohol (CumOH), dicumyl alcohol (DiCumOH), 2,4,4-trimethylpentan-2-ol (TMPOH), 2,6-dihydroxy-2,4,4,6-tetramethylheptane MHdiOH), are efficient in the polymerization of isobutylene (IB) in CH_3Cl or CH_2Cl_2 solvents in the -10°C to -50°C range; unfortunately the resulting polymers exhibit broad molar mass distributions [1-4]. However, the addition of electron-pair donors such as *N,N*-dimethylacetamide, dimethylsulfoxide and more recently triethylamine or 1-methylpyrrolidine to systems including various *tert*-alcohols as initiators leads to a living polymerization and to well-defined monodisperse polyisobutylenes end-capped with *tert*-chloro groups [5-8]. Pratap *et al.* have successfully demonstrated the living nature of isobutylene polymerization when the *tert*-alcohol is *tert*-amyl alcohol, 2-cyclohexylpropan-2-ol or dicumyl alcohol in conjunction with BCl_3 and 1-methyl-2-pyrrolidinone (NMP) as electron-pair donor, in CH_2Cl_2 solvent [9-11].

This article is devoted to the synthesis of monodisperse low molar mass α -(*tert*-butyl) ω -(*tert*-chloro) and α -cumyl ω -(*tert*-chloro) oligoisobutylenes using 1-methyl-2-pyrrolidinone associated with TMPOH/ BCl_3 and CumOH/ BCl_3 as initiating systems and methyl chloride as solvent. In order to compare the mechanism of the oligomerizations initiated by these two systems, kinetic studies were carried out using conventional AMI and IMA techniques [12].

EXPERIMENTAL

Materials

2,4,4-trimethylpentan-2-ol was prepared from 2,4,4-trimethylpent-1-ene according to Brown *et al.* [13]. 2-Phenylpropan-2-ol (i.e. cumyl alcohol) and 1-methyl-2-pyrrolidinone (from Aldrich) were used as received.

Methyl chloride and isobutylene (from Setic Labo) were separately dried by passing the gases through two columns packed with molecular sieves (4 Å) and BaO. Boron trichloride (from Setic Labo) was used as received.

Procedures

Polymerizations were carried out under vacuum at low temperature, using both the conventional *All-Monomer-In* (AMI) and *Incremental-Monomer-Addition* (IMA) techniques [12]. Specific oligomerization conditions and the

TABLE 1. Experimental Conditions of the Isobutylene Oligomerization Initiated by *tert*-alcohol (Initiator)/BCl₃/NMP (Except Runs 1, 2, 8 and 9) in Methyl Chloride - $\overline{Mn}_{th} \approx 1000 \text{ g}\cdot\text{mol}^{-1}$ - AMI Technique.

Initiator	Run	T (°C)	Time (min)	[C ₄ H ₈] ₀ (mol L ⁻¹)	[I] ₀ ^a (mol L ⁻¹) × 10 ²	[NMP] ₀ (mol L ⁻¹) × 10 ²	[BCl ₃] ₀ (mol L ⁻¹) × 10 ¹	$\frac{[\text{BCl}_3]_0}{[\text{I}]_0}$	$\frac{[\text{NMP}]_0}{[\text{I}]_0}$	CH ₃ Cl (mL)
TMPOH	1	-40	65	0.84	4.3	None	4.1	9.6	—	49
	2	-40	155	0.87	5.2	None	4.2	8.1	—	50
	3	-40	15	0.86	5.4	8.1	4.2	7.8	1.5	50
	4	-40	30	0.85	5.1	7.6	4.1	8.1	1.5	50
	5	-40	45	0.83	5.1	7.6	4.1	8.1	1.5	50
	6	-40	65	0.86	5.2	7.8	4.2	8.1	1.5	50
	7	-40	135	0.92	5.8	8.7	4.6	7.9	1.5	51
CumOH	8	-70	65	0.86	6.1	None	3.1	5.1	—	39
	9	-70	120	0.86	5.8	None	3.0	5.3	—	40
	10	-70	15	0.86	6.3	9.4	5.0	7.9	1.5	39
	11	-70	30	0.82	5.9	8.8	5.1	8.7	1.5	42
	12	-70	45	0.85	5.7	8.6	4.5	7.9	1.5	40
	13	-70	65	0.86	5.7	8.6	4.5	7.9	1.5	40
	14	-70	130	0.85	5.7	8.6	4.6	8.1	1.5	40

^a Initiator : *tert*-alcohol

reagent concentrations are given in Tables 1 and 5. In the AMI method, the introduction order of the chemicals in the reactor was as follows: initiator, methyl chloride, isobutylene and 1-methyl-2-pyrrolidinone. Oligomerizations were initiated with the introduction of boron trichloride after 15 minutes of premixing the solution, and were quenched with the addition of prechilled methanol. In the IMA method, the beginning of the procedure was the same as previously seen, but after 2 hours polymerization time intervals, an increment of isobutylene was added to the reactive mixture. At the end of polymerization, the solvent was removed under atmospheric pressure and at room temperature. The crude oligomer was then redissolved in hexane; the organic solution was washed with distilled water until it was neutral and the resulting organic layer was dried over anhydrous MgSO₄ and filtered. The oligomer was recovered by evaporating the solvent and dried under vacuum at room temperature.

