

Cationic polymerization of 1,3-pentadiene and 2-methylpropene: Direct initiation is a general mechanism with AlCl_3 in polar medium

He Wang^a, Véronique Bennevault-Celton^b, Bin Cheng^a, Hervé Cheradame^{b,*}

^a *The Key Laboratory of Novel Polymers, The Beijing University of Chemical Technology, Heping Street, 100029 Beijing, PR China*

^b *Laboratoire Matériaux Polymères aux Interfaces (MPI), UMR CNRS 7581, Université d'Evry Val d'Essonne, 91025 Evry Cedex, France*

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Abstract

Following previous results showing that direct initiation was operating in the cationic polymerization of 1,3-pentadiene in the presence of AlCl_3 in non-polar medium, it is shown on the same system that direct initiation also occurs in polar medium. In the case of 2-methylpropene the use of a proton trap (DtBP) allowed to show that at -30°C , direct initiation mechanism was operating either in 64/36 or in 36/64 (v/v) CH_2Cl_2 /pentane mixtures. These results show that direct initiation is a general mechanism with AlCl_3 . SEC studies showed that for 2-methylpropene transfer can be minimized.

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1. Introduction

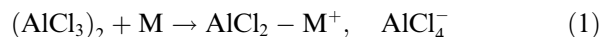
The cationic polymerization of monomers having carbon–carbon double bonds initiated in the presence of aluminum derivatives is still a field of interest [1]. However, papers devoted to polymerization initiated in the presence of aluminum halides alone are rather scarce. To date, some monomers have not been polymerized by controlled or quasi-living process [2]. However, living and controlled polymerization of 2-methylpropene with alkylaluminum halides as coiniciators has been extensively studied.

In the case of 1,3-pentadiene, it has been shown that the difficulty of obtaining controlled polymerization initiated by aluminum trichloride was essentially due to side reactions on the polymer [3]. For olefins, the initiation chemistry can be important in that the macromolecules produced by direct initiation from the Lewis acid have not the same functionalization as the ones produced by cointiation. It is worth also noting that aluminum trichloride is a cheap Lewis acid still extensively used in the industry. It has been shown that the polymerization of 1,3-pentadiene initiated by aluminum trichloride in non-polar solvent at room temperature was initiated by a direct reaction mechanism between the monomer and the Lewis acid (direct initiation) [4]. This result was surprising because the most widely admitted

* Corresponding author. Fax: +33 1 69 47 77 27.

E-mail address: Herve.Cheradame@univ-evry.fr (H. Cheradame).

mechanism of direct initiation is the self-ionization mechanism, which involves a charge separation, according to:



It has been considered sometimes that this charge separation in non polar solvent requires too much energy to be a general mechanism. In the case of 1,3-pentadiene cationic polymerization, this charge separation could be favoured by the fact that the positive moiety is a delocalized carbocation due to the mesomeric effect of the neighbouring double bond. In order to determine whether it is a general mechanism, it was decided to investigate the mechanism of initiation of the same monomer but in a polar solvent, and to compare its behaviour with a monomer which cannot delocalize the positive charge, such as 2-methylpropene.

2. Experimental

2.1. Materials

1,3-Pentadiene (composed of 34% in moles of *cis* pentadiene and 66% in moles of *trans* pentadiene, Aldrich, analytical grade, 90%), 2-methylpropene (Aldrich, 99%), pentane (SdS) and methylene chloride (SdS) were purified on calcium hydride under vacuum before use. Aluminum trichloride (Aldrich) was used as received from the supplier, but for some samples kept in a glove box under nitrogen.

2.2. Polymerization

The polymerization procedure was as follows: for experiments using anhydrous AlCl_3 , a freshly opened storage bottle was used, while always carefully stored under nitrogen. Preparation of the polymerization was carried out in the glove box. In a 250 mL glass bulb equipped with stopcocks, Teflon stirrer, and Teflon taps for connection to the vacuum line, the required amount of aluminum trichloride was weighed and introduced. After being closed, the reactor was then connected to the vacuum line, cooled down with liquid nitrogen, and the required amount of solvent was admitted. The reactor was then placed in a cooling bath at the required temperature under magnetic stirring. At last, the monomers were introduced in the reactor. After the desired polymerization time, the medium was quenched with a small excess of *n*-butylamine.

