European Polymer Journal 45 (2009) 837–845

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Cationic polymerization of dienes VIII: Is the elimination of cross-linking by a bulky electron donor a general behavior in the presence of aluminium trichloride? ☆

Véronique Bennevault-Celton *, Nezha Badi, Hervé Cheradame

Laboratoire Matériaux Polymères aux Interfaces (MPI), Université d'Evry Val d'Essonne, Rue du Père Jarlan, 91025 Evry Cedex, France

ARTICLE INFO

Article history:
Received 23 September 2008
Received in revised form 21 November 2008
Accepted 24 November 2008
Available online 3 December 2008

Keywords:
Electron donor
Cationic polymerization
Aluminium trichloride
Isoprene
1,3-Pentadiene

ABSTRACT

Previous works on the polymerization of 1,3-pentadiene initiated by aluminium trichloride in non polar solvent at room temperature in the presence of bulky electron donor (ED) as tri-*p*-tolylamine have highlighted a stabilization of the polymerizing actives centres by ED, which allowed a reduction of some side reactions and the formation of more precisely defined polypentadienes than ever by cationic polymerization in non polar medium. The aim of this research was to investigate the role of bulky EDs such as tri-*p*-tolylamine and similar compounds in polar medium in order to obtain if possible a complete control of the polymerization of isoprene and 1,3-pentadiene. The beneficial effect of tri-*p*-tolylamine was shown in the case of isoprene polymerization at room temperature, with an important reduction of the cross-linked fraction for long reaction times and strong reduction of termination reactions. At −30 °C in the presence of tri-*p*-tolylamine, polypentadienes more controlled than in non polar solvent could be obtained, with a nearly complete elimination of the cross-linked fraction, while keeping the microstructure approximately constant.

1. Introduction

In the domain of cationic polymerization, to date, some monomers have not been polymerized by controlled or quasi living process [1]. This is the case of dienes. It is mainly due to reactions between the active centres and the double bonds of the polymer leading to cyclization, isomerization, grafting and cross-linking reactions [2–6]. In some cases, the partial insolubility of the catalyst in the polymerization medium also contributes to the formation of insoluble polymer. Indeed, a previous paper reported on the formation of cross-linked polymer at the surface of the insoluble catalyst in the polymerization of 1,3-pentadiene (PD) initiated by aluminium trichloride in pentane [7].

In cationic polymerization, electron donors (EDs) were widely used to mediate the reactivity of the active species through carbocation stabilization method. Many controlled polymerizations could be obtained and were described in the literature [8–10]. Working on the cationic polymerization of PD initiated by $AlCl_3$ in non polar medium, it was shown that stabilizing the active centres with some bulky EDs gave a way to a strong reduction of some side reactions [11,12]. For example, at room temperature the introduction of OPh_2 or SPh_2, NPh_3, $N(PhBr)_3$ in the polymerization medium allowed to reduced the formation of cross-linked polymer, with an overall yield higher than that of the polymerization realized without ED after 2 h of reaction. Isomerisation was also reduced in the presence of SPh_2 and the total content of isomerization and cyclization was found lower in the presence of NPh_3. In the case of these last EDs, it was evidenced an interaction between the active

☆ PartVII: Eur Polym J 2004;40:1387–1398.

* Corresponding author. Tel.: +33 1 69 47 77 19; fax: +33 1 69 47 77 27.
E-mail address: Veronique.Celton@univ-evry.fr (V. Bennevault-Celton).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.11.032

centres and ED, which increased decreasing the temperature. Besides this interaction, a higher solubilization of the Lewis acid due to the formation of a complex between $AlCl_3$ and ED was suggested to explain all the results. The behavior of NPh_3 and 9-phenylcarbazole is different from the other EDs, since these additives induced transfer reaction by the alkylation of the aromatic rings at the para position by the growing polymer chains [12,13]. Thus we focused on para-substituted triphenylamine, for which this side reaction was prohibited. Best results were obtained in the case of tri-*p*-tolylamine ($N(PhMe)_3$). In these conditions it was observed a decrease of both proton and carbon relative unsaturation losses – witnessing the content of isomerization and cyclization [6] – with a nearly complete disappearance of the high molar masses (grafted molecules) leading to narrower polydispersity indexes and a drastic fall of the insoluble polymer [12]. When using a ratio $[N(PhMe)_3]/[AlCl_3]$ of 4, the remaining insoluble fraction (IF) was only about 5% even after 72 h of reaction at 20 °C with a polydispersity index (I_p) for the corresponding soluble polymer equal to 4.9. For comparison, in the absence of ED, IF reached about 50% after 30 h of reaction and I_p of the soluble polymer was equal to 24.5 [14]. In spite of these encouraging results, the control of the polymerization was not yet achieved, mainly due to the existence of few grafted molecules.

In the search of new conditions providing controlled $AlCl_3$/1,3-pentadiene polymerization, we focused in the present paper on bulky EDs used at different temperature in polar solvent.

2. Experimental

2.1. Materials

1,3-Pentadiene (Aldrich, analytical grade, 90%), is composed of 34% in moles of *cis* pentadiene and 66% in moles of *trans* pentadiene; before use it was dried under vacuum over calcium hydride under magnetic stirring. Isoprene (Aldrich, 99%) was dried in the same way. Aluminium trichloride (Aldrich, 99.99%) was handled and stored under N_2 atmosphere in a glove box and used as received. Methylene chloride (SdS) was refluxed over CaH_2 and distilled under nitrogen just before use. The solid electron donors were used as received without further purification: triphenylamine (Aldrich, 98%), tri-*p*-tolylamine (Aldrich, 97%), tribenzylamine (Acros, 99%), tris(4-bromophenyl)amine (Aldrich, 98%), triphenylphosphine (Acros, 99%), 1,3,5-triphenylbenzene (Aldrich), whereas the liquid electron donors were dried over a 3 Å molecular sieves under nitrogen: diethylether (Aldrich), diphenylether (Aldrich, 99%), diphenylsulfide (Aldrich, 98%) and ditertiobutylsulfide (Acros, 98%). *n*-Butylamine (Aldrich, 99%) was used without further purification.

