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Cationic polymerization of dienes
VII. New electron donors in the polymerization of 1,3-pentadiene initiated by aluminum trichloride in non-polar solvent ☆

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Abstract

The aim of this research was to investigate new bulky electron donors (EDs) generating hindered active species in the cationic polymerization of 1,3-pentadiene initiated by $AlCl_3$ in pentane, in order to avoid or strongly reduce the reaction between the active species and the double bonds of the polymer which are responsible for side reactions. At room temperature, the polymerization in the presence of new ED, such as OPh_2, $N(PhBr)_3$, NPh_3 and SPh_2, allowed to obtain higher conversions and lower insoluble fractions than without electron donor. The formation of a complex ED/$AlCl_3$ was shown for each electron donor. However, in the case of NPh_3 and SPh_2, variations of the polymer microstructure demonstrated an interaction between active species and these EDs. Similar results were obtained at lower temperature (−10 °C). The beneficial effect of the presence of electron donors such as NPh_3 and SPh_2 demonstrated the validity of the concept of sterically hindered active species, but the polymerization was still uncontrolled.

Keywords: Electron donor; Cationic polymerization; 1,3-Pentadiene; Aluminum trichloride

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1. Introduction

The cationic polymerization of pure *cis*- or *trans*-1,3-pentadiene (PD) or isomer mixture was initiated by various Lewis acids [1–5]. In many cases, insoluble cross-linked polymer was produced and side reactions like cyclization, double bond isomerization and branching were observed on the soluble chains, inducing a noticeable loss of unsaturation in the polymer. For example, unsaturation losses as high as 90% were observed in some operating conditions [1]. The molar mass distributions of the soluble polymers were broad in tune with the absence of control of the polymerization.

Electron donors (EDs) were widely used in cationic polymerization to mediate the reactivity of the active species through carbocation stabilization method [6–8]. For instance, the polymerization of vinyl ethers was mediated by esters [9], ethers [10], pyridines [11], sulfides [12] and phosphines [13] to give living polymerizations. Similar results were obtained in the isobutylene polymerization and in the polymerization of styrene

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(or derivative) using sulfoxides, amides, esters or amines [14,15]. No reports on the living carbocationic homopolymerization of linear dienes were published in the literature [15] and very few papers were interested in the use of electron donors to stabilize this kind of active centers [16,17]. Peng et al. [16] studied the influence of tetrahydrofuran, isopropyl ether, ethyl acetate, ethylbenzoate and triethylamine in the cationic polymerization of 1,3-pentadiene initiated by $SnCl_4$ in methylene chloride. They found that the introduction of ED greatly reduced the polymer yield, molecular weight and strong EDs such as EtN_3 totally inhibited the polymerization. No further investigations were carried out. In a previous work [17], we reported polymerizations of 1,3-pentadiene initiated by aluminum trichloride in non-polar solvent in the presence of some nucleophilic compounds such as ethyl acetate, *tert*-butyl acetate, dimethylphtalate, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide and dimethylsulfoxide. Addition of an ED whatever its nature, in a one-to-one molar ratio relative to the Lewis acid, resulted in a decrease of the overall yield and an increase of the cross-linked polymer proportion. The molecular weight distribution of the soluble fraction was narrower than in polymerizations carried out without ED and it was shown by the modification of the polymer microstructure that the ED interacted with the active species.

Thus, no ED allowing control of PD homopolymerization has been found yet. The aim of this research was to investigate new electron donors at two temperatures (−10 and 20 °C) so as to determine whether they could be sufficiently bulky to generate hindered active species in order to avoid or strongly reduce their reaction with the double bonds of the polymer, the residual double bonds in the polymer being responsible for the observed side reactions.

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. Aluminum chloride (Aldrich) was handled and stored under N_2 atmosphere in a glove box. Pentane (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%), 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%). *n*-Butylamine (Aldrich, 99%) was used without further purification.

2.2. Polymerizations

$AlCl_3$ and the solid electron donor if any were introduced in the reactor in a glove box under N_2 atmosphere. The solvent was introduced into the reactor under secondary vacuum by cryodistillation, then the reaction mixture was brought either to room temperature or to −10 °C using a cryothermostat before the introduction of the monomer. In the case of a liquid electron donor, the latter was added with a syringe to the polymerization medium before monomer introduction. After 2 h of reaction (unless otherwise stated), the polymerization was quenched by the addition of excess *n*-butylamine. The reaction solution was filtered to separate the insoluble cross-linked polymer, and after several washes with water the resulting solution was evaporated under reduced pressure to recover the soluble polymer. The latter was then purified by precipitation in acetone.

2.3. Polymer characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. ^{13}C measurements were performed using an Inverse Gate procedure (no NOE), allowing 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. The proton relative unsaturation loss per monomer unit was calculated by ^1H NMR and 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: $\alpha_H = (0.25 - d_{\text{exp}})/0.25$. In the same manner, the carbon relative unsaturation loss per monomer unit 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: $\alpha_C = (0.40 - d_{\text{exp}})/0.40$.

The molar masses and molar mass distributions of the polymers were determined by size exclusion chromatography (SEC) in tetrahydrofuran on a chromatograph equipped with two columns (PL Gel, mixte C), an IR cell and a UV at 254 nm detector. The number-average molecular weights ($\overline{M_n}$) and the weight-average molecular weights ($\overline{M_w}$) were calculated on the basis of a polystyrene calibration.

The IR spectra of the polymer solutions in CS_2 were recorded on a FTIR Perkin–Elmer 1760 spectrometer. The microstructure of the polymers were characterized using the molar extension coefficients of the linear units determined by Beebe [18].

