Cationic Polymerization of Dienes. 5.[†] Study of the Polymerization of 1,3-Pentadiene *cis*/*trans* Isomers and Evidences of the Origins of the Insoluble Fraction

Marilyn Delfour, Véronique Bennevault-Celton, and Hervé Cheradame*

Laboratoire Matériaux Polymères aux Interfaces (MPI), UMR CNRS 7581,
Université d'Evry Val d'Essonne, Bâtiment IMEVE, rue du Père Jarlan 91025 Evry Cedex, France

Florence Mercier and Nicole Barré

UMR Analyse et Environnement, Université d'Evry Val d'Essonne, Bâtiment IMEVE,
rue du Père Jarlan 91025 Evry Cedex, France

Received June 13, 2002; Revised Manuscript Received October 30, 2002

ABSTRACT: The cationic polymerization of 1,3-pentadiene isomers initiated by $AlCl_3$ was investigated in nonpolar solvent. It was shown that the polymerization was very sensitive to the initial monomer composition (proportion between the cis and trans isomers). The cis isomer favors the cross-linking reactions and double bond isomerization, whereas the trans isomer induces more cyclization. However, the behavior of the mixture of the two isomers cannot be simply deduced from a linear combination of the behavior of each isomer independently considered. Some polymerizations were realized in different alkanes (pentane, hexane, heptane, and decane). Despite similar polarity, it was observed that the higher the solvent molecular weight, the lower the total polymerization yield. These results were assigned to a different solubility of the Lewis acid and of polymer chains in the different solvents investigated. Finally, two origins of the cross-linked polymer were identified: the heterogeneity of the polymerization medium and intermolecular reactions of the active species with the polymer.

Introduction

The cationic polymerization of 1,3-pentadiene initiated by aluminum trichloride in nonpolar solvent is known to produce both insoluble polymer (which corresponds to cross-linked chains) and soluble polymer (linear or grafted macromolecules).[1−3] The polymer structure is complicated by the different microstructures of the monomer units (1,4-, 1,2-, and 3,4-polymerizations), by the involved stereochemistry (cis and trans enchainments) and by the occurrence of various side reactions like cyclization, double bond isomerization, termination, etc.[1−3] The aim of this work is to achieve a better understanding of the different mechanisms involved in the polymerization of this monomer, which is generally composed of a mixture of cis and trans isomers, the cost of pure isomers being expensive. This polymerization is very sensitive to experimental conditions (polarity of the solvent, nature of the initiator, monomer concentration, temperature, ...).[2,4,5] In this paper, the influence of each compound on the polymerization ($AlCl_3$, nonpolar solvents, 1,3-pentadiene isomers) was first examined. In a second part, the origin of the cross-linked chains was investigated.

Experimental Section

Materials. Aluminum chloride (Aldrich) was stored under N_2 atmosphere in a glovebox. Pentane (SdS), *n*-hexane (SdS), and heptane (SdS) were refluxed over CaH_2 and then distilled under nitrogen just before use. Because of its higher molecular weight, decane (Aldrich) was cryodistilled over CaH_2 under secondary vacuum. 1,3-Pentadiene (Aldrich) was either an analytical grade (90%), composed of 34 mol % of *cis*-pentadiene and 66 mol % of *trans*-pentadiene or a single isomer (*cis*-1,3-pentadiene, 98%, or *trans*-1,3-pentadiene, 96%). 1,3-Pentadiene and 2,3-dimethyl-2-butene (Aldrich, 99%) were also dried over calcium hydride.

Polymerization. Polymerizations were carried out under high vacuum at room temperature. $AlCl_3$ was handled in a glovebox and introduced into the reactor. It was dried 1 h under secondary vacuum before use. The dried solvent and if necessary the olefin were then added by cryodistillation. The mixture warmed to room temperature and the monomer was added. After 2 h of reaction, polymerizations were deactivated by the addition of pure *n*-butylamine. The crude polymerization medium was filtered to separate the insoluble polymer from the soluble fraction. The cross-linked polymer was dried under vacuum. The soluble fraction was washed with water. After evaporation of the solvent, the soluble polymer was dried under vacuum.

Analytical Techniques. Nuclear Magnetic Resonance (NMR). ^1H and ^{13}C spectra were recorded on a Bruker Avance 300 MHz. ^{13}C measurements were performed using an inverse gate procedure (no NOE), allowing a quantitative determination of the carbon unsaturation loss. The NMR pulse conditions were chosen to ensure that all the analyzed ^{13}C nuclei (including quaternary carbons) were detected.

Size Exclusion Chromatography (SEC). Number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$, respectively) were determined by SEC in tetrahydrofuran on a chromatograph equipped with two columns (PL Gel, mixed C), an IR cell, and a UV at 254 nm detector. Polystyrene standards were used to generate the calibration curve.

Fourier Transform Infrared Spectroscopy (FTIR). IR spectra of polymer solutions in CS_2 were recorded on an FTIR Perkin-Elmer 1760 spectrometer by using liquid cells. The microstructure of the polymers were then characterized using the molar extension coefficients of the linear units determined by Beebe.[11]

Differential Scanning Calorimeter (DSC). The polymer glass transition temperatures were determined on a differential scanning calorimeter (DSC), Perkin Elmer 4, calibrated with cyclohexane. Two heating programs were used: the first program operating in the range −120 to +250 °C, with the second program operating from −120 to +150 °C when no first-order transition occurred between 100 and 250 °C. The heating rate was 20 °C/min.

[†] Part 4: *Eur. Polym. J.* **2002**, *38*, 587−596.

10.1021/ma020921p CCC: $25.00

Table 1. Influence of the AlCl$_3$ Aging and Lot on the Polymerization Yields

run^a	AlCl$_3$ aging (day)	AlCl$_3$ lot no.	tot. yield (%)	IF (%)	$\overline{M}_n{}^b$ (g/mol)	$I_p{}^b$
1	0	2	83	49	8400	12.1
2	0	3	70	50	8900	11.0
3	0	6	78	45	10 400	10.3
4	7	5	69	86	1600	7.7
5	11	2	68	65	6400	10.0
6	13	8	78	38	10 000	11.2
7	14	5	75	53	5400	14.5
8	29	1	70	74	4500	8.9
9	43	1	76	71	5000	10.4
10	50	6	71	42	10 900	9.3
11	58	4	57	75	3300	8.2
12	114	1	73	73	3200	17.6
		av	72	60	7000	10.9
		σ^c	±7	±16	±3100	±2.8

^{a} [AlCl$_3$] = 2.3×10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, pentane, $T = 20$ °C, $t = 2$ h, deactivation by BuNH$_2$. ^{b} Determined by SEC (polystyrene standard). ^{c} Standard deviation.

