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## Carbocationic polymerization of isoprene using cumyl initiators: progress in understanding side reactions†

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The cationic polymerization of isoprene using cumyl chloride/ $\text{B}(\text{C}_6\text{F}_5)_3$  and cumyl ether/ $\text{TiCl}_4$  systems was investigated in dichloromethane or in dichloromethane/methylcyclohexane mixtures varying the polymerization conditions. Polymerizations were performed in all cases in the presence of a large excess of a proton trap (2,6-di-*tert*-butyl pyridine,  $\text{d}^t\text{BP}$ ) compared to initiator in order to suppress any protic side reactions. As a consequence, no polymerization went to completion. Independently of the reaction conditions, *trans*-1,4-oligomers were exclusively obtained with mainly an olefinic terminal group. It was highlighted that an important loss of double bonds yielding saturated parts was observed, even in the absence of protons, assuming that a great amount of double bond loss generally observed in isoprene cationic polymerization could be due to intramolecular cyclization reactions. Nevertheless, under particular conditions (low temperature and/or low polarity medium), branching and cross-linking reactions were also found responsible for double bond loss.

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## Introduction

Isoprene (IP) cationic polymerization has been studied since more than 70 years with various catalytic systems<sup>1</sup> but it was only recently that it was suggested that similar elementary processes proceeded in Natural Rubber (NR) biosynthesis, a *cis*-1,4-polyisoprene, produced by *Hevea Brasiliensis* crops.<sup>2,3</sup> Up until the end of the 60's, Friedel–Crafts catalysts, Lewis acids and/or other organometallic compounds were mainly used as initiating systems for the cationic polymerization of isoprene, whereas from the 70's protic promoters were preferred. Furthermore, many polymerization conditions were investigated, varying the solvent, the temperature and the monomer concentration. Whatever the conditions, *trans*-1,4-polyisoprenes with unusual microstructures, more specifically cyclized sequences leading to double bond loss, were obtained. Recent works showed that dimethylallyl derivatives (DMAX), homologues of the DMAPP natural initiator, were ionizable by Lewis acids (LAs) and the primary allylic carbocation was able to initiate isoprene polymerization.<sup>4</sup> Using a IP/DMABr/ $\text{TiCl}_4$  system, transfer reactions

were highlighted *via* the observation of a partial decomposition of the DMABr carbocation moiety into isoprene, which mimic the transfer reaction of an active allylic chain end into an unsaturated chain end.<sup>5</sup> This point was later proved by Puskas *et al.*, Kostjuk *et al.* and Ouadad *et al.* using, DMAOH/ $\text{TiCl}_4$  or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,<sup>6</sup> 1-(4-methoxyphenyl)ethanol/ $\text{B}(\text{C}_6\text{F}_5)_3$  (ref. 7) and 2-cyclohexylidene ethanol/ $\text{B}(\text{C}_6\text{F}_5)_3$  (ref. 8) or DMAOH/ $\text{B}(\text{C}_6\text{F}_5)_3$  (ref. 9) as initiating systems respectively, in organic media. Furthermore, 1-(4-methoxyphenyl)ethanol/ $\text{B}(\text{C}_6\text{F}_5)_3$  initiating system allowed the synthesis of *trans*-1,4-polyisoprenes without double bond loss in aqueous media<sup>7</sup> while in organic media a loss of double bonds was observed whatever the initiating system used.<sup>5–9</sup>

In this paper, the investigation of cationic polymerization of isoprene was conducted in order to better understand the elementary processes involved and more precisely the side reactions responsible for double bonds' loss. All the former studied systems, more particularly when allylic initiators were associated to boron Lewis acid, led to a loss of information regarding side reactions. Indeed, it was difficult to evaluate the extent of protic initiation, as a proton trap was added in default with regard to the initiator, or of the intermolecular branching reactions. Moreover,  $\text{B}(\text{C}_6\text{F}_5)_3$  was shown to form strong complex with allylic alcohol initiators at low temperature, inhibiting their ionization and thus the polymerization. To this end, initiating systems inducing rapid ionization and initiation rates were needed. Thus, as the well-known (di-)cumyl initiators associated to several Lewis acids proved to be efficient initiating systems for the carbocationic polymerization of isobutene and

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its copolymerization with isoprene,<sup>10–15</sup> they were used for isoprene homopolymerization in this study.

## Experimental part

### Materials

Isoprene (Aldrich, 99%) was cryo-distilled twice over CaH<sub>2</sub> and then over di-*n*-butyl-magnesium, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, Aldrich, 99.5%) and methylcyclohexane (Mecyclo, Aldrich, 99%) were distilled respectively from CaH<sub>2</sub> and sodium cubes under an inert atmosphere prior to use. 2,6-di-*tert*-butylpyridine (d<sup>t</sup>BP) was dried over KOH pellets before distillation. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (TCI, 97%) and TiCl<sub>4</sub> were used as received. The purity of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was checked by <sup>1</sup>H or <sup>19</sup>F NMR. Dioxane (DO) and ethyl acetate (EA) were cryo-distilled over CaH<sub>2</sub>.  $\alpha$ -methylstyrene ( $\alpha$ -MS, 99%, Aldrich) and Amberlist 15 were used as received.

