Macromolecules **1980,** *13,* 1104–1110

On the Cationic Polymerization of Olefins and the Structure of the Product Polymers.[1] 3. Polypropylene[2]

G. Ferraris, C. Corno, A. Priola, and S. Cesca*

Assoreni, Polymer Research Laboratories, San Donato Milanese, 20097 Italy.

Received November 6, 1979

ABSTRACT: The structure of cationic polypropylene obtained both from natural-abundance ^{13}C monomer and from monomers selectively enriched with ^{13}C in positions 1, 2, and 3 was studied through ^{13}C NMR spectroscopy. The presence of methyl, ethyl, *n*-propyl, *n*-butyl, isopropyl, *gem*-dimethyl, isobutyl, and *tert*-butyl groups was ascertained in samples obtained under different conditions. The content of the branched groups increased with the oligomerization temperature and the monomer conversion. The study showed that appreciable amounts of 1,3 enchainment of the monomer are ruled out and the irregular tail-to-head addition is of small importance. The formation of the linear groups is accounted for by 1,2-hydride and -methide shifts, while some branched groups can arise through protonic initiation followed by classical cationic rearrangements. Other unusual rearrangement mechanisms must operate if experimental results are to be explained. These possibilities are discussed in light of current views on carbenium ion chemistry.

In previous work we have shown that ^{13}C NMR spectroscopy provides detailed information on the structure of cationic polyolefins, i.e., poly(1-butene)[1] and poly(4-methyl-1-pentene),[4] which usually cannot be achieved through other spectroscopic investigations. When the olefin is linear the resulting polymer displays a very complicated structure[1] because of the lack of preferred rearrangements which, conversely, occur when the monomers contain tertiary[4,5] or quaternary[6,7] carbon atoms. However, the structure of cationic poly(1-butene) (PB1) can still be described in terms of "structural units" which are mainly formed through classical intramolecular hydride and methide shifts. Cationic polypropylene (PP) is much more complicated than PB1 since structural groups containing more than three carbon atoms are present in it and hence the concept of a structural unit is lost. Furthermore, some structural groups may arise only through unusual rearrangements. This situation accounts for the inadequacy of previous investigations on PP which were carried out mainly through IR spectroscopy.[8–11]

Very recently, it has been confirmed by means of spectroscopic and chemical analyses that PP contains ethyl, *n*-propyl, and *vic*- and *gem*-dialkyl groups as well as different types of unsaturation.[12]

In the present paper we describe the ^{13}C NMR study of the structure of PP carried out by preparing and polymerizing the monomer selectively enriched with ^{13}C in positions 1, 2, and 3 in order to improve knowledge of the structure and reaction mechanisms involved in the synthesis of PP. A similar approach has been adopted also for confirming some previous findings obtained during the polymerization of 1-butene.[1]

Experimental Section

Reagents. Propylene (Phillips, polymerization-grade product; purity 99.5% (VPC), the remaining products being ethane (0.1%), propane (0.2%), and isobutane (0.2%)) was dried by passing it through a 1-m column filled with activated molecular sieves (4A type). Solvents and catalyst components were purified, dried, and handled as reported elsewhere.[1,4]

Synthesis of $CH_2{=}CH{-}^{13}CH_3$. The preparation was carried out by using $^{13}CH_3I$ (Prochem product; ^{13}C enrichment 90%) and through the reaction scheme

$$CH_2{=}CHMgBr + {}^{13}CH_3I \rightarrow CH_2{=}CH{-}{}^{13}CH_3 + MgBrI$$

Vinylmagnesium bromide was prepared according to Normant[14] as a tetrahydrofuran (THF) solution which was filtered (sintered glass filter). The excess of vinyl bromide was vented and the solution titrated (1.5 M). Forty millimoles of this solution was introduced under an inert atmosphere into a three-necked round-bottom flask equipped with a magnetic stirrer, dropping funnel, and an efficient condenser which was connected with a trap cooled at −78 °C for collecting volatile products. A solution of 40 mmol of $^{13}CH_3I$ in 5 mL of THF was slowly added to the vinylmagnesium bromide solution which was stirred and maintained at 40–50 °C with a heating bath. The solutions were allowed to react for 2 h after mixing. During this interval 1.2 mL of liquid was collected in the trap. It showed the following composition by VPC analysis (column, EAS 10%, 5 m; T_c = 60 °C, T_e = 180 °C; carrier, He, 60 mL/min): 77% propylene (by area), 7% CH_3I, 1% CH_3Br, 15% THF. ^{13}C NMR analysis confirmed that propylene was selectively enriched in position 3 (methyl). The reaction product was dissolved in 6 mL of *n*-pentane and chilled at −78 °C, and a small molar excess of $AlEt_3$ with respect to THF was added. After complexation of the ether, the reaction mixture was maintained at −20 °C and gently distilled in vacuo through a trap cooled with liquid N_2. The condensed product was shown by VPC analysis to be a mixture of *n*-pentane, propylene, CH_3I, and CH_3Br in the ratios reported above. This solution of propylene, completely free from THF, was used for polymerization experiments (see below) without further purification.

$CH_2{=}^{13}CH{-}CH_3$. This was a commercial sample (Merck Sharp and Dohme), 90% enriched with ^{13}C in position 2, and was contained (100 mL of gaseous product) in a vial equipped with a break seal. The vial was connected by means of a manifold to a vacuum line which, in turn, was joined through a flexible steel tube to a small stainless steel autoclave (capacity 50 mL) where polymerization experiments were performed after condensation (at −78 °C) of the monomer (no preliminary purification was used).