Analysis

SEC Analysis

Molar masses and molar mass distributions of these oligomers were determined by Size Exclusion Chromatography using a Waters liquid chromat-

ograph (Model 510) equipped with a differential refractometer (Model 410) linked to the Maxima 820/Baseline 810 workstation. Tetrahydrofuran was used as the mobil phase. With regard to the analysis of oligomers resulting from the IMA technique (or oligomers with mass-average molar mass above 1000), four μ -styragel columns (50, 500, 103 and 104 Å), having a particle size of 5 μ m, were used (flow rate: 1 mL/min); the calibration curve was made with polystyrene standards. As for the analysis of oligomers resulting from the AMI technique (or oligomers with mass-average molar mass below 1000), three PL-Gel columns (50, 100 and 500 Å), having a particle size of 5 μ m and a 60 cm long, were used (flow rate: 0.5 mL/min); in this case, the molar masses were calculated from an internal calibration curve.

NMR Spectroscopy

NMR spectra were recorded in CDCl_3 on a Bruker AM 500 Spectrometer. The ^1H and ^{13}C chemical shifts were referenced to residual CHCl_3 at 7.26 ppm and to CDCl_3 at 76.9 ppm, respectively. The two-dimensional ^1H - ^{13}C spectra were recorded using the XHCORR impulsion sequence ($\Delta t = 0.5J_{\text{C-H}}$ with $J_{\text{C-H}} = 140$ Hz).

Determination of Kinetic Parameters

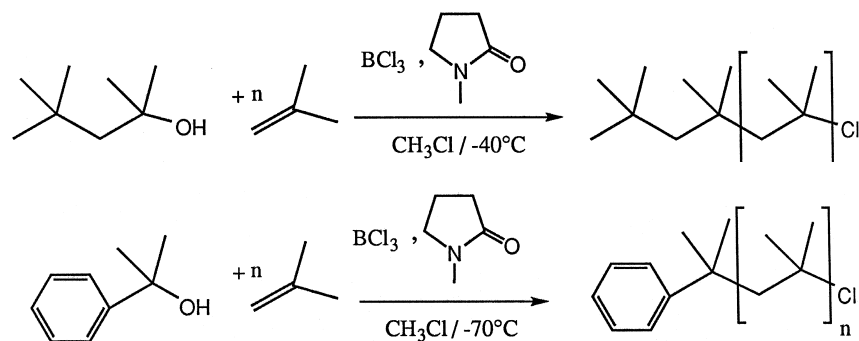
Calculations of $k_{\text{c}}^{\text{app}}$ and $k_{\text{p}}^{\text{app}}$ were carried out using the “Mathematica” software of Wolfram Research Co.

RESULTS AND DISCUSSION

Kinetic Study of $\text{R}'\text{OH}/\text{BCl}_3/\text{IB}/\text{NMP}/\text{CH}_3\text{Cl}$ Oligomerization Systems (AMI Technique)

The living oligomerization of isobutylene by an aliphatic (TMPOH) or an aromatic (CumOH) *tert*-alcohol initiator in conjunction with BCl_3 coinitiator and 1-methyl-2-pyrrolidinone (NMP) in methyl chloride, was investigated (Scheme 1).

On the basis of previous reports [14], we could determine experimental oligomerization conditions allowing us to prepare well-defined α -(*tert*-butyl) ω -(*tert*-chloro) and α -cumyl ω -(*tert*-chloro) oligoisobutylenes and the corresponding oligomerizations were not accompanied by side reactions such as protic initiation, chain transfer, cycloalkylation (formation of indanyl end group in the



Scheme 1. Oligomerization of isobutylene initiated by TMPOH/ BCl_3 /NMP/ -40°C and CumOH/ BCl_3 /NMP/ -70°C systems, respectively.

TABLE 2. Results of the Isobutylene Oligomerization Initiated by *tert*-alcohol (Initiator)/ BCl_3 /NMP (Except Runs 1, 2, 8 and 9) in Methyl Chloride - $\overline{Mn}^{\text{th}} \approx 1000 \text{ g}\cdot\text{mol}^{-1}$ - AMI Technique.

Initiator	Run	Time (min)	W_p^a (g)	\overline{Mn}^b	$\overline{Mw}/\overline{Mn}^b$	I_{eff}^c (%)	C^d (%)
TMPOH	1	65	2.95	2330	3.80	52	105
	2	155	3.05	1820	3.50	56	99
	3	15	0.72	380	1.10	62	16
	4	30	1.15	520	1.09	74	30
	5	45	1.53	615	1.09	82	43
	6	65	1.89	730	1.08	87	55
	7	135	3.39	945	1.06	102	92
CumOH	8	65	1.75	710	5.90	92	64
	9	120	1.77	750	6.20	89	65
	10	15	0.65	295	1.22	82	14
	11	30	0.99	410	1.26	90	27
	12	45	1.22	490	1.27	93	37
	13	65	1.78	670	1.19	93	60
	14	130	2.37	795	1.16	104	85

^a Amount of PIB-formed

^b Calculated from SEC measurements

^c Initiating efficiency corresponds to the ratio : (chain number / initial initiator number) 100 : $(W_p/\overline{Mn}) (100/I_0)$, where I_0 is the mole number of initial initiator

