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MODEL KINETIC STUDY OF $TiCl_4$-INDUCED IONIZATION OF POLYISOBUTENE CAPPED WITH DIPHENYLETHYLENE APPLICATION TO THE SYNTHESIS OF BLOCK COPOLYMERS

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Abstract : The use of non-homopolymerizable monomers such as 1,1-diphenylethylene (DPE) in the synthesis of functional polymers and block copolymers by cationic polymerization has been recently reported. The most important parameters in this process, the kinetics and extent of ionization and capping as well as the stability of the cation, were investigated by studying the reaction with $TiCl_4$ of 1-methoxy-1,1-diphenyl-3,3,5,5-tetramethylhexane, a model for DPE-capped polyisobutene chain-end. This study was performed using ^1H NMR and the high-purity stopped-flow device coupled with UV-visible spectroscopy.

INTRODUCTION

For the synthesis of block copolymers using living carbocationic polymerization, low cross-over efficiencies are generally found when the second monomer is more reactive than the first one. This drawback may be overcome by capping the first block with a highly reactive but non-homopolymerizable monomer such as 1,1-diphenylethylene in order to produce a more stable cation able to initiate the second stage polymerization. Efficiency of this method has been demonstrated by the synthesis of various di- and tri-block copolymers as well as end-functionalized polymers based on polyisobutene (PIB) as a first or central block [Ref.1]. In this process, living PIB is capped with DPE and, in the conditions generally applied, analysis of end-groups show that 100% capping is reached with monoaddition of DPE. The second polymerization is carried out in the presence of suitable solvent and Lewis acid. The DPE -

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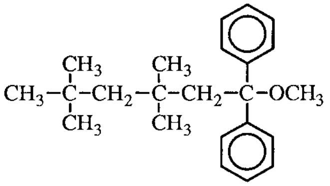
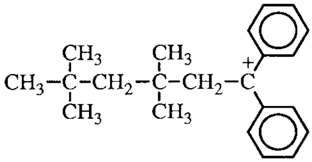
-capped PIB can be isolated after quenching with methanol which results in addition of one methoxy end-group per chain [Ref.2]. The aim of this work was to study the most important parameters concerning formation of the second block that are the kinetics and extent of ionization of the methoxy-terminated DPE-capped PIB and the stability of the formed β-substituted diphenylethyl cation. A capped di-isobutene, the 1-methoxy-1,1-diphenyl-3,3,5,5-tetramethylhexane (DIB-DPE-OMe) was used as a model molecule for this study. Ionization was performed in dichloromethane solvent with $TiCl_4$ as a Lewis acid and was followed using the high-purity stopped-flow device with very short mixing time (5 ms) which allows fast kinetic measurements owing to a UV-visible photodiodes array detector. Stability of the cation was also studied using low temperature NMR spectroscopy in CD_2Cl_2 solvent.



DIB-DPE-OMe



DIB-DPE$^+$

EXPERIMENTAL PART

Materials : Synthesis of DIB-DPE-OMe was performed by capping 2-chloro-2,4,4-trimethyl pentane (DIBCl) with diphenylethylene in the presence of $TiCl_4$ and 2,6-di-*tert*-butylpyridine (DTBP) as a proton trap at -80°C and quenching with methanol ; details on synthesis and characterization are reported in the reference 2. Proton NMR spectroscopy was performed in CD_2Cl_2 solvent and chemical shifts are the following : δ (ppm) = 0.63 (s, 6H, $-C(CH_3)_2-$) ; 0.93 (s, 9H, *tert*-butyl) ; 1.17 (s, 2H, $-CH_2-$ of DIB) ; 2.43 (s, 2H, $-CH_2-$ of DPE) ; 2.93 (s, 3H, $-O-CH_3$) ; 7.1 - 7.4 (m, 10H, aromatic H). This species was found relatively unstable in solution at room temperature owing to methanol elimination and formation of the corresponding olefinic compound taking place within some hours ; for this reason, solutions were always prepared just before use.