Nuclear Microprobe Analysis (NMA). The nuclear microprobe of the Pierre Süe Laboratory (CEA, Saclay, France) was used by coupling particle induced X-ray emission (PIXE) and the ^{12}C(p,p)^{12}C reaction with incident protons of 1.725 MeV energy. The capabilities of NMA and particularly the use of these two spectroscopic modes for characterization of organic matter has been demonstrated in papers.[12,13] For our study, PIXE permits one to determine Al and Cl at contents as low as 1 μg/g of sample. The ^{12}C(p,p)^{12}C nuclear reaction at the resonance energy of 1.725 MeV gives the C concentrations with an excellent sensitivity (because of this nuclear reaction high cross section at backward detection angles: 900 mb/sr at 175°).[14] The sensitivity of the organic matter to beam irradiation and temperature as well as the volatility of halogen elements (chlorine in this study) are well-known phenomena.[15] So, a beam size of 10 μm × 10 μm and a current density of 0.5 pA/μm^2 with a total integrated charge of 0.1 μC collected by the sample surface permits one to avoid elemental losses. Nuclear microprobe analyses consisted of point mode measurements (beam fixed on the analyzed zone) and of elemental maps of polymers surfaces of 500 μm × 500 μm dimensions to follow the correlations or anticorrelations between the elements C, Al, and Cl. The elemental maps and their corresponding spectra were treated by using the RISMIN software.[16]

Results and Discussion

Influence of the AlCl$_3$ Lot and its Aging. Before investigating polymerization mechanisms, it seemed to be interesting to study the influence of the AlCl$_3$ lot and its aging on the polymerization in term of yield and chain structure. Indeed, the Lewis acid may be progressively hydrolyzed despite the storage and handling cares under nitrogen atmosphere. The lot may be also an important factor because the granulometry can change from one sample to another used in this study. Consequently, a standard polymerization was realized 12 times with different Lewis acid lots and with different time lags between the opening and the use of the catalyst bottle. The polymerizations were carried out in pentane at room temperature using the same mixture of cis and trans isomers as monomer. The total yield, the insoluble fraction (proportion of cross-linked polymer, denoted as IF) as well as the molar mass and the polydispersity index of the soluble polypentadienes synthesized are reported in Table 1. These results showed that the AlCl$_3$ opening delay had little influence on the total yield. Indeed, even after 114 days (about 3 months), the global yield remained relatively constant. It was about 72% with a standard deviation of 7. This observation is in tune with previous works which showed that the direct initiation was responsible for this polymerization and that cocatalysis was of little influence if any.[1] As for as the insoluble fraction (IF), it substantially varied from one polymerization to another. The IF variation did not seem to be correlated with catalyst lot and with Lewis acid opening delay. The heterogeneous polymerization medium could explain these results. Indeed, AlCl$_3$ is poorly soluble in nonpolar solvent, and it was observed that the insoluble fraction aspect changed in the different polymerizations, showing that the 1,3-pentadiene cationic polymerization is very sensitive to medium homogeneity. For example, AlCl$_3$ is more soluble in polar solvent than in nonpolar solvent so that the 1,3-pentadiene polymerization in methylene chloride generated nearly no cross-linked polymer (IF = 6%).

As can be seen in Table 1, the values of the polymer number-average molar mass are very scattered since the standard deviation is close to 3000 g/mol. This fact is to be related to the variation of the insoluble fraction and will be explained below in the paragraph dealing with the origin of the cross-linked polymer.

The polymer microstructure was characterized by several analyses. The complementarity of infrared (IR) and ^{13}C NMR spectroscopies allowed us to describe accurately the linear pentadiene units. IR provides the molar percentages of 1,4-cis, 1,2-cis, and 3,4 units and the global percentage (1,4+1,2)-trans, while using quantitative ^{13}C NMR it was possible, by the existence of a signal at 18 ppm characteristic of the 1,2-trans units methylic carbons and a signal at 13,3 ppm characteristic of the 1,2-cis units methylic carbons, to quantify each unit. Therefore, the subtraction of the 1,2-trans content determined by NMR to the global percentage (1,4+1,2)-trans obtained by IR gives the 1,4-trans content. Figures 1 and 2 give examples of IR and ^{13}C spectra.

The polymer structural analysis showed that the linear microstructure of the polymers was not sensitive to AlCl$_3$ lot and to the time lag between the opening and the use of the catalyst bottle (Table 2). The polymers were mainly composed of 1,4- and 1,2-trans units, the others (1,2-cis, 1,4-cis, and 3,4 units) not exceeding 3−4%. It can be noted that the sum of the different pentadiene units did not give 100%. The missing fraction was assigned to cyclic units.

The ^{1}H and ^{13}C NMR analysis of the polymers allowed to study the unsaturation ratio contained in the polymer chains. It is well-known that an unsaturation loss was always observed in the cationic polymerization of dienes.[4,5] This loss is due to the existence of side reactions like isomerization, cyclization and grafting. In previous investigations,[2] we showed that cyclization and branching reaction are both responsible for a loss of olefinic protons and carbons at the same time, while double bond isomerization alone only leads to a loss of olefinic protons, according to Zaytzev's rule. Since the soluble polymer must contain less than two cross-linking points per macromolecule (beyond this average value the polymer becomes cross-linked), the branching reaction was assumed to be negligible. In conclusion, the ratio of the carbon relative unsaturation loss on the proton one (α_C/α_H) provides an estimation of the relative importance of the cyclization vs isomerization. Some authors[6] studied the cyclization reactions by IR and defined a cyclization degree (τ) as the loss of linear units ($t = 100\% -$ sum of the percentages of the linear units).