3. Results and discussion

3.1. Study of the 1,3-pentadiene polymerization initiated by $AlCl_3$ in pentane at −10 °C in the presence of EDs

The EDs selected in this study are ethers, sulfurs, amines or phosphines, mainly with aromatic substituents in order to have a bulky nucleophile with a moderate nucleophilicity due to mesomeric effect. The results of the polymerizations are listed in Table 1, including a standard polymerization (polymerization carried out without ED). Each polymerization was conducted with an ED concentration equal to the Lewis acid concentration, since excess of electron donor was commonly considered as a "poison" for the polymerization [19,20]. Yields were determined by neglecting the contribution of the mass of the ED.

At this temperature, only 1,3,5-triphenylbenzene induced an increase of the polymer yield (from 67% to 76%). However, in this run, the insoluble fraction (I.F.) was also strongly increased. Due to its high cross-linked polymer fraction, this additive was not investigated any more. As seen in Table 1, many EDs induced a consistent reduction of the conversion. Triphenylphosphine and tribenzylamine completely inhibited the polymerization (runs 8 and 9). The polymerization inhibition was assigned to the non-bonding orbital of the ED heteroatom which is not delocalized. In the case of PPh_3, the size of the phosphorous 3p atomic orbital and the carbon 2p orbital are too different to allow an orbital overlapping. The hybridization of the phosphorous atom is sp^3 in this molecule. Triphenylphosphine is well known to be an efficient nucleophile and is usually used in organic chemistry to synthesize quaternary phosphonium salts by reaction with methyliodide [21]. In conclusion, PPh_3 and $N(CH_2Ph)_3$ are too strong nucleophiles so that no polymerization occurs.

The comparison of the different polymerizations shows that five EDs induced a decrease of the insoluble fraction, namely OPh_2, $N(PhBr)_3$, NPh_3, OEt_2 and SPh_2 (runs 3–7), however only OPh_2 and $N(PhBr)_3$ (runs 3 and 4) induced conversions close to the standard polymerization, the others resulting in lower yields. The lower insoluble fraction is to be assigned to a stabilization of the active centers, a higher solubilization of the catalyst through the formation of a complex $ED/AlCl_3$, but also to lower yields in the case of NPh_3, OEt_2 and SPh_2 since it was shown that the cross-linking reaction was favored by a high polymer concentration [4].

From this study, two kinds of electron donors can be distinguished according to their effects on the polymerization. The higher conversions were obtained with electron donors having an aromatic group or a heteroatom substituted by phenyl groups allowing the delocalization of the heteroatom non-bonding orbital or the central phenyl group π orbitals. $C_6H_3Ph_3$, OPh_2, $N(PhBr)_3$ and NPh_3 (runs 2–5) belong to this class of ED. In the second kind of ED (runs 6–9), no mesomerism with the central heteroatom can occur. OEt_2 and SPh_2 induced relatively similar results as regards I.F. and conversion, which suggest that they have similar nucleophilicity. For the same reasons as PPh_3, the hybridization of the sulfur atom is sp^3. The difference between PPh_3 and SPh_2 only results from the different electronegativity of the central atom.

The polymer fractions were analyzed by size exclusion chromatography (SEC). Low molar masses were obtained for the polymers synthesized in the presence of triphenylamine and diethylether in comparison with the standard polymerization (see Table 1), that could suggest a transfer and/or termination behavior. In order to study the ED influence on the isomerization and cyclization reactions, the relative proton and carbon

Table 1
1,3-Pentadiene polymerizations performed in the presence of ED at −10 °C

Run[a]	ED	Total yield (%)	I.F. (%)	$\overline{M_n}$[b] (g/mol)	I_p[b]	α_H[c]	α_C[c]
1	–	67	34	14100	10.6	0.32	0.27
2	$C_6H_3Ph_3$	76	85				
3	OPh_2	69	19	8500	11.1	0.29	0.28
4	$N(PhBr)_3$	65	23	15100	8.1	0.30	0.30
5	NPh_3	41	22	2800	4.5	0.23	
6	OEt_2	32	25	2400	3.7	0.32	0.29
7	SPh_2	30	23	9200	4.4	0.33	0.22
8	$N(CH_2Ph)_3$	0	0				
9	PPh_3	0	0				

[a] Pentane, $[AlCl_3] = [ED] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = -10$ °C, deactivated by $BuNH_2$.

[b] Determined by SEC, $I_p = \overline{M_w}/\overline{M_n}$.

[c] Proton and carbon unsaturation losses determined by NMR.

unsaturation losses (α_H and α_C) were determined by NMR from purified polymers (polymers free of ED). It must be kept in mind that cyclization is responsible at the same time for a loss of olefinic carbons and protons, while double bond isomerization alone only leads to a loss of olefinic protons [4]. Due to a partial alkylation of the NPh_3 aromatic groups by the polymer chains in growth during the polymerization, the α_C value could not be determined in this case: the signals belonging to the phenyl groups of the incorporated NPh_3 and the signals of the olefinic carbons of the pentadiene units are overlapping on the spectrum. Table 1 shows that diphenylsulfide reduces the cyclization reactions and favors isomerization reactions. Indeed, in the presence of this ED, α_C was lower while α_H was in the same magnitude as the standard polymer (run 1). The results also show that NPh_3 reduces both isomerization and cyclization. For the other EDs, no noticeable variation was observed. Thus, the interaction between the additive and the active centers was evidenced for two electron donors, SPh_2 and NPh_3.