### Initiator synthesis

Cumyl chloride (cumylCl) was synthesized by the reaction of  $\alpha$ -MS with dry HCl gas over a period of 5 h. The reaction is total and excess of HCl gas is removed by flushing with argon. Cumyl ether (cumylOCH<sub>3</sub>) was synthesized by the reaction of  $\alpha$ -MS with methanol in presence of Amberlist 15 over a period of 24 h. The desired product, obtained with a yield of 80%, was isolated by a column using a mixture of dichloromethane/methanol (v/v 99.5/0.5). The purity of cumyl initiators was checked by <sup>1</sup>H NMR. <sup>1</sup>H NMR:  $\alpha$ -MS: 2.22 ppm (–CH<sub>3</sub>), 5.15 ppm (–CH<sub>2</sub>), 5.44 ppm (–CH<sub>2</sub>), 7.39 ppm and 7.54 ppm (aromatic protons, Ar); cumylCl: 1.88 ppm (–CH<sub>3</sub>), 7.17 ppm (*p*-Ar), 7.24 ppm (*m*-Ar), and 7.54 ppm (*o*-Ar); cumylOCH<sub>3</sub>: 1.37 ppm (–CH<sub>3</sub>), 2.91 ppm (–OCH<sub>3</sub>), 7.11 ppm (*p*-Ar), 7.21 ppm (*m*-Ar), and 7.28 ppm (*o*-Ar) (Fig. S1, ESI†).

### Polymerization procedure

The polymerization reactions were carried out in glass Schlenk tubes equipped with a stopcock in an argon atmosphere at 20 °C. As an example of a typical procedure in solution, polymerization was initiated by adding LA (0.8 mmol) dissolved in 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> to a mixture consisting of a cumyl initiator (0.4 mmol), isoprene (30 mmol, 3 mL), and CH<sub>2</sub>Cl<sub>2</sub> for a total volume of 25 mL. After a predetermined time, ~1 mL aliquots were withdrawn and poured into a methanol excess. The precipitated polymer was separated from the solution by centrifugation and dried in vacuum. Monomer conversions were determined by gravimetry.

### Instrumentation

Molar masses were determined by Size Exclusion Chromatography (SEC) at 40 °C in THF as the eluent (1 mL min<sup>–1</sup>), trichlorobenzene as a flow marker, using both refractometric (RI) and UV detectors (Varian). Analyses were performed using a three-column set of TSK gel TOSOH (G4000, G3000, G2000 with pore sizes of 20, 75, and 200 Å respectively, connected in series) calibrated with polystyrene standards. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and <sup>19</sup>F NMR (160 MHz) spectra were recorded in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> at 25 °C on a Bruker Avance 400 spectrometer

calibrated relative to the solvent peak in reference to tetramethylsilane and CFCl<sub>3</sub> standards. Maldi-TOF MS was performed on a Voyager mass spectrometer (AB Sciex). The instrument is equipped with a pulsed N<sub>2</sub> laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in THF at 10 mg mL<sup>–1</sup>. The DCTB matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile) solution was prepared by dissolving 10 mg in 1 mL of THF. A solution of cationation agent (AgTFA or CuCl, 10 mg mL<sup>–1</sup>) was also prepared. The solutions were combined in a 10 : 1 : 1 volume ratio of matrix to sample to cationation agent. 1–2  $\mu$ L of the obtained solution was deposited onto the sample target and vacuum dried. The instrument was calibrated externally using poly(ethylene glycol) standards at the appropriate molar mass. All mass-to-charge ratios (*m/z*) quoted are mono-isotopic; *i.e.* they include the most abundant isotopes of the elements present in the corresponding ion.

## Results and discussion

### CumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as initiating system

In several papers,<sup>7–9</sup> thanks to Maldi-TOF MS analysis, the presence of intensive transfer reaction during the cationic polymerization of isoprene was evidenced, even at low conversion. As a consequence, polyisoprene chains with unsaturated chain-ends were mainly obtained accompanied by a proton release which was later responsible of protic initiation and/or double bond protonation entailing double bond loss *via* cyclization and/or branching reactions. In this study, in order to understand the elementary processes involved in IP cationic polymerization, the side reactions due to protons were suppressed by adding a proton trap, namely d<sup>t</sup>BP. Here however, in contrast to our previous works,<sup>8,9</sup> an excess of d<sup>t</sup>BP was used (initiator/d<sup>t</sup>BP 1/2) to trap all protons coming from transfer reactions (maximum one per initiator molecule) and water traces. To avoid possible complexation of highly oxophilic B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with the selected cumyl initiator (as encountered with the 2-cyclohexylidene ethanol at low temperature), cumyl chloride (cumylCl) was chosen in place of cumyl ether (cumylOCH<sub>3</sub>). On the basis of this new initiating system, the influence of the isoprene cationic polymerization conditions were investigated at 20 °C (cumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/d<sup>t</sup>BP 1/2/2).

As expected, polymerizations were characterized by a fast initiation rate. Propagation was quite fast among the first hours to then almost stop after few hours (graph A, Fig. 1). Whatever the polymerization conditions, low conversions (<30%) were reached and only oligomers characterized by low dispersities were obtained. Nevertheless, it can be noticed that working at high IP concentration (green *vs.* blue curves, graph A, Fig. 1) and lower medium polarity (pink *vs.* blue curves, graph A, Fig. 1) lead to lower yield at the plateau but no significant effect was noticed regarding molar mass or dispersity (graph B, Fig. 1). The observed rate deceleration was probably due to the large amount of added d<sup>t</sup>BP that trap all the protons generated during transfer reactions, transforming these latter into termination reactions by inhibiting protic side reactions (initiation or