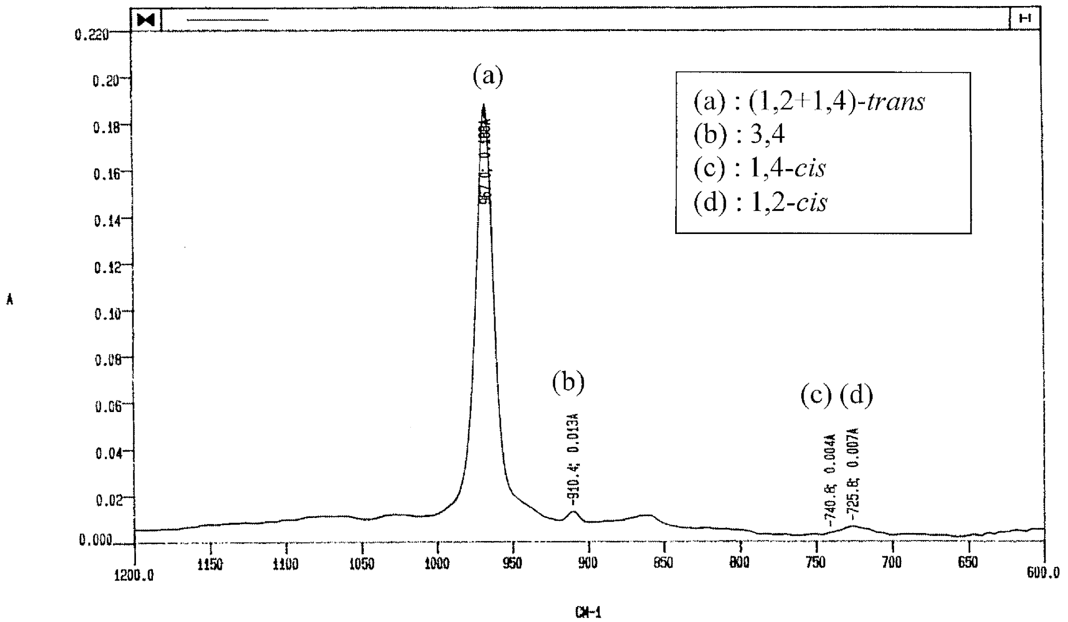

Figure 1. IR spectrum of a polypentadiene in solution in CS_2.

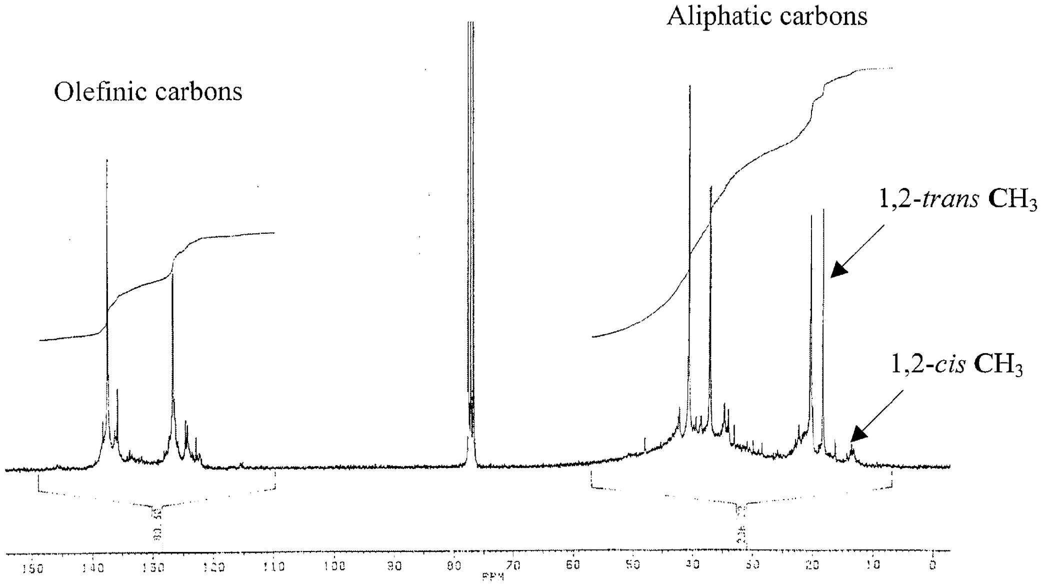

Figure 2. ^{13}C NMR spectrum of a soluble polypentadiene in $CDCl_3$.

Table 2. Influence of the $AlCl_3$ Aging and Lot on the Linear Unit Microstructure and on the Cyclization and Isomerization Reactions[a]

	1,2-trans[c]	1,2-cis[d]	1,4-trans[e]	1,4-cis	3,4	α_H[f]	α_C[f]	α_C/α_H	τ[g]	T_g onset (°C)
av	16	3	32	4	3	0.40	0.31	0.77	0.42	−6.5
σ[b]	±4	±1	±4	±2	±1	±0.02	±0.03	±0.04	±0.06	±5

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, pentane, $T = 20$ °C, $t = 2$ h, deactivation by $BuNH_2$. [b] Standard deviation. [c] Determined by ^{13}C NMR; 1,2-trans % = $(1 - \tau)(I_{1,2-\mathrm{trans}}/I_{\mathrm{Me}})$ with τ = sum of linear units. $I_{1,2-\mathrm{trans}}$ = Integration of CH_3 belonging to 1,2-trans units at 18 ppm, I_{Me} = Integration of CH_3 belonging to 1,4-(cis+trans), 1,2-(cis+trans), and 3,4 between 10 and 25 ppm. [d] Determined by IR. [e] Determined by ^{13}C NMR and IR. [f] Relative unsaturation losses determined by ^1H or ^{13}C NMR. [g] Cyclization degree determined by IR.

This last characteristic was also determined in this work and compared to α_C. At last, the polymers were investigated by differential scanning calorimetry (DSC). The glass transition temperatures may give information on the stiffness of the cyclic structures. As shown in Table 2, α_C, α_H, τ, and T_g remained nearly constant within experimental accuracy whatever the catalyst lot and the opening delay. The ratio α_C/α_H of the polymers being about 0.77 meant that cyclization reactions dominated compared to isomerization reactions, but the low T_g average value obtained indicated that the polymers were not stiff material. The comparison between α_C and τ of the different polymers showed that τ was always higher than α_C.

In conclusion, this preliminary work showed that $AlCl_3$ lot and its aging had a little influence if any on polymerization. The variations of the insoluble fraction and number-average molecular weights were assigned to the homogeneity of the polymerization medium and to cross-linking reactions.