For vacuum experiments, CH_2Cl_2, CD_2Cl_2 and $TiCl_4$ were purified according to the techniques generally used in the french laboratory [Ref.3] and no proton trap was used. For the experiments under inert atmosphere conducted in Lowell, CH_2Cl_2 and CD_2Cl_2 were refluxed at least for 4 hours and distilled over CaH_2 just before use, $TiCl_4$ (Aldrich) was used as received and a proton trap (DTBP, 99%, Aldrich) was added in the medium, without any purification.

Proton NMR spectroscopy : Direct low temperature ^1H NMR analysis of the reaction of DIB-DPE-OMe with $TiCl_4$ in CD_2Cl_2 were performed using a Bruker 200 MHz and a Bruker 250 MHz spectrometers respectively in Paris and in Lowell. Mixing of the reagents was performed at the lowest temperature (-78°C and -80°C) after that the temperature was gradually increased. Experimental conditions are reported in Table 1.

Table 1 : Proton NMR spectroscopy of the reaction of DIB-DPE-OMe with $TiCl_4$ in CD_2Cl_2 at various temperatures.

Expt.	Experimental conditions	[DIB-DPE-OMe] (mol/L)	[$TiCl_4$] (mol/L)	[DTBP] (mol/L)	Temperature (°C)
R1	vacuum	0.0049	0.086	0	- 78 - 61 - 40
R2	inert atmosphere	0.0030	0.090	0.006	- 80 - 60
R3	vacuum	0.0193	0.023	0	- 78 - 63 - 45

Scanning UV-visible spectroscopy : Analysis were performed in a sealed, 0.1 cm optical path thermostated quartz cell, using a Cary 118 scanning spectrophotometer from Varian. Highly purified dichloromethane and reagents were used and solutions were prepared under vacuum. Experimental conditions are reported in Table 2. For both experiments, mixing of the reagents was performed at the lowest temperature. Then temperature was gradually increased and absorbance at the maximum of the peak was measured for each temperature after about one hour.

Table 2 : Experimental conditions for the UV-visible spectrometric analysis of the reaction of DIB-DPE-OMe with $TiCl_4$ in CD_2Cl_2 at various temperatures.

Expt.	[DIB-DPE-OMe] (mol/L) (1)	[$TiCl_4$] (mol/L) (1)	Temperature (°C)	A_{444} after 1 hour	% cation (2)
UV1	9.4 10^{-4}	1.9 10^{-2}	- 78	3.2 (not accurate)	100
			- 57	2.05	55
			- 45	1.08	31
			- 35	0.66	19
			- 25	0.38	11
UV2	4.5 10^{-4}	4.8 10^{-3}	- 79	1.68	100
			- 54	1.01	61

(1) calculated at -79°C with CH_2Cl_2 volumic contraction coefficient = 0.00137 K^{-1}

(2) based on concentrations calculated at the reaction temperature

Stopped-flow experiments : A complete description of the stopped-flow apparatus has been reported previously [Ref.4]. For the experiments, highly purified reagents and CH_2Cl_2 were used and no proton trap was added. Experimental conditions are summarized in Table 3.

Table 3 : Stopped-flow experiments of the reaction of DIB-DPE-OMe with $TiCl_4$ in CH_2Cl_2 Characteristics of the absorbance at 444 nm.

Expt	[DIB-DPE-OMe] ($mol.L^{-1}$)	[$TiCl_4$] ($mol.L^{-1}$)	$\frac{[TiCl_4]}{[DIB\text{-}DPE\text{-}OMe]}$	T (°C)	Initial Slope ($A\ unit.s^{-1}$)	t_{max} (s)
SF1	$3.4\ 10^{-4}$	$3.3\ 10^{-4}$	1	- 60	0.8	10 - 14
SF2	"	$1.0\ 10^{-3}$	3	"	3,2	1.4
SF3	"	$3.3\ 10^{-3}$	10	"	24	0.25
SF4	"	$1.3\ 10^{-2}$	40	"	> 100	< 0.05
SF5	$1.7\ 10^{-4}$	$1.3\ 10^{-2}$	80	"	> 55	0.02
SF6	$2.2\ 10^{-4}$	$4.5\ 10^{-4}$	2	- 63	0.9	4
SF7	"	$2.2\ 10^{-3}$	10	"	13	0.5 - 0.6