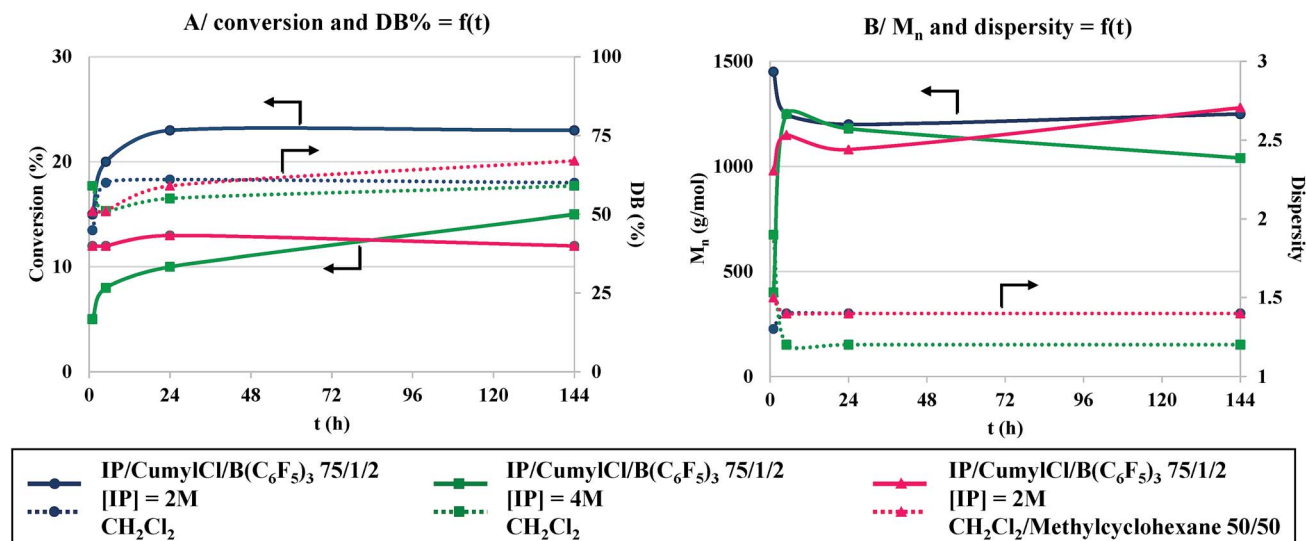


Fig. 1 Cationic polymerization of isoprene at 20 °C in different conditions; DB% determined by  $^1\text{H}$  NMR (100% if no DB loss),  $M_n$  and dispersity determined by SEC (PS calibration, THF, 40 °C, 1 mL  $\text{min}^{-1}$ ).

DB protonation). Control polymerization reactions performed in the absence of the proton trap showed much higher conversion with PI characterized by low molar masses, quite low dispersities and low DB contents.

For more insight on the microstructures, NMR analyses were performed (Fig. 2). Thanks to the  $^1\text{H}$  NMR, it was observed that even in presence of  $d^t\text{BP}$ , the oligoisoprenes were not fully unsaturated. The double bonds' loss was only due in this case to the active chain ends which reacted with the oligoisoprenes double bonds as well as with the IP monomer. It could be thus concluded that the loss of double bonds observed in previous works,<sup>8,9</sup> where  $d^t\text{BP}$  was added in lack compared to the

initiator, was not only due to protic side reactions but also to some other processes. No significant double bond conservation could be obtained in the various studied conditions (graph A, Fig. 1) as at the very beginning of the polymerization, 40% of the expected double bonds were already consumed.

The NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) analyses showed that in all conditions, oligoisoprenes were mainly *trans*-1,4- with saturated segments. As an example, in  $^1\text{H}$  NMR spectra of oligoisoprene obtained in dichloromethane using the system IP/cumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/ $d^t\text{BP}$  75/1/2/2 (Fig. 2; corresponding to the blue curves in Fig. 1), it can be seen that the oligoisoprenes were mainly made of 1,4- unit ( $-\text{CH}_2-\text{CCH}_3=\text{CH}-\text{CH}_2-$  at 5.04 ppm), traces of 1,2- and 3,4-

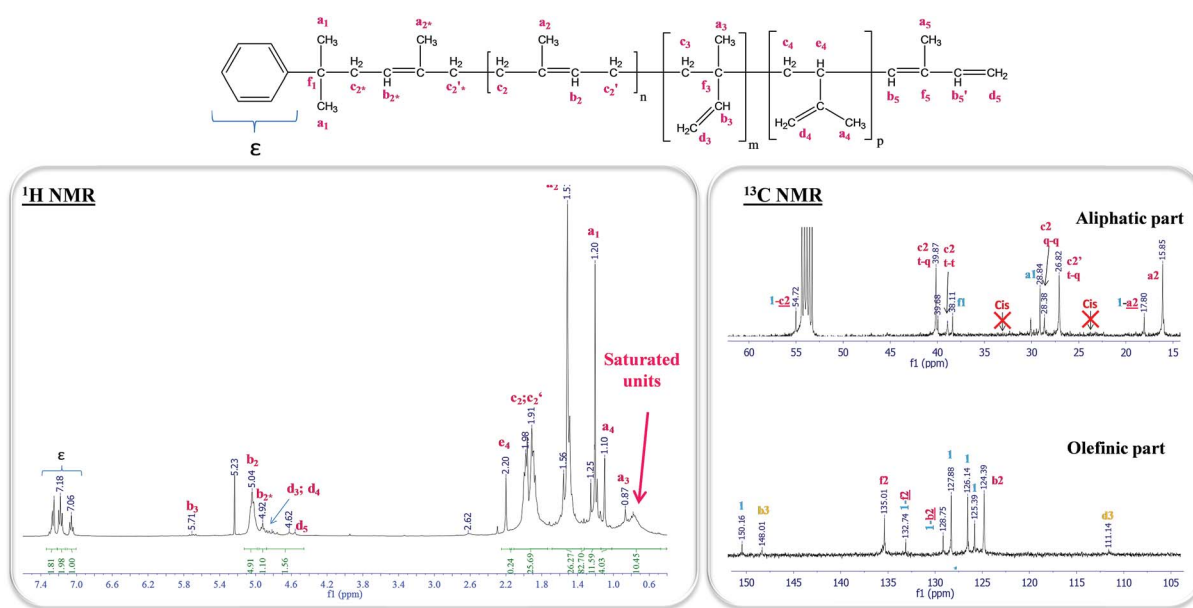


Fig. 2  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of oligoisoprenes obtained with the system IP/cumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/ $d^t\text{BP}$  75/1/2/2 in  $\text{CH}_2\text{Cl}_2$  at 20 °C,  $t = 24$  h (corresponding to blue curves in Fig. 1).