When it applied, the cross-linked polymer was recovered by filtration and drying under vacuum. The filtrate was washed by water to neutralization, then evaporated and dried under vacuum.

2.3. Analytical techniques

Size exclusion chromatography (SEC): The SEC analyses were carried out in THF using polystyrene standards on a chromatograph equipped with one column (Styragel HR 4E: molecular separation range: $100\text{--}5 \times 10^5$ 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.

Nuclear Magnetic Resonance (NMR): NMR spectroscopy was effected in deuterated chloroform on a Bruker Avance 300 MHz spectrometer at room temperature.

3. Results and discussion

3.1. Polymerization mechanism of 1,3-pentadiene initiated by AlCl_3 in polar medium

It was first necessary to examine the point of the quality of the aluminum trichloride and its hydration degree. It is worth recalling here that it was demonstrated that one mechanism of initiation of the 1,3-pentadiene polymerization proceeded through a direct reaction between aluminum trichloride and the monomer (direct initiation) in non polar medium [4], but that a protonic initiation mechanism could also be operating. For instance, it was shown earlier that trifluoromethanesulfonic acid could initiate 1,3-pentadiene polymerization in CH_2Cl_2 giving polymer in high yield [5]. Thus, it was anticipated that the comparison between an extremely dry aluminum trichloride and an hydrated one could give information on the point of the possible simultaneity of the two initiation processes. Some results are shown on Table 1.

Experiments 1 and 2 were carried out with hydrated AlCl_3 samples stored in phials under nitrogen, while experiment 3 involved a dry Lewis acid stored in a freshly opened phial kept in a glove box under nitrogen. It is clear that the non-anhydrous Lewis acid gave a much lower polymerization yield and molar mass than a dry one. The comparison of the SEC traces showed that a hydrated Lewis acid induced a polymer giving an approximately monomodal trace, while the trace corre-

Table 1
Study of the influence of the hydration state of AlCl_3 (2.3×10^{-2} mol/L) on the behaviour of 1,3-pentadiene (1.6 mol/L) polymerization in methylene chloride

Run	T^a (°C)	t^b (h)	AlCl_3	Storage conditions of AlCl_3	Polymer yield ^c (%)	IF ^d (%)	M_n^e (Da)	I_p^f	[Macromolecules] (mol/L)
1	-10	2	Hydrated	Bottle kept under N_2	25	10	1300	4.6	2.1×10^{-2}
2	-10	2	Hydrated	Bottle kept under N_2	27	11	1000	5.6	2.9×10^{-2}
3	-10	2	Anhydrous	Freshly opened bottle under N_2	89	13	12,300	4.0	7.9×10^{-3}
4	-30	2	Anhydrous	Freshly opened bottle under N_2	49	26	5900	3.7	9.0×10^{-3}
5	-10	0.5	Anhydrous	Freshly opened bottle under N_2	20	22	2300	3.5	9.5×10^{-3}

^a Polymerization temperature.

^b Reaction time.

^c Yield of soluble and insoluble polymer.

^d Fraction of insoluble polymer.

^e Molar mass in equivalent polystyrene.

^f Polymolecularity index.