Table 3. Influence of Different Alkane Solvent on the Pentadiene Polymerization[a]

solvent	ϵ[b]	tot. yield (%)	IF (%)	$\overline{M}_n$[c] (g/mol)	I_p[c]	α_H[d]	α_C[d]
pentane	1.844	78	45	10 400	10.3	0.39	0.32
hexane	1.890	65	54	8200	7.1	0.39	0.32
heptane		61	64			0.40	
decane	1.991	43	56	8200	5.7	0.38	

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, $T = 20$ °C, $t = 2$ h, deactivation by $BuNH_2$. [b] Dielectric constant at 20 °C. [c] Determined by SEC (polystyrene standard). [d] Relative unsaturation losses determined by ^1H or ^{13}C NMR.

Influence of Solvent. As mentioned above, the cationic polymerization of 1,3-pentadiene is very sensitive to the solvent and in particular to its polarity. In this work, different alkanes (pentane, hexane, heptane, and decane), of similar polarity, were examined as polymerization solvents. The results listed in Table 3 showed that the higher the molar mass of the solvent, the lower the total yield. Indeed, a significant and progressive decrease of the conversion was observed. The total yield decreased from 78% to 43% when changing from pentane to decane. It is unlikely that these variations result from the difference of polarity, since there is only an increase of 0.147 of the dielectric constant value passing from pentane to decane. The suggested assumption to explain these observations lies in the difference of macromolecular chains and Lewis acid solubility in these different solvents even though there was no noticeable visual difference. A better solubilization of $AlCl_3$ in the polymerization medium could increase its efficiency and thus the yield. The insoluble fraction varied also according to the solvent used. However, the variation of this characteristic is so important for a given solvent (see Table 1), so that it is not reasonable to comment on this point in relation with the change of solvent.

The nature of the alkane seemed to have no influence on the existence and the relative proportion of cyclization and isomerization reactions, which suggested no significant modification of the active center structure in these four solvents (no variation of α_H and α_C).

In the literature, Fodor,[7] Puskas,[8] and Paulo[9] reported different behaviors in hexane (Hx) and methylcyclohexane (MeCHx) for the cationic polymerization of isobutylene. Indeed, the polymerization rate was found lower in methylcyclohexane. After further investigations, the authors showed that these variations did not result from differences in polarity ($\epsilon_{MeCHx} = 2.0240$ and $\epsilon_{Hx} = 1.8865$) but instead resulted from the presence of carbonyl impurities contained in higher quantity in methylcyclohexane. Therefore, in our case, we verified by IR spectroscopy that no such impurity was present in the different nonpolar solvents used.

Influence of Monomer Composition. Study of the Polymerization Yields. The polymerization of the pure 1,3-pentadiene isomers (cis and trans) has been studied in different papers.[5,6] Several catalyst systems were investigated and the higher reactivity of the trans isomer was shown. In previous works, we also showed that monomer concentration is an important factor in the PD polymerization, since the cross-linking reaction is strongly favored by a concentrated medium. Thus, a monomer concentration lower than 0.5 mol/L must be used in order to limit the formation of insoluble polymer. However, at this concentration, the polymerization rate was rather low. In this paper, the influence of the monomer composition on the different mechanisms and in particular on the side reactions involved in the PD polymerization is examined. The polymerizations of each pure isomer and of the isomers mixture in the proportion 66% trans and 34% cis were achieved in pentane at a concentration of 1.6 mol/L (Table 4).

Table 4. Influence of Monomer Composition

	monomer composition (%)		yields (%)						
run[a]	cis	trans	tot.	cis	trans	IF	$\overline{M}_n$[d] (g/mol)	I_p[d]	f_{Cl}[e]
1[b]	0	100	97	0	97	56	5600	13.7	0.32
2[c]	34	66	72	56	80	60	7000	10.9	0.33
3[b]	100	0	18	18	0	86	1000	21.8	–

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, pentane, $T = 20$ °C, $t = 2$ h. [b] Deactivation by $BuNH_2$. [c] Deactivation by nonylamine. [d] Determined by SEC (polystyrene standard). [e] Chlorine functionality.

In the isomers mixture polymerization, the residual isomer molecules were cryodistilled from the polymerization medium after deactivation of the active centers by addition of nonylamine after 2 h of reaction and were analyzed by quantitative ^{13}C NMR. This heavy amine was added instead of the usual *n*-butylamine because the latter has a too low boiling point temperature (63 °C) and would be extracted with the residual monomers. The boiling point of nonylamine being 201 °C, it remains with the polymer in the reactor. This analysis, which was possible because of an incomplete polymerization yield (72%), provided the polymerization yields in trans and cis isomer.

The comparison of the pure isomer polymerizations clearly showed the highest reactivity of the *trans*-1,3-pentadiene, as mentioned in the literature, the yield of the trans isomer polymerization after 2 h of reaction being 97% whereas it was equal to 18% for the cis isomer under the same conditions. Comparing the three experiments, it was observed a linear increase of the total yield with the initial content of *trans*-1,3-pentadiene in the medium polymerization. These results cannot be explained by some variations of termination reactions, the extent of which would vary according to the monomer composition used, since the chlorine content of the polymer remained constant (not determined in run 3, Table 4, because of the too low yield). The assumed termination is the reaction with the counterion $AlCl_4^-$ since it was shown that the initiation step occurred via a direct mechanism.[1]

In the polymerization of the mixture of the two isomers, if one calculates a yield from the initial monomer composition linearly combining the yields obtained in the polymerization of each isomer, the yield would be equal to $(0.34 \times 0.18 + 0.66 \times 0.97)$, i.e., 70%. As the experimental percentage was 72%, it could be concluded that the two isomers behaved similarly, being alone or in the presence of the other isomer. However, this conclusion is too straightforward and the two isomers have to be considered separately. Indeed, the evolutions of each isomer consumption vs their initial proportion in the monomer mixture revealed a different behavior of the two isomers when they are polymerized together. The consumption of the trans isomer increased with its initial fraction, whereas the consumption of cis monomer reached a maximum (56%) in the case of the mixture polymerization and was only 18% when polymerized alone. The insertion of cis monomer in the growing macromolecular chain was therefore favored by the presence of the other isomer in the polymerization

Table 5. Linear Units Microstructure

run[a]	pentadiene cis/trans	% 1,4-*trans*[b]	% 1,2-*trans*[c]	% 1,4-*cis*[d]	% 1,2-*cis*[d]	% 3,4[d]
1	0/100	47	13	0	0	0
2	34/66	31	16	4	3	3
3	100/0	41	4	6	8	5

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, $T =$ 20 °C, $t = 2$ h. [b] IR–RMN ^{13}C. [c] RMN ^{13}C. [d] IR.

medium. If its behavior was independent of the trans isomer, a consumption equal to $0.34 \times 0.18 = 6\%$ would be expected in run 2, whereas the experimental one was 56%. In the same way, the trans monomer consumption expected in the mixture polymerization could be calculated and would be equal to $0.97 \times 0.66 = 64\%$. The experimental yield being in this case 80%, the trans monomer polymerization was thus also favored, although this increase was smaller than in the case of the cis monomer.