2.2. Procedures

$AlCl_3$ and the solid electron donor if any were introduced in the reactor in a glove box under N_2 atmosphere. The reactor was connected to the vacuum line and CH_2Cl_2 was added by cryodistillation. The reactor was placed either at room temperature or at −10 °C or −30 °C using a cryothermostat before the introduction of the monomer. After the required time, the polymerization was quenched by addition of excess butylamine. An insoluble and a soluble fraction can be obtained. After filtration, the soluble fraction was washed with water then evaporated to dryness under vacuum. The insoluble fraction, i.e. the cross-linked polymer, was only dried under vacuum.

2.3. Polymer characterization

2.3.1. Nuclear magnetic resonance (NMR)

^1H and ^{13}C spectra were recorded on a Bruker Avance 300 MHz in deuterated chloroform or methylene chloride. The proton relative unsaturation loss per monomer unit α_H calculated by ^1H NMR (in $CDCl_3$) was defined as the difference between the theoretical unsaturation degree (equal to 25% of the total of protons, assuming negligible the ratio of 3,4-units) and the experimental unsaturation degree (d_{exp} = integration of olefinic proton peaks/integration of aliphatic and olefinic proton peaks) divided by the theoretical unsaturation degree: $\alpha_H = (0.25 - d_{exp})/0.25$. In the same manner, the carbon relative unsaturation loss per monomer unit α_C was calculated from quantitative ^{13}C NMR spectra and was equal to the difference between the theoretical unsaturation degree (equal to 40%) and the experimental unsaturation degree (d_{exp}) divided by the theoretical unsaturation degree: $\alpha_C = (0.40 - d_{exp})/0.40$. ^{13}C measurements were performed using an Inverse Gate procedure, allowing a quantitative determination of the carbon unsaturation loss. The NMR pulse conditions were chosen to ensure that all the analyzed ^{13}C nuclei (including quaternary carbons) were detected.

2.3.2. Size exclusion chromatography (SEC)

Number- and weight-average molar mass ($\overline{M_n}$ and $\overline{M_w}$, respectively) were determined by SEC in tetrahydrofuran on a chromatograph equipped with one column (Styragel HR 4E: molecular separation range: 100–5.10^5 g/mol), a refractive index (RI) cell (Waters 410) and an UV detector (Waters 2487). The analyses were realized at room temperature with a flow rate equal to 0.3 mL/min. Polystyrene standards were used to generate the calibration curve.

3. Results and discussion

3.1. Influence of the tri-p-tolylamine on the isoprene polymerization at room temperature in methylene chloride

In order to investigate the importance of the bulkiness of the EDs, they were used in the cationic polymerization of an important diene, 2-methyl-butadiene (isoprene). The polymerizations were performed at room temperature, because this polymerization is very slow at low temperature. Different tri-*p*-tolylamine concentrations ($[ED]/[AlCl_3] = 0.5–4$) were introduced and the polymerizations were compared to two polymerizations realized without ED (runs 1 and 2, Table 1). After 2 h

Table 1
Influence of tri-*p*-tolylamine concentration on the isoprene polymerization at room temperature in a polar solvent.

Run[a]	[ED]/[$AlCl_3$]	Overall Yield (%)	IF [b] (%)	$\overline{M}_n$ [c] (g/mol)	I_p[c]
1	0	12.3	14.6	100	19.4
2	0	13.6	10.3	100	29.1
3	0.5	9.7	27.9	300	5.14
4	1	10	10.6	300	5.17
5	2	7.5	34.6	1100	1.62
6	4	1.9	43.5	-	-

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [isoprene] = 1.6 mol/L, CH_2Cl_2, t = 2 h, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/overall yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.

of reaction, the overall yield for runs 1 and 2 was low, about 13%, with a polymer containing an insoluble fraction close to 12% and it can be noticed that in the presence of the tri-*p*-tolylamine, the higher the ED concentration, the lower the total yield. These results were assigned to a kinetic effect, due to a complexation between the active centres C^+ and ED. It was observed that the amount of the insoluble polymer changed little (in the 1–3% range of the initial monomer content) while the soluble polymer yield decreased with increasing [ED], which led to an increase of the insoluble fraction. Our previous findings showed that a part of the insoluble polymer is formed on the surface of the insoluble catalyst [7]. The fact that the insoluble polymer is produced in constant yield is a consequence of the constant heterogeneity of the polymerization medium in the experiments carried out in constant conditions (temperature, solvent, [$AlCl_3$], time). For all the polymerizations, only oligomers were obtained. The increasing tri-*p*-tolylamine concentrations would seem to induce a slight increase of the molar mass of the chains and a decrease of the polydispersity index. No alkylation of the ED aromatic groups by the growing chains was detected by SEC using the double detection, refractive index and UV detections.

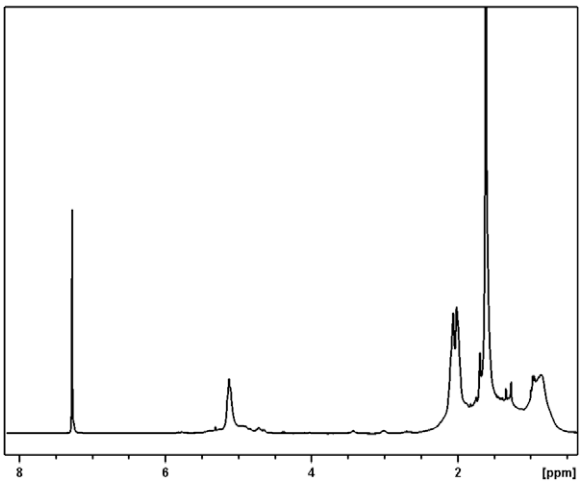

Fig. 1. ^{1}H NMR spectrum of a polyisoprene synthesized in the presence of the tri-*p*-tolylamine at room temperature (run 4, Table 1) after precipitation in acetone.