^d Monomer conversion corresponds to the ratio : (reacted monomer / introduced monomer) 100 :

$$((\overline{Mn} - y)/56) (W_p/\overline{Mn}) (1/(C_4H_8)_0) 100$$

with $y = 148.5$ for the TMPOH/ BCl_3 /NMP initiating system

$y = 154.5$ for the CumOH/ BCl_3 /NMP initiating system

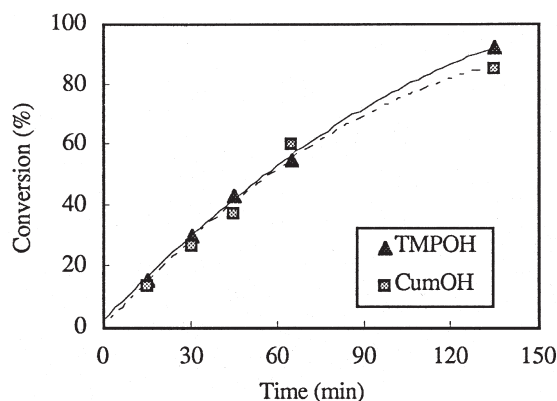


Figure 1. Monomer conversion as a function of time in TMPOH/BCl₃/IB/NMP/CH₃Cl/-40°C and CumOH/BCl₃/IB/NMP/CH₃Cl/-70°C experiments. (AMI technique: the reaction conditions are listed in Tables 1 and 2; $\overline{Mn}_{th} \approx 1000 \text{ g}\cdot\text{mol}^{-1}$).

case of cumyl initiator) and irreversible termination [15]. For each initiating system, these optimal experimental conditions are listed in Table 1; they particularly require a low polymerization temperature, an excess of BCl₃ over the initiator (BCl₃/*tert*-alcohol ≈ 8) and a molar ratio NMP/*tert*-alcohol equal to 1.5 [9].

The kinetics of these systems were studied using the AMI technique (see Experimental); the reactions were stopped at different times by quenching with prechilled methanol. The results of isobutylene polymerizations are reported in Table 2.

Polymerizations carried out without electron-pair donor (Runs 1, 2, 8 and 9) lead to very broad molar mass distributions and initiating efficiencies (I_{eff}) below 100%; moreover monomer conversion (C) is limited to 65% when the initiator is CumOH whereas, it reaches 100% when the initiator is TMPOH.

On the other hand, in the presence of NMP, I_{eff} and C are close to 100% after 130 minutes. The plots corresponding to monomer conversion as a function of time (Figure 1) and total number of polymer chains (N) as a function of time (Figure 2) are in agreement with a mechanism where both initiation and propagation are slow. However, we can observe that after 15 minutes, initiating efficiency reaches a comparatively high value: 62% in the case of TMPOH as initiator and 82% in the case of CumOH, whereas in both systems monomer conversion is only 15%. In these systems, \overline{Mn} does not linearly increase with conversion (Figure 3) corroborating that the number of polymer chains formed increases during oligomerization, which supports the hypothesis assuming that

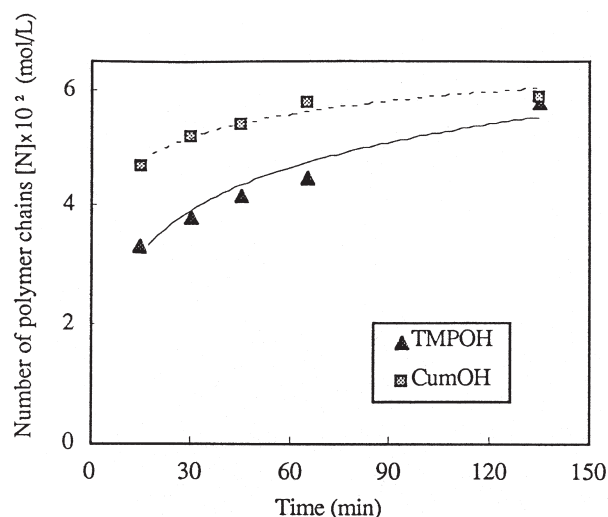


Figure 2. Total number of polymer chains $[N]$ as a function of time in TMPOH/ BCl_3 /IB/NMP/ CH_3Cl / -40°C and CumOH/ BCl_3 /NMP/ CH_3Cl / -70°C experiments. (AMI technique: the reaction conditions are listed in Tables 1 and 2 ; $[N] \approx (\text{Wp}/\overline{Mn})(1000/\text{V})$; Wp is the amount of PIB-formed and V is the total volume (mL); $[N]_0 = [\text{I}]_0 \approx 0.058 \text{ mol L}^{-1}$).

initiation is slow. But, \overline{Mn} reaches theoretical value ($\overline{Mn}_{\text{th}} \approx 1000$) after 2 hours, with a narrow molar mass distribution (see Table 2). However, the molar mass distribution with the CumOH/ BCl_3 /NMP initiating system is slightly broader than that obtained with the TMPOH/ BCl_3 /NMP system (1.16 against 1.06).

Size Exclusion Chromatography studies provide further evidence for slow initiation and propagation steps (Figures 4 and 5). After 15 minutes, (Figure 5), a low amount of chlorinated initiators ($n = 0$) are detected: cumyl chloride (CumCl) or 2-chloro-2,4,4-trimethylpentane (TMPCl) resulting in the chlorination of the initial *tert*-alcohols with BCl_3 . Chromatograms 4a and 4b clearly show the successive incorporation of isobutylene units in growing chains which accounts for a slow propagation (Scheme 2): all the peaks corresponding to the oligomers from $n = 1$ to $n = 9$ are distinctly observed up to 45 minutes. It is worth mentioning that the amounts of CumCl and TMPCl present in the final samples are probably smaller than the actual values because the oligomer recovery step includes a washing step (see Experimental) and some part of these molecules can be washed away.