In the literature[5] it is reported that in the trans isomer polymerization the active center reacts with the monomer rather than with a polymer chain, contrary to the cis monomer. Indeed, some experimental conditions allow the synthesis of entirely soluble polymer from trans monomer, whereas these same conditions can result in the formation of cross-linked chains in the case of the cis isomer. This difference was observed either at the beginning of the polymerization or when the yield became high. In our case, the comparison of the insoluble fraction obtained from each pure isomer showed that cis 1,3-pentadiene induced more cross-linking (IF = 86% for the cis compound and IF = 56% for the trans one). Moreover the results show a relatively good linear correlation between the insoluble fraction and the initial cis fraction in the polymerization medium (Table 4).

Study of the Soluble Polymer Microstructure. The linear microstructure of the polypentadienes was studied by IR and quantitative ^{13}C NMR as described above. The results listed in Table 5 show that the isomer configuration influenced the linear microstructure of the polymers. In the case of the polymerization performed with the trans isomer, the polymer was exclusively composed of linear units (1,4+1,2)-trans, whereas the polymers synthesized with the cis monomer or from the isomer mixture contained (1,4+1,2)-trans, (1,4+1,2)-cis, and 3,4 units, indicating that the cis isomer was responsible for the production of the 3,4, 1,4-cis, and 1,2-cis linear units. This point was already described in the literature,[5,6] but this study showed an approximately linear correlation between the 3,4 and (1,4+1,2)-cis units and the quantity of cis isomer introduced in the polymerization medium (Figure 3).

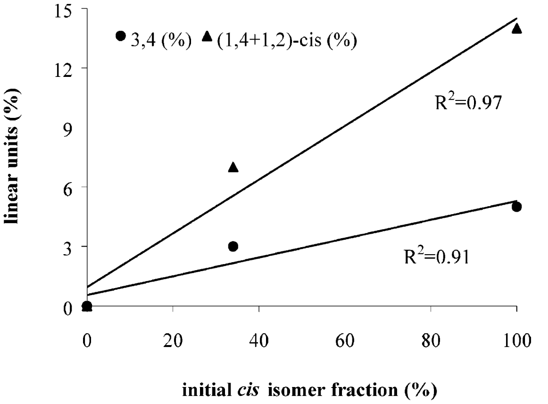

Figure 3. Influence of the cis isomer on the 3,4 and (1,4+1,2) cis units contents in the polymers.

Table 6. Chemical Shifts (in ppm) of the 1,3-pentadiene Isomers in ^{13}C NMR[a]

	$C_1{=}C_2{-}C_3{=}C_4{-}C_5$				
isomer	C_1	C_2	C_3	C_4	C_5
cis	116.36	132.17	130.50	126.47	13.14
trans	114.21	137.43	132.80	129.51	17.71

[a] In $CDCl_3$.

Table 7. Influence of the Initial Monomer Composition on Cyclization and Double Bond Isomerization

run[a]	pentadiene cis/trans	α_H[b]	α_C[b]	τ[c]	α_C/α_H
1	0/100	0.36	0.24	0.40	0.67
2	34/66	0.40	0.31	0.44	0.78
3	100/0	0.35	0.19	0.35	0.54

[a] $[AlCl_3] = 2.3 \times 10^{-2}$ mol/L, [1,3-pentadiene] = 1.6 mol/L, $T =$ 20 °C, $t = 2$ h, pentane. [b] Relative unsaturation losses determined by ^{1}H or ^{13}C NMR. [c] Cyclization degree determined by IR.

According to Higashimura,[10] the difference of reactivity between the two isomers is to be owed to the highest electronic density of the carbon C_1 in the trans structure. Table 6 gives the chemical shifts of the two isomers obtained in ^{13}C NMR in $CDCl_3$. In agreement with Higashimura, the carbon C_1 had a weaker chemical shift in the trans monomer. The presence of 3,4 units contained in the polymers synthesized from the cis isomer can be also explained by comparing the chemical shifts of the C_4 carbon in the two isomers. The C_4 chemical shift of the cis isomer was lower than that of the trans isomer, which suggested a higher reactivity of cis monomer C_4 and therefore a better ability to generate the 3,4-addition for this monomer. However, considering both cis and trans isomers, the chemical shift of the carbon C_1 is lower than that of the carbon C_4, the difference being above 10 ppm. Whatever the considered isomer, the 1,2- and 1,4-additions remain strongly favored with regard to 3,4-addition in the polymerization of 1,3-pentadiene, according to the above explanation.

This study suggests a final comment. Considering the different contents in linear units of the polymers (reported in Table 5), it can be said that the cis/trans isomerization occurs at the level of the active centers and not in the polymer after propagation. If the isomerization occurred in the polymer chain (involving sequences of proton addition and elimination), the proportion of cis and trans units would be constant whatever the monomer composition used. The isomerization of the active center is kinetically and not thermodynamically controlled. In conclusion, there are in the polymerization medium two kinds of active centers, the one resulting from cis isomer able to be isomerized in trans configuration and the trans one undergoing no isomerization reaction. Then the two active centers would react with the two monomers, the observed effect of synergism between the two monomers being assigned to the copolymerization of the two isomers.