This result was confirmed by ^{1}H NMR after precipitation of the polymers in acetone (Fig. 1).

A kinetic study was then realized with very high reaction duration in order to accurately characterize the influence of tri-*p*-tolylamine on the isoprene polymerization. Table 2 reports the results of polymerizations carried without ED or in the presence of ED with a ratio [ED]/[$AlCl_3$] equal to 1 or 2. Because of the polymerization medium heterogenity which prevented sampling out, each result corresponded to one experiment. For the polymerizations realized without ED, the total yield was almost constant while the insoluble fraction slightly increased with time, possibly due to grafting onto reactions. It is known that the cross-linked polymer formation was favored by high reaction time [6,7]. The very low variation of the overall yield would mean that many active centres were deactivated or could not propagate due to steric hindrance reasons. On the contrary, when the tri-*p*-tolylamine was added in the polymerization medium, the total yield increased with time and reached about 90% after 49 h for the experiments using a ratio [ED]/[$AlCl_3$] equal to 1 or 2. These results evidenced the beneficial effect of this ED on the polymerization. However, when the ratio [ED]/[$AlCl_3$] was equal to 1, the quantity of ED was not sufficient to avoid or limit the formation of insoluble polymer, since IF varied from about 11% to 77% between 2 h and 49 h of reaction. It was necessary to use an excess of ED (runs 8–10) to strongly reduce IF. For these experiments, IF decreased from 35% to 8%: the last experimental conditions allowed limiting the formation of cross-linked polymer (insoluble polymer yield being equal to 3% and 7% of the initial monomer content, respectively, for runs 8 and 10) and on the contrary favoring the formation of soluble polymer by stabilization of the active centres (soluble polymer yield = 5% and 84.5%, respectively, for runs 8 and 10). Another important point was the increase of the molar masses of the polymer chains with time. When [ED]/[$AlCl_3$] = 1, $\overline{M}_n$ reached 4000 g/mol after 30 h and when [ED]/[$AlCl_3$] = 2, $\overline{M}_n$ was of 5200 g/mol after 49 h. In the case of the experiments realized with the ratio equal to

Table 2
Kinetic study of isoprene polymerization carried without or in the presence of tri-*p*-tolylamine at room temperature in a polar solvent.

Run [a]	[ED]/[$AlCl_3$]	Time (h)	Overall Yield (%)	IF [b] (%)	$\overline{M}_n$ [c](g/mol)	I_p [c]	$\overline{M}_n$th[d] (g/mol)
1	0	2	13.6	10	100	29.1	
2	0	21	14.1	38	200	10.6	
3	0	49	15.3	43	200	9.9	
4	1	2	10	11	300	5.2	
5	1	21	17	11.5	1700	2.1	
6	1	30	44	23	4000	4.8	
7	1	49	87.5	77	2400	6.2	
8	2	2	7.5	35	1100	1.6	700
9	2	21	48.3	9	3400	4.0	4400
10	2	49	91.2	8	5200	1.5	8600

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [isoprene] = 1.6 mol/L, CH_2Cl_2, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/Overall yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.
[d] Calculated molar mass assuming direct initiation from $AlCl_3$ assuming self-ionization.

1, the molar mass of the soluble chains decreased between 30 h and 49 h of reaction due to the increase of the insoluble fraction which consumed the highest molar mass chains (IF growing from 23% to 77%). When IF was low, it was possible to compare the molar masses of the soluble chains and the theoretical values, calculated assuming a direct initiation from $AlCl_3$ by self-ionization, because in the case of a low IF, its influence on the theoretical calculation can be neglected. Table 2 shows an acceptable agreement between the experimental and calculated values when the tri-*p*-tolylamine was introduced in excess in the polymerization medium.

After this short study devoted to the role of bulky ED in the polymerization of isoprene, highlighting the reduction of the cross-linked fraction, the same type of study was carried out on the 1,3-pentadiene polymerization.

3.2. Influence of the solvent polarity on the 1,3-pentadiene (PD) polymerization

Side reactions were first examined without introducing ED in the polymerization medium but varying the polarity of the solvent (Table 3). When polymerizations were realized in methylene chloride, the polymerization medium was almost homogeneous and nearly no cross-linked polymer was produced at room temperature and at −10 °C. The polydispersity indexes were lower at −10 °C in the two solvents. The examination of the proton and carbon unsaturations losses of the polymers gave information on cyclization and isomerization reactions which were on the whole less important at low temperature. Table 3 also shows that at room temperature the isomerization and cyclization content is greater in polar solvent (higher α_H and α_C). This result was assigned to the formation of more dissociated active species. This effect is less pronounced at −10 °C.

To conclude on this preliminary investigation, in order to obtain the best control of the polymerization, it is preferable to operate in polar solvent and at low temperature. The polymerization temperature cannot be strongly decreased because the polymerization rate becomes too low. For example, the total yield was only equal to 6% when the polymerization was performed at −70 °C after 24 h of reaction with [PD] = 2.3 mol/L and $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L.

Table 3
Influence of the solvent polarity on the 1,3-pentadiene polymerization initiated by $AlCl_3$ in the absence of ED.