$^{13}CH_2{=}CH{-}CH_3$. This was kindly supplied by Professor A. Zambelli.[15] The labeling reagent ($^{13}CH_3I$ from Prochem) was used in the reaction scheme

$$P(C_6H_5)_3 + {}^{13}CH_3I \rightarrow (C_6H_5)_3\overset{+}{P}{}^{13}CH_3\overset{-}{I} \xrightarrow[THF]{LiC_6H_5}$$
$$(C_6H_5)_3P{=}{}^{13}CH_2 \xrightarrow[THF]{CH_3CHO} (C_6H_5)_3PO + {}^{13}CH_2{=}CH{-}CH_3$$

The purity of the monomer was 99% (VPC; column, Poropack, 3 m; T_c = 100 °C) and ^{13}C NMR analysis confirmed the selective enrichment of position 1. Other experimental details are reported elsewhere.[15]

Polymerization of ^{13}C-Enriched Propylenes. Polymerization experiments carried out at 20 and 70 °C were performed in a stainless steel autoclave (capacity 50 mL) equipped with a magnetic stirrer and a thermocouple. The monomer (ca. 5 mmol), solvent (*n*-pentane, 10 mL), and cocatalyst (0.5 mmol of isopropyl chloride) were introduced in the autoclave at −78 °C and, after the chosen temperature was reached, the catalyst ($EtAlCl_2$, 0.5 mmol in 5 mL of *n*-pentane) was introduced by means of N_2 overpressure. The reaction time was usually 30 min. Experiments at −78 °C were carried out in glass equipment similar to that used in previous investigations,[4] adopting the general procedure de-

0024-9297/80/2213-1104\$01.00/0

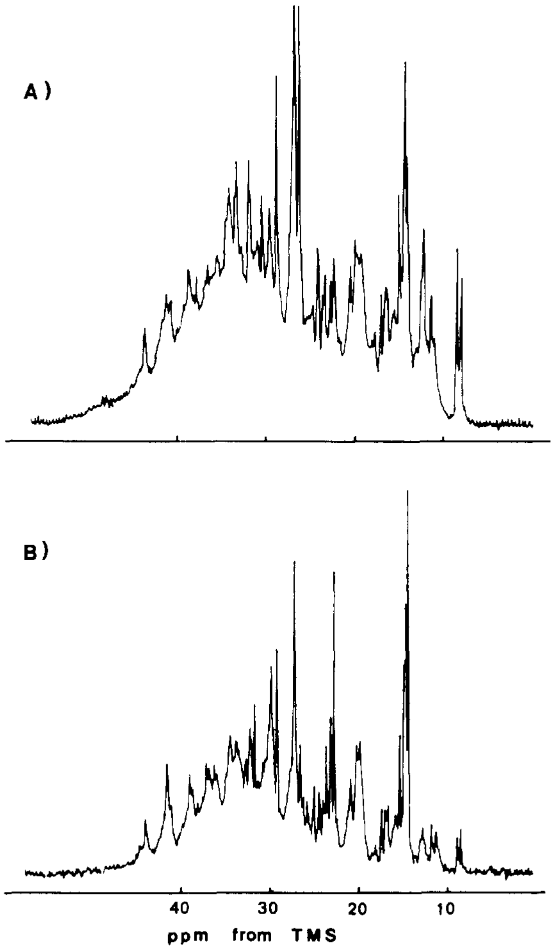


Figure 1. (A) ^{13}C NMR spectrum of cationic polypropylene (PP). (B) ^{13}C NMR spectrum of cationic poly(1-butene) (PB1).

scribed above. Monomer conversions were almost quantitative in each experiment, either at high or low temperature.

Polymerization of Propylene Having Natural ^{13}C Abundance. Experiments at temperatures below -20 °C were carried out in glass equipment under a dry N_2 atmosphere as described previously.[4] When the polymerization temperature was higher than -20 °C, a stainless steel autoclave was used as reactor.[1] Other experimental details are reported in Table III. Both low and high conversions were obtained by using an appropriate catalyst concentration.

Analyses. Analyses of the polymers were carried out as described elsewhere.[1] ^{13}C NMR spectra were recorded with a Varian FT XL-100-15 instrument, according to conditions reported previously.[1,4]

Results and Discussion

^{13}C NMR Investigations on PP Obtained from Natural-Abundance ^{13}C Monomer. Figure 1A shows the ^{13}C NMR spectrum of a typical sample of PP synthesized at 70 °C with catalyst $EtAlCl_2 + i\text{-}C_3H_7Cl$ in *n*-pentane. The spectrum is analogous to that of cationic PB1 (Figure 1B) prepared under similar conditions. All the signals evident in Figure 1B are also observable in the spectrum of PP, but their respective intensities differ. Table I lists the chemical shifts and the assignments of the methyls belonging to the identified structural groups.[16] An inspection of Table I shows the presence of unit D arising from the regular 1,2 addition of propylene and also some units deriving from single (unit A) or multiple hydride shifts (units A′, B, B′, D′, and C) subsequent to the regular addition of the monomer.

