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Cationic Polymerization of 1,3-Pentadiene Initiated by Aluminum Chloride: Determination of the Various Side Reactions

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ABSTRACT: The polymerization of 1,3-pentadiene initiated by $AlCl_3$ was investigated in a nonpolar medium at room temperature. It was shown that, besides propagation, the system undergoes various side reactions such as cross-linking, cyclization, double bond isomerization, ... An examination of the various possible structures of the polymer showed that the comparison of the ^{1}H and ^{13}C quantitative NMR spectroscopies allows the determination of the relative importance of cyclization and double bond isomerization. It is shown that some of these side reactions can be kept under control: for instance cross-linking could be avoided at low monomer concentration, while cyclization could be strongly decreased at high monomer concentration and by catalyst sublimation. Double bond isomerization was eliminated in the presence of a transfer agent such as methyl-2-butene-2.

Introduction

In a previous paper,[1] we reported experimental evidences in favor of a direct initiation mechanism by aluminum chloride in the polymerization of 1,3-pentadiene in hexane. The present paper also deals with the cationic polymerization of 1,3-pentadiene (PD) initiated by $AlCl_3$ in a nonpolar solvent; experiments were carried out under various conditions, and the structure of the resulting polymers was examined by NMR spectroscopy.

Various publications showed[1−3] that the cationic polymerization of PD produced both soluble polymer (which corresponds to linear and grafted macromolecules) and insoluble polymer (rubberlike solid particles, corresponding to the participation of cross-linking reaction to the polymerization mechanism). In general terms, the allylic carbenium ions formed from PD may attack the next diolefin in one of three ways, leading to a 1,4-, or 1,2-, or 3,4-propagation. The mechanism is further complicated by the stereochemistry involved (for example cis or trans enchainment) and by the presence of head-to-head and tail-to-tail enchainments in the structural units. Some authors[4−13] investigated the structure of cationic poly(1,3-pentadiene)s (PPD) and some other poly(conjugated dienes) by FTIR and ^{1}H NMR spectroscopies. They claimed the participation of side reactions to the polymerization mechanism: for example, a consumption of some polymer double bonds was observed from an unsaturation loss on ^{1}H NMR spectra and was attributed to cyclization reactions. It is difficult to control these side routes in conventional cationic polymerization systems, and a mixture of ill-defined products is obtained, which makes the analysis of the polymer structure complicated.

In the present study, the microstructure of the soluble polymers obtained from the cationic polymerization of PD initiated by aluminum chloride was investigated both by ^{1}H NMR and quantitative^{13}C NMR spectroscopies. Indeed the FTIR analysis does not allow an accurate determination of the structures because the two main monomer units along the polymer chain (*trans*-1,4 and *trans*-1,2) give absorption maxima at around the same frequency. It should be noted that quantitative^{13}C NMR spectroscopy has been employed to a limited extent for the structure determination of polydienes in cationic polymerization but appeared here to be decisive for a better understanding of the side reactions occurring during the polymerization.

The purpose of this paper is to outline a series of significant observations leading to a proposition of side reactions.

Experimental Section

Materials. Before use, 1,3-pentadiene (analytical grade Aldrich) and 2-methyl-2-butene (Merck) were dried over CaH_2 under vacuum. Hexane (SDS) was refluxed over calcium hydride at least 4 h and then distilled under N_2 stream. Aluminum chloride (Aldrich) was handled and stored under N_2 atmosphere in a glovebox. It was dried for 8 h under secondary vacuum before use.

Polymerization procedure. Polymerizations were carried out under high vacuum at room temperature. $AlCl_3$, hexane, 1,3-pentadiene, and, if necessary, 2-methyl-2-butene were successively introduced into the reactor. Except for the catalyst handled in a glovebox, all the reagents were introduced into the reactor by cryodistillation. The reaction mixture was rapidly brought to the required room temperature. After 2 h of reaction, polymerizations were deactivated by addition of MeOH. The crude polymerization medium was filtered. Insoluble polymer was dried under vacuum. The filtered solution was washed with water. After evaporation of the solvent, the soluble polymer was dried under vacuum.

Analyses. ^{1}H NMR spectra were recorded at 200 MHz in $CDCl_3$ with a Bruker AC 200 E spectrometer. ^{13}C NMR

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measurements were performed on a Bruker AM 400 spectrometer using an "Inverse Gate" (no NOE) procedure, allowing a quantitative determination. ^{13}C spectra were proton decoupled. The NMR pulse conditions were chosen so as to ensure that all the analyzed ^{13}C nuclei (included quaternary carbons) were detected on spectra.

The molecular weight and the molecular weight distribution of the polymers were determined by size exclusion chromatography (SEC) in tetrahydrofuran on a chromatograph equipped with three polystyrene gel columns (PL gel). Number-average molecular weight and weight-average molecular weight were calculated on the basis of a polystyrene calibration.

Results and Discussion

^{1}H NMR Spectroscopy. Several studies were devoted to the analysis of linear PPD microstructure by ^{1}H NMR spectroscopy[6,7,15] and signals corresponding to the various structures were assigned. Cationic PPD spectra exhibited broad signals which were generally attributed to methyl, methylene, and methine groups present in cyclic structures and overlapping with well-known signals of linear PPD.[16]

Unsaturation loss of our polymers was calculated from the values of the signal areas due to olefinic and aliphatic hydrogens, assuming that the molar fraction of 3,4-units present in the polymer is negligible. Indeed, the 3,4-units were not detected by FTIR spectroscopy. This result is similar to what was observed in previous studies of the PD polymerization initiated by $FeCl_3$ and aluminum triflate.[2-3] This could be explained by the steric hindrance of the pendent groups in the 3,4-unit. Hence, if no side reactions occurred during the polymerization, the signal at 5.3 ppm should be proportional to the olefinic hydrogens of 1,2-units and 1,4-units (i.e. to two olefinic protons per unit) and the integration of the peaks between 0.5 and 2.8 ppm should correspond to six aliphatic protons per unit. Thus, we defined the relative unsaturation loss per monomer unit as the difference between the theoretical unsaturation degree (equal to 25% of the total of protons) and the experimental unsaturation degree (d_{exp}) divided by the theoretical unsaturation degree: $\alpha_H = (0.25 - d_{exp})/0.25 = (a - 3b)/(a + b)$, where a is the integration of the peaks of the aliphatic protons, and b is the peak area of the olefinic protons (see Figure 1).