Figure 5 provides interesting information with regard to the contribution of each oligomer and the reactivity of the oligomeric carbocation. When the initiating system is CumOH/BCl₃/NMP (Figure 5a), only a very small amount of 1,1,3,3-tetramethyl indane (arising from P₁) is formed [16], whereas the P₁ (n = 1) content is very high. On the other hand, the TMPOH/BCl₃/IB/NMP system presents a slightly different behavior (Figure 5b) : the concentration of P'1 (n = 1) is low compared to those of the higher oligomers P'2 - P'6. These observations are discussed further.

These oligomers were also characterized by NMR spectroscopy. The NMR analysis of polyisobutylenes with end groups of various nature has been extensively described [16-19]. Very recently, Mayr *et al.* have published ¹³C chemical shift data of low molar mass α -cumyl ω -(*tert*-chloro) oligoisobutylenes (from P₁ to P₇) [20].

The samples we prepared were analyzed by ¹³C and ¹H NMR. In particular, the comprehensive assignment of ¹H NMR spectra of α -cumyl ω -(*tert*-chloro) oligoisobutylenes was realized from two-dimensional ¹H-¹³C NMR spectra. For instance, in the ¹H NMR spectrum of the sample resulting from CumOH/BCl₃/IB/NMP polymerization system after 15 minutes reaction time (Figure 6b), we observe clearly the different peaks corresponding to various species present in the sample (Figure 6a). This ¹H NMR analysis confirms that the contents of side compounds such as 1,1,3,3-tetramethyl indane and the poly-

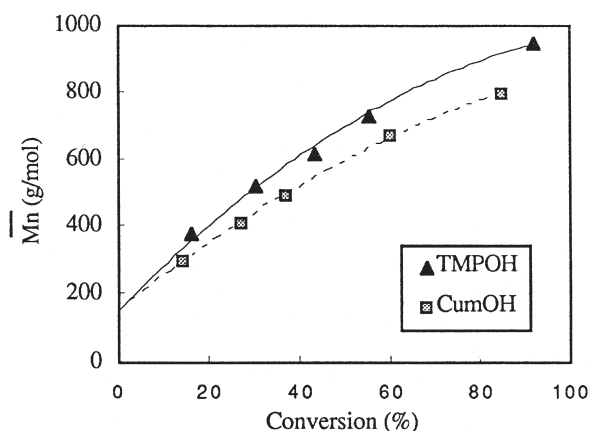


Figure 3. Variation \overline{Mn}_{th} versus conversion in TMPOH/BCl₃/IB/NMP/CH₃Cl /-40°C and CumOH/BCl₃/IB/NMP/CH₃Cl/-70°C experiments. (AMI technique: the reaction conditions are listed in Tables 1 and 2; $\overline{Mn}_{th} \approx 1000 \text{ g.mol}^{-1}$).

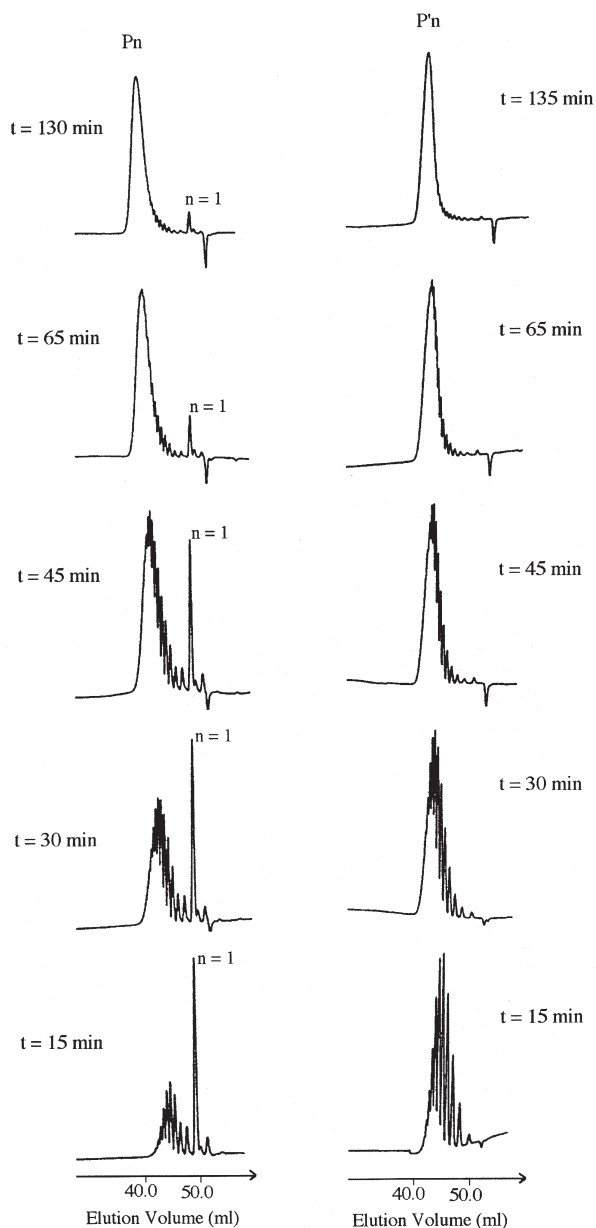


Figure 4. SEC (refractive index) chromatograms of oligoisobutenes: 4a) prepared from the CumOH/ BCl_3 /IB/NMP/ CH_3Cl / -70°C system at different reaction times (15, 30, 45, 65, and 130 minutes); 4b) prepared from the TMPOH/ BCl_3 /IB/NMP/ CH_3Cl / -40°C system at different reaction times (15, 30, 45, 65, and 135 minutes). (AMI technique: the reaction conditions are listed in Tables 1 and 2; $\overline{Mn}_{th} \approx 1000 \text{ g}\cdot\text{mol}^{-1}$).