As a preliminary conclusion, this first work at −10 °C allowed to select five electron donors: OPh_2, $N(PhBr)_3$, NPh_3, OEt_2 and SPh_2. They were particularly interesting because the cross-linked polymer fraction was reduced in their presence. The lower conversion obtained in the case of some ED could be due to a decreased rate of polymerization (stabilization of the active centers) and could be a kinetic effect.

The influence of these electron donors was investigated at room temperature. At this temperature, higher conversions were expected, although side reactions could also be favored.

3.2. Study of the 1,3-pentadiene polymerization initiated by $AlCl_3$ in pentane at 20 °C

3.2.1. No ED

A kinetic study without electron donor first carried out (Table 2) in order to get more information on the mechanisms of the 1,3-pentadiene polymerization. The influence of the electron donors on these mechanisms was then studied. Table 2 shows that the experimental molar mass of the polymers increased with polymerization time, which means that the monomer transfer did not predominantly occur in comparison with other elementary reactions. Polymer transfer is usually mentioned in the polymerization of dienes to explain the formation of the high molar mass chains (responsible for broad and bimodal distributions in SEC) and of cross-linked polymer. The latter was due to the concomitant existence of transfer reactions to polymer followed by grafting from reactions (1) and grafting onto reactions (2) and to the partly insoluble catalyst in the polymerization medium [5]

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\ C^+ + P \rightarrow \sim\sim\sim\sim\sim\sim\sim\sim\sim\ C + P^+$$
$$\text{then } P^+ + nM \rightarrow P \sim\sim\sim\sim\sim\sim\sim\sim\sim\ C^+ \qquad (1)$$

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\ C^+ + P \rightarrow \sim\sim\sim\sim\sim\sim\sim\sim\sim\ CP + H^+ \qquad (2)$$

where P and M, respectively, represent a polymer chain and the monomer.

Whatever the considered scheme (1 or 2), two macromolecular chains are produced from two other chains. Therefore, the polymer transfer does not modify the molar mass of the polymer, while the cross-linking mechanism can modify it due to the incorporation of the high molar mass macromolecules in the network [5]. When there is little cross-linked polymer, the molar mass of the soluble polymer can be compared to the theoretical value since the influence of the high molar mass chains which are possibly lost on the average number molar mass would be low. The results reported in Table 2 (last column) shows that the lower the insoluble fraction, the better the agreement between the experimental and theoretical $\overline{M_n}$, the theoretical value being calculated according to a direct initiation mechanism by self-ionization [22] (i.e. half the catalyst molecules initiate macromolecular chains). In all the experiments, part of the catalyst was embedded inside the network [5], which could induce a higher experimental molar mass than the

Table 2
Kinetic study at 20 °C

Run[a]	Time (h)	Total yield (%)	I.F. (%)	$\overline{M}_{\mathrm{nexp.}}$[b] (g/mol)	I_p[b]	$\overline{M}_{\mathrm{nth.}}$[c] (g/mol)	$\overline{M}_{\mathrm{nexp.}}/\overline{M}_{\mathrm{nth.}}$
1	0.25	39	62	7200	5.3	3700	1.95
2	0.5	51	59	7300	7.0	4800	1.52
3	1	62	50	9100	7.6	5900	1.54
4	1.5	70	53	8200	8.5	6600	1.24
5	2	78	45	10400	10.3	7400	1.41
6	3	81	46	9900	10.0	7700	1.29
7	10	89	43	11400	13.3	8400	1.36
8	17	94	44	11700	15.6	8900	1.31

[a] $[AlCl_3] = 2.3\times10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, pentane, $T = 20$ °C, deactivation by $BuNH_2$.

[b] Determined by SEC (polystyrene standards).

[c] $\overline{M}_{\mathrm{nth.}} = 2[M]_0 \times \mathrm{yield}/[AlCl_3]_0$.

theoretical one. The calculation of the molar masses in SEC from a polystyrene calibration can also be responsible for this difference.

3.2.2. In the presence of EDs

The polymerizations in the presence of the five previously selected EDs were carried out at room temperature under identical conditions. The yields were calculated by neglecting the weight of possibly incorporated EDs.

At this temperature (20 °C), all the additives induced an increase of the total yield and a decrease of the cross-linked polymer proportion (Table 3). Note that a complete conversion with an insoluble fraction of 46% was obtained in the case of tris(4-bromophenyl)amine. Lower I.F. could be reached using triphenylamine (I.F. = 13%) and diethylether (I.F. = 8%); these results can be correlated to the lower molar masses of the corresponding polymers, since it was shown that cross-linking reactions mainly occurred from the highest molar mass polymer chains [5]. The lower $\overline{M_n}$ obtained for these two polymers in spite of high conversions (NPh_3: 92%, OEt_2: 78%) was in agreement with a transfer behavior.