^{13}C NMR Spectroscopy. ^{13}C NMR gives more information on the polymer sequences than ^{1}H NMR spectroscopy since this analytic method is sensitive to stereoregularity of the structural units. Thus, characteristic spectra of the examined polymer samples (shown in Figure 2) exhibit a large number of peaks both in the aliphatic carbons area (ca. 9–43 ppm) and in the olefinic carbons area (ca. 123–138 ppm), few of which were assigned. Developments in stereospecific catalysts (Ziegler–Natta type for example) allowed the synthesis of isotactic *trans*-1,4-, isotactic *cis*-1,4-, syndiotactic *cis*-1,4-, and syndiotactic *trans*-1,2-PPDs. The assignments of carbon-13 chemical shift data of these highly stereoregular polymers allowed an easier interpretation of the cationic PPDs[4-6] spectra. In the polymerization of PD by cationic process described in the present paper, the carbon-13 spectra of polymers obtained under our experimental conditions were divided into four large signal groups. Some peaks agreed in terms of position with those reported in the mentioned studies, but were broader. As in the case of ^{1}H NMR spectra, the broadening can be explained among other considerations by a mixture of various structures and by an overlapping of the typical signals of linear PPDs by the nonequivalent but similar carbons present in cyclic structures.

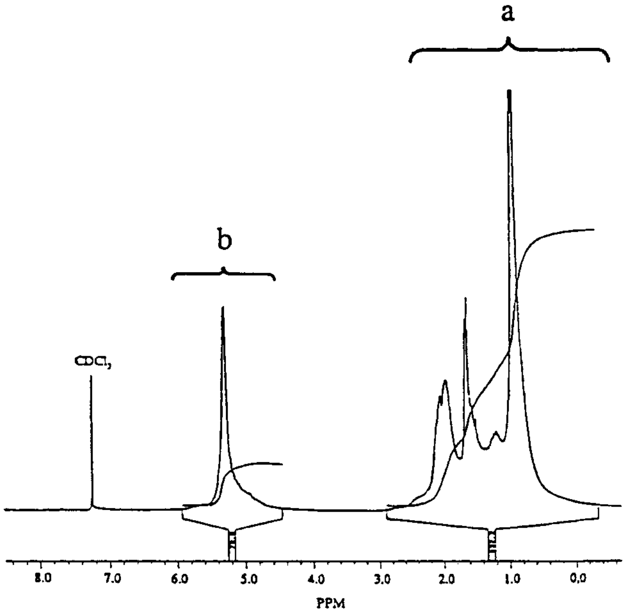


Figure 1. ^{1}H NMR spectrum of a PPD.

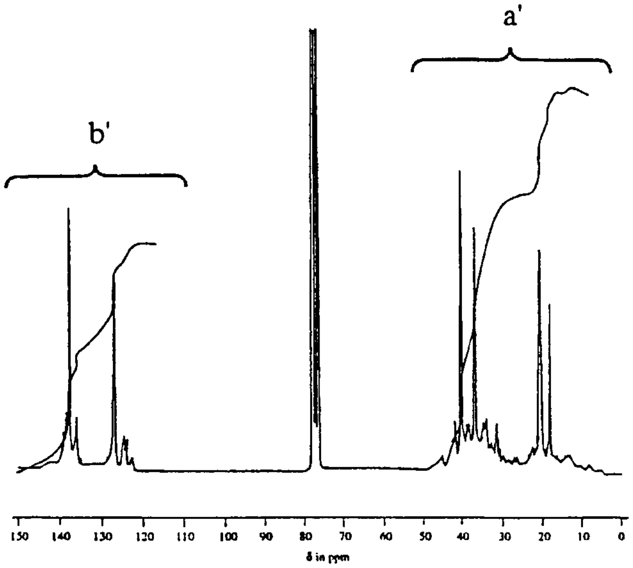
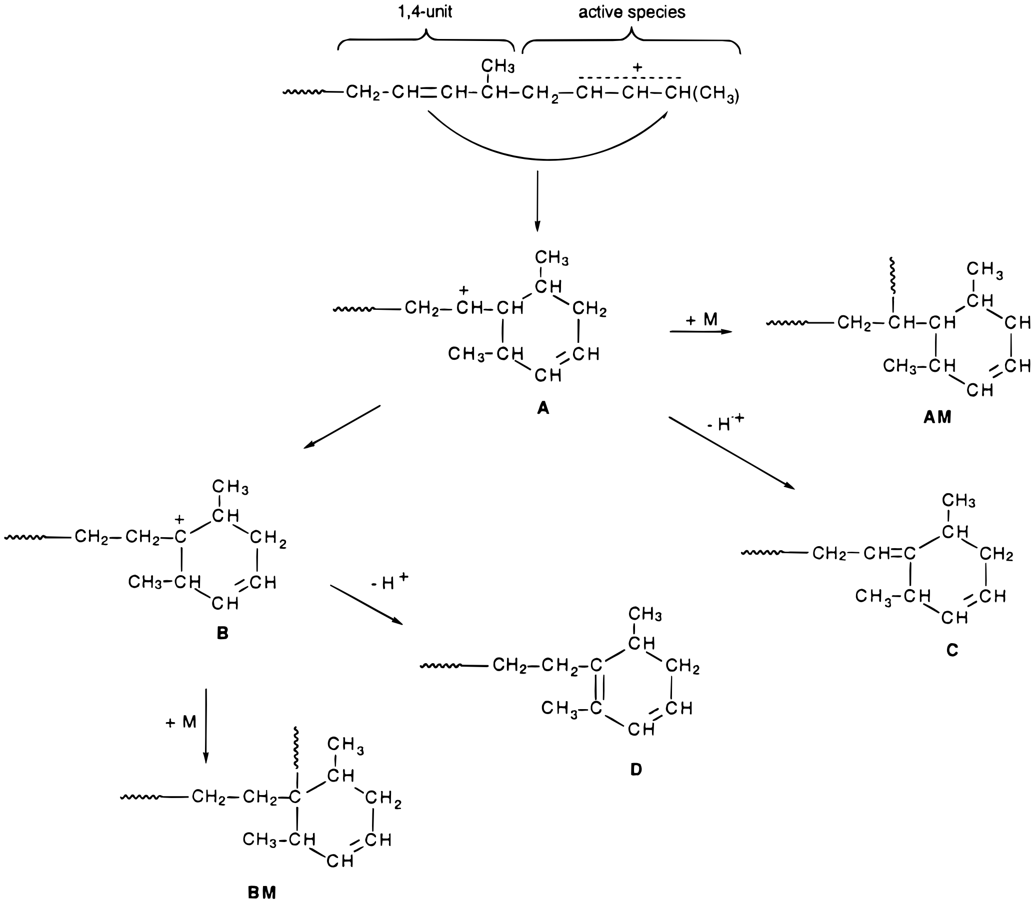


Figure 2. ^{13}C NMR spectrum of soluble PPD (run 3, Table 2).