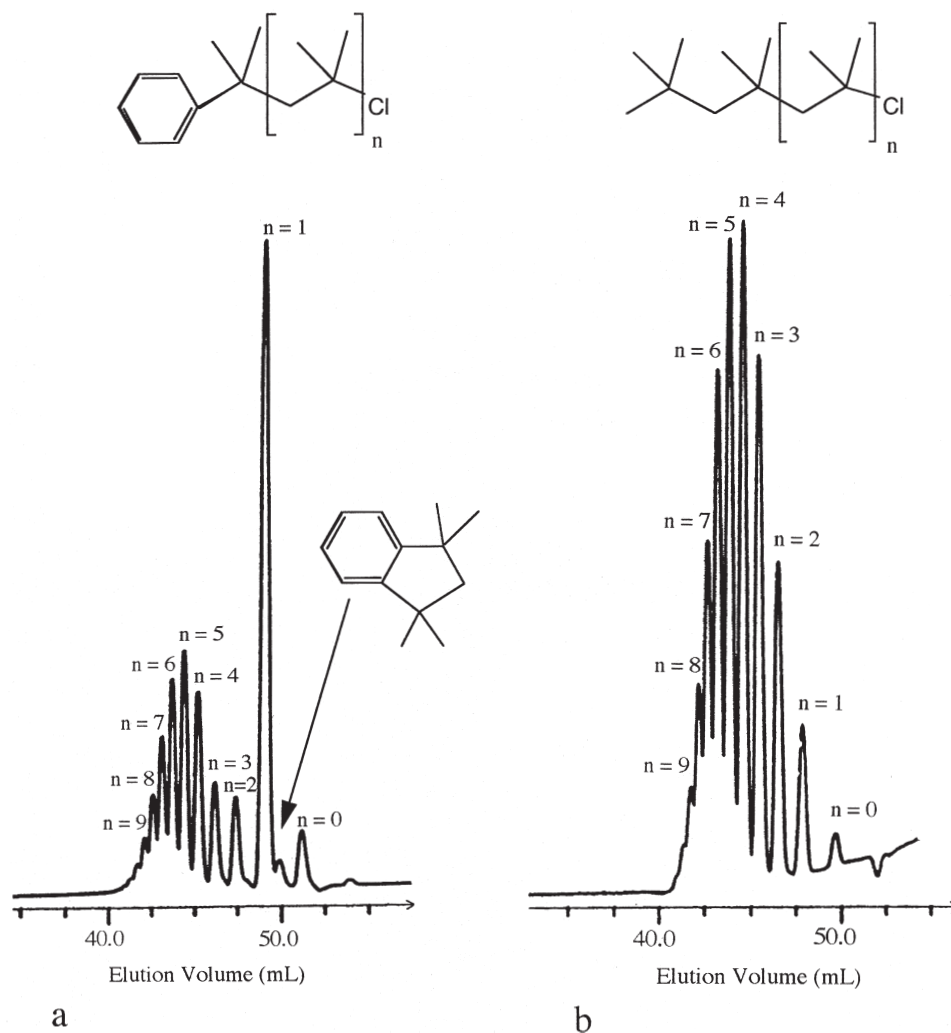
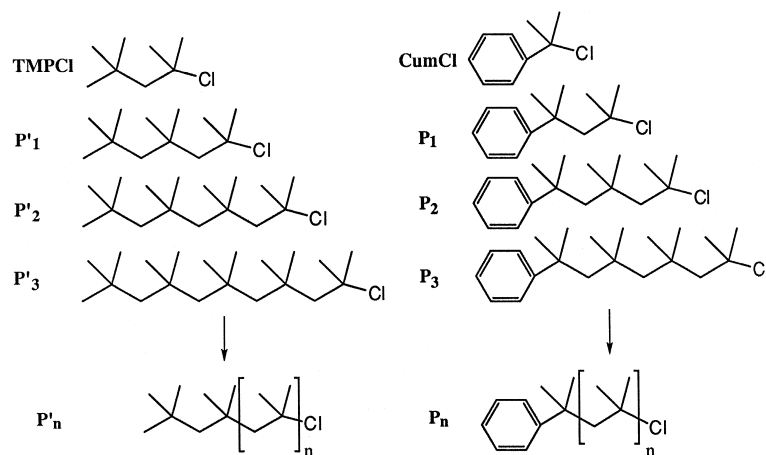


Figure 5. SEC (refractive index) chromatograms of oligoisobutene: 5a) prepared from the CumOH/ BCl_3 /IB/NMP/ CH_3Cl /-70°C system at reaction time of =15 minutes; 5b) prepared from the TMPOH/ BCl_3 /IB/NMP/ CH_3Cl /-40°C system at reaction time of 15 minutes. (AMI technique: the reaction conditions are listed in Tables 1 and 2; $\overline{Mn}_{\text{th}} \approx 1000 \text{ g}\cdot\text{mol}^{-1}$).

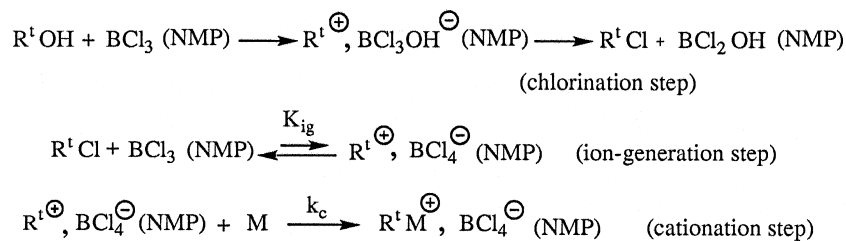
mer resulting from a protic initiation (P^n with $n \geq 0$) are low when NMP is present (Table 3); moreover, it confirms the high P_1 content, even at the end of polymerization. The CumCl content was not taken into account because some part of this compound was removed during the polymer recovery step.