Table I
Methyl Assignments in the ^{13}C NMR Spectrum of PP Obtained from Natural-Abundance ^{13}C Monomer

structural group		chem shift, ppm
type	name	
$>\!\!C-CH_2-CH_3$	A′	8-9
$>CH-CH_2-CH_3$	A	10-12
$-CH_2-CH_2-CH_2-CH_3$	C	14.1
$>\!\!C-CH_2-CH_2-CH_3$	B′	14.5-15
$>CH-CH_2-CH_2-CH_3$	B	
$-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-CH<$	D	15-17
$-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-CH_2$		19-20
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH<$	H	19-20
$-CH_2-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-CH_2-$	E	27.4
tert-butyl	F	29.5

Chart I
Schematic Representation of Possible Intramolecular Rearrangements Leading to Seven Structural Groups Identified in Cationic PP

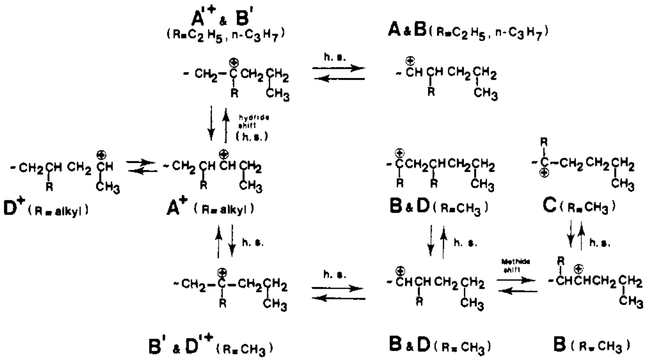


Chart I summarizes the reaction schemes which may explain the formation of these units through intramolecular rearrangement.[17] As pointed out in the case of PB1,[1] intermolecular rearrangements may also account for the structural groups of Table I. The presence among them of significant amounts of branched groups E, F, and H suggests that additional reactions take place during the synthesis of PP. Some of the constitutional groups listed in Table I were previously identified by means of IR studies.[8-11] Their formation was sometimes accounted for by invoking the 1,3 enchainment of the monomer and its unusual tail-to-head addition,[18] besides hydride and methide shifts typical of the cationic polymerization of olefins. However, no direct evidence of these unusual mechanisms was given. Therefore, in order to check the existence of the mechanistic possibilities mentioned above, we have undertaken the polymerization of propylene selectively enriched with ^{13}C in each position of the molecule.

^{13}C NMR Investigations of PP Synthesized with ^{13}C-Enriched Monomers. Since the identification of the structural groups of PP was done in general through the methyl resonances, the first polymer studied was enriched in the CH_3 position.

$CH_2{=}CH{-}^{13}CH_3$. Figures 2 and 3A show the spectra of two polymers prepared at -78 and +70 °C, respectively. They are much simpler than the spectrum of Figure 1A. In particular, the broad band between 20 and 45 ppm in Figure 1A and due to the signals of carbons belonging to the polymer backbone is completely missing. Both Figures

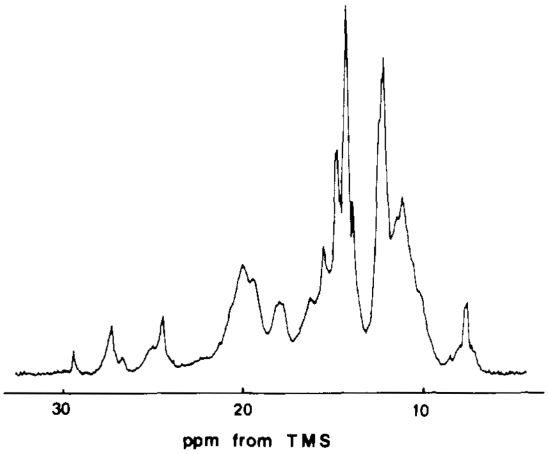
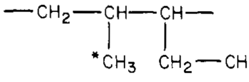


Figure 2. ^{13}C NMR spectrum of PP obtained at -78 °C from $^{13}CH_3$-enriched monomer.

2 and 3A show all the signals identified and assigned in Table I to methyls in various environments. Besides the resonances listed in Table I there are additional signals of low-to-medium intensity at 30.1, 25.2, 24.6, 24.1, and 22.7 ppm.

Selective decoupling experiments suggested that all these signals arise from methyl carbons. In fact, irradiation at 87 Hz (this frequency corresponds to the maximum absorption for methyl protons in the ^{1}H NMR spectrum) yielded singlets (Figure 3B). On the other hand, irradiation at 130 Hz (frequency typical of methylene and methine protons) produced signals which were split (Figure 3C). Therefore, no methyl group originally present on the monomer is transformed during the polymerization process into any methylene, methine, or quaternary carbon. This finding rules out the existence in the samples studied of any appreciable amount of 1,3-enchained propylene.[10] The signal occurring at 24.6 ppm (rather strong) may be assigned to *gem*-dimethyl groups linked to tertiary carbons, whose vicinity appears unfavored for steric hindrance, or, more probably, to the methyl of the 1,2 unit when it is bonded to a quaternary carbon (unit D′; see subsequent reaction scheme 2). The same possibility exists for the weak peaks observed at 25.2 and 24.1 ppm. The resonance observed at 22.7 ppm is typical of the isobutyl group which was previously identified in PB1[1] (where this structure was named G), while the weak peak at 30.1 ppm should be assigned to the *tert*-butyl group having an additional δ substitution relative to the peak at 29.5 ppm.

In conclusion, the analysis of the polymer obtained from the $^{13}CH_3$-enriched monomer indicates clearly the absence of appreciable amounts of 1,3 enchainment and identifies a new structural group (unit G) and the peaks of unit D′. However, no information about the irregular tail-to-head monomer addition was obtained. In fact, the signals occurring between 15 and 17 ppm, which might be attributed to *vic*-methyls, are assignable also to the methyl of unit D in dyad D–A, i.e.



$$-\mathrm{CH_2}-\underset{{}^{*}\mathrm{CH_3}}{\mathrm{CH}}-\underset{\mathrm{CH_2}-\mathrm{CH_3}}{\mathrm{CH}}-$$

$CH_2={}^{13}CH-CH_3$. The spectrum of the polymer resulting from the monomer enriched in the =CH— position (Figure 4A) is clearly more complicated than that of Figures 2 and 3A. In the downfield region (20–40 ppm) there is a broad band due to the labeled carbons of the polymer backbone. However, a series of rather strong, sharp peaks is superimposed on the broad line of Figure 4A.