Run [a]	Solvent	T (°C)	Overall yield (%)	IF[b] (%)	$\overline{M}_n$[c] (g/mol)	I_p[c]	α_H[d]	α_C[d]
1	Pentane	20	64	52.5	2200	10.2	0.36	0.26
2	Pentane	−10	30	73	5400	6.0	0.27	0.28
3	CH_2Cl_2	20	83	3	2800	25.9	0.64	0.50
4	CH_2Cl_2	−10	67	5	4000	2.4	0.37	0.28

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, t = 2 h, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/Overall yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.
[d] Proton and carbon unsaturation losses determined by NMR.

3.3. Influence of some ED on the 1,3-pentadiene polymerization at room temperature in methylene chloride

The solvent (methylene chloride) being selected, the influence of different EDs was first investigated at room temperature with a ratio [ED]/[$AlCl_3$] equal to 1, since 20 °C is the temperature used in industry to synthesize polypentadienes [15]. The results are reported in Table 4. In the presence of diphenylsulfide (run 2), the overall yield was complete and higher than the one obtained without additive (run 1). Except diphenylether, the overall yields obtained with the other EDs were higher or in the same magnitude as the standard polymerization (run 1). The lower yield observed with OPh_2 could be due to a lowering of the polymerization rate or to termination reactions. Indeed, it was shown in non polar solvent that this ED slightly favored unimolecular termination by reaction with the counter-ion $AlCl_4^-$ [11] (direct initiation [16]). Only two electron donors, triphenylamine and tri-*p*-tolylamine, allowed totally suppressing the formation of cross-linked polymer. 1,3,5-triphenylbenzene ($C_6H_3Ph_3$, run 8, Table 4) led to a slightly higher insoluble fraction compared to the standard polymerization (result assigned to the partial solubilization of this ED in our conditions) and the other additives gave similar insoluble fractions as run 1.

Table 4 shows that all the EDs induced interactions with the active centres since the branching reactions are strongly reduced in their presence (runs 2–9). Indeed, the I_p of the corresponding polymers were much lower than one of the polymer performed without ED. It was also observed a slight reduction of the total isomerization and cyclization content for runs 2, 3 and 5–9. Based on the values of I_p and α_H of the polymers, it might be concluded that this interaction would be the highest in the case of $StBu_2$ since the latter would induce the highest decrease of the total isomerization and cyclization content and branching reactions. Unfortunately it was shown previously that this ED was a transfer agent and the transfer reactions still occurred, even when reducing temperature at 0 °C [17]. It was proposed the following mechanism:

$$P^+ + SR_2 \rightleftharpoons P(-H^+) + HSR_2{}^+$$
$$HSR_2{}^+ + M \rightarrow HM^+ + SR_2$$

where P^+, M, SR_2 respectively represent a growing chain, the monomer and ditertiobutylsulfide.

Like in non polar medium [12], it was found that the triphenylamine and 9-phenylcarbazole reacted with the growing polymer chains by alkylation of the aromatic groups, which obviously induce transfer reactions, while thanks to methyl groups in para position this side reaction was inhibited in the case of the tri-*p*-tolylamine. The polymers were analyzed by size exclusion chromatography (SEC) using a double detection, refractive index and UV detections. The UV detector was set at 345 nm, since at this wavelength the chromatograms only show the aromatic groups absorption. The RI and UV SEC chromatograms traces of the polymer synthesized in the presence of 9-phenylcarbazole are given Fig. 2. The superposition of the two detections clearly showed the incorporation of the triphenylamine and 9-phenylcarbazole to the polymer, whatever

Table 4
Influence of some ED on the polymerization of 1,3-pentadiene at room temperature with a ratio [ED]/[$AlCl_3$] = 1.

Run [a]	ED	Overall yield (%)	IF [b] (%)	$\overline{M}_n$ [c] (g/mol)	I_p [c]	α_H [d]
1	None	83	3	2800	25.9	0.64
2	SPh_2	100	1	2400	6.3	0.60
3	9-Phenylcarbazole	94	1.5	2200	9.5	0.57
4	$StBu_2$	90	2	1100	3.4	0.35
5	$N(PhMe)_3$	86	0	3300	7.0	0.56
6	NPh_3	85	0	2400	7.4	0.53
7	$N(PhBr)_3$	77	4	4400	9.5	0.59
8	$C_6H_3Ph_3$	75	9.5	3400	8.1	0.57
9	OPh_2	63	2	2900	12.1	0.56

[a] [$AlCl_3$] = ED] = 2.3×10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/Overall yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.
[d] Proton unsaturation loss determined by ^{1}H NMR.

the length of the polymer chains. On the contrary no UV signal corresponding to the polymer chains was observed in the case of $N(PhMe)_3$ and, in the ^{1}H NMR, no aromatic protons were observed on the spectra of the purified polymer (Fig. 3).

To summarize, these results showed that it was easier to limit intermolecular reactions (branching, cross-linking) than intramolecular reactions (isomerization, cyclization...) in the studied operating conditions. The studied conditions were not yet sufficient to induce a complete control of the polymerization. In order to see whether the control might be improved, increasing tri-*p*-tolylamine concentrations were tested. As seen in Table 5, the overall yield did not vary, while the SEC analysis showed a narrowing of the molar mass distribution and a decrease of the average number molar mass when [$N(PhMe)_3$] increased. This result is due to the more and more important reduction of the grafted chains (highest molar mass chains), thanks to the stabilization of the active species by the ED. The SEC chromatograms given Fig. 4 showed that, for a ratio [ED]/[$AlCl_3$] equal to 4, the molar mass distribution was monomodal with a polydispersity index of 3.2. No insoluble polymer was observed whatever the used quantity of ED and concerning the isomerization and cyclization content, it can be noticed a light decrease with the increasing ED concentration. α_H decreased from 0.64 to 0.52. If one compares this study to the same one realized in non polar solvent [12], better results were obtained in methylene chloride as far as grafting reactions and insoluble fraction were concerned. It is worth noting that in non polar solvent, when [$N(PhMe)_3$]/[$AlCl_3$] = 4, it still remained cross-linked polymer (IF = 11%) and the molar mass distribution was not monomodal. However, α_H was lower in non polar medium: α_H = 0.30 in pentane and 0.52 in methylene chloride. The latter solvent which induced a higher dissociation of the active species, thus favors isomerisation and cyclization reactions.