– Study of Cyclization and Double Bond Isomerization Reactions. The cyclization and isomerization reactions were investigated by studying the relative unsaturation losses of the soluble polymers determined by ^{1}H and ^{13}C NMR (Table 7). The comparison of the α_C of the polymers synthesized from each single isomer shows that the unsaturated carbons loss is higher in the case of the trans monomer. Thus, the latter would induce more cyclization. As for α_H, it was similar in the two experiments, which means that the isomerization ratio is lower in the polymerization of trans monomer. The ratio α_C/α_H indicating the importance of the cyclization reactions relative to isomerization, it could be noted that the proportion of cyclic units was higher in the mixture polymerization. Therefore, these side reactions would be influenced by the initial monomer composition and an effect of synergism was again observed. However, whatever the composition used, the cyclization reactions remained the more important ones ($\alpha_C/\alpha_H > 0.5$).

In conclusion, this survey shows that the polypentadienes microstructure is sensitive to the cis/trans isomers proportion and two qualitative tendencies could be clearly underlined. The cis isomer would favor the cross-linking reactions and double bond isomerization, whereas the trans isomer would induce more cyclization. However, the mixture of the two isomers did not follow a linearly correlated behavior which was assigned to an effect of isomers copolymerization.

Origin of the Insoluble Fraction. The formation of the cross-linked polymer is a main characteristic of the cationic diene polymerization. It obviously shows the absence of control of the polymerization, and it is a drawback because of the loss of polymer (only the soluble polymer is useful). The determination of the origin of the insoluble fraction would be a first step toward its elimination in the future.

To our best knowledge, there is no elemental or structural characterization of the insoluble polymer in the literature, whatever the diene investigated. Thus, elemental maps of Al, Cl, and C corresponding to the same area of a cross-linked polymer (polymer synthesized in pentane according to the usual procedure) were carried out by using NMA (Figure 4, parts a–c). The different colors contrasts represent the elemental concentrations variations of the map and the intensities corresponding to the signals (Al, Cl, or C) can be seen on the right side of the map. These three elemental maps first reveal a heterogeneity of the insoluble fraction. Second, aluminum and chlorine distributions are well correlated but strictly anticorrelated to carbon. These NMA results about the heterogeneous constitution of the insoluble polymer give information about its origin. A straightforward explanation of these observations is that the cross-linked chains would be formed at the surface of the insoluble Lewis acid entrapped in the bulk of the polymer. The concentrations of Al, Cl, and C were quantified in the areas with high and low contents, which gives a quantitative appreciation of the elemental heterogeneities (Table 8).

Table 8. Content of Aluminum, Chlorine, and Carbon Atoms in the Mapping of Insoluble Polymer

polymer contents	aluminum[a] in ppm	chlorine[a] in ppm	carbon[b] in %
insoluble	Al < 53291	25730 < Cl < 113858	48.4 < C < 77.7
soluble	nd[c]	181	88.4

[a] Determined by atomic interaction: particle induced X-ray emission (PIXE). [b] Determined by nuclear reaction analysis (NRA). [c] No determined.

Similar NMA elemental maps of Al, Cl, and C made by using the same experimental approach (scanned polymer surface: 500 μm × 500 μm) for the soluble chains of the same polymer were also realized. As seen in Figure 5, parts a–c, the soluble fraction of the polymer was homogeneous and the Cl content was not correlated to the Al one, as in the case of the insoluble fraction. The Al content was in too small quantity to be quantified (inferior to the detection limit of PIXE). Here, the presence of Cl in the polymer (181 ppm) would result from reaction of the active species with the counterion.

These NMA elemental maps demonstrate that the cross-linked polymer comes from the partial insolubility of the catalyst in the polymerization medium. This observation is in tune with results already published by Peng et al.[17] showing that a ratio of [toluene]/[$AlCl_3$] of 10 is sufficient to dramatically decrease the cross-linked polymer content. The reason for that is the well-known solubility of complexes of aromatic compounds with $AlCl_3$. Of course, the transfer reaction also mentioned by these authors can contribute to the elimination of cross-linking. This is the reason an insoluble fraction is always observed in the apolar solvents which are not susceptible to aromatic electrophilic substitution. Indeed, a second origin of the cross-linked chains had to be considered, examining all the polymers previously described above using the different alkanes. A linear decrease of the number-average molar masses of the soluble chains with the insoluble fraction was observed (Figure 6). So, the higher the IF, the lower $\overline{M}_n$. It means that the cross-linked chains were partly due to intermolecular reactions and the higher the molar mass the higher the chance to be incorporated in the gel. It was also noted a weak decrease of the polydispersity index with IF, due to the progressive disappearance of the chains with the highest molar mass. This correlation was observed whatever the nonpolar solvent used and must be considered as a general rule between IF and $\overline{M}_n$ of the soluble chains

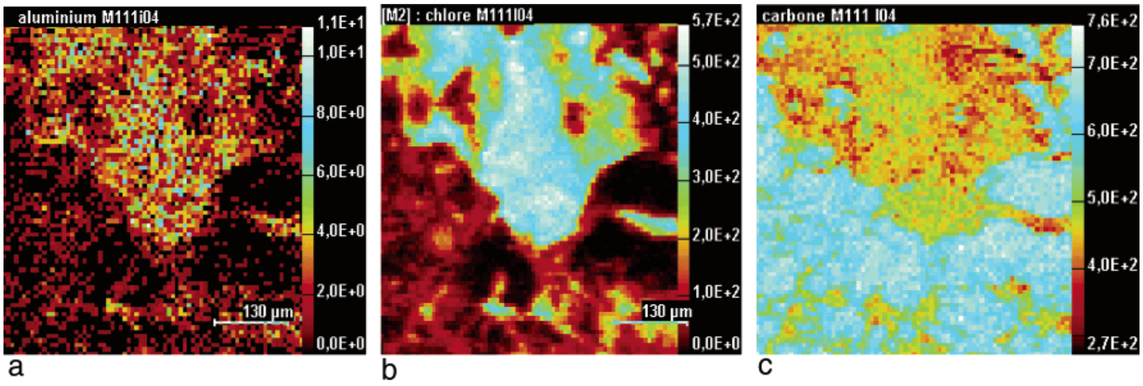

Figure 4. (a) Al, (b) Cl, and (c) C NMA elemental maps of a surface (500 μm × 500 μm) of a cross-linked polypentadiene.