The relative unsaturation loss per monomer unit is also calculated from quantitative ^{13}C NMR spectra. It is equal to the difference of the theoretical unsaturation degree (equal to 40%, assuming that the olefinic carbons region corresponds to two carbons and that the aliphatic carbons region corresponds to three carbons per unit) to the experimental unsaturation degree (d_{exp}), divided by the theoretical unsaturation degree: $\alpha_C = (0.40 - d_{exp})/0.40 = (2a' - 3b')/2(a' + b')$, where a' is the integration of the peaks corresponding to the aliphatic carbons and b' is the peak area of the olefinic carbons (see Figure 2).

Cyclization, Double Bond Isomerization, and Branching Reactions. Until now, few works have been devoted to the study of the cyclization mechanism in PPDs.[2,3,14,17-19] The most abundant work related to the cyclization reaction in cationic polymerization is

Scheme 1. Chemical Reactions Leading to the Formation of Cyclic Structures Assuming that Cyclization Occurs in the Course of Polymerization, from the Active Species



described in some papers concerning polyisoprenes and polybutadienes.[20–29] The authors mentioned the formation of monocyclic structures as well as polycyclic structures. However no direct proof of the cyclic structures were given though several teams announced a cyclization rate, estimated mainly by ^1H NMR analysis. We point here to the fact that an unsaturation loss calculated by ^1H NMR may find its origin either in cyclization reactions or in double bond isomerizations: this means that ^1H NMR spectroscopy is not an appropriate method to calculate the cyclization degree. Only a more recent publication by Vautrin-Ul et al.[14] based its discussion on carbon-13 analysis, in combination with FTIR and ^1H NMR results, but the proposed calculation leading to the cyclization content is not satisfactory either. Indeed these authors proposed a calculation of the proportion of cyclic unsaturations, from the ^1H NMR and ^{13}C NMR analyses, leading to their proposal of a tetrasubstituted double bond in a cyclic sequence. While they noticed a difference in the cyclization ratios measured from proton and carbon NMR, they did not take into account the fact that cyclization does not always result in α_H equal to α_C since different mechanisms of cyclization could exist.

We used a novel strategy to gain an insight into side reactions occurring in the course of PD polymerization. For example, cyclization is responsible both for a loss of olefinic carbons and for a loss of olefinic protons at the same time, while double bond isomerization alone leads to only a loss of olefinic protons, according to Zaytzev's rule. This means that the microstructure can be understood *only* from a comparison of both ^1H NMR and ^{13}C NMR spectroscopic analyses.

A general study is described in the present work to determine the mechanism responsible for the cyclization reaction, from ^1H and ^{13}C NMR spectra analysis of the polymers. Our discussion is based on the assumption made in the literature that two types of cyclization mechanism may occur: a direct cyclization of the macromolecular chains during the propagation step (intramolecular transfer) and a cyclization reaction independent of the polymerization reaction. These two mechanisms will be discussed separately, assuming that cyclization may be followed by either propagation or proton elimination. The following discussion will also take into account the double bond isomerization and branching reactions.

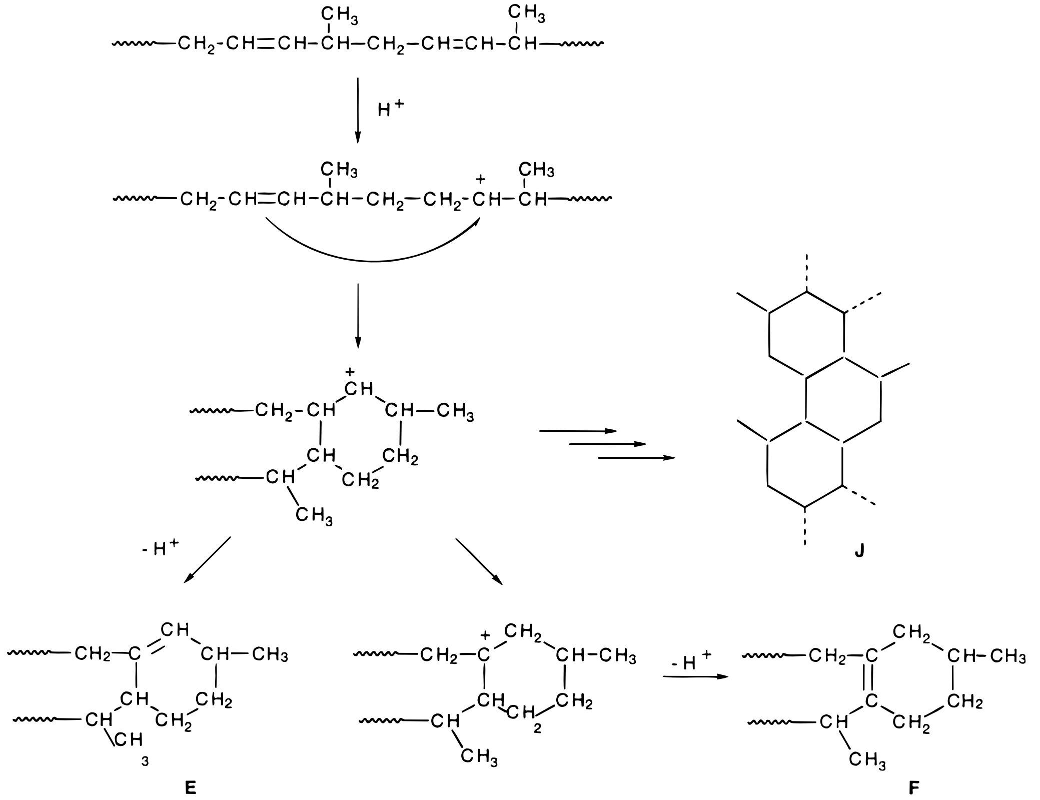
(1) Cyclization by the Reaction of a Growing Active Species onto an Unsaturation of the Penultimate Structural Unit. Cyclization may occur through the reaction of the active species with the double bond borne by the penultimate unit. Scheme 1 shows this reaction for a 1,4-type penultimate unit.

This reaction would lead to the cyclic structure **A**, which could then undergo one of three changes.

(1) The first is propagation, resulting in a loss of olefinic protons and of olefinic carbons equal to 1/2 per cyclized unit ($\alpha_H = \alpha_C = {}^1/_2$). Gaylord et al.[30] proposed a similar mechanism in the cationic polymerization of isoprene on the 1,4-units.