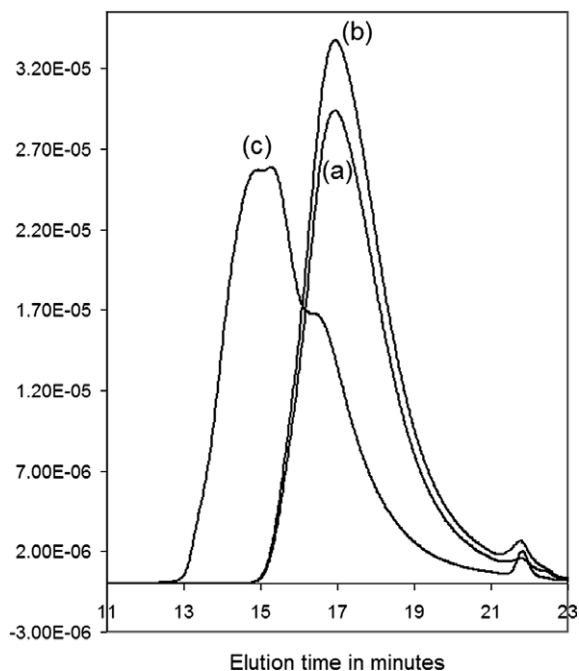


Fig. 1. Influence of the AlCl_3 hydration degree on the SEC curves: (a), (b) and (c) respectively, corresponding to runs 1, 2 and 3 of Table 1. ($[1,3\text{-pentadiene}] = 1.6$ mol/L; $[\text{AlCl}_3] = 2.3 \times 10^{-2}$ mol/L) polymerization at -10 °C in CH_2Cl_2 .)

sponding to the dry one was clearly bimodal (Fig. 1). Looking at the various SEC traces, the lower mass distribution of the SEC trace corresponding to run 3 can be clearly assigned to the hydrated part of the Lewis acid, while the high molar mass distribution corresponded to the macromolecules generated by the dry part of the Lewis acid, i.e. by direct initiation. It also seemed that the proportion of insoluble polymer was not sensitive to the hydration state of AlCl_3 .

The concentration of the macromolecules has been calculated with the total yield but using the molar mass determined by SEC, as if the polymer was totally soluble. Since the proportion of insoluble polymer was low at -10 °C (between 10% and 13%), this calculation is assumed to give a relevant indication. Looking at the concentration of macromolecules generated in these experiments, it can be seen that the dry Lewis acid generated less macromolecules than the hydrated ones. Whatever the initiation kinetics, the molar mass distributions are to be explained. In the case of experiments 1 and 2, the apparently monomodal distribution could be assigned to the predominant initiation by protonic species contained in the hydrated Lewis acid. The

bimodal distribution for sample No. 3 is accounted for by the existence of two different initiating species not exchanging their counteranion despite the fact that the medium is polar. However, the non-protonic initiation for this experiment is clearly more important than with hydrated catalysts. Experiment 4 shows that decreasing temperature at $-30\text{ }^{\circ}\text{C}$ did not decrease the number of macromolecules produced by direct initiation but rather the polymerization degree and yield. This observation shows that the initiation reaction is approximately as efficient at $-30\text{ }^{\circ}\text{C}$ as at $-10\text{ }^{\circ}\text{C}$, which indicates that in these conditions it is possible to consider that the polymerization is under control. Experiment 5 compared with experiment 3 brings a confirmation of this conclusion: a shorter polymerization time at $-10\text{ }^{\circ}\text{C}$ did not decrease the number of macromolecules produced by direct initiation but rather the polymerization degree. The direct initiation mechanism gives a sufficiently fast initiation with a sufficiently low rate of spontaneous transfer to allow to consider that in the temperature range $-10\text{ }^{\circ}\text{C}$, $-30\text{ }^{\circ}\text{C}$ the polymerization is apparently controlled, the number of macromolecules in given conditions of concentration being constant, while it remains some cross-linked material. It is worth recalling that transfer to polymer (branching) does not modify the concentration of macromolecules and cannot explain why the number average molar mass increases with the yield [6], but rather why the polymolecularity index is high.

These experiments allowed to complete the knowledge on the initiation mechanism by AlCl_3 in polar medium, this Lewis acid being at the same time an initiator, and if a proton donating species is present a coinitiator. It is clear that the overall chemistry was not modified by the change of polarity of the solvent. It was interesting to carry out sim-

ilar investigations with a more reactive monomer such as 2-methylpropene, which has been shown long time ago to polymerize by both initiation mechanism, coinitiation and direct initiation.