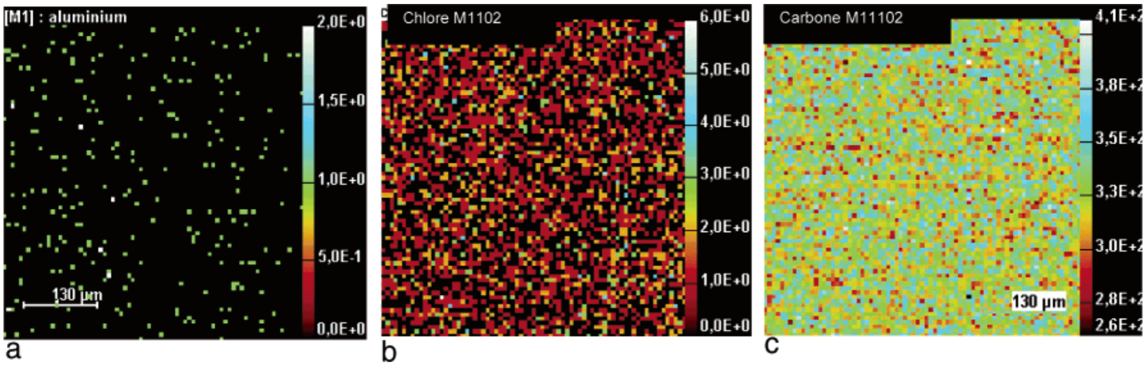

Figure 5. (a) Al, (b) Cl, and (c) C NMA elemental maps of a surface (500 μm × 500 μm) of a soluble polypentadiene.

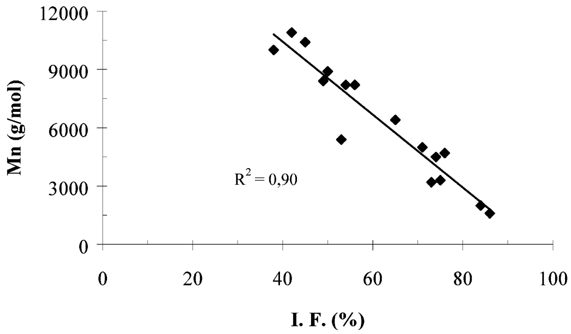

Figure 6. Correlation between the molar mass of the soluble chains and IF

in the 1,3-pentadiene cationic polymerization. Although this polymerization has been studied for a long time, this point was never mentioned. The fair integration of all the polymers within the general rule was confirmed by achieving other polymerizations in hexane.

The intermolecular reactions, responsible for the insoluble polymer production, generated first branched chains by reaction of the active center of one chain with a double bond of a second chain. The cross-linking occurred after that more than two sites were involved in a macromolecule. The double bond involved in these mechanisms might come from a linear unit (disubstituted double bond) or from a tri- or tetrasubstituted

Table 9. Influence of DMB on the 1,3-Pentadiene

run[a]	[DMB]/ [AlCl$_3$]	total yield (%)	IF (%)	$\overline{M_n}$[b] (g/mol)	I_p[b]	α_H[c]	α_C[c]	Cl content[d]
1	0	75	53	5400	14.5	0.43	0.32	<0.2
2	0	78	45	10 400	10.3	0.39		0.10
3	1	83	46	5200	16.5	0.44	0.35	0.16
4	7	87	52	3400	12.2	0.49	0.41	0.08

[a] [AlCl$_3$] = 2.3×10^{-2} mol/L, [1,3-pentadiene] = 1.6 mol/L, T = 20 °C, t = 2 h, deactivation by BuNH$_2$. [b] Determined by SEC (polystyrene standard). [c] Relative unsaturation losses determined by ^{1}H or ^{13}C NMR. [d] Percentages by weight.

double bond. The trisubstituted one could result from a double bond isomerization or a branching reaction followed by a deprotonation. The former could be induced by a cyclization reaction due to a H$^+$ transfer followed by an isomerization and deprotonation.[2] To show that the active center reacted easily with a di-, tri-, or tetrasubstituted double bond, copolymerizations with a hindered olefin were realized. The olefin investigated in this study was a tetrasubstituted one: 2,3-dimethyl-2-butene (DMB). We already reported that a trisubstituted olefin such as 2-methyl-2-butene was incorporated in the polymer when PD was polymerized in its presence and behaved as a transfer agent.[2] Different polymerizations were performed with increasing DMB concentration (Table 9). The ^{1}H and ^{13}C NMR analysis of the polymer synthesized with the highest

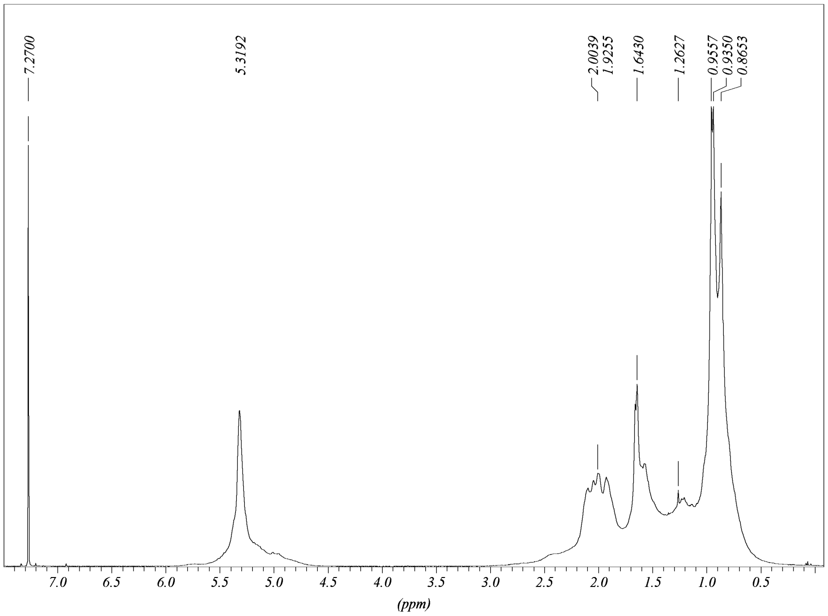

Figure 7. ^{1}H NMR of a copolymer PD/DMB.