Scheme 2. Chlorinated initiators and the different oligoisobutenes P'1 → P'n and P1 → Pn resulting from oligomerizations initiated by MPOH/BCl₃/NMP/-40°C and CumOH/BCl₃/NMP/-70°C systems, respectively.

Moreover, in these spectra no ethylenic end group signals are observed whatever the system (CumOH or TMPOH) showing that chain transfer to monomer does not take place, at least in the experimental conditions we used.

On the basis of Kennedy *et al.* [1, 5, 14, 21, 22] works, we propose the following mechanism for the isobutylene polymerization from the R^tOH/BCl₃/NMP initiating system (R^t = tertiary aliphatic or aromatic group). It takes into account the most important features of the polymerizations we investigated: no chain transfer to monomer and initiator, and no irreversible chain termination; moreover, the above studies show that the indanic cyclization and the formation of chains resulting from protic initiation can be neglected.



Initiation

Where K_{ig} is the equilibrium constant corresponding to the ion-generation step, k_c is the cationation rate constant, and M is the monomer. $\text{R}^t\oplus, \text{BCl}_4^\ominus (\text{NMP})$ represents all the species formed from R^tCl in the presence of the electron donor leading to a living polymerization.

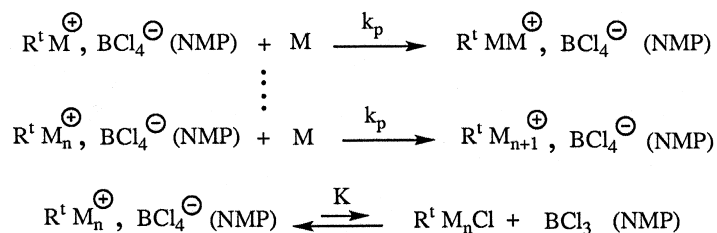
TABLE 3. Percentage of Various Species Calculated by ^1H NMR Analysis for the CumOH/ BCl_3 /IB/NMP Polymerization System.

Run	Time (min)	$P_n, n \geq 4$ (%)	P_1 (%)	P_2 (%)	P_3 (%)	Indanic structure (%)	$P', n \geq 0$ (%)
8	65	53.7	9.4	4.5	3.3	20.5	8.6
9	120	56.7	8.5	6.3	3.8	17.2	7.5
10	15	36.0	52.3	4.7	4.3	1.5	1.3
11	30	57.4	34.7	2.6	2.5	1.1	1.8
12	45	66.1	26.5	1.6	2.2	1.0	2.6
13	65	71.9	22.4	1.7	0.6	0.9	2.5
14	130	84.4	10.6	1.6	0.5	0.4	2.5

According to the results obtained from various $\text{R}'\text{OH}/\text{BCl}_3$ initiating systems [1, 5, 21], the chlorination step is very fast and the ion-generation step is involved in a rapid equilibrium.

Propagation

Where k_p is the overall rate constant of propagation. $\text{R}'\text{M}_n^+$, BCl_4^- (NMP) represents all active species capable of propagation in presence of NMP. These propagating species are in rapid dynamic equilibrium with dormant species (K is the corresponding equilibrium constant). Up to now, the role of the electron-pair donor remains a controversial subject [22-25].



The monomer is consumed by both propagation and cationation. This mechanism leads to two differential equations (1) and (2) which were solved by computer processing

$$\frac{d[\text{N}]_t}{dt} = k_c^{\text{app}} ([\text{I}]_0 - [\text{N}]_t) [\text{M}]_t \quad (1)$$

$$-\frac{d[M]_t}{dt} = k_p^{\text{app}} [N]_t [M]_t + k_c^{\text{app}} ([I]_0 - [N]_t) [M]_t \quad (2)$$

where k_c^{app} and k_p^{app} are the apparent cationation and propagation rate constants, respectively, $[M]_t$ and $[N]_t$ are monomer and polymer chain concentrations at reaction time t , respectively, and $[I]_0$ is the initial *tert*-alcohol concentration.

The low resulting values k_c^{app} and k_p^{app} (Table 4) show that both initiating systems lead to polymerizations with similar behavior; in the presence of the electron-pair donor, these slow polymerizations give rise to narrow molar mass distribution oligomers ($\overline{M}_w / \overline{M}_n = 1.1\text{-}1.2$). These results must be compared to those of Storey and Shoemake [26] and Kennedy *et al.* [22]. The first authors reported kinetic investigations of the living isobutylene polymerization initiated by the TMPCl or CumCl/TiCl₄/pyridine system using 60:40 hexane: CH₃Cl as solvent mixture and -80°C as temperature; a rapid initiation and a same low apparent propagation rate constant were observed for both initiating systems. In contrast, slow initiation and propagation were observed by Kennedy *et al.* [22] with the TMPCl/TiCl₄/triethylamine initiating system in CH₂Cl₂:hexane (60:40) at a temperature ranging from -25 to -82 °C.