The beneficial effect of the EDs on conversion and the insoluble polymer fraction might be due to the stabilization of C^+ through an interaction between C^+ and ED or by the formation a weaker Lewis acid (ED/$AlCl_3$). However one can also consider an enhanced solubilization of the Lewis acid in pentane due to the formation of a more soluble ED/$AlCl_3$ complex. The color variations of the polymerization medium after monomer addition observed for example in the presence of triphenylamine could be viewed as demonstration of the interaction between the carbocations and ED. In the absence of ED, the polymerization medium was orange yellow and in the presence of NPh_3 the solution was a red wine-like color (the initial amine and catalyst were white compounds and the color of the ED/$AlCl_3$ mixture was green). The change in color observed after that NPh_3 and $AlCl_3$ were mixed also indicated an interaction between these two products. Thus each ED/$AlCl_3$ mixture was characterized by ^{1}H NMR and the resulting spectrum was compared to that of the pure ED in order to determine whether a complex was formed. Table 4 shows the multiplicity and the chemical shifts of the signals and some example spectra are given in Figs. 1 and 2. The spectra were obtained in dried non-deuterated pentane (polymerization solvent) and locked on $CDCl_2$ introduced in an insert tube. $AlCl_3$ and ED were mixed in equimolar proportions, but only the soluble part was analyzed by NMR. In these conditions, the actual molar ratio between the catalyst and ED in the NMR tube can be different of the theoretical one, some ED being partly soluble in pentane as well as $AlCl_3$. A change of each ED proton spectrum was observed after the catalyst addition, showing the formation of a complex in each experiment. The changes were either a total modification of the signals or only a shift of the signals.

The linear microstructure of the purified soluble poly(1,3-pentadiene)s were then determined by IR and ^{13}C NMR. Average values of the PD unit contents with their standard deviations for the standard polymerization were determined in a previous paper [5] and were reported in first line in Tables 5, 7, 9 and 11. Table 5 showed that the different linear units contents of the polymers synthesized in the presence of ED were close to that of run 1 (standard polymerization), except for SPh_2 and NPh_3. In the case of SPh_2, the contents of 1,4-*trans* and 1,2-*trans* units were a little lower and in the case of NPh_3 the contents of 1,4-*cis* and 1,2-*cis* units were a little higher. However, whatever the polymer, the *trans* units were predominant (about 45%) and the 3,4-units were present in the lowest amount (about 3%). The relative proton and carbon unsaturation losses (α_H and α_C) of the polymers were reported in Table 3. As for experiments carried out at −10 °C, α_C of the polymer synthesized in the presence of triphenylamine could not be determined. More cyclizations (Table 3) occurred in the presence of SPh_2 ($\alpha_C = 0.40$), the cyclizations contents of the other polymers being similar ($\alpha_C \approx 0.33$). In the

Table 3
1,3-Pentadiene polymerizations performed in the presence of ED at 20 °C

Run[a]	ED	Total yield (%)	I.F. (%)	$\overline{M_n}$[b] (g/mol)	I_p[b]	α_H[c]	α_C[c]
1	–	76	71	5000	10.4	0.40	0.31
2	$N(PhBr)_3$	100	46	8800	11.7	0.42	0.33
3	SPh_2	94	36	6400	17.4	0.41	0.40
4	NPh_3	92	13	3800	8.7	0.33	–
5	OPh_2	89	26	9800	23.7	0.41	0.34
6	OEt_2	78	8	1100	4.5	0.40	0.35

[a] Pentane, $[AlCl_3] = [ED] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.

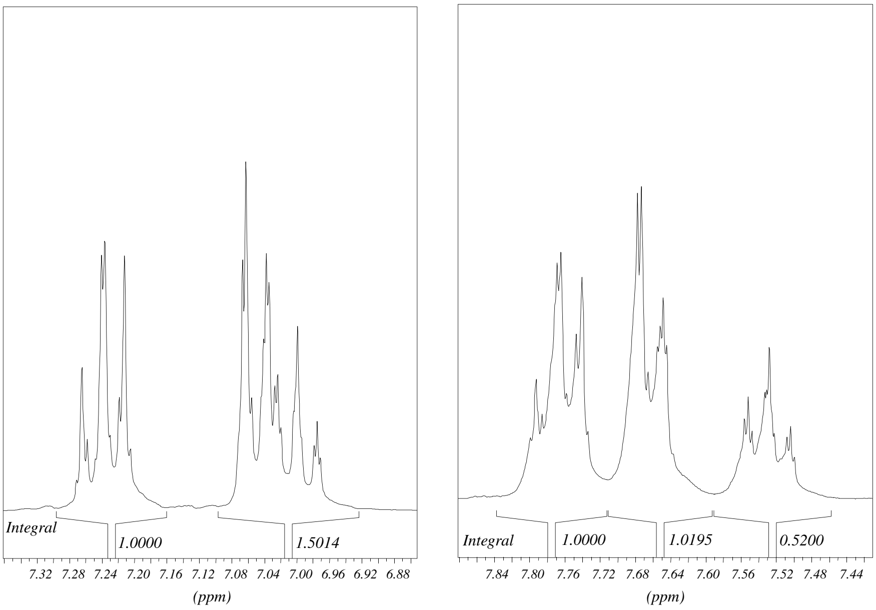
[b] Determined by SEC, $I_p = \overline{M_w}/\overline{M_n}$.

[c] Proton and carbon unsaturation losses determined by NMR.

Table 4
Chemical shifts and multiplicity of ^{1}H NMR signals of pure ED and $AlCl_3$/ED mixtures

Alone ED			ED/$AlCl_3$		
Multiplicity	Relative intensity	δ (in ppm)	Multiplicity	Relative intensity	δ (in ppm)
$N(PhBr)_3$					
Doublet	50	7.37; 7.34	Doublet	50	7.96; 7.93
Doublet	50	6.94; 6.91	Doublet	50	7.53; 7.50
SPh_2					
Multiplet		7.38	Multiplet	40	7.92
			Multiplet	60	7.78
NPh_3					
Triplet	40	7.24	Multiplet	40	7.76
Multiplet	60	7.02	Multiplet	40	7.66
			Multiplet	20	7.53
OPh_2					
Triplet	40	7.38	Multiplet	40	7.83
Triplet	20	7.15	Multiplet	60	7.58
Doublet	40	7.07; 7.05			
OEt_2					
Quadruplet	40	3.43	Quadruplet		4.30
Triplet	60	1.16	?[a]		?[a]