Based on these different results and keeping in mind that the best control of the polymerization in non polar solvent at room temperature was obtained with tri-*p*-tolylamine and that the polymerization temperature reduction could contribute to the stabilization of the active centres, the PD polymerization was investigated in the presence of tri-*p*-tolylamine and additives with similar structure at low temperature.

3.4. Influence of some ED on the 1,3-pentadiene polymerization at low –10 °C in methylene chloride

Different polymerizations with increasing tri-*p*-tolylamine concentrations were performed at −10 °C using anhydrous aluminium trichloride with the same purity as above (99.99%) in order to improve the control of the polymerization. As shown in Table 6, the overall yield decreased at constant polymerization duration with increasing ED concentration. The insoluble fraction was nearly suppressed in the presence of tri-*p*-tolylamine for a [ED]/[$AlCl_3$] ratio of 2. Using size exclusion chromatography it can be seen a decrease of the molar mass of the soluble polymer with the increasing ED concentration, due to a reduction of the highest molar mass chains (Fig. 5), while no visible effect was observed on the polydispersity index and on the proton relative unsaturation loss. These results could be explained by an interaction between C^+ and tri-*p*-tolylamine, leading to a slowing down of the polymerization (kinetic effect), but the interaction would not be sufficient to suppress intramolecular reactions like cyclization, isomerisation... The effect of tri-*p*-tolylamine on the isomerization and cyclization was negligible at −10 °C.

Like at room temperature, it was shown that the ED did not react with the active centres by alkylation of the aromatic group. The superposition of the RI and UV chromatograms confirmed that no incorporation of the ED to the polymer occurred (Fig. 6) whatever the [ED] used. Apparently, no alkylation reaction was induced on this ED. This result was supported by the ^{1}H NMR analysis of the polymer synthesized in run 2 (Table 6) precipated in acetone (Fig. 7).

Assuming a direct initiation, the theoretical molar mass of the polymers were calculated and compared to the experimental values (Table 6). For run 3 realized with a ratio [ED]/[$AlCl_3$] = 2, the calculated value ($\overline{M}_n$ = 7200) does not closely agree with the experimental determination ($\overline{M}_n$ = 4400), while the agreement is better for experiment 2. This result suggests a possible slight transfer effect of the ED: the ED can extract proton from the active species and transfer it to incoming monomer molecule. In other word, the ED could be a weak catalyst of transfer when used in excess. It was proposed the following mechanism:

$$P^+/ED_1 + ED_2 \rightarrow P(-H^+) + H^+/ED_2 + ED_1$$
$$H^+/ED_2 + M \rightarrow HM^+/ED_2$$

where P^+, M, ED_1 and ED_2 respectively represent a growing chain, the monomer, a first and a second molecule of ED.

Moreover, the polydispersity index showed that the system is not controlled, while the insoluble fraction was low. Keeping in mind that the ED is not incorporated in the polymer, it can be assumed that the ED is a part of the active species, and this is why it prevents the reaction with the polymer by steric hindrance.

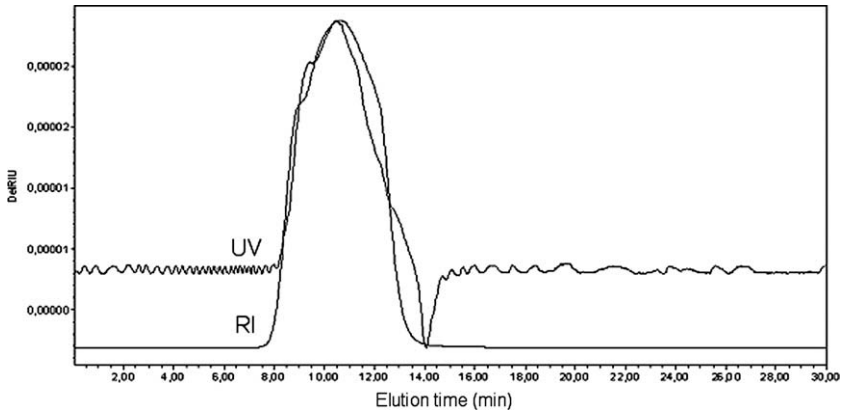

Fig. 2. RI and UV chromatograms of a crude poly(1,3-pentadiene) synthesized in the presence of the 9-phenylcarbazole ([ED]/[$AlCl_3$] = 1; run 3, Table 4), [$AlCl_3$] = 2.3×10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h.

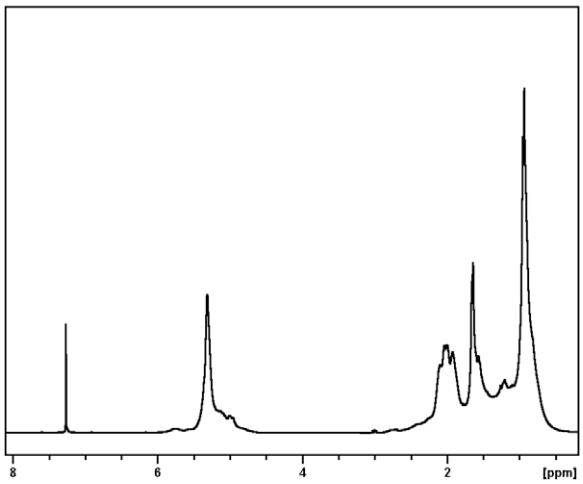

Fig. 3. ^{1}H NMR spectrum of a poly(1,3-pentadiene) synthesized in the presence of the tri-*p*-tolylamine at room temperature (run 5, Table 4) after precipitation in acetone.