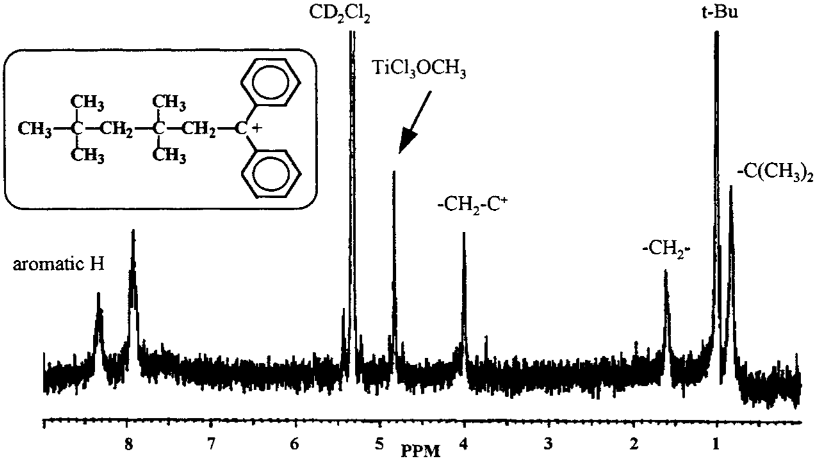
RESULTS AND DISCUSSION

NMR and UV-visible characterization of the DIB-DPE$^+$ cation

The ionization of DIB-DPE-OMe with $TiCl_4$ was studied at very low temperature (-78°C) in CD_2Cl_2 using direct ^1H NMR spectroscopy of the medium. At such a temperature with excess Lewis acid (18 equivalents), complete ionization was observed upon mixing and the resulting 1,1-diphenyl-3,3,5,5-tetramethylhexyl cation (DIB-DPE$^+$) was characterized (Expt. R1). Spectrum is reported on Figure 1 together with assignments of the peaks. The peak observed at 4.8 ppm was attributed to the methoxy group of $TiCl_3OCH_3$ and chemical shift was checked by NMR analysis of a 3:1 molar mixture of $TiCl_4$ and $Ti(OCH_3)_4$. The existence of this species in the medium indicates that the counter-anion of the DIB-DPE$^+$ cation is not mainly $TiCl_4OMe^-$ but may be $TiCl_5^-$ or $Ti_2Cl_9^-$ as previously postulated [Refs.5,6] and this will be discussed later.

As observed by UV-visible spectroscopy, the ionization of DIB-DPE-OMe with $TiCl_4$ in dichloromethane gives a main peak with the maximum absorption at $\lambda_{max} = 444$ nm (see Figure 2) ; it was obviously ascribed to the DIB-DPE$^+$ cation. Other low wavelength absorptions ($\lambda <$ 380 nm) result from $TiCl_4$, from the counter-anions and from complexes existing between $TiCl_4$ and the aromatic rings. The value of the extinction coefficient at 444 nm, $\varepsilon = 37\ 000$ $L.mol^{-1}.cm^{-1}$ could be determined at -79°C with excess $TiCl_4$ (experiment UV2) since it was shown from NMR analysis that ionization was complete under those conditions. Such values of λ_{max} and ε are similar to the ones found for diarylic cations and especially 1,1-diphenyl ethylium which has the maximum absorption at 435 nm with ε at about 30000 $L.mol^{-1}.cm^{-1}$ [Ref.7].

Figure 1 : ^1H NMR spectroscopy of the DIB-DPE$^+$ cation in CD_2Cl_2 (sealed tube ; expt. R1)
[DIB-DPE-OMe] = 4.9 10^{-3} mol/L ; [$TiCl_4$] = 0.086 mol/L ; T = -78 °C