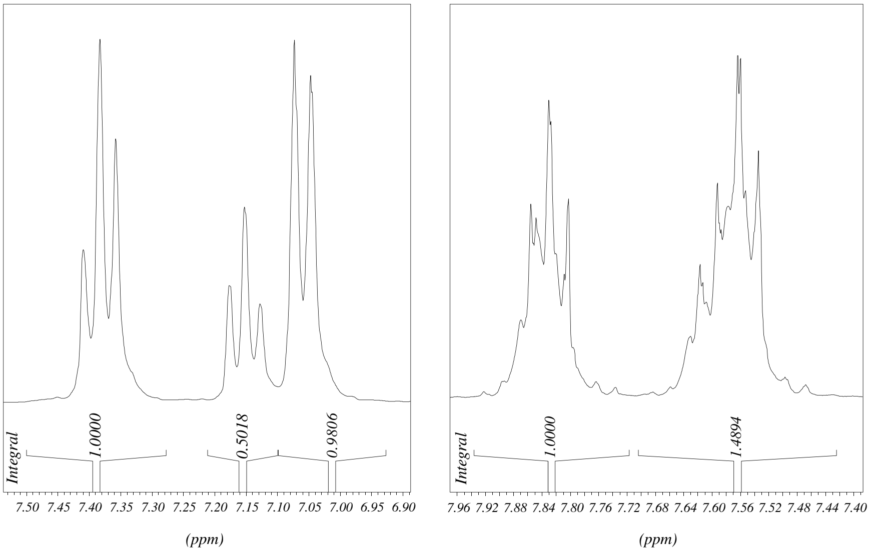
[a] Peak under pentane signals.



(a) **(b)**

Fig. 1. ^{1}H NMR of triphenylamine in the absence (a) and in the presence (b) of $AlCl_3$.

same way, the α_H values of the different polymers little varied ($\alpha_H \approx 0.41$), except for the polymer obtained in the presence of triphenylamine ($\alpha_H \approx 0.33$). To conclude, the introduction of diphenylsulfide in the polymerization medium favored cyclization and disfavored isomerization and NPh_3 reduced the sum of isomerization and cyclization contents. The other EDs did not induce noticeable modifications. Thus, as above for



(a) (b)

Fig. 2. ^{1}H NMR of diphenylether in the absence (a) and in the presence (b) of $AlCl_3$.

Table 5
Poly(1,3-pentadiene)s linear microstructure

Run[a]	ED	% 1,4-*trans*[b]	% 1,2-*trans*[c]	% 1,4-*cis*[d]	% 1,2-*cis*[d]	% 3,4[d]
1	–	32 ± 4	16 ± 4	4 ± 2	3 ± 1	3 ± 1
2	$N(PhBr)_3$	29	15	6	5	5
3	SPh_2	23	11	4	3	2
4	NPh_3	30	12	11	7	4
5	OPh_2	33	12	7	5	4
6	OEt_2	37	13	6	5	3

[a] Pentane, $[AlCl_3] = [ED] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.

[b] Determined by IR and ^{13}C NMR.

[c] Determined by ^{13}C NMR.

[d] Determined by IR.

experiments carried out at −10 °C, it was found that diphenylsulfide and triphenylamine caused changes in the polymer microstructure, which is an argument supporting the occurrence of a stabilization effect of the active species by ED.

In conclusion, the following electron donors OPh_2, $N(PhBr)_3$, NPh_3, OEt_2 and SPh_2 allowed to have higher conversions and lower cross-linked polymer fractions than the standard polymerization. On the basis of IR and NMR analyses, these interesting results could result from a stabilization of the active centers through an interaction between C^+ and ED in the case of NPh_3 and SPh_2, as shown by the modification of the polymer microstructure. For the other EDs, these interactions could be too weak to induce consistent changes in the polymer microstructure or the results would only come from a higher solubilization of the Lewis acid due to the formation of a complex between $AlCl_3$ and ED. This complexation also occurred in the case of NPh_3 and SPh_2.

All these electron donors were investigated with a one-to-one molar $[ED]/[AlCl_3]$ ratio, however, a better control of the polymerization could be obtained in other conditions. In order to better understand the influence of ED on the polymerization mechanisms, different experiments were performed varying the $[ED]/[AlCl_3]$ from 0 to 1.5 or 2. A more particular study in the presence of triphenylamine and derivatives is to be presented in other papers [23].

4. Influence of OPh_2 concentration on the 1,3-pentadiene polymerization at 20°C

The results of the polymerizations realized in the presence of OPh_2 are listed in Table 6. The proton

Table 6
1,3-Pentadiene polymerizations performed in the presence of OPh_2 at 20 °C

Run[a]	$[OPh_2]/[AlCl_3]$	Total yield[b] (%)	I.F.[c] (%)	$\overline{M_n}$[d] g/mol	I_p[d]	α_H[e]	α_C[e]
1	0	76	71	5000	10.4	0.40	0.31
2	0.13	87	29	10900	24.0	0.40	0.35
3	0.25	83	27	10700	22.1	0.40	0.36
4	0.5	87	28	9700	25.8	0.42	0.33
5	1	87	29	9800	23.7	0.41	0.34
6	1.5	82	20	9300	24.9	0.41	0.34

[a] Pentane, $[AlCl_3] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.

[b] Total yield $= (m_{polymer} - m_{ED})/m_{monomer}$.