units were detected ( $-\text{CH}=\text{CH}_2$  at 4.92 ppm at  $-\text{CH}=\text{CH}_2$  at 5.71 ppm) and saturated units (broad band between 0.5 ppm and 1 ppm, Fig. 2). Regarding the 1,4- units,  $^{13}\text{C}$  NMR confirmed the exclusive presence of *trans* configuration ( $-\text{CH}_2-\text{CCH}_3=\text{CH}-\text{CH}_2-$  at 15.85 ppm) mainly made up by “head-to-tail” enchainments ( $-\text{CH}_2-\text{CCH}_3=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CCH}_3=\text{CH}-\text{CH}_2-$  at 39.87 ppm) and of few “head-to-head” and “tail-to-tail” enchainments characterized by signals at 38.67 ppm and at 28.38 ppm, respectively. In addition to signals of the various IP units, signals corresponding to the cumyl head unit were also detected; at 7 ppm and 7.5 ppm (aromatic protons) and at 1.2 ppm (methyl group) on  $^1\text{H}$  NMR spectra, and at 28.98 ppm (methyl groups), 38.11 ppm ( $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-$ ) and 125.39 ppm, 126.14 ppm and 127.88 ppm (aromatic carbons) on  $^{13}\text{C}$  NMR spectra. Absence of dimethylallyl head signals ( $(\text{CH}_3)_2=\text{C}-\text{CH}_2-$  at 17.52 ppm and  $(\text{CH}_3)_2=\text{C}-\text{CH}_2-$  at 25.55 ppm), proved the absence of protic initiation thanks to the efficiency of proton trapping by  $\text{d}^t\text{BP}$ .

For more insight on side reactions, Maldi-TOF MS characterization was performed (Fig. 3 and S2 in ESI†). Results obtained for all the investigated conditions were similar. At low molar mass only one family ( $\text{F}_1$ ) was detected corresponding to polyisoprene ( $n^*\text{C}_5\text{H}_8$ ) initiated by a cumyl cation ( $\text{C}_9\text{H}_{11}^+$ ) and bearing terminal unsaturation ( $\text{C}_5\text{H}_7$ ) due to termination by  $\beta$ -H elimination (transfer reaction process). At higher molar mass, for all the investigated conditions, a second family ( $\text{F}_2$ ) is detected in addition to the first one ( $\text{F}_1$ ). The  $\text{F}_2$  family corresponds also to polyisoprene chains but here bearing two cumyl fragments. The first family,  $\text{F}_1$  ( $\text{C}_9\text{H}_{11}-\text{PI}-\text{C}_5\text{H}_7$ ), is in larger amount than the second one,  $\text{F}_2$ , present only at higher molar

mass. The  $\text{F}_2$  family could thus be explained by an intermolecular branching between two chains initiated by a cumyl cation (path (a), Scheme 1), by a Friedel-Crafts (FC) reaction of an active chain bearing a cumyl head with any chain (path (b), Scheme 1) or by a partial decomposition of cumyl chloride initiator after ionization leading to  $\alpha$ -methylstyrene which is then incorporated as a *co*-monomer (path (c), Scheme 1).

Previous results on the IP cationic polymerization at 20 °C using 2-cyclohexylidene ethanol/ $\text{B}(\text{C}_6\text{F}_5)_3$  as initiating systems showed the absence of branching reactions at low conversion based on absence of family bearing two 2-ethylcyclohexylidene fragments.<sup>8</sup> In the present study, as conversions did not exceed 25%, the intermolecular branching as the side reaction responsible of the  $\text{F}_2$  family formation can be reasonably discarded. Besides, the presence of a FC reaction would induce the formation of *p*- or *o*-substituted aromatic group inside a polyisoprene chain. Therefore, in addition to the peaks of the cumyl chain head one or different new sets of aromatic peaks (depending on the aromatic position attack and degree of substitution) should be observed in  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Since just one set of aromatic peaks, corresponding to the mono-substituted cumyl fragment at the chain head was observed in  $^1\text{H}$  and  $^{13}\text{C}$  NMR, Friedel-Craft reactions can be also discarded. Finally, on HSQC NMR spectrum (Fig. S3, ESI†), two sets of three peaks were detected in the aromatic region, one of high intensity corresponding to the cumyl fragment head and a second less intense one (hidden in the  $^1\text{H}$  NMR spectrum) corresponding to  $\alpha$ -MS incorporated in the PI chain. This assumption that the presence of  $\text{F}_2$ , chain bearing two cumyl