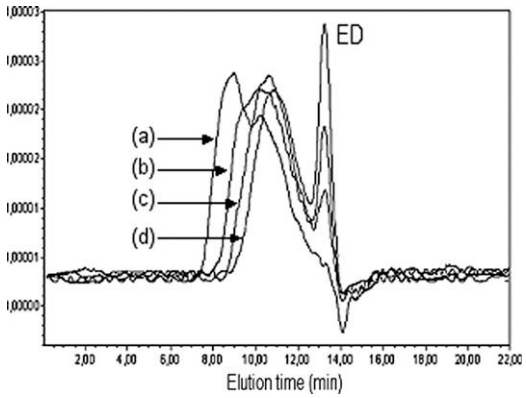

Fig. 4. SEC chromatograms of the crude poly(1,3-pentadiene)s synthesized in the presence of the tri-*p*-tolylamine at room temperature [$AlCl_3$] = 2.3×10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h ([ED]/[$AlCl_3$] = 0 (a); 1 (b); 2 (c); 4 (d)).

Table 5
Influence of the increasing tri-*p*-tolylamine concentration on the polymerization of 1,3-pentadiene at 20 °C.

Run [a]	[ED]/[$AlCl_3$]	Overall Yield (%)	IF [b] (%)	$\overline{M_n}$ [c] (g/mol)	I_p [c]	α_H [d]
1	0	83	3	2800	26	0.64
2	1	86	0	3300	7.0	0.56
3	2	82	0	2700	4.5	0.53
4	4	86	0	2200	3.2	0.52

[a] [$AlCl_3$] = 2.3×10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/Overall yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.
[d] Proton unsaturation loss determined by ^{1}H NMR.

EDs with similar chemical structure as tri-*p*-tolylamine were investigated in order that varying the nucleophilicity would allow suppressing or limiting the side reactions taking place during the polymerization. The results are listed in Table 7. Different runs were performed in the presence of the *N*,*N*-dimethyl-*p*-toluidine (Me_2N(PhMe)) or di-*p*-tolylamine (HN(PhMe)$_2$) at two temperatures (−10 °C and −30 °C) with a ratio [ED]/[$AlCl_3$] = 1 and were compared to polymerizations realized with the tri-*p*-tolylamine (runs 3 and 4) or without ED (runs 1 and 2). The polymerization was inhibited in the case of HN(PhMe)$_2$ at −10 °C. As for Me_2N(PhMe), nearly no polymer was obtained at −10 °C and no polymerization occurred at −30 °C. These two EDs are probably too nucleophilic (insufficient delocalization of the azote non-bonding orbital) together with an insufficient steric hindrance around the nitrogen atom. In this last case, they would behave like butylamine used for quench the polymerizations. In spite of the low quantity of synthesized polymer in run 5, the polymer was characterized in SEC with the double detection. SEC analysis showed the incorporation of the ED to the polymer whatever the chain length (Fig. 8). In this experiment, the active species are neutralized by the quaternization of the nitrogen atom. Therefore, the two methyl groups are not en-

Table 6
Influence of the increasing tri-*p*-tolylamine concentration on the polymerization of 1,3-pentadiene at −10 °C.

Run [a]	[ED]/[$AlCl_3$]	Overall Yield (%)	IF [b] (%)	$\overline{M}_n$ [c] (g/mol)	I_p [c]	α_H [d]	$\overline{M}_n$th[e] (g/mol)
1	0	89	14	12300	4.0	0.42	8400
2	1	83	3	8800	4.1	0.43	7900
3	2	76	2	4400	5.2	0.42	7200

[a] [$AlCl_3$] = 2. × 10^{-2} mol/L (anhydrous catalyst), [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, *t* = 2 h, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/Overall yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.
[d] Proton unsaturation loss determined by ^1H NMR.
[e] Calculated molar mass assuming direct initiation from $AlCl_3$ by self-ionization.

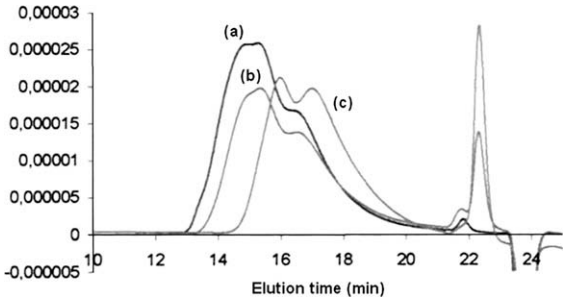

Fig. 5. SEC chromatograms of the crude polypentadienes synthesized in the presence of tri-*p*-tolylamine at −10 °C [$AlCl_3$] = 2.3 × 10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, *t* = 2 h ([ED]/[$AlCl_3$] = 0 (a); 1 (b); 2 (c)).

ough bulky to prevent the quaternization reaction. To conclude, these two EDs have not an adequate nucleophily to allow the control of the polymerization in the studied conditions.