3.2. Polymerization of 2-methylpropene initiated by AlCl_3 in polar medium

This work was trying to characterise the 2-methylpropene polymerization in order to understand the various chemical events involved in the initiation process when AlCl_3 is used. It has been known for a long time that when the Lewis acid was TiCl_4 , the initiation process of 2-methylpropene could follow both reaction pathways (direct initiation by a mechanism which is not totally elucidated, or coinitiation called long time ago cocatalysis) [7]. The problem at that time was to be able to eliminate all available source of proton donating species and to make sure that this elimination was complete.

3.2.1. Characteristics of the initiation mechanism

In the present work, various experiments were realized to examine this point of the initiation mechanism in the presence of increasing quantities of a classical “proton trap”, 2,6-ditertibutylpyridine (DtBP), and are described on Table 2. Of note is the fact that the reactivity of 2-methylpropene is so high that the methodology used hereby in the case of 1,3-pentadiene (see previous section) could not allow to easily distinguish the two mechanisms. Using a so-called proton trap was the best way to shed some light on this initiation chemistry.

The solvent mixture for polymerization was chosen relatively polar but still able to dissolve the polymer produced by the reaction, a 64/36 (v/v) mixture of CH_2Cl_2 /pentane. Experiments 1 and 2 are showing the polymerization behaviour in the absence of

Table 2

Study of the 2-methylpropene (1.1 mol/L) polymerization initiated by AlCl_3 (1.1×10^{-2} mol/L) in a 64/36 (v/v) mixture of CH_2Cl_2 /pentane at $-30\text{ }^{\circ}\text{C}$ in the presence of DtBP^a

Run	[DtBP]/[AlCl_3]	Yield (%)	\bar{M}_n^b (Da)	I_p^c	[Macromolecules] (mol/L)
1	0	74	2400	15	1.9×10^{-2}
2 ^d	0	99	2100	8.8	2.9×10^{-2}
3	1	47	1900	9	1.5×10^{-2}
4	2.1	39	1800	9	1.3×10^{-2}
5	4.4	22	1900	7	0.7×10^{-2}
6	6	21	1800	7	0.7×10^{-2}

^a Polymerization duration = 16 h.

^b Molar mass in equivalent polystyrene.

^c Polymolecularity index.

^d Time = 1.5 h.

any additive, all reactants being dried under vacuum on calcium hydride, and the AlCl_3 coming from ordinary storage (non-anhydrous Lewis acid). The polymerization yield at -30°C was high but variable. These variations were attributed to the presence of adventitious moisture which is difficult to accurately control. Experiments 3–6 involved increasing quantities of DtBP. As it can be seen on Table 2, increasing concentration of DtBP induced a decrease of the polymerization yield which reached a plateau value when $[\text{DtBP}]$ was higher than 2.3×10^{-2} mol/L in the reaction medium. Since the adventitious water concentration is obviously much lower than this value, being given the technique used in these experiments, it was concluded that the remaining initiation was due to direct initiation. Several reasons can be produced to explain the decrease of the yield with increasing DtBP concentration. Of course, it must be assumed that the protonic initiation is quenched. It can also be assumed that spontaneous transfer can be quenched by the reaction of the complex acid, generated by such transfer, with the proton trap. This is the reason why, according to the published literature [8] it is believed that the presence of DtBP eliminates not only protonic initiation but also unimolecular transfer. This point will also be discussed below.

It must be also noted that if the direct initiation process is represented by reaction (1), the theoretical average number molar mass for complete initiation should be 2300 for experiment 6, which is in tune with the observed polymer molar mass (1800 in equivalent polystyrene). On the other hand, experiments 1 and 2 show that in the absence of “proton trap” the experimental molar mass is lower than the theoretical one (calculated on the same basis of a process involving direct initiation without transfer) showing that some protonic initiation occurred and/or some transfer was operating. The number of macromolecules which are produced by the system is another point which deserves to be discussed.