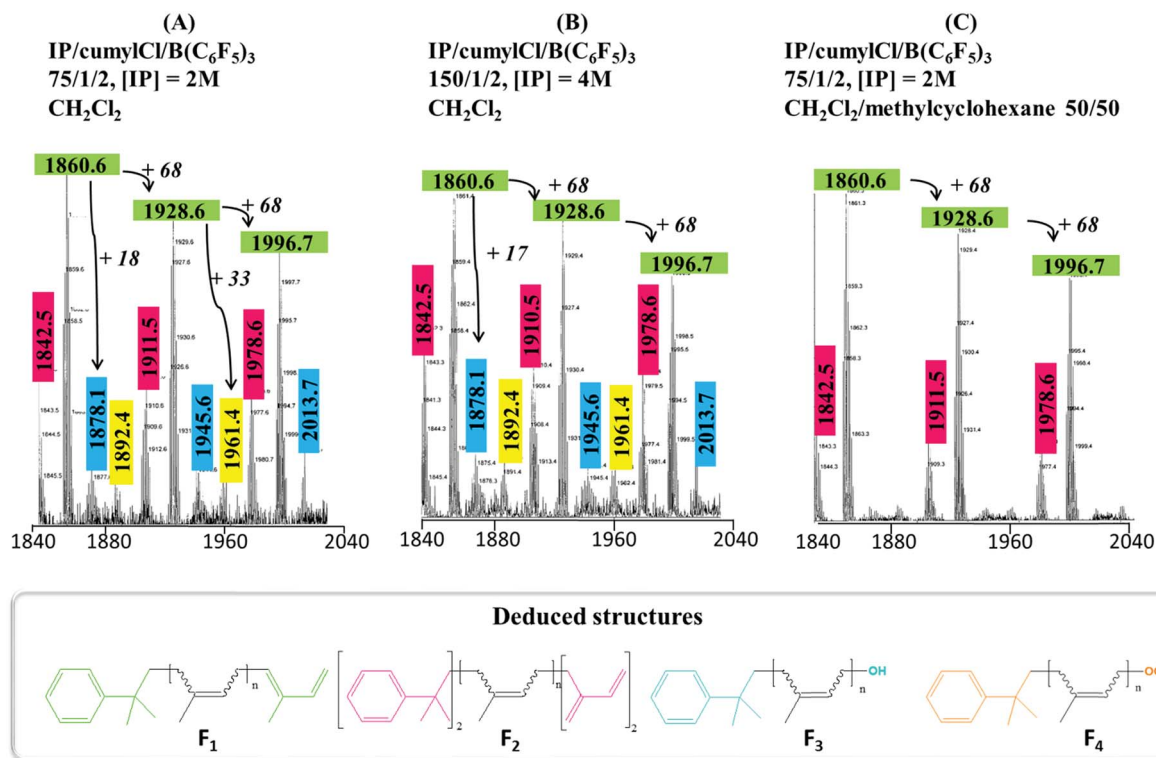
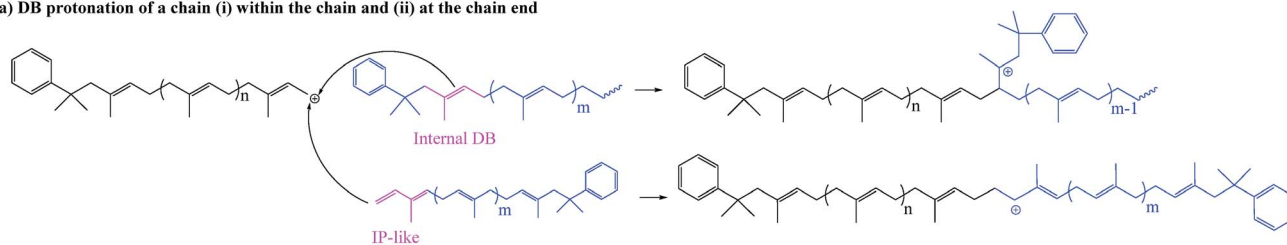


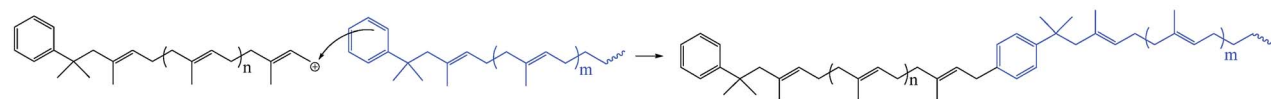
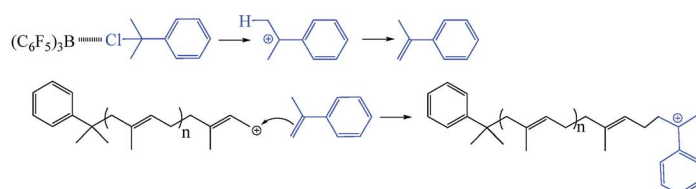
Fig. 3 Maldi-TOF MS spectra of oligoisoprenes obtained by the system IP/cumylCl/ $\text{B}(\text{C}_6\text{F}_5)_3/\text{d}^t\text{BP}$  at 20 °C.



## (a) DB protonation of a chain (i) within the chain and (ii) at the chain end



## (b) Friedel-Crafts reaction

(c) Incorporation of an  $\alpha$ -methylstyrene moiety via a partial decomposition of CumylCl initiator

Scheme 1 Possible pathways for the formation of chains bearing two cumyl fragments.

fragments, is due to the incorporation of  $\alpha$ -MS (coming from a partial decomposition of the initiator) is in good accordance with a previous work that highlighted a partial decomposition of 1-(4-methoxyphenyl)ethanol.<sup>7</sup> When experiments were performed in 100% dichloromethane, two others families, F<sub>3</sub> and F<sub>4</sub>, were observed, both of them bearing a cumyl fragment and a hydroxy or methoxy chain-end respectively. The formation of F<sub>3</sub> could be due to the presence of adventitious water, whereas F<sub>4</sub> could be formed during precipitation in methanol at the end of the polymerization. As these chain-ends are most probably present in very low amounts, they were not observed by NMR. In addition, no chain initiated by protons was observed which is in good correlation with NMR results. On the contrary, for experiments performed in the absence of the proton trap, chains were mainly initiated by the protons released during transfer reactions.

From this first set of experiments, it can be concluded that transfer reactions are in these conditions the major termination process limiting the conversion and that the intramolecular cyclization is responsible of the loss of DB (absence of DB protonation and interchain branching reaction).