The P₁ concentration is high during the whole polymerization whereas P₁' concentration becomes rapidly low. These results are corroborated by recent works reported by Mayr *et al.* [20, 27] who studied the living isobutylene oligomerization initiated by CumCl or TMPCl/BCl₃ system in the presence of benzyltriethylammonium tetraborate, particularly the kinetics of the initiation and the early propagation steps. When the initiator is CumCl, the reaction CumCl → P₁ is fast compared to the propagation steps; the following reaction P₁ → P₂ is very slow, and the complete sequence CumCl → P₂ is slower than the later chain growth steps which accounted for the high concentration of P₁ and a slightly broad molar mass distribution ($\overline{M}_w / \overline{M}_n \approx 1.1\text{-}1.2$) observed during the whole

TABLE 4. Values of Apparent Cationation and Propagation Rate Constants for the *tert*-alcohol RtOH/BCl₃/IB/NMP/CH₃Cl Carbocationic Polymerization Systems.

Initiating system	$\frac{k_c^{\text{app}} \times 10^3}{(\text{L mol}^{-1} \text{ s}^{-1})}$	$\frac{k_p^{\text{app}} \times 10^3}{(\text{L mol}^{-1} \text{ s}^{-1})}$
TMPOH / BCl ₃ / NMP / -40°C	1.08 ± 0.08	6.7 ± 0.8
CumOH / BCl ₃ / NMP / -70°C	1.83 ± 0.08	4.2 ± 0.8

TABLE 5. Results of the Living Isobutylene Oligomerization Initiated by *tert*-alcohol (Initiator)/BCl₃/NMP in Methyl Chloride-IMA Technique.
 [CumOH]₀ = 0.054 mol L⁻¹; [TMPOH]₀ = 0.053 mol L⁻¹; [BCl₃]₀/[I]₀ ≈ 8;
 [NMP]₀/[I]₀ = 1.5.

Initiator	Run	Time (min)	Δ[C ₄ H ₈] ₀ (mol L ⁻¹)	\overline{Mn}_{th} ^a	\overline{Mn}_{SEC} ^b	$\overline{Mw}/\overline{Mn}$	W _p ^c (g)	I _{eff} ^d (%)	C ^d (%)
TMPOH	15	135	0.92	1040	1200	1.1	3.39	81	95
	16	260	0.81	1880	1950	1.2	6.83	94	99
	17	390	0.65	2700	2620	1.2	9.54	97	93
	18	510	0.61	3550	3180	1.2	13.50	112	100
CumOH	19	130	0.82	935	1000	1.3	2.37	82	89
	20	250	0.65	1630	1750	1.1	3.89	77	83
	21	375	0.59	2380	2795	1.1	6.90	85	100
	22	500	0.55	3210	3420	1.1	9.00	94	100

^a \overline{Mn}_{th} (TMPOH) = 56n_{th} + 148.5; \overline{Mn}_{th} (CumOH) = 56 n_{th} + 154.5 with n_{th} = ΣΔ[C₄H₈]₀ / [I]₀

^b Calculated from SEC measurements

^c Amount of PIB-formed

^d I_{eff} and C evaluation : see Table 2

oligomerization process. On the other hand, when the initiator is TMPCl, there is much less difference of reactivity between TMPCl, P'₁, P'₂, etc... (the P'₁ reactivity is only 2.6 times as high as that of TMPCl), and consequently P'₁ concentration is lower. In conclusion, the two polymerization systems we investigated and using *tert*-alcohol initiators and NMP as an electron-pair donor seem to show a kinetic behavior analogous to that of corresponding chloride initiators in conjunction with benzyltriethylammonium tetraborate.

Living Carbocationic Oligomerization Initiated by R^tOH/BCl₃/IB/NMP/CH₃Cl Systems (IMA Technique)

The living character of these polymerizations was established by the IMA technique (see Experimental) which has been routinely used for this purpose [5, 12, 14]. Because of the slow polymerization in these systems, successive fresh monomer increments were added every two hours; the initial molar ratio NMP/*tert*-alcohol was equal to 1.5 and experimental conditions are listed in Table 5.

The \overline{Mn} versus PIB amount (W_p) plots are straight lines from origin up

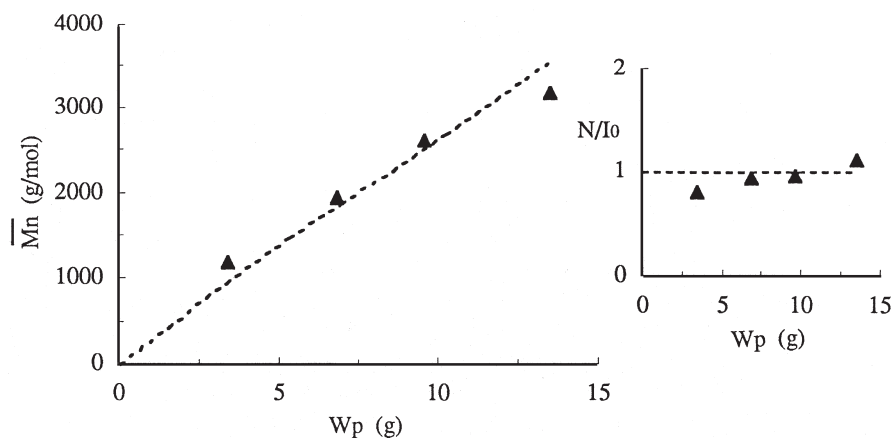


Figure 7. \overline{Mn} (SEC) and N/I_0 , the ratio of number of polyisobutylene chains per number of initiator molecules introduced (inset), versus the amount of polymer formed (W_p) from the TMPOH/ BCl_3 /IB/NMP/ CH_3Cl system at $-40^\circ C$ using the IMA technique; $[TMPOH]_0 = 0.053 \text{ mol L}^{-1}$; $[NMP]_0/[TMPOH]_0 = 1.5$; $[BCl_3]_0/[TMPOH]_0 = 7.9$; $V(CH_3Cl) = 51 \text{ mL}$; $\Delta[C_4H_8]_0 \approx 0.60\text{-}0.95 \text{ mol L}^{-1}$; $\Delta t = 120$ minutes. Dotted lines represent theoretical values.