It is clear that the higher the “proton trap” concentration, the lower the number of macromolecules produced in a given time. The remaining macromolecules produced at high DtBP concentration (runs 5 and 6) are due to direct initiation. The concentration of macromolecules produced by the system brings a confirmation of the direct initiation mechanism. In the presence of DtBP this concentration decreased, and when $[\text{DtBP}]$ was higher than 2.1 $[\text{AlCl}_3]$ (run 4, Table 2), the concentration of macromolecules (calculated on the basis of the molar mass given by SEC) became constant and lower than $[\text{AlCl}_3]$. This set of experiments clearly showed that the direct initiation phenomenology which was evidenced in the case of 1,3-pentadiene polymerization in a polar solvent can also explain the initiation of 2-methylpropene polymerization by the same Lewis acid in a polar medium.

In order to remain for the solvent mixture in the validity domain of polarity of the direct initiation mechanism as determined above, but trying to decrease slightly the reactivity by the use of a less polar medium and to see whether the chemistry could be changed, 2-methylpropene polymerization was briefly investigated in the mixture 36/64 (v/v) CH_2Cl_2 /pentane in various conditions, all experiments carried out under vacuum and using a non-anhydrous Lewis acid in absence of DtBP (Table 3). The comparison between experiments 1 and 3 demonstrates the importance of the initial monomer concentration for the polymer production: the quantity of polymer produced in experiment 3 is 40 times higher than for experiment 1. Looking at the concentration of macromolecules, respectively produced by experiments 1 and 3, it can be seen that the concentration of macromolecules is approximately increasing in proportion to the increasing monomer concentration. The macromolecule concentration is much lower than the Lewis acid concentration at -75°C , while it is higher at -30°C (compare runs 3 and 4, Table 3). It can be seen that the same phenomenology is operating in the 36/64 (v/v) CH_2Cl_2 /pentane as in

Table 3
2-Methylpropene polymerization initiated by aluminum trichloride (10^{-2} mol/L) in a mixture 36/64 (v/v) CH_2Cl_2 /pentane

Run	$[\text{M}]$ (mol/L)	T ($^\circ\text{C}$)	Time (h)	Yield (%)	\bar{M}_n^a (Da)	I_p^b	$[\text{Macromolecules}]$ (mol/L)
1	0.1	-75	1	20	9200	6.6	1.2×10^{-4}
2	0.1 + 1	-75	1 + 2	54	130,000	3.1	2.5×10^{-4}
3	1	-75	2	80	530,000	2.6	8.4×10^{-4}
4	1	-30	2	62	1200	18.6	2.9×10^{-2}

^a Molar mass in equivalent polystyrene.

^b Polymolecularity index.

the 64/36 (v/v) CH_2Cl_2 /pentane mixture (compare with run 2, Table 2, carried out at the same temperature in comparable polymerization conditions). It is worth mentioning that the observed overall chemistry is similar to the one of the 1,3-pentadiene but showing that some transfer is operating.

Experiment 2 (Table 3) was carried out in a different way: first a low initial 2-methylpropene concentration (0.1 M) was introduced in the reaction vessel and the polymerization was allowed for 1 h, in order to reproduce the conditions of experiment 1 (Table 3). Then, instead of quenching the system, a new monomer charge (10 times higher) was added and the polymerization was again allowed to run for 2 h, mimicking the conditions of run 3. After this time, the polymerization medium was quenched. It can be seen that this technique did not allow for a macromolecule concentration as high as in experiment 3. This result demonstrates that the active species are mainly produced at the beginning of the polymerization reaction, and that the new monomer charge introduced after 1 h was mainly reacting with the active species already present in the system, the effective AlCl_3 concentration falling over time. The above interpretation explains the higher macromolecule concentration for run 3 (Table 3) than for runs 1 and 2 by a more efficient initiation due to a higher monomer concentration present at the beginning of the reaction. If this initiation reaction would simply result from the direct initiation reaction (1), the introduction of the second monomer charge (run 2) should be as efficient as in the case of run 3, which is far from being the case. Since the second monomer charge was less efficient in producing active species than in the case of experiment 3, it must be deduced that the active species are produced according to reaction 1, but when the active species concentration becomes high enough, the monomer molecules react more readily with the active species than with AlCl_3 , taking into account that its concentration can be decreasing due to some depletion mechanism. It then concluded that the polymerization kinetics can be assimilated to a stationary state of active species concentration. Experiment 2 (Table 3) demonstrated that initiation is rather fast since after 1 h there was not much newly produced active species.