CumylOCH<sub>3</sub>/TiCl<sub>4</sub> as initiating system

CumylOCH<sub>3</sub>/TiCl<sub>4</sub> and more generally cumylX/TiCl<sub>4</sub>, initiating systems have been widely used for living cationic polymerization of isobutene<sup>16,17</sup> or cationic copolymerization of isoprene with isobutene allowing higher incorporation of isoprene unit with a lower loss of DB.<sup>15</sup> Therefore, this system was also studied with the aim to disfavour the transfer reaction and to obtain PI with higher mass and DB content than those obtained with cumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> initiating system. Besides, cationic polymerization of isobutene was shown to be free of transfer

reactions when performed below  $-60$  °C, whereas they became more and more important with temperature above  $-60$  °C.<sup>18</sup>

Polymerizations were then mainly performed at  $-80$  °C. Again, 2 equivalents of d<sup>4</sup>BP with regard to cumylOCH<sub>3</sub> initiator were used in order to trap all protons. Polymerization conditions were varied (temperature, *M/I* ratio, monomer concentration and solvent polarity). Moreover, since a total gelation was observed after 30 min at  $-80$  °C in plain CH<sub>2</sub>Cl<sub>2</sub>, experiments were performed in solvent mixture. Main results are summarized in Table 1.

When polymerization were conducted in a 50/50 CH<sub>2</sub>Cl<sub>2</sub>/methylcyclohexane mixture, even at  $-80$  °C, transfer reactions were still present but retarded as higher conversions were obtained compared to reactions performed at 20 °C (Run 1 vs. Run 2, Table 1). Temperature decrease was also beneficial to molar masses as they increased from 520 g mol<sup>-1</sup> to 3680 g mol<sup>-1</sup> at 20 °C and  $-80$  °C respectively after 24 h, with a dispersity increase but without gel formation. Finally, lowering the temperature induced a slight higher DB content. A decrease of the medium polarity at  $-80$  °C (Run 3 vs. Run 4, Table 1) by increasing the amount of methylcyclohexane in the solvent mixture (50/50 vs. 25/75), lowered the yield, the molar mass and the dispersity without noticeable DB content change. Increasing *M/I* ratio at volume total constant and thus increasing monomer concentration (Run 4 vs. Run 5, Table 1) led to a large multi-modal molar mass distribution and high gel content (Fig. S4, ESI†). Therefore, high monomer concentration combined to apolar medium and low temperature seemed to be the worst condition for isoprene cationic polymerization. In these conditions, intermolecular branching reactions were present in contrast to polymerizations conducted at 20 °C with the 2-cyclohexylidene ethanol/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (ref. 8) and cumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> initiating systems. In these conditions, polyisoprene is probably

**Table 1** Isoprene cationic polymerization with cumylOCH<sub>3</sub>/TiCl<sub>4</sub> as the initiating system<sup>a</sup>

Run	CH <sub>2</sub> Cl <sub>2</sub> /mecyclo	IP/cumylOCH <sub>3</sub>	[IP] (M)	T (°C)	t (h)	Yield (%)	M <sub>n</sub> <sup>b</sup> (g mol <sup>-1</sup> )	D <sup>b</sup>	DB <sup>c</sup> (%)
1	50/50	75/1	1.2	20	0.5	23	560	1.2	45
					24	29	520	1.1	53
2	50/50	75/1	1.2	-80	0.5	27	2180	1.7	60
					24	46	3680	1.9	55
3	50/50	150/1	2.4	-80	0.5	29	3040	2.1	55
					24	48	7180	3.5	58
4	25/75	150/1	2.4	-80	0.5	15	1330	2.0	57
					24	30	2090	2.1	57
5	25/75	299/1	4.8	-80	23	36	3770 <sup>d</sup>	3.9	65
					48	100	3640 <sup>d</sup>	8.7	66

<sup>a</sup> IP/cumylOCH<sub>3</sub>/TiCl<sub>4</sub>/d<sup>4</sup>BP = IP/cumylOCH<sub>3</sub>/2/2. <sup>b</sup> Molar mass and dispersity of the soluble fraction determined by SEC (PS calibration, THF, 40 °C, 1 mL min<sup>-1</sup>). <sup>c</sup> DB% determined by <sup>1</sup>H NMR (100% if no loss). <sup>d</sup> Observation of gel formation.

not fully soluble. For instance, with other initiating systems, Rozentsvet *et al.* showed the presence of intermolecular branching reactions at low temperature and an increase of the degree of branching and the amount of gel content with decreasing temperatures.<sup>19–21</sup>

In a second set of experiments, we tried to overcome gel formation observed in the worst conditions defined previously. To this end, the influence of monomer concentration or of the presence of an electron donor (ED) was investigated. These latter were expected to stabilize the active chain end or to modulate the Lewis acid acidity. Dioxane and ethyl acetate were thus selected. Results are summarized in Table 2. In all experiments, a decrease of the polymerization rate was observed leading to oligoisoprenes with lower dispersity but similar DB content. The gel formation was successfully avoided either by lowering the monomer concentration or by adding an electron donor. Furthermore, while the polyisoprene microstructure was unchanged by lowering the IP concentration, changes were observed on NMR spectra (Fig. 4) in the presence of electron donors (runs 7 and 8, Table 2). Indeed, the broad peaks attributed to cyclized segments become more defined (0.5–1 ppm) and higher functionalization degree is obtained (peaks between 3.2–3.7 ppm and between 3.9–4.2 ppm corresponding respectively to -CH-X and -CH<sub>2</sub>-X protons). The effect of ethyl

acetate was more pronounced than that of dioxane. Electron donors may thus interact with active species, directly or *via* association with the Lewis acid.

As expected, Maldi-TOF MS analysis (Fig. 5) showed that no protic initiation occurred (exclusive initiation by a cumyl fragment). Transfer reaction was again the major termination process (F<sub>1</sub> family). As with cumylCl/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> initiating system, a second family bearing two cumyl fragments was observed at higher molar mass. In presence of electron donors, functionalized families could also be detected, cumyl-PI-OH (F<sub>3</sub> family) and cumyl-PI-OCH<sub>3</sub> (F<sub>4</sub> family), in good correlation with NMR results.