As observed in Table 3, decreasing the temperature of the polymerization medium in a polar solvent induced a decrease of α_H, which means a reduction of the isomerization and cyclization content. This result was again observed for the polymerizations performed without ED and with $N(PhMe)_3$ (Table 7). It must be noticed that the agreement between the experimental and the theoretical values of molar mass is good in the case of the tri-*p*-tolylamine. This agreement was not obtained when polymerizations were performed in non polar or polar medium at room temperature. An other interesting point observed in the presence of this ED in the present study is that the insoluble fraction remained very low at −10 °C and −30 °C, while the latter was not negligible without ED and increased when temperature decreased. However, the SEC chromatogram of the polypentadiene synthesized at −30 °C in the presence of the tri-*p*-tolylamine (Fig. 9) showed that the molar mass distribution was not mono-

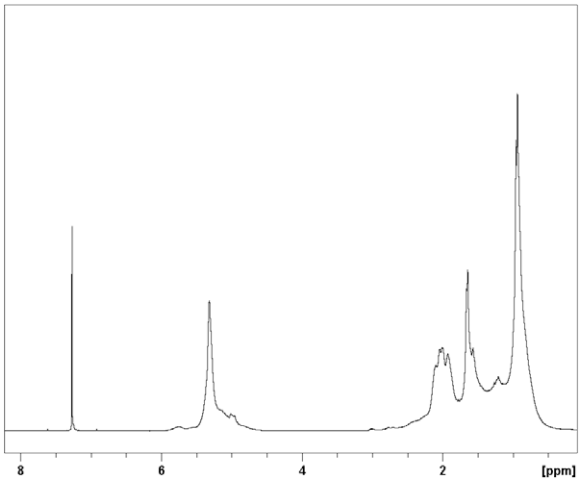

Fig. 7. ^1H NMR spectrum of a poly(1,3-pentadiene) synthesized in the presence of the tri-*p*-tolylamine at −10 °C (run 2, Table 6) after precipitation in acetone.

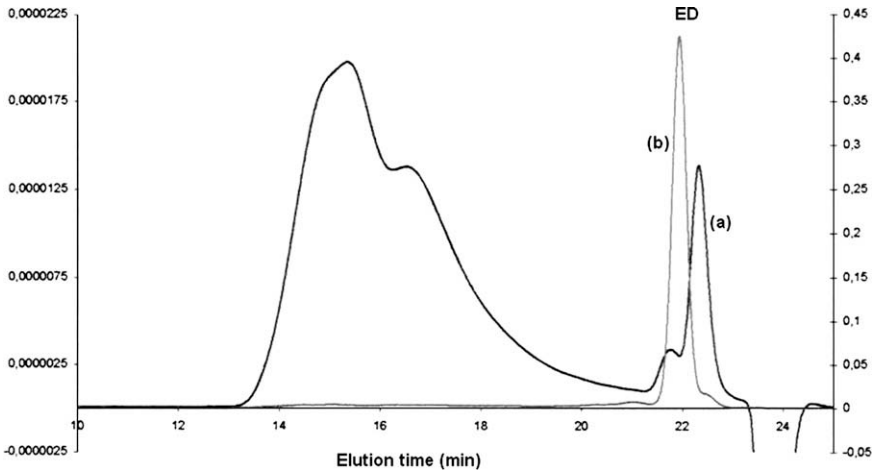

Fig. 6. RI (a) and UV (b) chromatograms of a crude polymer synthesized in the presence of tri-*p*-tolylamine [$AlCl_3$] = 2.3 × 10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, *t* = 2 h ([ED]/[$AlCl_3$] = 1; run 2, Table 6).

Table 7
Influence of tri-*p*-tolylamine and derivatives on the polymerization of 1,3-pentadiene at −10 °C or −30 °C initiated by $AlCl_3$ in the presence of various amines.

Run [a]	ED	T (°C)	Total Yield (%)	IF [b] (%)	$\overline{M}_n$ [c] (g/mol)	I_p [c]	α_H [d]	$\overline{M}_n$th[e] (g/mol)
1	–	−10	89	14	12300	4.0	0.42	
2	–	−30	49	26	5900	3.7	0.32	
3	$N(PhMe)_3$	−10	83	3	8800	4.1	0.43	7900
4	$N(PhMe)_3$	−30	69	5	6600	3.9	0.34	6500
5	$Me_2N(PhMe)$	−10	4	8	4200	5.0	–	400
6	$Me_2N(PhMe)$	−30	0	0	–	–	–	
7	$HN(PhMe)_2$	−10	0	0	–	–	–	

[a] $[AlCl_3] = [ED] = 2.3 \times 10^{-2}$ mol/L (anhydrous catalyst), [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h, deactivated by $BuNH_2$.
[b] Insoluble fraction = Insoluble polymer yield/total yield.
[c] Soluble fraction, determined by SEC, $I_p = \overline{M}_w/\overline{M}_n$.
[d] Proton unsaturation loss determined by ^1H NMR.
[e] Calculated molar mass assuming direct initiation from $AlCl_3$ by self-ionization.

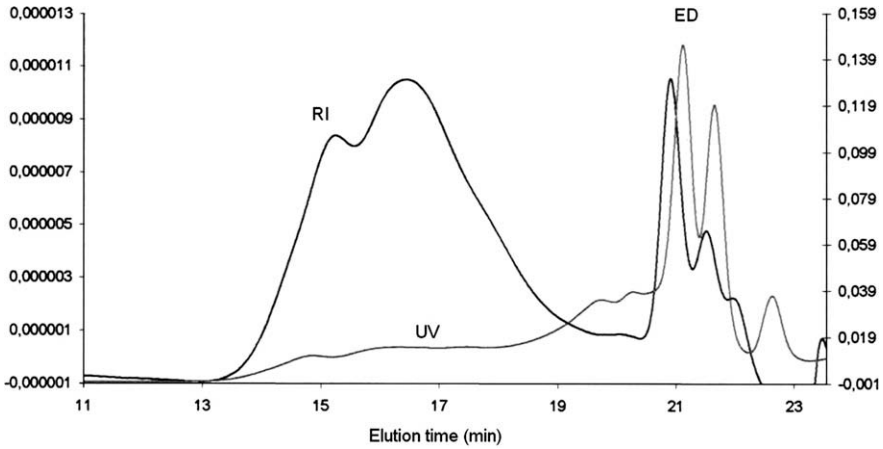

Fig. 8. RI and UV chromatograms of a crude polymer synthesized in the presence of $Me_2N(PhMe)$ $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h ([ED]/[$AlCl_3$] = 1; run 5, Table 7).