SEC analysis of the polymer produced by experiment 4, Table 3, gave a trace with a clear bimodal distribution (Fig. 2). Taking into account the results obtained in the case of 1,3-pentadiene, one distribution is to be assigned to polymer given by direct ini-

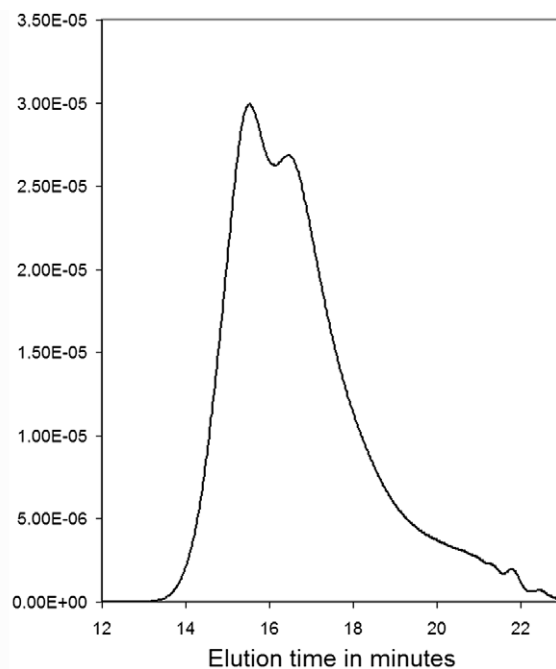


Fig. 2. SEC trace of the polymer synthesized in experiment 4 of Table 3 (2-methylpropene polymerization at $-30\text{ }^\circ\text{C}$ in a mixture 36/64 (v/v) CH_2Cl_2 /pentane).

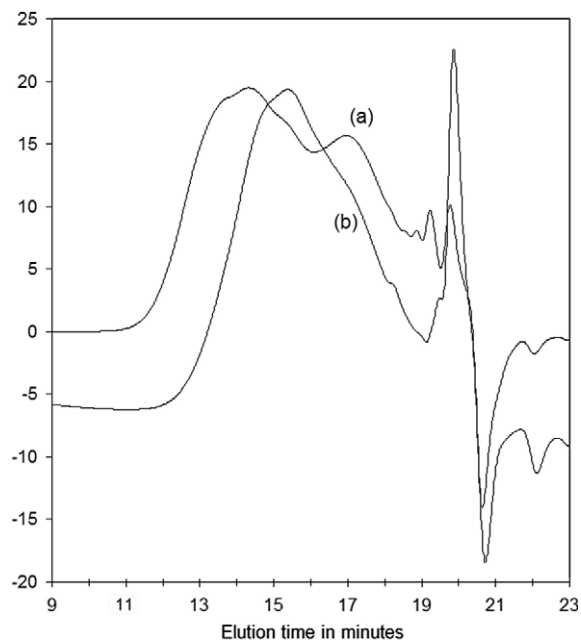


Fig. 3. SEC traces of a polyisobutylene synthesized without DtPB and a polyisobutylene synthesized with DtBP: (a): run 1, Table 2; (b): run 3, Table 2.

tiation and the other one to protonic initiation, the two active species not exchanging their counteran-

ion. The average number molar mass of poly (2-methylpropene) is lower for experiment 4 at $-30\text{ }^{\circ}\text{C}$ (Table 3), where protonic initiation was active, than when protonic initiation was quenched (Table 2). However, due to the difference of polarity between the two series of experiments, it is not possible to safely conclude on the assignment of each distribution relying only on these observations. SEC analysis of the experiments 1 and 3, Table 2, showed that the distribution of lower molar mass decreased when the DtBP concentration increased (Fig. 3). Then, it can be concluded that the distribution of lower mass was due to protonic initiation, as in the case of the polymerization of 1,3-pentadiene. SEC analysis of polymer No. 3, Table 3, showed that the polymer distribution was monomodal with a polydispersity index of 2.6. It is proposed that at such a low temperature, direct initiation was mainly responsible for the polymerization.