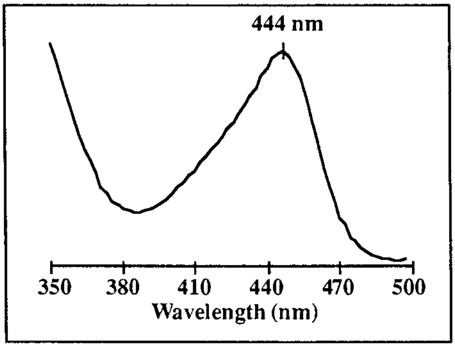


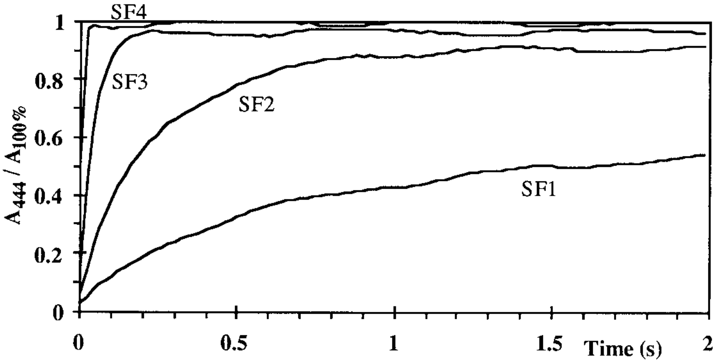
Figure 2 :
UV-visible spectrum of the DIB-DPE$^+$ cation (Absorbance unit versus Wavelength)

Kinetics and extent of ionization of DIB-DPE-OMe with $TiCl_4$ in dichloromethane

Ionization is very fast and initial rates could not be measured using classical analytical techniques since reaction was always completed within less than a few seconds, even at the lowest temperature. For that reason, initial rates of appearance of the DIB-DPE$^+$ cation were measured using the stopped-flow technique by following the absorbance at 444 nm (A_{444}) for various initial concentrations at -60°C (see Table 3). Typical plots of the absorbance A_{444} versus time are reported on Figure 3 for short reaction times where it appears that a plateau is reached after a short period of increase which corresponds to the ionization. It was shown, for constant DIB-DPE-OMe initial concentration, that time to reach the plateau was strongly dependent upon $TiCl_4$ initial concentration. For instance, for the experiments SF1 to SF4, the plateau was reached in 10 s when the [$TiCl_4$]/[DIB-DPE-OMe] ratio was 1 and in less than 0.05 s when the ratio was 40. The kinetics of ionization was deduced from the initial slopes.

Assuming a first order with respect to DIB-DPE-OMe, the order with respect to $TiCl_4$ was found equal to 1.5 (see Figure 4) and an apparent rate constant of ionization (k_i) could be estimated : at -60°C, k_i is approximately 0.5 - 1.10^5 $L^{1.5}.mol^{-1.5}.s^{-1}$.

Figure 3 : A_{444} / $A_{100\%}$ versus time for the experiments SF1 - SF4 carried out at -60°C ($A_{100\%}$ corresponds to the absorbance at 100 % ionization)



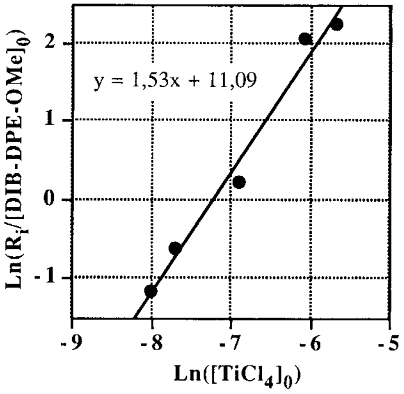


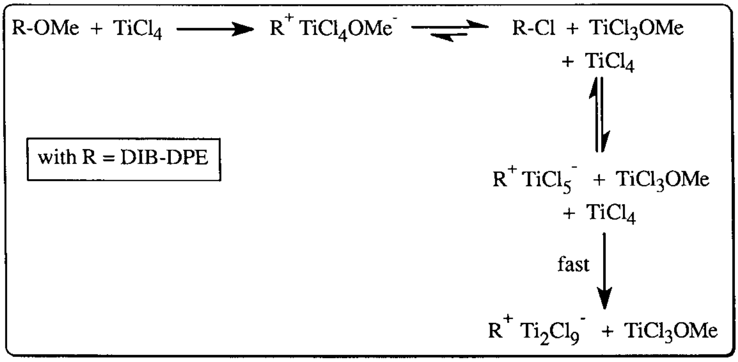
Figure 4 :
Determination of the external order with respect to $TiCl_4$:
Plot of $\ln(R_i/[\text{DIB-DPE-OMe}]_0)$ versus $\ln([TiCl_4]_0)$ for the experiments SF1-SF3 and SF6-SF7 where R_i represents the initial rate of appearance of DIB-DPE^+