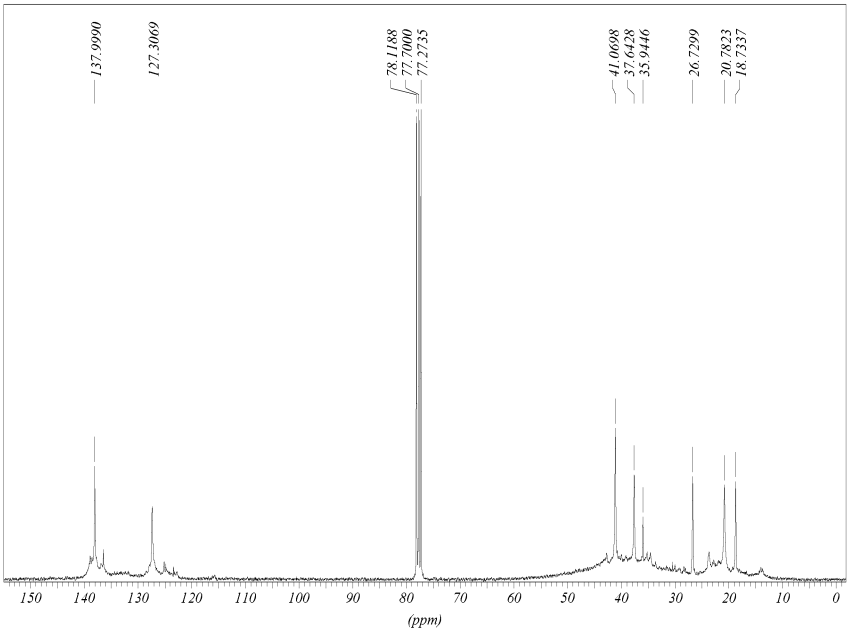

Figure 8. ^{13}C NMR of a copolymer PD/DMB.

[DMB] (run 4) clearly showed the incorporation of the olefin in the polymer. Run 3 realized with a too low DMB concentration did not allowed to conclude. In the ^1H NMR spectrum of the former polymer (Figure 7), a new signal at 0.87 ppm was easily observed, which was attributed to the saturated CH_3 of the olefin units. In the same way, two new signals appeared in the ^{13}C spectrum of the polymer at 26.73 and 35.94 ppm, which were respectively assigned to the methyl groups and the quaternary carbons of the polymerized olefin (Figure 8). Indeed, these chemical shifts are close to the ones of 2,2,3,3-tetramethylbutane. In agreement with the assumption of the incorporation of the olefin in the polymer, α_H and α_C increased. In conclusion, these results show that the active centers in the PD cationic polymerization can react with a hindered double bond.

Although no signal belonging to the initial olefin was clearly noted at 1.64 ppm for the CH_3 in ^1H NMR and at 123.5 ppm for the unsaturated carbons in ^{13}C NMR, it was difficult to conclude on the complete incorporation of DMB in the polymer. Indeed, the polymer was dried under vacuum and since the olefin boiling point is only 73 °C under atmospheric pressure, the latter could be eliminated during the drying step of the polymer. The yields reported in Table 9 were calculated assuming a total incorporation of the olefin. They were a little higher (about 10%) than for the polymerization performed only with 1,3-pentadiene (runs 1 and 2). Like 2-methyl-2-butene, DMB seemed to behave as a transfer agent, since $\overline{M}_n$ decreased with increasing DMB concentration.

Conclusions

This study allowed us to show that the PD cationic polymerization was not influenced by the lot and the aging of $AlCl_3$ but was very sensitive to the monomer composition and to the used nonpolar solvent. For example, the highest yield was obtained in the alkane with the lowest molecular weight, and it was noted that the cis isomer would favor the cross-linking reactions and double bond isomerization, whereas the trans isomer would induce more cyclization.

An important point of this work is the investigation of the cross-linked polymer showing its double origin: the heterogeneity of the polymerization medium (due to a partial solubilization of the Lewis acid) and intermolecular reactions occurring on the chains with the highest $\overline{M}_n$. This work confirms that the polymer must be prevented to react with the active species in order to get a controlled system.

References and Notes

(1) Duchemin, F.; Bennevault-Celton, V.; Cheradame, H.; Macedo, A. *Macromol. Chem. Phys.* **1998**, *199*, 2533−2539.
(2) Duchemin, F.; Bennevault-Celton, V.; Cheradame, H.; Merienne, C.; Macedo, A. *Macromolecules* **1998**, *31*, 7627−7635.
(3) Peng, Y. X.; Liu, J. L.; Cun, L. F.; Dai, H. S. *Polym. Bull. (Berlin)* **1995**, *35*, 393−397.
(4) Hasegawa, K. I.; Asami, R.; Higashimura, T. *Macromolecules* **1977**, *10*, 592−599.
(5) Denisova, T. T.; Lisvshits, I. A.; Gershtein, Y. R. *Polym. Sci. USSR* **1974**, 1017−1023.
(6) Vautrin-Ul, C.; Pla, F. *Macromol. Symp.* **1997**, *119*, 197−205.
(7) Fodor, Z.; Faust, R. *J. Macromol. Sci.—Pure Appl. Chem.* **1998**, *A35* (2), 375−394.
(8) Puskas, J. E.; Lanzendörfer, M. G. *Macromolecules* **1998**, *31*, 8684−8690.
(9) Paulo, C.; Puskas, J. E.; Angepat, S. *Macromolecules* **2000**, *33*, 4634−4638.
(10) Higashimura, T.; Yamamoto, K. *Makromol. Chem.* **1974**, *175*, 1139−1156.
(11) Beebe, D. H.; Gordon, C. E.; Thudium, R. N.; Throckmorton, M. C.; Hanlon, T. L. *J. Polym. Sci.: Polym. Chem. Ed.* **1978**, *16*, 2285−2301.
(12) Mercier, F.; Moulin, V.; Guittet, M. J.; Barré, N.; Toulhoat, N.; Gautier-Soyer, M.; Toulhoat, P. *Radiochim. Acta* **2000**, *88*, 779.
(13) Mercier, F.; Moulin, V.; Barre, N.; Casanova, F.; Toulhoat, P. *Anal. Chim. Acta* **2001**, *427*, 101.
(14) Amirikas. Jamieson, D. N.; Dooley, S. P. *Nucl. Instrum. Methods Phys. Res.* **1993**, *B77*, 110.
(15) Trocellier, P.; Toulhoat, N.; Mercier, F.; Courel, P. *Nucl. Instrum. Methods Phys. Res.* **1993**, *B83*, 545−551.
(16) Daudin, L. 2000. Personal communication.
(17) Peng, Y. X.; Liu, J. L.; Cun, L. F.; Dai, H. S. *Polym. Bull. (Berlin)* **1995**, *35*, 393−397.

MA020921P