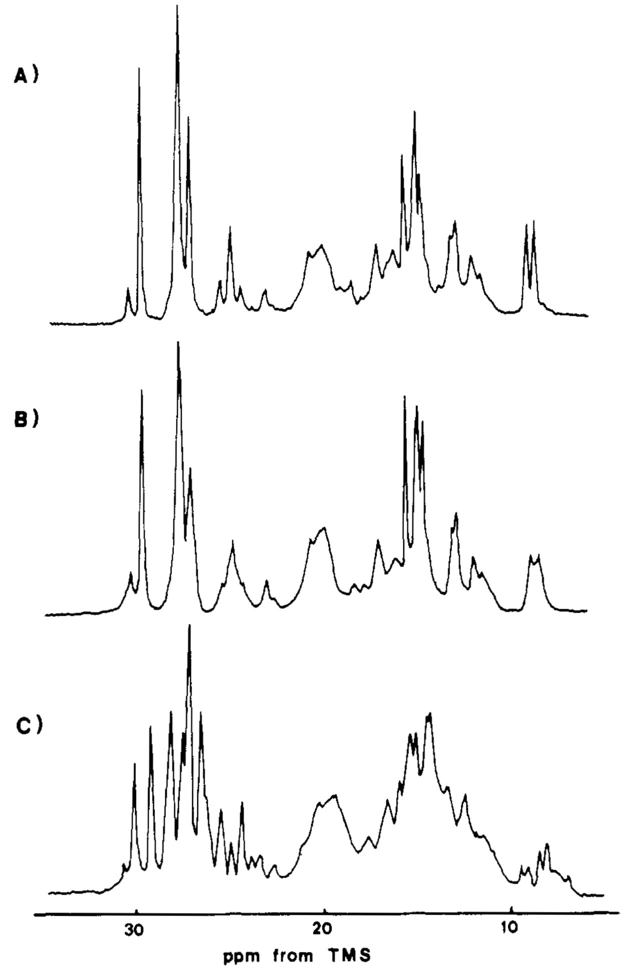
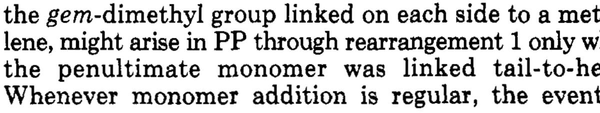


Figure 3. ^{13}C NMR spectra of PP obtained at +70 °C from $^{13}CH_3$-enriched monomer: (A) noise decoupled; (B) selectively decoupled at 87 Hz; (C) selectively decoupled at 130 Hz.

Selective decoupling experiments (see the previous section) were carried out with the aim of characterizing the type of carbons corresponding to different resonances and, in particular, to identify eventual ^{13}C-labeled methyls arising from the labeled methine of the monomer. Figure 4C shows that irradiation at 130 Hz causes a resulting spectrum practically coincident with the noise decoupled spectrum, while the use of the frequency at 87 Hz induces the formation of a doublet at 27 ppm (Figure 4B). These results reveal that no signal having appreciable intensity is due to methyls, whereas a tertiary carbon makes the major contribution to the signal at ca. 27 ppm. Therefore, the rearrangement based on the simultaneous concerted exchange of hydride and methide ion, i.e.



$$\mathrm{R-CH_2-\underset{CH_3}{{}^{13}CH^+}} \longrightarrow \mathrm{R-\underset{{}^{13}CH_2-CH_3}{CH^+}} \longrightarrow \mathrm{R-\overset{CH_3}{\underset{{}^{13}CH_3}{C^+}}} \qquad (1)$$

invoked to explain the presence of *gem*-dimethyl groups in cationic PB1,[1] does not occur during the synthesis of PP since one of the two methyls of the *gem*-dimethyl (or isopropyl) group should be ^{13}C labeled. However, it must be pointed out that the situation of propylene is different from that of 1-butene. In fact, the structural group E, i.e., the *gem*-dimethyl group linked on each side to a methylene, might arise in PP through rearrangement 1 only when the penultimate monomer was linked tail-to-head. Whenever monomer addition is regular, the eventual