(2) The carbocation **A** can rearrange before resuming propagating, to give a more stable endocyclic species **B**. The species **B** could propagate inducing for the cyclized unit unsaturation losses α_H and α_C equal to ${}^1/_2$ (structure **BM**) or eject a proton giving two conjugated

Scheme 2. Chemical Reactions Leading to the Formation of Cyclic Structures Assuming that Cyclization Occurs by H^+ Transfer on a Polymer Unsaturation



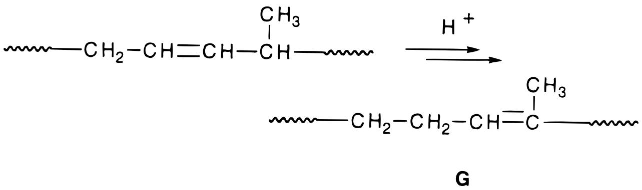
endocyclic double bonds, which might be more stable than **B**. Structure **D** formed in this last case is responsible for $\alpha_{\mathrm{H}} \approx 1/2$ and $\alpha_{\mathrm{C}} = 0$.

(3) The structure **A** could eject a proton (transfer) giving structure **C**, for which $\alpha_{\mathrm{H}} = 1/5$ and $\alpha_{\mathrm{C}} = 0$.

It must be noted that the above reactions would generate the same losses of unsaturation if the penultimate unit was resulting from a 1,2-type propagation or if the resulting cycle was a less favored five-membered or seven-membered structure.

(2) Cyclization Due To a H^+ Transfer on an Unsaturation Borne by the Polymer Chain. The cyclization mechanism may result from a proton transfer onto a polymer chain unsaturation. This cyclization is described in Scheme 2 on a sequence of two 1,4-units of the macromolecular chain. It can be easily shown that this mechanism is valid whatever the propagation type (1,4 or 1,2) and whatever the attack site of the proton. Structure **E** was formed from a protonation of the polymer, followed by cyclization and then transfer. This mechanism is similar to what was proposed by Golub and Heller on the 1,4-units of polyisoprene.[23] Structure **E** was also proposed by Denisova et al.[17] without any explanation in the cationic polymerization of PD. This structure yields α_{H} equal to $3/4$ and α_{C} equal to $1/2$ per cyclized unit. Structure **F**, which results from an additional isomerization of the active carbocation, corresponds to $\alpha_{\mathrm{H}} = 1$ and $\alpha_{\mathrm{C}} = 1/2$. The formation of polycondensed structures may be also considered. Indeed, after the first cyclization, the cation may attack the double bond of the preceding monomer unit, forming a new cation which again may attack the double bond of the preceding monomer unit and so on, forming type **J** structures. In this process (which is similar to the cyclization mechanism of 1,4 polyisoprene proposed by Golub[23]) olefinic protons and olefinic carbons disappear ($\alpha_{\mathrm{H}} = \alpha_{\mathrm{C}} = 1$).

Scheme 3. Double Bond Isomerization of a 1,4-Unit



(3) Double Bond Isomerization. As described in Schemes 1 and 2, the double bond isomerization may result from processes involving cyclization reactions. However, this isomerization may also exist independently of cyclization. Scheme 3 shows an example from a 1,4-unit unsaturation in the presence of a proton donor. It should be mentioned that, whatever the propagation type and microstructure, this double bond isomerization is responsible for $\alpha_{\mathrm{H}} = 1/2$ and $\alpha_{\mathrm{C}} = 0$ per modified unit.

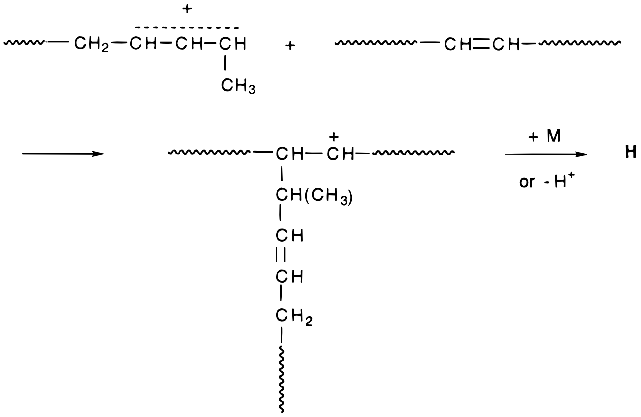
(4) Branching Reactions. Branching reactions (Scheme 4) would result from the reaction of a polymer chain active species with another chain unsaturation, followed if necessary by a propagation step depending on the new active species steric hindrance. This side reaction, which leads to the formation of a high molecular weight chain, would precede the formation of cross-linked polymer. The unsaturation losses α_{H} and α_{C} resulting from branching reactions are equal to 1. It is worth noting that the cross-linked polymer chains result from macromolecules which react at least twice with an active species by a “branching through” chemical event. Only soluble polymers are considered here by the NMR spectroscopies. Thus, it can be assumed that only macromolecules having undergone less than two “branching through” per macromolecule are present in the samples under investigation. Consequently, it can be

Table 1. Losses of Olefinic Protons and Olefinic Carbons in the Main Envisaged Structures

mechanism type	scheme	structure	α_H	α_C	α_C/α_H
cyclization	1	AM	$^{1}/_{2}$	$^{1}/_{2}$	1
cyclization	1	BM	$^{1}/_{2}$	$^{1}/_{2}$	1
cyclization (polycondensed structure)	2	J	1	1	1
cyclization + double bond isomerization[a]	2	E	$^{3}/_{4}$	$^{1}/_{2}$	$^{2}/_{3}$
cyclization + double bond isomerization[a]	2	F	1	$^{1}/_{2}$	$^{1}/_{2}$
double bond isomerization	3	G	$^{1}/_{2}$	0	0

[a] Results from the cyclization reaction.

Scheme 4. Branching Reaction



assumed that branching reaction has a negligible influence on the unsaturation losses.

(5) Comments. In the aim of a better understanding of the following discussion, the unsaturation losses resulting from the main mechanisms previously described are collected in Table 1. Structures **C** and **D** are not listed. Indeed, it can be hypothesized that the cyclic structures **AM**, **BM**, **J**, **E**, **F**, and **G** are present in the polymer chain in greater proportion than the cyclic structures **C** and **D** since the former are formed all along the macromolecular chain, while the latter result from cyclization of chain ends, followed by the interruption of the growing chain. This assumption must be valid, even if one or two **C**/**D** type structure(s) exit(s) per macromolecule due to branching reactions (see section 4).