3.2.2. Discussion of the transfer mechanism

Still having for experiments 5 and 6 (Table 2) a polymolecularity index much higher than 2, this result raises the question of the phenomenon leading to such a high value ($I_p = 7$). If the acidic species resulting from a unimolecular transfer was eliminated by the “proton trap”, such a high I_p is to be assigned to the dead macromolecules produced by the loss of proton. In this situation, i.e. in the presence of a proton trap, such a transfer is a termination reaction. The instantaneous polymerization degree of the polymer produced at any time is given by:

$$\begin{aligned} \overline{DP}_n &= v_p/v_{tr} = k_p \cdot [C^+] \times [M]/k_{tr} \cdot [C^+] \\ &= K \times [M] \end{aligned} \quad (2)$$

with k_p , k_{tr} , $[C^+]$, $[M]$, respectively representing the propagation rate constant, the spontaneous transfer rate constant, the active species concentration and the monomer concentration. Since each polymer sample produced at any given time must have a polymolecularity index equal or close to 2, the total polymer sample is the sum of all samples centered on a \overline{DP}_n which decreases with the monomer concentration, which gives an index higher than 2.

It is known that, the propagation rate being first order in monomer concentration, when transfer to monomer is predominant among the chemical events leading to the interruption of chain growth, the number average molar mass is approximately constant with time and the polymolecularity index

is equal to 2. So it is concluded that monomer transfer is negligible (see runs 1 and 2, Table 2). Taking into account that direct initiation gave a concentration of macromolecules lower than $[AlCl_3]$, and that protonic initiation gave a maximum macromolecule concentration of the order of $[AlCl_3]$, it is deduced that unimolecular transfer is operating at $-30\text{ }^{\circ}\text{C}$ (Table 2).

About experiments carried out at $-75\text{ }^{\circ}\text{C}$, it is interesting to note that despite the higher concentration of macromolecules in run 3 (Table 3) than in run 1, the molar mass in run 3 is higher than in run 1. Consequently, the increase of molar mass with initial monomer concentration is to be explained either by transfer to the counteranion (spontaneous transfer) or control of the polymerization. Considering the lower polymerization yield of run 2 (Table 3) than that of run 3 and the high polymolecularity index, it is proposed that at $-75\text{ }^{\circ}\text{C}$ the molar mass are mainly governed by unimolecular transfer.

One can see that the polymerization involving spontaneous transfer can be distinguished from a controlled polymerization by two aspects, besides the fact that \overline{M}_n must decrease with yield, one characteristic point of the former is a high polymolecularity index.

4. Conclusion

This work, which is the continuation of a previous work carried out with the help of proton trap in 1,3-pentadiene cationic polymerization, showed that not only direct initiation from $AlCl_3$ can induce the polymerization of 1,3-pentadiene in polar or non-polar solvent [1], but also for a simple olefin such as 2-methylpropene in polar solvent. It suggests also that both active species, created from the Lewis acid by initiation or coinicitation, behave independently without exchanging their counteranion, for both monomers, and this aspect explains why bimodal distributions of molar mass are observed when the two initiating systems are simultaneously at work, at least in the $-10\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$ range. About transfer, indications are provided here showing that spontaneous transfer is only operating at a negligible rate in the case of 1,3-pentadiene at $-30\text{ }^{\circ}\text{C}$ in a polar solvent, and at low rate in the case of 2-methylpropene at $-75\text{ }^{\circ}\text{C}$ in polar medium, in conditions where direct initiation is thought to be the main mechanism responsible for polymerization. It is verified here that spontaneous transfer

mainly depends on the counteranion. The high poly-molecularity indices observed even in the presence of a proton trap can be explained by spontaneous transfer, which becomes a termination process in these conditions. The fact that direct initiation can compete with other initiating systems can explain why in some conditions a controlled polymerization is difficult to obtain.

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