[c] I.F. = insoluble yield/total yield $= [m_{insoluble\ polymer}/m_{monomer}]/[(m_{polymer} - m_{ED})/m_{monomer}]$.

[d] Determined by SEC (polystyrene standards), $I_p = \overline{M_w}/\overline{M_n}$.

[e] Proton and carbon unsaturation losses determined by NMR.

NMR spectra of the purified polymers (polymers precipitated in acetone) showed that this electron donor was not incorporated in the polymer. Since the additive was not eliminated during the drying step of the polymer due to its high boiling point (b.p. = 259 °C), the crude total yield was calculated substracting the introduced ED mass from the polymer mass. The results showed that even at very low concentration (run 2), the ED addition induced an increase of the total yield and did not change introducing more ED in the polymerization medium. Indeed from a $[OPh_2]/[AlCl_3]$ ratio equal to 0.13, maximum conversion was reached. No noticeable variations were observed in regard to insoluble fraction, polymer molar mass and polydispersity index when $[OPh_2]/[AlCl_3]$ increased from 0.13 to 1.5. The experimental molar mass of the soluble polymers ($\overline{M_n} \approx 10\,000$ g/mol) was in a relative good agreement with the theoretical one calculated as above for a yield ≈85% ($\overline{M_{n th.}} \approx 8100$ g/mol). The experimental value was higher than in the polymerizations performed without ED (see Table 2) and the SEC distribution was still bimodal and broad (Fig. 3). It would mean that OPh_2 did not strongly interact with the active centers, but only inducing a reduction of the cross-linking reaction. The limited effect of diphenylether can be assigned to its too low nucleophilicity to efficiently stabilize the active centers.

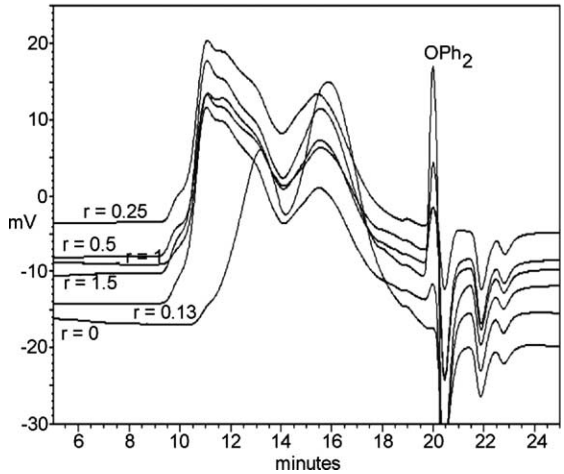


Fig. 3. SEC chromatograms of the crude polymers synthesized in the presence of OPh_2. r = $[OPh_2]/[AlCl_3]$.

Table 7 reports the linear units contents of the purified polymers. In spite of the increase of OPh_2 concen-

Table 7
Linear microstructure of the polymers synthesized in the presence of OPh_2

Run[a]	$[OPh_2]/[AlCl_3]$	% 1,4-*trans*[b]	% 1,2-*trans*[c]	% 1,4-*cis*[d]	% 1,2-*cis*[d]	% 3,4[d]
1	0	32 ± 4	16 ± 4	4 ± 2	3 ± 1	3 ± 1
2	0.13	36	18	8	6	5
3	0.25	29	18	9	7	4
4	0.5	29	15	11	8	5
5	1	33	12	7	5	4
6	1.5	35	14	10	7	5

[a] Pentane, $[AlCl_3] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.

[b] Determined by IR and ^{13}C NMR.

[c] Determined by ^{13}C NMR.

[d] Determined by IR.

tration, the 1,4-*trans* and 1,2-*trans* contents did not vary and were similar to the values determined in run 1 (without ED). On the other hand, a slight increase of the 1,4-*cis* and 1,2-*cis* molar fractions were observed with the addition of OPh_2. This point was not previously mentioned because in the experiment with $[OPh_2]/[AlCl_3] = 1$, the variations were within experimental accuracy (standard polymerization: 1,4-*cis* = 4 ± 2 and 1,2-*cis* = 3 ± 1). In conclusion, this electron donor modified the linear microstructure of the polymers slightly. Concerning the proton and carbon unsaturation losses (see Table 6), no consistent variations were observed with the OPh_2 concentration (standard deviation of α_C for a standard polymerization being 0.03). In order to examine the influence of OPh_2 on the termination reactions, and in particular on the termination by the counter-ion, the chlorine content of the soluble polymers was determined. According to Fig. 4, it would seem that the electron donor favored unimolecular termination reactions. It could suggest that large ED excess would react with the counter-ion $AlCl_4^-$ to generate an ED/$AlCl_3$ complex and a Cl^- ion (according to the direct initiation scheme).

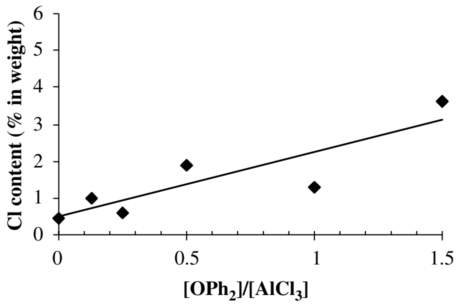


Fig. 4. Chlorine contents of the polymers synthesized in the presence of OPh_2.