It is important to keep in mind that both unsaturation losses calculated from ^{1}H NMR and ^{13}C NMR spectra would be equal to 0 in the absence of side reaction. From Table 1 results, it was observed that the double bond isomerization alone yields a loss of olefinic protons equal to $^{1}/_{2}$ whereas cyclization could be responsible for various values of unsaturation loss depending on the extent of the reaction. In ^{13}C NMR, only the isomerization alone induces a loss of olefinic carbons equal to 0. Therefore, an unsaturation loss different from 0, determined by ^{1}H NMR spectroscopy, could be significant both for isomerization and cyclization, whereas an unsaturation loss different from 0, observed in ^{13}C NMR spectroscopy, demonstrates the participation of cyclization reactions to the polymer structure. In this case, the ratio α_C/α_H may provide an estimation of the relative importance of the cylization reaction mechanism. It can also be noted that, only in the case of structures **AM**, **BM**, and **J** (cyclization without double bond isomerization), α_H is equal to α_C.

At last, it was noticed that the double bond isomerization induces the formation of a trisubstituted or tetrasubstituted double bond, whereas the unsaturations of 1,2- and 1,4-units are disubstituted.

Table 2. Yields, Molecular Weights, and Unsaturation Losses in the Study of the Reproducibility of the PD Polymerization in Hexane at Room Temperature ($[AlCl_3]_0 = 2.3 \times 10^{-2}$ mol·L^{-1}, $[PD]_0 = 2.3$ mol·L^{-1})

run	overall yield, %	proportion of insoluble material	soluble polymer		
			M_n[a]	α_H[b]	α_C[c]
1[d]	93	0.39	7000	0.43	0.16
2[d]	83	0.41	7500	0.40	0.16
3[e]	86	0.63	2000	0.44	0.05

[a] Determined by SEC chromatography (polystyrene standards). [b] Unsaturation loss calculated from ^{1}H NMR spectra. [c] Unsaturation loss calculated from ^{13}C NMR spectra. [d] $AlCl_3$ dried under vacuum for 8 h before polymerization. [e] Twice sublimed catalyst.

These points have never been mentioned until now in the literature concerning the analysis of the cationic polymerization of conjugated diolefins.

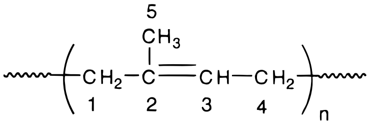
Study of Side Reactions under Various Experimental Conditions. Study of the Polymerization Reproducibility. Experiments using the same experimental conditions were carried out aiming at the determination of the polymerization reproducibility. Typical results are shown in Table 2. As mentioned elsewhere[1], PD polymerization initiated by $AlCl_3$ in nonpolar solvent yields both soluble and insoluble polymers. From the results in Table 2, the relative proportion of cross-linked insoluble polymer varied appreciably with the catalyst drying conditions, whereas the overall polymerization yields are similar, being equal to 87 ± 7%. The latter observation leads to the conclusion that the overall yield is reproducible in the experimental accuracy. The existence of the cross-linking reaction is due to nucleophilic polymer double bonds which can react with growing active species. The variation of insoluble proportion seems to be correlated to the unsaturation loss variation measured by ^{13}C NMR spectroscopy: indeed, run 3 (Table 2) exhibited the highest cross-linked fraction and the lowest α_C. On the contrary, run 1 and run 2 (Table 2) exhibited a lower cross-linked proportion and a higher unsaturation loss, α_C.

The unsaturation losses given in Table 2 could be explained by a double bond isomerization and by an additional cyclization step for runs 1 and 2. In the experiment 3, the unsaturation losses in proton and carbon NMR are respectively close to 0.5 and 0, suggesting that the main side reaction is an isomerization alone which leads to structures **G**. In runs 1 and 2, α_H was also close to 0.5, but an increase of α_C was observed. This result was explained by the participation of cyclization to the polymer structure; different cyclic structures may be envisaged in this case (**AM**, **BM**, **E**, ...). The assumption of **G**-type unsaturation isomerization in experiment 3 is in agreement with an increase in the cross-linked polymer. Indeed double bond isomerization of an 1,4-unit which leads to structure **G** is identical to the 1,4-units of polyisoprene:

Table 3. ^{13}C NMR Shifts of Polyisoprene in the 1,4-Propagation[32]

no. of the carbon[a]	structure	chemical shifts (in ppm)	
		cis	trans
2	$-\mathbf{C}(CH_3)=CH-$	135.2	134.9
3	$-C(CH_3)=\mathbf{C}H-$	125.0	124.3
1	$-\mathbf{C}H_2-C(CH_3)=$	32.2	39.7
4	$=CH-\mathbf{C}H_2-$	26.7	26.8
5	$-\mathbf{C}H_3-C=CH-$	23.1	15.6

[a] Referring to structure **I**.



I

The trisubstituted double bond of this polyisoprene-like **I** structure is more nucleophilic than the corresponding PPD unsaturation. As a consequence, the cross-linking reaction was enhanced in comparison to PD polymerization.[32] Moreover, this reaction is confirmed by the comparison of the ^{13}C NMR spectrum of this polymer (run 3) with the chemical shifts of polyisoprene carbons (Table 3). The ^{13}C NMR spectrum of run 3 (Figure 2) exhibited two peaks around 15.6 and 26.8 ppm which have not been attributed in the literature and which could correspond respectively to carbon 4 and carbon 5 of polyisoprene in the 1,4 trans propagation. No peak corresponding to carbons 1, 2, and 3 of polyisoprene have been specifically detected, but the latter could be screened by the PPD carbons (which appear as broad peaks) and from which their chemical shifts are close by less than 1 ppm. On the contrary, carbon-13 spectra of experiments 1 and 2 do not exhibit any peak which could be attributed to polyisoprene. This observation is in favor of our assumption that the linear PDD is modified both by cyclization and by unsaturation isomerization. This is also in agreement with the fact that the higher the cyclization, the lower the cross-linked polymer. Indeed the cross-linking reaction is explained by the intermolecular reaction of the active species with the polymer unsaturations, while the reaction leading to cyclization produces more hindered unsaturation.