### Further polyisoprene characterization

To this date, details on the microstructure of polyisoprenes synthesized through cationic polymerization were only based on the unsaturated part.<sup>1,7–9,19–21</sup> It was thus shown using <sup>1</sup>H and <sup>13</sup>C NMRs that they were *trans*-1,4-PI mainly linked in a regular fashion “head-to-tail” with few “head-to-head” and “tail-to-tail” linkages, with some saturated structures. Nevertheless, the presence of saturated parts was highlighted since the first studies on cationic polymerization of IP. Several assumptions were given with time, going from mono-, bi-, tri-, tetra- or polycycles but without any fully convincing proofs. Assumption of the presence of cycles was based on the presence of a broad band between 0.5 and 1 ppm on <sup>1</sup>H NMR spectra. In order to have more details on this saturated part, PIs have been analyzed combining various NMR techniques (<sup>1</sup>H, <sup>13</sup>C, NOESY, TOCSY, HSQC, HMBC, JMOD). All PIs obtained in our conditions were analyzed by the same techniques (<sup>1</sup>H NMR in Fig. S5, ESI†) but also by 2D NMR (COSY, HSQC, HMBC, TOCSY, NOESY) and JMOD (Fig. S6, ESI†) for deeper local and spatial microstructural analyses. TOCSY (Fig. S7, ESI†) and NOESY (Fig. S8, ESI†) analyses led to artefacts only while combination of COSY (Fig. S9, ESI†), HSQC (Fig. S3, ESI†), HMBC (Fig. S10, ESI†) confirmed the *trans*-1,4 configuration of polyisoprenes but unfortunately no additional information was obtained. It can be assumed that side reactions leading to double bond loss and thus to saturated units formation did not lead to regular units, otherwise, few specific saturated units would have been formed

**Table 2** Isoprene cationic polymerization using cumylOCH<sub>3</sub>/TiCl<sub>4</sub> initiating system<sup>a</sup>

Run	[IP] (M)	ED	t (days)	Yield (%)	M <sub>n</sub> <sup>b</sup> (g mol <sup>-1</sup> )	D <sup>b</sup>	DB <sup>c</sup> (%)
5	4.8	—	1	36	3770 <sup>d</sup>	3.9	65
			2	100	3640 <sup>d</sup>	8.7	66
6	2.4	—	1	17	970	1.4	70
			2	21	1180	1.4	76
7	4.8	DO	1	14	1170	2.0	69
			2	17	1245	2.0	69
8	4.8	EA	1	9	1770	1.3	64
			2	12	1210	1.6	66

<sup>a</sup> IP/cumylOCH<sub>3</sub>/TiCl<sub>4</sub>/d<sup>4</sup>BP = 299/1/2/2; CH<sub>2</sub>Cl<sub>2</sub>/mecyclo: 25/75; T = -80 °C. <sup>b</sup> Molar mass and dispersity of the soluble fraction determined by SEC (PS calibration, THF, 40 °C, 1 mL min<sup>-1</sup>). <sup>c</sup> DB% determined by <sup>1</sup>H NMR (100% if no DB loss). <sup>d</sup> Observation of gel formation.