5. Influence of SPh_2 concentration on the 1,3-pentadiene polymerization at 20 °C

The results of the polymerizations performed in the presence of diphenylsulfide are reported in Table 8. The yields were calculated as above for the same reasons (SPh_2 was not incorporated in the polymer and was not removed because of its high boiling point). The SPh_2 addition in the polymerization medium induced an increase in conversion, which was however weaker with increasing ED concentration. On the other hand, the higher $[SPh_2]$, the lower insoluble fraction. A $[SPh_2]/[AlCl_3]$ ratio close to 1 was a good compromise to optimize at same time these two features (for a reaction time of 2 h). It would seem that the interaction between the active centers and the electron donor was a little more pronounced in the case of SPh_2 in comparison with OPh_2, since the total yield varied versus the diphenylsulfide concentration and was constant in the case of OPh_2.

The molar masses of the polymers synthesized in the presence of the ED were higher than that of the standard polymerization, but two distributions still appeared on the SEC chromatograms whatever the $[SPh_2]/[AlCl_3]$ ratio used was (Fig. 5).

The analysis of the polymer linear microstructure and of isomerization and cyclization reactions (Tables 8 and 9) showed that the ED effect varied a little as a function of the ED concentration: for example, a decrease of 1,4-*trans* content and more cyclization were observed when $[SPh_2]/[AlCl_3]$ was close to 1. The α_H variations were much weaker than the α_C variations. As seen in Fig. 6, the analysis of polymer chloride contents led to similar results as with OPh_2. Thus, up to a $[SPh_2]/[AlCl_3]$ ratio equal to 1.5, the higher the $[SPh_2]$ the higher chlorine percentage was found. Beyond this value, the chlorine content decreased but was higher than that obtained in the polymerization without ED. Consequently, as OPh_2, the addition of SPh_2 in the polymerization medium

Table 8
1,3-Pentadiene polymerizations performed in the presence of SPh_2 at 20 °C

Run[a]	$[SPh_2]/[AlCl_3]$	Total yield[b] (%)	I.F.[c] (%)	$\overline{M_n}$[d] g/mol	I_p[d]	α_H[e]	α_C[e]
1	0	73	73	3200	17.6	0.40	0.31
2	0.5	90	44	9100	16.4	0.44	0.31
3	1	94	36	6400	17.4	0.41	0.40
4	1.5	84	17	4500	17.4	0.46	0.44
5	2	76	32	5700	13.2	0.42	0.36

[a] Pentane, $[AlCl_3] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, t = 2 h, T = 20 °C, deactivated by $BuNH_2$.

[b] Total yield $= (m_{\text{polymer}} - m_{\text{ED}})/m_{\text{monomer}}$.

[c] I.F. = insoluble yield/total yield $= [m_{\text{insoluble}}/m_{\text{monomer}}]/[(m_{\text{polymer}} - m_{\text{ED}})/m_{\text{monomer}}]$.

[d] Determined by SEC (polystyrene standards), $I_p = \overline{M_w}/\overline{M_n}$.

[e] Proton and carbon unsaturation losses determined by NMR.

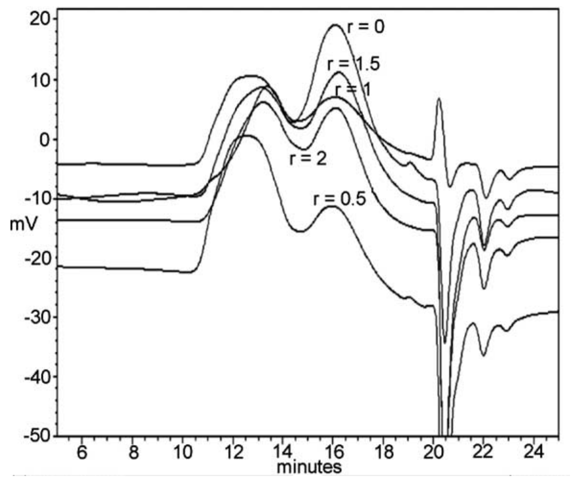


Fig. 5. SEC chromatograms of the crude polymers synthesized in the presence of SPh_2. $r = [SPh_2]/[AlCl_3]$.

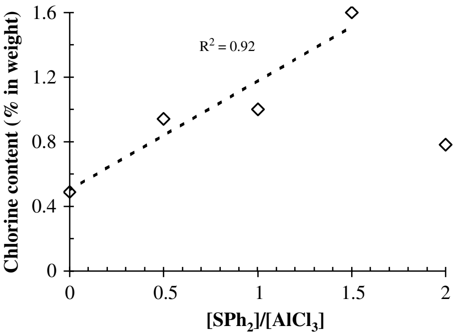


Fig. 6. Chlorine contents of the polymers synthesized in the presence of SPh_2.

favored the termination reactions by the counter-ion. Since high conversions were obtained, it can be assumed that reinitiation by the regenerated aluminum trichloride is operating.

6. Influence of OEt_2 concentration on the 1,3-pentadiene polymerization at 20 °C

Taking into account the structural difference of diethylether in comparison with the other EDs, differences in behavior were expected. Tables 10 and 11 show that no consistent variation was observed for conversion, linear microstructure, isomerization and cyclization reactions and the chlorine ratio when OEt_2 was introduced in the polymerization medium with a ratio $[OEt_2]/[AlCl_3]$ varying between 0 and 2. Consequently, OEt_2 would not interact with the active centers or very weakly if any. The actual effect is the reduction of the cross-linked polymer proportion which fell from 73% in the absence of ED to only about 8%. This value is the lowest obtained in this study and can obviously be correlated to the drastic decrease of $\overline{M_n}$ and I_p. As suggested earlier, OEt_2 is a transfer agent. Indeed as soon as the ether was added, the highest molar mass population completely disappeared to give only the lowest molar mass population (Fig. 7). The polydispersity index values showed that transfer reactions became predominant when OEt_2 concentration increased: from a ratio $[OEt_2]/[AlCl_3]$ equal to 1.5, the polydispersity index becomes close to the theoretical value of a predominant transfer ($I_p = 2$). Diethylether cannot be incorporated in the polymer. The oxygen non-bonding orbital extracts a proton from the active centers, which then initiates a new macromolecular chain as follows:

$$\begin{aligned}&-CH{=}CH{-}CH(CH_3)^+ + OEt_2\\&\quad\rightarrow -CH{=}CH{-}CH{=}CH_2 + Et_2O^+H\end{aligned}$$

$$Et_2O^+H + M \rightarrow Et_2O + HM^+$$

In conclusion, this compound would be more basic than nucleophilic.