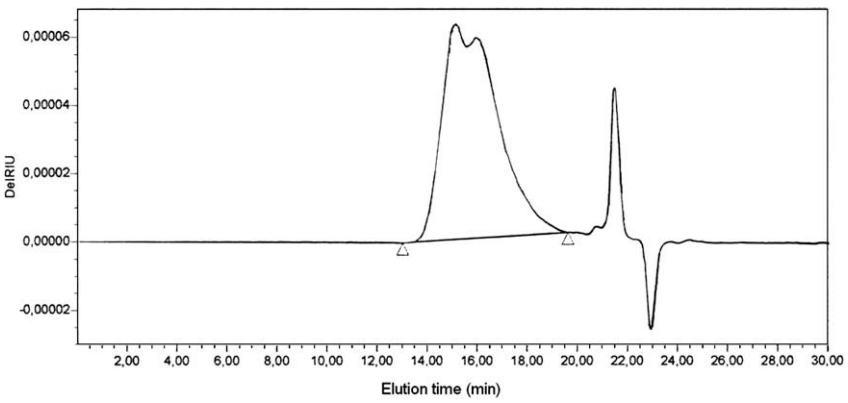

Fig. 9. RI chromatogram of the polypentadiene synthesized at −30 °C in the presence of tri-*p*-tolylamine $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, CH_2Cl_2, t = 2 h ([ED]/[$AlCl_3$] = 1; run 4, Table 7).

modal, suggesting the existence of remaining grafted chains. Operating at a temperature lower than −30 °C would allow reducing again the isomerization, cyclization and grafting reactions, thus improving the control of the polymerization, but it is worth reminding that decreasing too much the temperature is not possible due to the too important slowering down of the polymerization rate as mentioned above.

4. Conclusion

It is demonstrated that the use of a bulky electron donor such as tri-*p*-tolylamine in the cationic polymerization of dienes initiated by $AlCl_3$ in methylene chloride can strongly decrease (isoprene) or totally eliminate (1,3-pentadiene) the cross-linking reaction. This result can be assigned to the complexation of the active species by the ED. However, the polydispersity index indicates that the system is still out of control in the usual sense of polymer synthesis. This can be due to the occurrence of "grafting through" reaction to the polymer to a small extent, as shown by the reduction of the insoluble fraction when tri-*p*-tolylamine concentration increases. In order to further decrease the polydispersity index which is still higher than 2, it should be necessary to prevent the reaction of the active species with the double bonds of the polymer, while giving enough access to the monomer molecule. In this vein, a more hindering ED would be required. It must be kept in mind that a more complexing ED could also be a cause of increased transfer. More investigations are necessary to find a compromise between the complexing ability, steric hindrance and nucleophilicity.

The fact that the presence of tri-*p*-tolylamine did not influence the microstructure more particularly at $-10\,^{\circ}C$ and $-30\,^{\circ}C$ can be interpreted as showing that the 1,3-pentadiene monomer can have access to the active species as well in the presence of the ED as in its absence. This observation is accounted for as showing that the effect of the ED is a pure steric effect, only visible for the double bonds of the polymer units. It is also clear that preventing the reaction of the polymer also decreases termination reaction as shown by the behavior of isoprene (Table 2).

References

[1] Puskas JE, Kaszas G. Prog Polym Sci 2000;25:403–52.
[2] Rozentsvet VA, Kozlov VG. J Appl Polym Sci Appl Polym Symp 1992;51:183–93.
[3] Pla F, Vautrin-Ul C. Macromol Symp 1997;119:197–205.
[4] Asami R, Hasegawa K. Polym J 1976;8:67–73.
[5] Audisio G, Priola A, Rossini A. Macromol Chem Macromol Symp 1991;47:263–70.
[6] Duchemin F, Bennevault-Celton V, Cheradame H, Mérienne C, Macedo A. Macromolecules 1998;31:7627–35.
[7] Delfour M, Bennevault-Celton V, Cheradame H, Mercier F, Barre N. Macromolecules 2003;36:991–8.
[8] Miyamoto M, Sawamoto M, Higashimura T. Macromolecules 1984;17:265.
[9] Kaszas G, Puskas JE, Kennedy JP, Chen CC. J Macromol Sci Chem 1989;A26(8):1099.
[10] Kaszas G, Puskas JE, Chen CC, Kennedy JP. Macromolecules 1990;23:3909–15.
[11] Delfour M, Bennevault-Celton V, Anh Nguyen H, Macedo A, Cheradame H. Eur Polym J 2004;40:1387–98.
[12] Delfour-Sabater M, Bennevault-Celton V. Cheradame H Eur Polym J 2005;41:2761–9.
[13] Delfour M, Bennevault-Celton V, Anh Nguyen H, Cheradame H. Macedo A Macromol Chem Phys 2004;205:2312–26.
[14] Bennevault-Celton V, Delfour M, Cheradame H. Macromol Chem Phys 2004;205:1620–32.
[15] Delfour M, Bennevault-Celton V, Cheradame H, Macedo A. University Technology Day, Machelen (Belgique); 1999 .
[16] Duchemin F, Bennevault-Celton V, Cheradame H, Macedo A. Macromol Chem Phys 1998;199:2533–9.
[17] Bin C, Badi N, Bennevault-Celton V, Cheradame H. Polym Bull 2004;51:343–9.