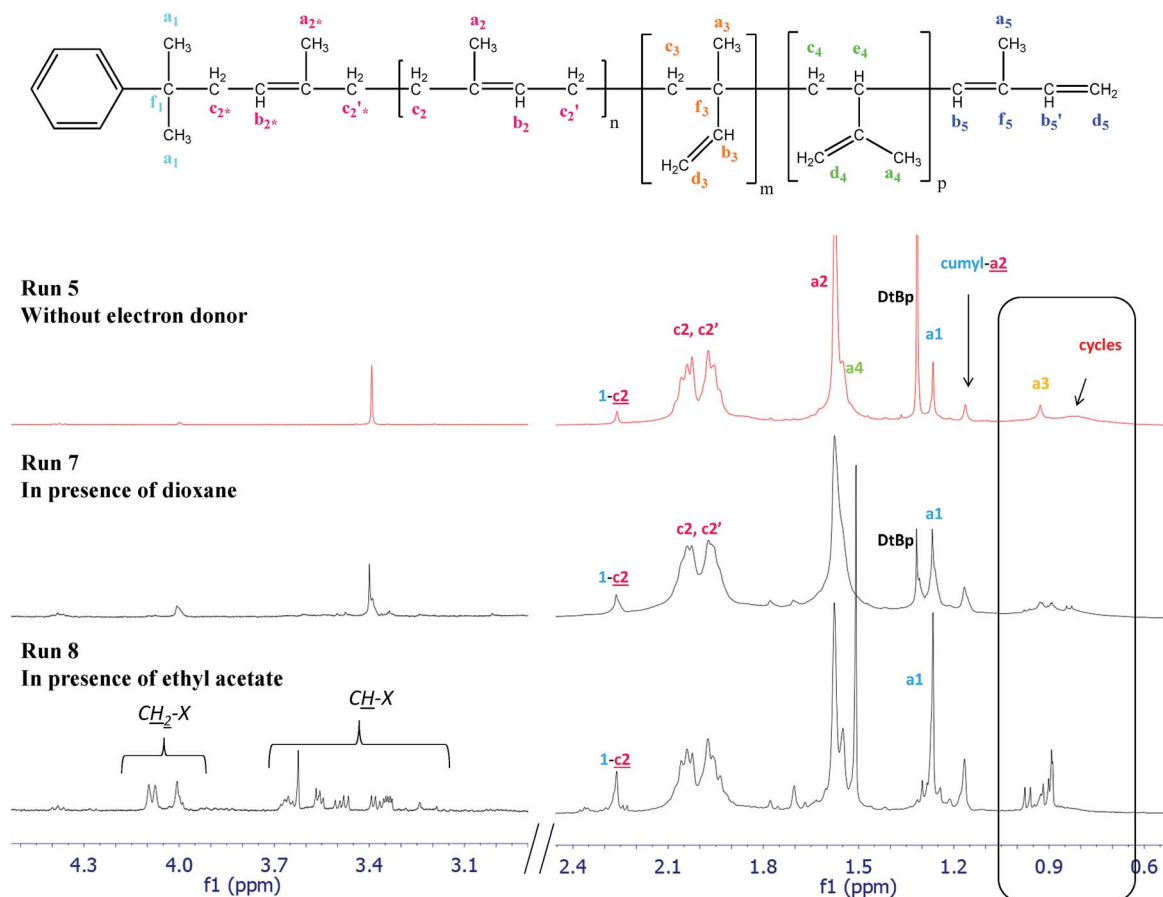


Fig. 4  $^1\text{H}$  NMR spectra of polyisoprenes obtained with IP/cumylOCH<sub>3</sub>/TiCl<sub>4</sub>/d<sup>t</sup>BP/ED 299/1/2/2/1, [IP] = 4.8 M, 24 h at  $-80^\circ\text{C}$  in presence or absence of an electron-donor additive.

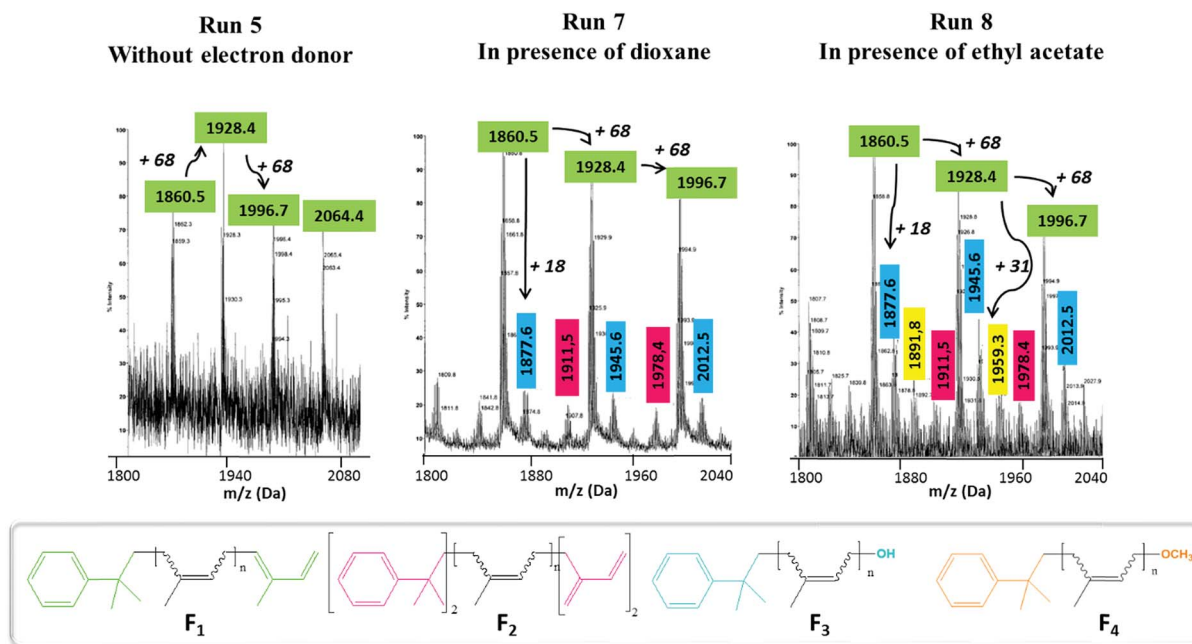


Fig. 5 Maldi-TOF MS spectra of oligoisoprenes obtained with cumylOCH<sub>3</sub>/TiCl<sub>4</sub> initiating system at  $-80^\circ\text{C}$  (IP/cumylOCH<sub>3</sub>/TiCl<sub>4</sub>/d<sup>t</sup>BP/ED = 299/1/2/2/1, [IP] = 4.8 M,  $t$  = 24 h).

and could be thus detectable by NMR analysis, considering the significant amount of double bond loss.

As the NMR investigation was not conclusive, it was also performed pyrolysis studies coupled to gas chromatography-mass spectrometry technique (GC-MS) in order to identify oligoisoprenes subunits. Unfortunately, again it was not possible to find possible structures for the cyclized units. Finally, controlled degradation techniques in the presence of ozone or periodic acid were performed. Again the elucidation of the saturated units was not possible as it was only detected the fragments arising from the 1,4-*trans* units.

## Conclusions

This article showed that, whatever the polymerization conditions, the presence of a large excess of d<sup>4</sup>BP prevented polymerization completion, as transfer reactions were transformed in termination reactions, the released protons being trapped by d<sup>4</sup>BP. As expected for isoprene cationic polymerization, *trans*-1,4- oligoisoprenes were produced with some saturated units. In this study, no polymerization conditions could avoid the consumption of double bond, whereas the best polymerization conditions described so far for the conservation of the double bonds in the cationic polymerization of isoprene are in aqueous medium.<sup>7,22</sup> Besides, the important double bond loss (30–60%) observed in this work was always detected since the very beginning of the polymerization, involving most probably intramolecular cyclization reactions, as it was present even in conditions where protons and interchain branching were absent. Indeed, sufficient proton trap was added to remove all free protons (coming from transfer reactions and water traces) and avoid gelation at 20 °C. It was also shown that the cross-linking reactions observed at lower temperature (gelation temperature depending on the solvent polarity) could be suppressed by addition of an electron donor or by lowering the isoprene concentration. Finally, further attempts to characterize the saturated segments turned out to be difficult because of a probable diversity of the segment units.

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