For the sake of accuracy, one should take into account the chlorine content of the soluble polymers, which witnesses for the participation of termination reactions during the polymerization or hydrochlorination reactions generated during the polymerization quench. The former do not modify the unsaturation losses (α_H and α_C), whereas the latter leads to the formation of saturated chlorinated monomer units along the polymer chain, yielding a loss of olefinic hydrogens and olefinic carbons equal to 1 per chlorinated unit. Thus, α_H and α_C values calculated from NMR spectra of soluble polymers correspond to the unsaturation losses due to the sum of cyclization, unsaturation isomerization and hydrochlorination reactions. The percentage of chlorinated units was calculated from the following formula: % chlorinated units = $(M_{PD} \times \%\ Cl)/M_{cl}$, where % Cl is the chlorine content in weight measured by elemental analysis, M_{PD} the molar mass of the monomer, and M_{Cl} the molar mass of chlorine. Then the unsaturation losses α_H' and α_C', corresponding only to modified polymer structural units either by cyclization or by unsaturation isomerization, were calculated from these two formulas:

Table 4. Unsaturation Losses (α_H' and α_C') of the Modified Units by Cyclization or Isomerization (Experimental Conditions Detailed in Table 2)

run	soluble polymer		chlorine content, % wt	chlorinated units, %	modified units	
	α_H[a]	α_C[b]			α_H'	α_C'
1	0.43	0.16	0.61	1.17	0.43	0.15
2	0.40	0.16	2.01	3.85	0.38	0.13
3	0.44	0.05	1.05	2.01	0.43	0.03

[a] Unsaturation loss calculated from ^{1}H NMR spectra. [b] Unsaturation loss calculated from ^{13}C NMR spectra.

$$\alpha_H = \%\ \text{chlorinated units} \times 1 + (100 - \%\ \text{chlorinated units}) \times \alpha_H'$$

$$\alpha_C = \%\ \text{chlorinated units} \times 1 + (100 - \%\ \text{chlorinated units}) \times \alpha_C'$$

Results are collected in Table 4. As can be seen, the percentage of chlorinated units was at best equal to ≈ 4% of the overall polymer constituting units and so they contributed only a few extent to the loss of olefinic hydrogens and carbons. Indeed α_H' and α_C' values are not far from the corresponding α_H and α_C values for the overall soluble polymer. In the following discussion, it was considered that the participation of cyclization and unsaturation isomerization to the polymerization could be calculated only from ^{1}H NMR and ^{13}C NMR spectra, neglecting hydrochlorination reaction.

Study of Copolymerization PD/2-Methyl-2-butene. Copolymerization of PD and 2-methyl-2-butene was previously studied with other initiators such as aluminum triflate:[3] the monoolefin seemed to behave as a transfer agent. Here, we were interested on the effect of this transfer agent in the PD polymerization initiated by aluminum chloride in hexane.

Several copolymerizations were realized with different 2-methyl-2-butene concentrations and were compared to the PD homopolymerization. The overall yields, reported in Table 5, were calculated from the sum of the two monomers. If we calculate the yield assuming that only PD is incorporated in the polymer, the yields for the three experiments would be respectively 93, 91, and 105%. Thus, the last figure shows that when the 2-methyl-2-butene concentration is high, it is somewhat incorporated in the copolymer. This incorporation was also confirmed by NMR spectroscopy. It is interesting to notice that when 2-methyl-2-butene was present, the proportion of cross-linked polymer was negligible and that, on the SEC chromatograms, the higher molecular weight fractions disappeared (Figure 3). These observations support the assumption that the higher molecular weight distribution is assigned to the branched polymer nonincorporated to the cross-linked material. From results of Table 5, it can be proposed that the introduction of 2-methyl-2-butene into the polymerization medium reduces cross-linking reaction by the formation of lower molecular weight chains (reduced probability of reaction for two unsaturations of the same polymer chain with active species, when the system is close to the percolation transition), but also by a solvation of the active species which prevents or slows down the approach of the polymer chains. The hypothesis of active species solvation is also discussed in the following paragraph in view of the polymer NMR analysis. These assumptions might explain the drastic fall of the insoluble ratio with the 2-methyl-2-butene concentration.

Table 5. Characteristics of PD Copolymerizations with 2-Methyl-2-butene in Hexane at Room Temperature ($[AlCl_3]_0 = 2.3 \times 10^{-2}$ mol·L^{-1}; $[PD]_0 +$ $[2\text{-methyl-2-butene}]_0 = 2.3$ mol·L^{-1}

		yield[a]		soluble polymer	
run	2-methyl-2-butene	overall yield, %	proportion of insoluble material	M_n[b]	M_w/M_n[b]
1	0	93	0.39	7000	35
2	5% molar	86.5	0.01	3400	4.8
3	20% molar	84	0.02	3000	6

[a] Calculated for the total of the comonomers. [b] Determined by SEC chromatography (polystyrene standards).

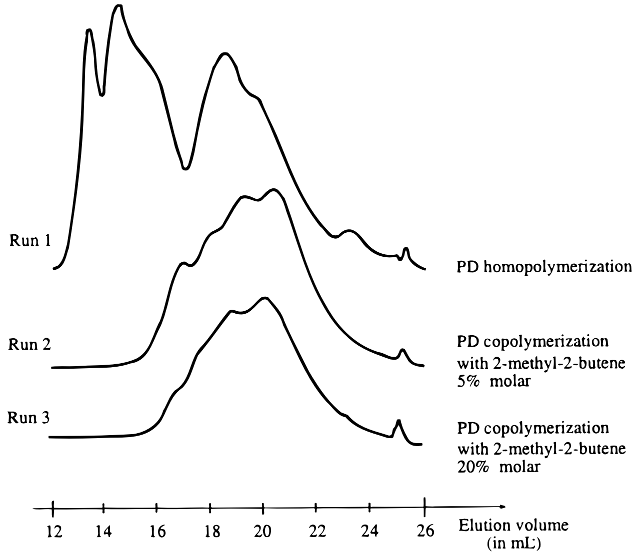


Figure 3. SEC traces of soluble polymers in PD copolymerization with 2-methyl-2-butene in hexane (Table 5).

Table 6. Unsaturation Losses Calculated on ^{1}H NMR and ^{13}C NMR Spectra in the Study of PD Copolymerization with 2-Methyl-2-butene in Hexane at Room Temperature (See Data in Table 5)

		soluble polymer		microstructure[a]
run	2-methyl-2-butene	α_H	α_C	1,4-units/ 1,2-units
1	0	0.43	0.16	2.2
2	5% molar	0.66	0.61	2.8
3	20% molar	0.74	0.63	2.7

[a] Determined from the proportion of methyl groups of each unit (1−4 and 1−2).