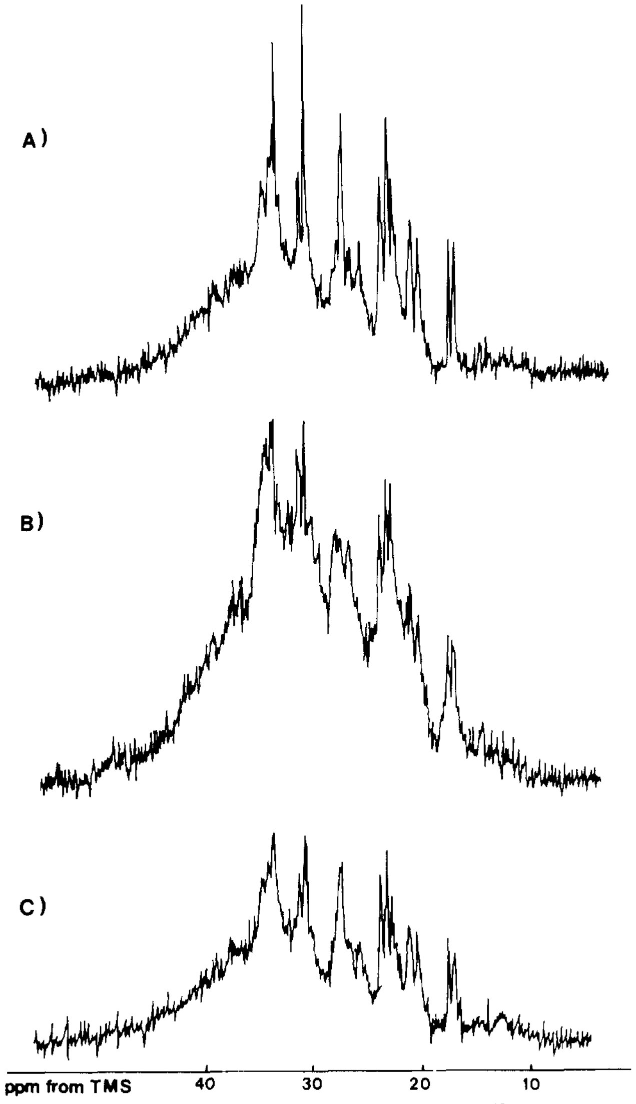
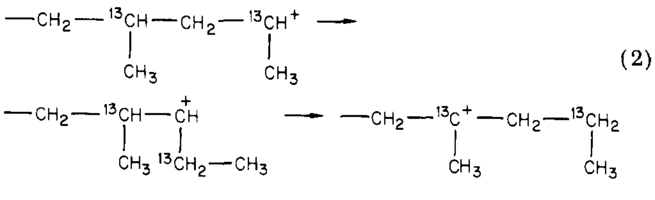


Figure 4. ^{13}C NMR spectra of PP obtained from ^{13}CH-enriched monomer at +70 °C: (A) noise decoupled; (B) selectively decoupled at 87 Hz; (C) selectively decoupled at 130 Hz.

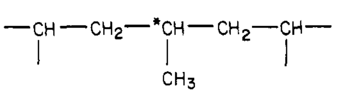
gem-dimethyl group will be in the α position relative to a tertiary carbon and as a result its signal should be shifted upfield by the γ effect. Furthermore, the hydride shift occurring in the first step of rearrangement 1 could be followed by a second energetically favored hydride shift which gives rise to a tertiary-carbenium ion, i.e.



$$\mathrm{-CH_2-{}^{13}\underset{\displaystyle CH_3}{CH}-CH_2-{}^{13}\underset{\displaystyle CH_3}{CH^+}} \longrightarrow \qquad (2)$$
$$\mathrm{-CH_2-{}^{13}\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle {}^{13}CH_2-CH_3}{\overset{+}{CH}}} \longrightarrow \mathrm{-CH_2-{}^{13}\underset{\displaystyle CH_3}{C^+}-CH_2-{}^{13}\underset{\displaystyle CH_3}{CH_2}}$$

An *n*-propyl group (unit B′) and a methyl group bonded to a quaternary carbon (unit D′) is the final result of this rearrangement. Therefore, the formation of structural group E takes place in PP through a reaction path different from that formerly proposed[1] for PB1 and subsequently confirmed by using 1-butene ^{13}C enriched in position $-CH_2-$.[13]

For the interpretation of the spectrum shown in Figure 4A, the main peaks coming out from the broad line which envelops the signals due to the carbons of the backbone are due to methylene groups with the exception of the peak at ca. 27 ppm. The latter, assigned to the tertiary carbon of the regular 1,2 unit belonging to a sequence of three or more units of the same type, i.e.



$$\mathrm{-\underset{|}{CH}-CH_2-{}^{*}\underset{\displaystyle CH_3}{CH}-CH_2-\underset{|}{CH}-}$$

is, in practice, the sole signal of the backbone which can be identified. Table II lists the main attributes of the spectrum of Figure 4A.