Table 9
Linear microstructure of the polymers synthesized in the presence of SPh_2

Run[a]	$[SPh_2]/[AlCl_3]$	% 1,4-*trans*[b]	% 1,2-*trans*[c]	% 1,4-*cis*[d]	% 1,2-*cis*[d]	% 3,4[d]
1	0	32 ± 4	16 ± 4	4 ± 2	3 ± 1	3 ± 1
2	0.5	29	10	6	4	3
3	1	23	11	4	3	2
4	1.5	26	11	7	4	3
5	2	28	10	6	3	2

[a] Pentane, $[AlCl_3] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.
[b] Determined by IR and ^{13}C NMR.
[c] Determined by ^{13}C NMR.
[d] Determined by IR.

Table 10
1,3-Pentadiene polymerizations performed in the presence of OEt_2 at 20 °C

Run[a]	$[OEt_2]/[AlCl_3]$	Total yield[b] (%)	I.F.[c] (%)	$\overline{M_n}$[d] g/mol	I_p[d]	α_H[e]	α_C[e]
1	0	73	73	3200	17.5	0.40	0.31
2	0.5	74	9	1400	8.6	0.40	0.34
3	1	78	8	1100	4.5	0.40	0.35
4	1.5	89	6	800	2.6	0.37	0.33
5	2	75	8	800	2.6	0.37	0.27

[a] Pentane, $[AlCl_3] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.

[b] Total yield $= m_{polymer}/m_{monomer}$.

[c] I.F. = insoluble yield/total yield.

[d] Determined by SEC (polystyrene standards), $I_p = \overline{M_w}/\overline{M_n}$.

[e] Proton and carbon unsaturation losses determined by NMR.

Table 11
Linear microstructure of the polymers synthesized in the presence of OEt_2

Run[a]	$[OEt_2]/[AlCl_3]$	% 1,4-*trans*[b]	% 1,2-*trans*[c]	% 1,4-*cis*[d]	% 1,2-*cis*[d]	% 3,4[d]
1	0	32 ± 4	16 ± 4	4 ± 2	3 ± 1	3 ± 1
2	0.5	37	13	5	4	3
3	1	36	14	6	5	3
4	1.5	35	14	5	5	3
5	2	29	12	5	4	3

[a] Pentane, $[AlCl_3] = 2.3 \times 10^{-2}$ mol/l, [1,3-pentadiene] = 1.6 mol/l, $t = 2$ h, $T = 20$ °C, deactivated by $BuNH_2$.

[b] Determined by IR and ^{13}C NMR.

[c] Determined by ^{13}C NMR.

[d] Determined by IR.

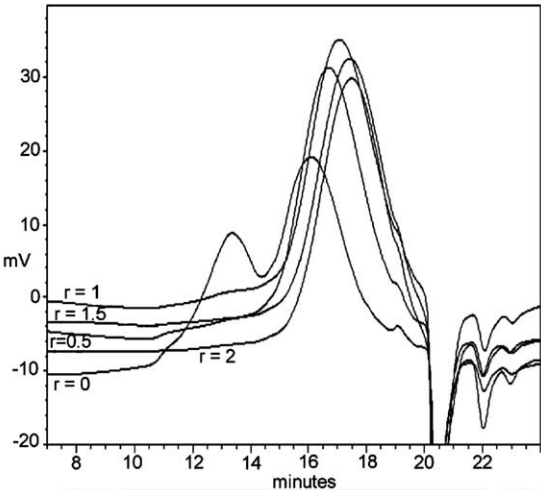


Fig. 7. SEC chromatograms of the polymers synthesized in the presence of OEt_2. r = $[OEt_2]/[AlCl_3]$.

7. Conclusion

This work allowed to focus on four electron donors, OPh_2, $N(PhBr)_3$, NPh_3 and SPh_2, in the cationic polymerization of 1,3-pentadiene initiated by $AlCl_3$ in pentane. At room temperature, they induced an increase of the conversion and a reduction of the cross-linked polymer proportion. Due to the modification of the polymer structure, it was suggested an interaction with the active centers in the case of NPh_3 and SPh_2. Thus this work validated the concept of sterically hindered active species. The conversions obtained at −10 °C in the presence of NPh_3 and SPh_2 lower than at room temperature suggested that the interaction C^+/ED was stronger at low temperature. The formation of a complex between OPh_2 or OEt_2 and $AlCl_3$ was also noticed.

In spite of the beneficial effect of the additives on the polymerization, it was not controlled: there was still cross-linked polymer left, the SEC distributions were still broad.... It means that the interaction of these electron donors with the active species were not sufficiently important to efficiently stabilize the active centers. The comparison between the effect of OEt_2 (a transfer agent), of OPh_2 and SPh_2 (sterically hindering the active species) suggests that this stabilization will be more efficient for the softer nucleophiles.

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