NMR analysis of the resulting polymers is described in Table 6. Unsaturation losses measured by ^{1}H and ^{13}C NMR spectroscopy increased in the presence of 2-methyl-2-butene. It can be noted that the increase of α_C is drastic, the latter becoming of the same order of magnitude as that given by the protonic spectroscopy. Even if it is assumed that all the 2-methyl-2-butene comonomer is incorporated in the copolymer, this incorporation would be far from explaining such a large increase of the unsaturation loss. This discussion shows that there is a change in the main side reaction when 2-methyl-2-butene is present. Unsaturation isomerization and cyclization are found as the main side reactions in the PD homopolymerization, whereas cyclization becomes predominant, if not exclusive, in the copolymerization. Indeed, in the presence of the transfer agent, α_C is close to $^1/_2$ and α_H is close to $^1/_2$ or $^3/_4$ according to the 2-methyl-2-butene concentration, suggesting that many cyclizations occurred involving, for example, the structures **AM**, **BM**, and **E**. One explanation of the cyclization increase could be that the active species are strongly solvated by the nucleophilic double bond of the transfer agent, preventing their reaction with the polymer due to the hindered structure of the double bonds. As a result, cyclization is important. The fact that both unsaturation losses are higher than 0.5 would be assigned to some polycyclization reactions (**J**- type structures) as previously suggested by some authors.[3,20]

Table 7. Yields, Molecular Weights, and Unsaturation Losses in the Study of PD Polymerization at Various Monomer Concentration in Hexane at Room Temperature ($[AlCl_3]_0 = 2.3 \times 10^{-2}$ mol·L^{-1}; Polymerization Time = 2 h)

		yield		soluble polymer			
run	$[PD]_0$, mol·L^{-1}	overall yield, %	proportion of insoluble polymer	M_n[a]	M_w/M_n[a]	α_H[b]	α_C[c]
1	0.5	74	0.06	6500	10	0.52	0.55
2	1	78	0.10	6100	33	0.48	
3	1.6	81	0.16	7500	49	0.45	
4	1.9	82	0.26				
5	2.1	90	0.39	6100	46	0.46	
6	2.3	95	0.94	4400	32		
7	2.3	93	0.41	7000	35	0.40	0.16

[a] Determined by SEC chromatography (polystyrene standards). [b] Unsaturation losses calculated from ^{1}H NMR spectra. [c] Unsaturation losses calculated from ^{13}C NMR spectra.

The ratio of unmodified 1,4 to 1,2 units (pentadiene units which did not undergo side reaction) was estimated in ^{1}H NMR for the copolymers and were compared to PD homopolymer values (Table 6). As it can be seen, the 1,4 to 1,2 units proportion increased in the copolymers. It must not be taken for granted that cyclization must consume more easily the 1,2 units. Another reason could be that 1,4-propagation is more favored in the presence of 2-methyl-2-butene. Indeed, it is not known to what extent cyclization is in competition with propagation.

Dependence of the Polymerization with the Initial Monomer Concentration. Polymerization of 1,3-pentadiene initiated by aluminum chloride in nonpolar solvent was carried out at various initial monomer concentrations. Results are listed in Table 7. As shown in Figure 4, the overall yield slightly linearly increased when the initial monomer concentration varied from 0.5 to 2.3 mol·L^{-1}. A first order dependence on monomer was shown up to a conversion of ≈ 80% for the polymerization realized with a initial monomer concentration equal to 1.6 mol·L^{-1} (see Figure 5). Thus, in this polymerization, the concentration of active species is constant at least in the first period of polymerization (for a polymerization time equal to 0.5 h). This kinetic study also allowed one to show the presence of termination reactions, since the overall yield was kept constant and equal to ≈ 80% after a reaction time of $^1/_2$ h (Figure 6). Termination reactions may result from the formation of hindered carbocations by side reactions (for instance by cyclization) which could not propagate. For the kinetic study realized at 0.5 mol·L^{-1}, the presence of an induction period can be noted (Figure 6).

Monomer concentration appeared to be the main parameter responsible for the formation of cross-linked polymer. The higher the monomer initial concentration, the greater the proportion of insoluble polymer. This observation is in good agreement with previous publications on the cationic polymerization of 1,3-pentadi-

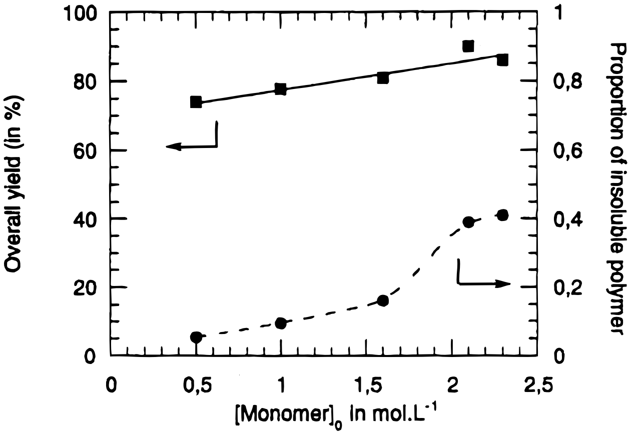


Figure 4. Overall yield (%) and relative proportion of cross-linked insoluble polymer (■, overall yield in %; ●, proportion of insoluble polymer) vs initial monomer concentration plot for the polymerization of PD in hexane at room temperature (for details, see data in Table 7).

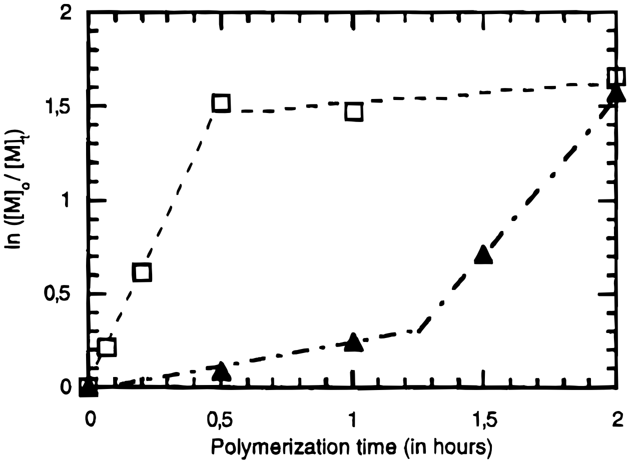


Figure 5. Plot of $\ln([M]_0/[M]_t)$ vs time for PD polymerization at various monomer concentrations (▲, [PD] = 0.5 mol·L^{-1}; □, PD] = 1.6 mol·L^{-1}) using hexane at room temperature. $[AlCl_3]_0$ = 2.3 × 10^{-2} mol·L^{-1}.