The same value of maximum A_{444} was found for the experiments with $[TiCl_4]$/[DIB-DPE-OMe] ≥ 3, indicating complete ionization. However, when the ratio was 1 and 2, the extent of ionization was lower (see Figure 3) as previously observed by conductivity measurements [Ref.2]. Incomplete ionization was also observed by NMR spectroscopy when using 1 equivalent $TiCl_4$ at -78°C (Expt. R3). In that case, within 2 minutes after mixing, the DIB-DPE^+ cation (75 mol.%) was observed together with DIB-DPE-Cl (25 mol.%), the end-chlorinated analogue of DIB-DPE-OMe (1-chloro-1,1-diphenyl-3,3,5,5-tetramethylhexane). This assignment was based on the disappearance of the peak at 2.93 ppm (terminal methoxy group) and the shift of the peak of the methylene from 2.43 ppm (for DIB-DPE-OMe) to 2.82

ppm. Since no DIB-DPE-OMe could be observed, this indicates very fast exchange of the leaving groups leading to DIB-DPE-Cl and $TiCl_3OCH_3$ followed by partial ionization of the chlorinated compound by $TiCl_3OCH_3$.

To explain that complete ionization occurs only when the $[TiCl_4]/[DIB\text{-}DPE\text{-}OMe]$ ratio is higher than 3, it is necessary to postulate that ionization takes place with rapid formation of $TiCl_3OCH_3$ together with $Ti_2Cl_9^-$ as a counter-anion. The existence of the $Ti_2Cl_9^-$ anion was experimentally evidenced for other systems [Refs.8,9] and it was proposed that an associated form of the acid (Ti_2Cl_8, [Ref.10]) could be active for ionization [Refs.2,5]. However, the existence of this dimer has been disputed [Refs.11-13] and is not absolutely necessary to explain the experimental results. Actually, the existence of $Ti_2Cl_9^-$ as well as the 1.5th order with respect to $TiCl_4$ may be explained by the ionization with monomeric $TiCl_4$ followed by fast rearrangement of the counter-ion by reaction with a second molecule of $TiCl_4$ (Scheme 1).

Scheme 1 : General scheme for the ionization of DIB-DPE-OME with excess $TiCl_4$



Stability of the DIB-DPE$^+$ cation

Although very stable at -80°C or -78°C with excess Lewis acid, the DIB-DPE$^+$ cation was found less stable at higher temperature and/or with lower $TiCl_4$ initial concentration since maximum ionization was followed by a relatively slow decrease of its concentration as observed by UV-visible spectroscopy as well as conductivity. This decrease was explained by decapping i.e. elimination of DPE since it has been recently reported that reaction of DIBCl or end-chlorinated PIB with DPE in the presence of $TiCl_4$ is equilibrated [Ref.1].

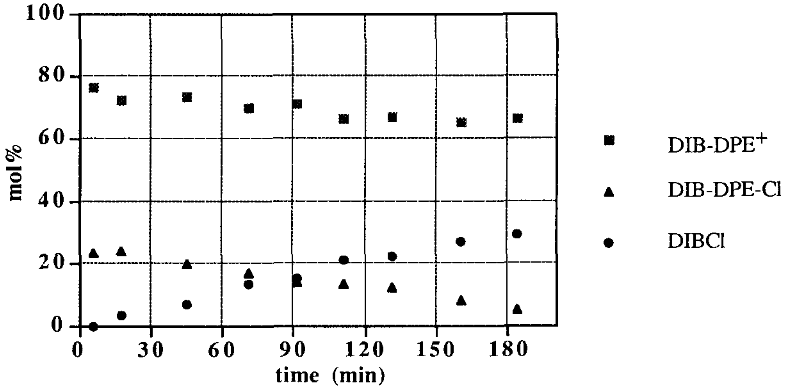
Equilibria of decapping of the DIB-DPE$^+$ cation

$$\mathrm{DIB\text{-}DPE^+\,Ti_2Cl_9^-} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{DIB^+\,Ti_2Cl_9^-} + \mathrm{DPE} \overset{K_2}{\rightleftharpoons} \mathrm{DIBCl} + \mathrm{DPE} + 2\,\mathrm{TiCl_4}$$