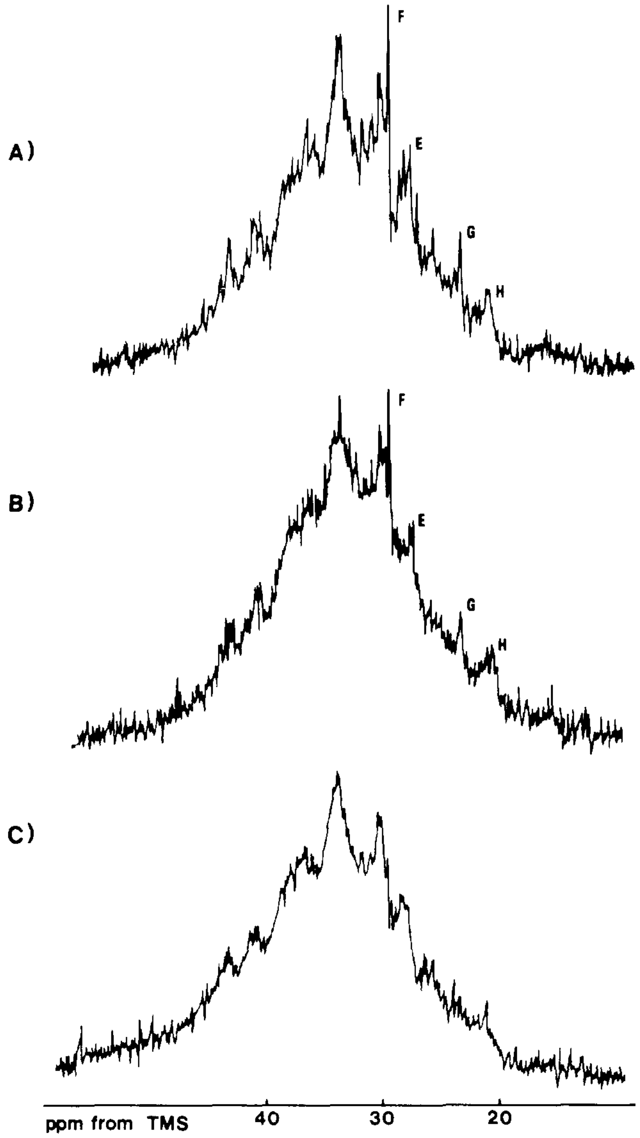


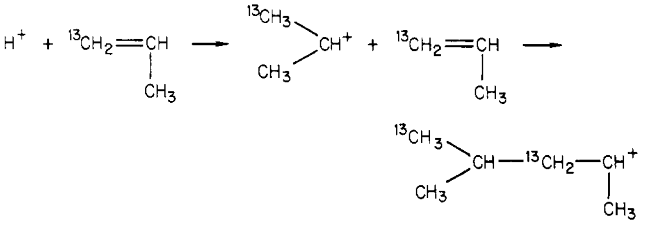
Figure 5. ^{13}C NMR spectra of PP obtained from ^{13}CH$_2$-enriched monomer at +70 °C: (A) noise decoupled; (B) selectively decoupled at 87 Hz; (C) selectively decoupled at 130 Hz.

^{13}CH$_2$=CH–CH$_3$. The spectrum of PP obtained with the monomer enriched in position ^{13}CH$_2$= (Figure 5A) is the most complicated because the labeled carbons mainly constitute the polymer chains. However, interesting information can be obtained from selective decoupling experiments. A very sharp signal at 29.5 ppm and three other rather weak peaks at 20, 22.4, and 27.4 ppm are certainly assignable to methyls on the basis of these experiments (Figure 5B,C; the peaks are denoted with the letters corresponding to the structures). The formation of labeled methyls originating from the ^{13}CH$_2$= group may be explained according to two hypotheses: (1) a proton attack on the double bond of the monomer in the initiation process and (2) a tail-to-head addition of the monomer followed by a rearrangement of the primary carbenium ion

Table II
Assignments in the ^{13}C NMR Spectrum of PP Obtained from $CH_2={}^{13}CHCH_3$

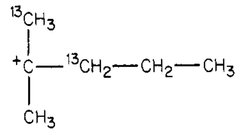
structure	chem shift, ppm
$CH_3-{*CH_2}-CH_2-C<$	16.8-17.3
$CH_3-{*CH_2}-CH_2-CH<$	20.3-20.9
$>CH-\underset{{*CH_2}-CH_3}{\underset{\vert}{CH}}-CH_2-$	22.7-23.8
$>CH-CH_2-\underset{CH_3}{\underset{\vert}{{*CH}}}-CH_2-CH<$	27.7
$>CH-\overset{\overset{\vert}{CH_2}}{\overset{\vert}{\underset{{*CH_2}-CH_3}{\underset{\vert}{C}}}}-CH_2-$	31.1

which yields the methyl group.[19] According to the first hypothesis we obtain

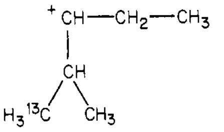


I

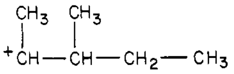
The carbenium ion I can rearrange by a hydride shift (as reported previously[2]) to the carbenium ions II and III,



II



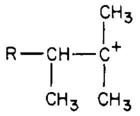
III



IV

while a methide shift[2] gives rise to ion IV. Therefore, ions I, II, and III give rise to isobutyl (G), *gem*-dimethyl (E), and isopropyl (H) groups, respectively, each of which contains one ^{13}C-labeled methyl. The absence of the signals due to the *vic*-dimethyl group, arising from ion IV, can be explained by the fact that the chemical shifts are markedly influenced by the structural environment.

The initiation process induced by protons accounts for three of the four structural groups identified in PP prepared with $^{13}CH_2=CHCH_3$. The formation of the *tert*-butyl group may be explained by a long-range methide shift, but, unfortunately, there are no experimental data in the literature supporting the hypothesis of long-distance methide jumps.[22] On the other hand, a tertiary carbenium ion having a methyl in the α position is hardly to be expected if a regular head-to-tail addition of the monomer is assumed. Evidently this structure, i.e.



$R-\underset{CH_3}{\underset{\vert}{CH}}-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C^+}}}}$

is easily obtained if one assumes a tail-to-head addition of propylene followed by a hydride shift which transforms the primary carbenium ion into a tertiary one.[19] However, we have not so far collected any experimental evidence supporting the tail-to-head addition of olefins during cationic polymerization, a step which is disfavored for electronic and steric reasons. Therefore, the explanation of the mechanism of *tert*-butyl group formation in PP is at present still obscure. We have attempted an evaluation of the amount of $^{13}CH_2=$ transformed into $^{13}CH_3$ groups. This estimation, performed by measuring the areas of signals, is clearly only approximate because of the spectral complexity. However, the estimated value is in the range 5–10%. Since the degree of oligomerization is ca. 15 under the conditions used, about 7% of the $CH_2=$ converted to CH_3 could arise from proton initiation. According to this evaluation, the supposed tail-to-head addition of the monomer, if present, would occur to a small extent.

Quantitative Analysis. As was observed in the case of PB1 the complexity of the ^{13}C NMR spectra of PP limits the precision of the quantitative analysis of the structural groups constituting the polymer. The reasons for the limitations encountered are essentially the same as discussed previously[1] and only a semiquantitative evaluation can be carried out on PP obtained from natural-abundance ^{13}C monomer.