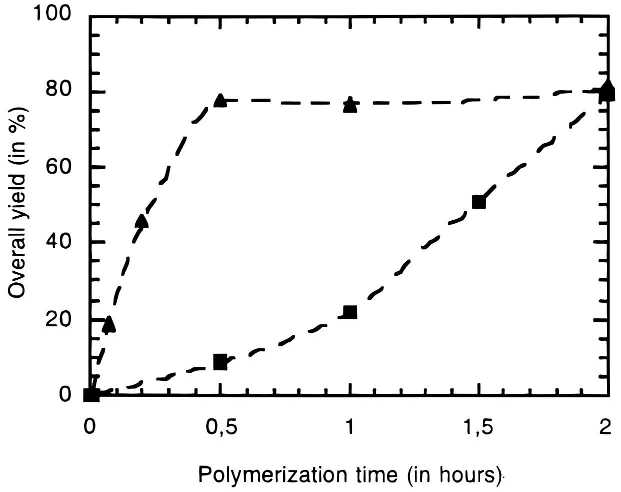


Figure 6. Overall yield (%) vs polymerization time plot in the polymerization of PD at various monomer initial concentration (■, [PD] = 0.5 mol·L^{-1}; ▲, [PD] = 1.6 mol·L^{-1}) in hexane at room temperature. $[AlCl_3]_0$ = 2.3 × 10^{-2} mol·L^{-1}.

ene.[3,32,33] It should be noted that the proportion of insoluble polymer was greatly different between run 6 and run 7 though the monomer initial concentration was kept equal to 2.3 mol·L^{-1} in both cases (Table 7). This difference is easily accounted for assuming that there was a small variation in the monomer concentration, thus placing run 7 between runs 6 and 5 in Table 7. Hence the cross-linking reaction appeared to be very sensitive to the experimental conditions when the monomer concentration was high.

At constant catalyst concentration, the α_H value slightly decreased when the monomer initial concentration increased from 0.5 to 2.3 mol·L^{-1}, while the loss of olefinic carbons decreased from 0.55 to 0.16. These variations would be attributed to a high cyclization rate at the lowest monomer initial concentration (0.5 mol·L^{-1}) which also exhibited the lowest proportion of insoluble (Table 7). This assumption was also confirmed by the shape of ^{13}C NMR spectrum of the polymer obtained in run 1. Indeed, the spectrum showed broad bands and a bad resolution between 25 and 50 ppm and more particularly at 20.1 ppm (which corresponds to the methyl carbon of the 1,4-unit). The ^{1}H NMR spectrum also exhibited an overlapping of the peaks in the aliphatic protons area which is significant of cyclization,[34] and new signals have been detected at 1.43, 1.76, and 1.79 ppm, which have not been attributed in the literature.

It could be assumed that cyclization and cross-linking are side reactions competing with the regular propagation leading to polymerization. Hence, cross-linking was decreased when the monomer initial concentration (with which the resulting polymer concentration is directly linked) was decreased (Table 7). On the contrary, cyclization, most probably involving **AM** and/or **BM**-type mechanisms (since α_H and α_C values are around 0.5), was encountered at low monomer concentration. The high rate of cyclization can be explained by the fact that the polymerization is slower at a PD concentration equal to 0.5 mol·L^{-1} (Figure 6) and the polymer concentration is kept low in the course of the polymerization. So cyclization which corresponds to the intramolecular reaction of the carbocations with the polymer unsaturations is favored. On the contrary, the highest PD concentration yielded much less cyclized polymer as showed by the lower α_C value (Table 7). Indeed the polymerization kinetics is faster under these conditions as plotted in Figure 6. Hence the intermolecular reaction of the active species with polymer unsaturations is favored, leading to more cross-linking.

Unsaturation isomerization is also competing with propagation, and it can even be assumed that at the highest monomer initial concentration, the main side reaction is isomerization taking into account that α_C is much lower than α_H. To explain this aspect, it is possible to assume that the active species solvation by the polymer produces isomerization steps, besides cross-linking.

PD polymerization in hexane resulted, whatever the monomer concentration, in plurimodal SEC traces as shown in Figure 7, and large polydispersities were obtained for the soluble polymer as indexed in Table 7. This polydispersity originates from the various side reactions (branching, transfer reactions, ...).

Conclusions

Our results showed that, to assign the effects of the various possible side reactions in the PD cationic polymerization initiated by $AlCl_3$ in hexane, it was essential to compare quantitatively ^{1}H NMR spectra

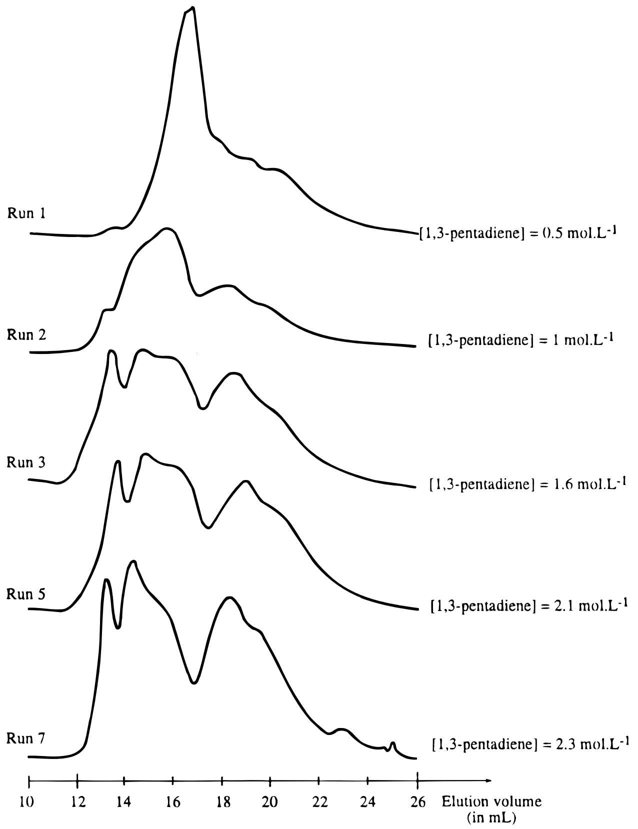


Figure 7. SEC traces of soluble polymers in PD polymerization initiated by aluminum chloride in hexane at various monomer concentration (experimental data detailed in Table 7).

with ^{13}C NMR spectra, taking into account the possibility of double bond isomerization. It was shown that under some conditions the protonic unsaturation loss was to be attributed to predominant unsaturation isomerization, for instance at high monomer concentration. Our study demonstrated that the competition between isomerization and cyclization was not a kinetic effect but must rather be assigned to variations in active species solvation, as shown by the experiments in the presence of methyl-2-butene-2. Finally, if cross-linking can be eliminated in the presence of a transfer agent such as methyl-2-butene-2, this side reaction is a function of the polymer concentration in agreement with the fact that the proportion of insoluble product increased with the initial monomer concentration. This work shows that it is possible to control side reactions in the cationic polymerization of dienes in a nonpolar medium by the proper choice of the reaction conditions.

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