At -78 °C, decapping occurred when 1 equivalent $TiCl_4$ was used for ionization (Expt. R3) to lead to DIBCl and DPE, as observed by NMR. The proportion of capped cation only slightly decreased but the extent of non ionized DIB-DPE-Cl decreased until almost complete disappearance in about 3 hours. At that stage, the molar proportion of DIB-DPE$^+$/DIBCl was 69/31 (Figure 5).

Figure 5 : Relative proportions of DIB-DPE$^+$, DIB-DPE-Cl and DIBCl versus time as measured by NMR spectroscopy at -78°C with 1 equivalent $TiCl_4$ (Expt. R3).

$$\text{DIB-DPE-Cl} + TiCl_3OCH_3 \rightleftharpoons \text{DIB-DPE}^+\ TiCl_4OCH_3^- \rightleftharpoons \text{DIBCl} + \text{DPE} + TiCl_3OCH_3$$



For the same experiment, when temperature was raised to -63°C, decapping was completed in less than 20 minutes. In that case, the equilibrium of decapping was strongly shifted towards the formation of DIBCl and DPE since the formed Lewis acid, $TiCl_3OCH_3$, is not strong enough to ensure sufficient ionization of DIBCl which is needed for the reverse reaction.

With excess $TiCl_4$, the cation was found stable at -80°C, but it has been shown that the rate of decapping increased when the temperature was increased and the concentration of remaining cation after a given time strongly decreased (see Table 2) ; for instance, percentage of ionization reached 11 % after 1 hour at - 25°C for the experiment UV1.

When the initial $TiCl_4$ concentration was increased at -60°C, the rate of decapping strongly decreased (Figure 6) since the capping reaction which comprises ionization of DIBCl and addition of DPE is accelerated with increasing free Lewis acid concentration.

An apparent constant K_e of the capping- decapping equilibrium can be written as follows :

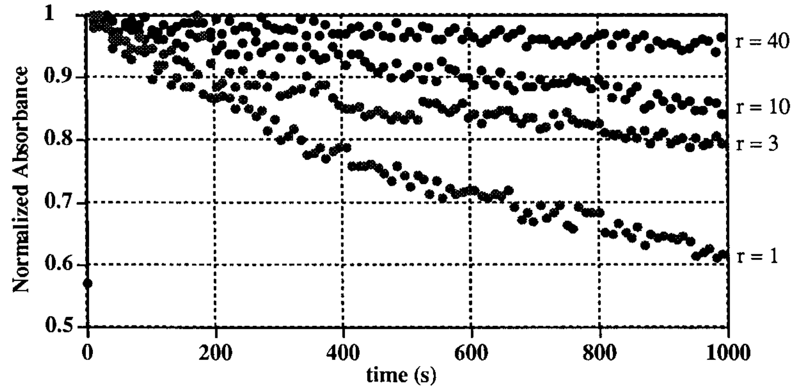
$$K_e = \frac{1}{K_1.K_2} = \frac{[\text{DIB-DPE}^+\ Ti_2Cl_9^-]}{[\text{DIBCl}].[TiCl_4]^2.[\text{DPE}]}$$

which indicates that an equilibrium concentration of the cation should be reached depending on the initial concentrations and temperature.

$$\frac{[\text{DIB-DPE}^+\ Ti_2Cl_9^-]_{eq.}}{[\text{DIB-DPE-OMe}]_0} = 1 + \frac{1 - \sqrt{1 + 4.K_e.[TiCl_4]_0^2.[\text{DIB-DPE-OMe}]_0}}{2.K_e.[TiCl_4]_0^2.[\text{DIB-DPE-OMe}]_0}$$

However, the determination of this equilibrium concentration and thus the value of K_e in CH_2Cl_2 at various temperatures failed owing to different reasons. The first one is that, using UV-visible spectroscopy in the absence of a proton trap, the decrease of A_{444} during decapping was accompanied by a hypsochromic shift of the maximum wavelength of a few nanometers indicating the existence of another species which prevents accurate measurement of A_{444}. Another main reason is that complete decapping occurred for some experiments instead of final equilibrium.