Despite this unfavorable situation, there is interest in the results of a semiquantitative analysis because of the possiblity of identifying some interesting features of the polymerization process. On the other hand, the availability of monomer ^{13}C enriched in the methyl group allowed us to collect more precise composition data because the spectrum is in this case simplified and the overlapping of signals is limited. The sole limitation of this approach was the very small amount of available monomer so that only very few polymerization experiments were performed during which the monomer was converted quantitatively to polymer.

PP Obtained from Natural-Abundance ^{13}C Monomer. The most important experimental parameter which controls the structure of PP is the temperature of oligomerization. This result is very evident in experiments performed with ^{13}C-enriched monomer (see next section) and is analogous to the corresponding finding in the cationic polymerization of 1-butene. The degree of conversion of the monomer is another parameter which significantly influences the structure of PP. The catalyst concentration (when it is low) influences the monomer conversion and hence the polymer structure. An excess of catalyst, such as used in experiments with ^{13}C-enriched monomer, does not significantly influence the structure, which is independent of the catalyst concentration when monomer conversion is complete. Table III shows the compositions of the polymers prepared at 70 °C in a polar and apolar solvent, at low and high conversion, and with different catalysts. The peak occurring between 19 and 20 ppm and assigned to two structural groups (D + H) containing a different number of methyls has been considered to arise mainly from the regular 1,2 unit (group D), because of the rather broad shape of the signal.

By taking into account only the signals due to the linear structural groups (i.e., A, A′, B, B′, and C) and the branched ones (E and F), it can be concluded (Table III) that the latter increase with conversion of the monomer. A quite similar situation was observed in cationic PB1[1] and can be attributed to postmodification reactions involving mainly the oligomer unsaturations (their relative abundance increases with the reaction temperature) and the carbons carrying a chlorine atom (from the catalyst). Conversely, the polarity of the solvent and the type of catalyst used do not modify substantially the PP structure, as in the case of PB1.[1]

Table III
Structure of PP Obtained under Different Experimental Conditions[a]

	catalyst				structural units,[e] %						
solvent	type	mmol/L	yield, %	$\overline{M}_n$	A	A′	B + B′	C	D + H	E[f]	F[f]
n-pentane	$EtAlCl_2$	25.0	6.3	nd	28	6	22	2	28	13	1
n-pentane	$EtAlCl_2$ [b]	25.0	59.0	510	20	7	17	2	31	18	5
CH_2Cl_2	$EtAlCl_2$	7.5	11.6	nd	34	7	26	1	26	6	0
CH_2Cl_2	$EtAlCl_2$	25.0	78.8	570	22	7	24	1	31	13	2
n-pentane	$AlCl_3$	4.0	10.1	nd	25	6	22	1	31	13	2
n-pentane	$AlBr_3$ [c]	25.0	58.0	600	19	8	20	2	31	17	3
n-pentane	$AlBr_3$ [c]	25.0	68.4[d]	640	43	3	23	1	24	6	0

[a] Conditions: [M] = 3.8 mol/L; T = +70 °C; time = 30 min. [b] Cocatalyst: $[(CH_3)_2CHCl]$ = 25 mol/L. [c] Cocatalyst: [HBr] = 25 mmol/L. [d] The $\overline{M}_n$ and structural data are referred to a fraction (15%) of the sample, obtained through preparative GPC, polymerized at −78 °C. [e] See footnote *b* of Table IV. [f] The contents of structural groups E and F were calculated by dividing the areas of their signals by 2 or 3, respectively, i.e., the number of the equivalent methyls constituting the considered groups.

Table IV
Percentage of Methyl Carbons in the Various Structural Units of PP Obtained from $CH_2{=}CH{-}^{13}CH_3$

	percentage of methyl in polymers made[b]	
units[a]	at −78 °C	at +70 °C
A′	4.1	4.8
A	35.4	9.4
C	0.5	0.7
B + B′	22.9	13.2
D + H	30.6	27.7
G	0.0	5.5
E	2.4	22.0
F	0.5	10.2
D′	3.6	6.6

[a] The structures of the listed units are shown in Table I except G and D′ which are $-CH_2-CH(CH_3)_2$ and $>\!C-CH_3$, respectively. [b] The percentages in Tables III and IV were calculated from the area of the peaks of methyls, but from a rigorous standpoint they cannot be compared. This happens because the spectra of the natural-abundance ^{13}C polymer contain the contribution of methyls formed from CH and CH_2 groups. Since these rearrangements are rather modest, the difference in the calculations is not large.

The last two runs of Table III compare the composition data of two samples having the same $\bar{M}_n$ value prepared at −78 and at +70 °C. It can be seen that the presence of branched groups depends markedly on the oligomerization temperature, again considering samples with the same chain length.