to $\overline{Mn} \approx 4000$; in the same way the number of PIB chains per number of initiator molecules introduced (N/I_0) versus W_p plots are horizontal straight lines (Figures 7 and 8). These plots indicate that the number of active sites remains unchanged during the runs. The living nature of these polymerizations was further substantiated by SEC and 1H NMR studies [15]: additions of fresh isobutylene to the reactive mixture led to polymers whose chromatograms showed no multimodal traces and their molar mass distributions remained narrow ($\overline{Mw}/\overline{Mn} = 1.1\text{-}1.2$) for both initiating systems. Moreover, no traces of ethylenic signals in the different sample NMR spectra were observed giving proof that no chain transfer to monomer occurs during these successive polymerizations.

CONCLUSION

The addition of an electron-pair donor such as 1-methyl-2-pyrrolidinone to monofunctional *tertiary* alcohol/ BCl_3 / initiating systems led to slow controlled polymerization of isobutylene giving rise to ω -(*tert*-chloro) oligoisobutylenes

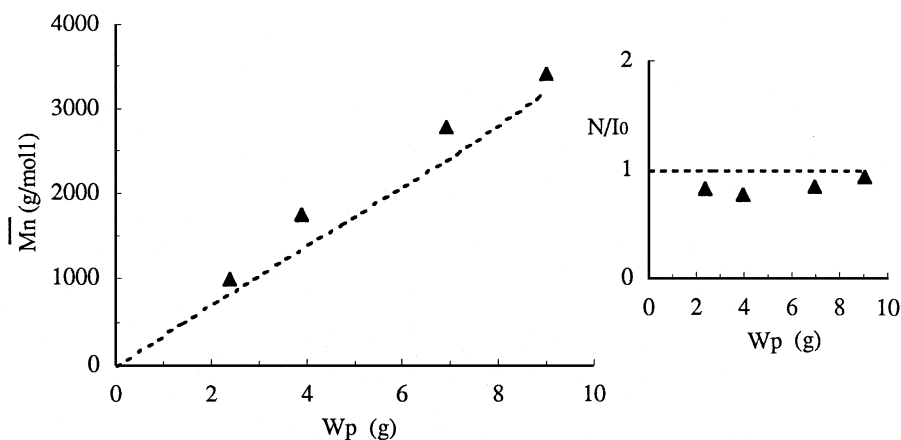
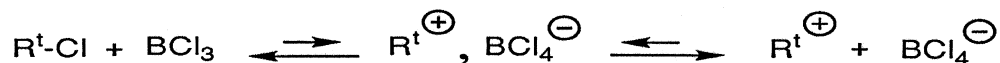
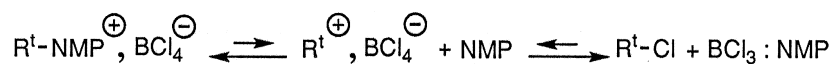


Figure 8. (SEC) and N/I_0 , the ratio of number of polyisobutylene chains per number of initiator molecules introduced (inset), versus the amount of polymer formed (W_p) from the CumOH/ BCl_3 /IB/NMP/ CH_3Cl system at $-70^\circ C$ using the IMA technique; $[CumOH]_0 = 0.054 \text{ mol L}^{-1}$; $[NMP]_0/[CumOH]_0 = 1.5$; $[BCl_3]_0/[CumOH]_0 = 8.6$; $V(CH_3Cl) = 51 \text{ mL}$; $\Delta[C_4H_8]_0 \approx 0.55\text{-}0.85 \text{ mol L}^{-1}$; $\Delta t = 120 \text{ minutes}$. Dotted lines represent theoretical values.

with low molar mass and narrow molar mass distribution. Such an addition reduces the high reactivity of growing cations, and side reactions such as uncontrolled initiation by protic impurities, chain transfer to monomer, intra-molecular alkylation by the growing carbocation (in the case of CumOH initiator) and irreversible chain termination, can be depressed or totally eliminated. The low values of the apparent rate constants of propagation generally observed in living carbocationic systems, and more particularly in these systems, can be explained by the small concentration of propagating carbocations which are in dynamic equilibrium with dormant species [24, 25]; the latter can be covalent species or onium ions. The ionization of covalent species $R^t\text{-Cl}$ by BCl_3 leads to ion-pairs which can dissociate to free ions :



Onium ions ($R\text{-NMP}^+$) are reversibly formed by the addition of a nucleophile like NMP, which reduces the lifetime of free carbocations (generally leading to non living polymerization) and of the corresponding ion-pairs:



These equilibria between the different species are fast in comparison with addition monomer. Thus, polymerization rates can be reduced by decreasing the momentary concentration of growing carbocations. In the systems on study, a relative long reaction time (~130 minutes) is required to obtain a complete initiation and high conversions. This process is particularly suitable for oligomer preparation.

The chlorine end-group of these various oligoisobutylenes was successively converted to ethylenic end group then to anhydride or dianhydride termination; the latter was condensed with α -methoxy ω -hydroxy oligooxyethylene leading to linear and multi-armed star-shaped amphiphilic copolymers [28].

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