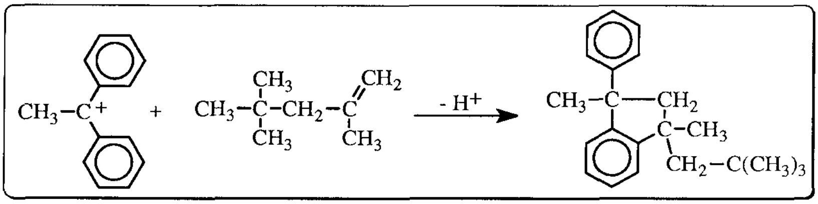
Figure 6 : Influence of $TiCl_4$ initial concentration on the rate of decapping (experiments SF1-SF4) as observed by stopped-flow UV-visible spectroscopy .
For each experiment, the normalized absorbance is the ratio of A_{444} over A_{max} which is the maximum A_{444} versus time and $r = [TiCl_4]_0/[DIB\text{-}DPE\text{-}OMe]_0$



Direct ^1H NMR observation of the reaction of DIB-DPE-OMe with excess $TiCl_4$ was carried out at various temperatures, in the presence and in the absence of DTBP (respectively (Expt. R2 and Expts. R1, R3) and allows a better understanding of the decapping reaction. At temperatures above -60°C decapping occurred and was evidenced, in the presence of DTBP, by the expected formation of DPE and DIBCl. The latter product was not stable enough to remain unreacted during long periods of time and decomposed probably into its ethylenic analogues leading to by-products such as dimers. The H^+ ions formed by this reaction were trapped by the unprotonated DTBP. In the absence of DTBP but with high vacuum purified reagents, decapping lead to DIBCl and to the diphenylethyl cation (DPE^+, chemical shift of CH_3 = 3.74 ppm) which was produced by fast protonation of DPE owing to protic impurity traces (cocatalysis with free $TiCl_4$) ; in the experiment R1, no free DPE could be detected. The DPE^+ cation which absorbs at 435 nm was responsible for the wavelength shift mentioned above. At the same time, the slow dehydrochlorination of DIBCl into its exo ethylenic analogue (2,4,4-trimethylpent-1-ene) occurred since the compound resulting from its addition with DPE^+ and further indanic cyclization was observed (1-phenyl-1,3-dimethyl-3-neopentylindan, see Scheme 2) and this product was the final species observed at room temperature. Both reactions, i.e.

HCl elimination from DIBCl and indanic cyclization lead to the continuous formation of H^+ in such an amount that complete protonation of DPE can occur. Therefore, in both situations i.e. with and without added proton trap, side reactions prevent from reaching the equilibrium concentrations and lead to a slow but complete decapping of the DIB-DPE^+ cation.

Scheme 2



CONCLUSION

The ionization with $TiCl_4$ of methoxy-terminated DPE-capped di-isobutene was studied as a model reaction for the formation of block copolymers using living cationic polymerization with PIB as a first block. It has been evidenced that ionization was a complete and very fast reaction provided that excess Lewis acid is used (more than 3 equivalents). The resulting diarylic cation has been shown to be very stable at -80°C with excess $TiCl_4$. However decapping reaction leading back to DIBCl and DPE became detectable at that temperature when only 1 equivalent $TiCl_4$ was used and also at temperatures above -60°C even with excess $TiCl_4$. To improve cross-over efficiency, the rate of decapping should be slow as compared with the rate of initiation. Such requirement may be achieved at very low temperature (typically -80°C) and with excess $TiCl_4$. However, concerning that last point, a compromise should be found depending on the second monomer and thus, nature and concentration of the Lewis acid should be adjusted in order to get a living second stage polymerization.

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