PP Obtained from $CH_2{=}CH{-}^{13}CH_3$. The compositions of two samples, synthesized at −78 and +70 °C with $CH_2{=}CH{-}^{13}CH_3$, are reported in Table IV, which shows that when the oligomerization temperature is relatively high, the content of branched groups (E, F, and G) increases markedly at the expense of linear groups. Although we have identified significant amounts of structures with crowded methyls (*tert*-butyl, isopropyl, isobutyl, and *gem*-dimethyl groups), we have found only a modest transformation of methine and methylene into methyl groups. Therefore, the branched structures observed seem to arise from jumping of methyls, which probably move from tertiary or quaternary carbons. Actually, the increase of the content of the branched structures, observed when the reaction temperature increases, is not accompanied by a dramatic decrease of the content of unit D and D′ (i.e., isolated methyls) but by a decrease of all the linear groups. Connected with the formation of the branched groups are the long-range shifts of the methide ion, which were sometimes invoked.[23] However, the more recent literature casts doubt on this assumption.[24,25] At present we do not know how these processes take place.[26]

Conclusions

The study of the structure of PP by means of ^{13}C NMR spectroscopy has revealed that the oligomers obtainable under different conditions have very complex structures. Eleven structural groups have been identified, four of which were branched, i.e., isopropyl, *gem*-dimethyl, isobutyl, and *tert*-butyl groups. Their amount in the polymer increases markedly with the temperature of polymerization and the conversion of the monomer. The latter finding, analogous to that observed during the synthesis of cationic PB1,[1] can be ascribed to postmodification reactions occurring on the reactive sites, e.g., unsaturations and chlorine atoms, of the oligomeric chains. The results obtained from polymer containing natural-abundance ^{13}C monomer were confirmed by polymers prepared with monomers selectively enriched with ^{13}C in positions 1, 2, and 3. The principal information of mechanistic significance obtained during this work may be summarized as follows.

(1) The claimed 1,3 enchainment of the monomer[10] is not observed in the samples investigated.

(2) The formation of linear structural groups can be accounted for by classical 1,2-hydride and -methide shifts (see Chart I).

(3) The formation of part of the branched structural groups arises from the proton initiation, but other mechanisms are also responsible for them, in particular for the formation of *tert*-butyl groups.

(4) No proof of a concerted exchange of 1,2-methide and -hydride ion, which was found to yield *gem*-dimethyl group in cationic PB1,[1,13] was obtained in the case of PP.

(5) No proof of the irregular tail-to-head monomer addition was obtained but, at the same time, this possibility could not be ruled out by direct evidence. However, some results suggest that its possible extent is quite low. In fact, a very low amount of the monomeric methylene is converted into CH_3 groups and a great part of these rearrangements can be explained by proton initiation.

(6) The high content of all the branched groups, which is over 60% in samples synthesized at 70 °C and ca. 10% in samples obtained at −78 °C, suggests that some rearrangements not prevalent in the cationic polymerization of higher α olefins are nevertheless very efficient during the polymerization of propylene. Tentatively, they may be identified with long-range methide shifts, favored by the relatively high concentration of methyls in the oligomers of propylene and, perhaps, by some cooperative conformational effects.

(7) The overlapping of signals assigned to the carbons of the backbone, which appears as a broad line between 20 and 45 ppm and increases when the content of branched groups increases, suggests that a significant modification

of the polymer backbone takes place when branches are formed. This means that the rearrangements occurring involve both side groups and the main chain. The main chain might be subjected to cyclization reactions and/or any process which reduces still further the already low degree of regularity of the polymer formed under mild conditions.

These last three conclusions point out the problems still remaining in the PP system despite the advances in the knowledge of the reaction mechanisms and the structure of PP obtainable by using ^{13}C-enriched monomers.

References and Notes

(1) Part 2: C. Corno, G. Ferraris, A. Priola, and S. Cesca, *Macromolecules*, **12**, 404 (1979).

(2) After the manuscript to this paper was mailed to the editor, Puskas et al.[3] published similar arguments. We could not take into account that paper in drawing our conclusions, even though we knew of it in preliminary form.[12]

(3) I. Puskas, E. M. Banas, A. G. Nerheim, and G. J. Ray, *Macromolecules*, **12**, 1024 (1979).

(4) G. Ferraris, C. Corno, A. Priola, and S. Cesca, *Macromolecules*, **10**, 188 (1977).

(5) J. P. Kennedy and J. E. Johnston, *Adv. Polym. Sci.*, **19**, 58 (1975).

(6) J. P. Kennedy, J. J. Elliot, and B. E. Hudson, *Makromol. Chem.*, **79**, 109 (1964).

(7) G. Sartori, H. Lammens, J. Siffert, and A. Bernard, *J. Polym. Sci., Part B*, **9**, 599 (1971).

(8) A. D. Ketley and M. C. Harvey, *J. Org. Chem.*, **26**, 4649 (1961).

(9) E. H. Immergut, G. Kollman, and A. Malatesta, *J. Polym. Sci.*, S57 (1961).

(10) G. Natta, A. Valvassori, F. Ciampelli, and G. Mazzanti, *J. Polym. Sci., Part A*, **3**, 1 (1965).

(11) G. Henrici-Olivê and S. Olivê, *Polym. Lett.*, **8**, 205 (1970).

(12) I. Puskas, E. M. Banas, A. G. Nerheim, and G. J. Ray, paper presented at the 2nd Joint CIC-ACS Conference, Montreal, Canada, May 29–June 2, 1977.

(13) See following paper in this issue.

(14) H. Normant, *C. R. Hebd. Seances Acad. Sci.*, **239**, 1510, 1811 (1954).

(15) A. Zambelli et al., submitted to *Makromol. Chem.*

(16) Owing to the close analogy of the structural groups reported in Table I with those identified in the previous work on poly(1-butene),[1] we have adopted the same letters for naming the different structural groups.

(17) The occurrence of several structural units in cationic polyolefins is the consequence of very fast rearrangements involving carbenium ions and suitable adjacent carbons of the oligomeric chain rather than other molecules (e.g., monomer) through intermolecular processes. The former appear to occur faster than the latter and are shown in Chart I.

(18) In our context "tail-to-head" addition refers merely to the possibility of the 2,1 addition of the monomer to the active centers, neglecting the arrangement of the ultimate unit. In this sense there it is not necessary to distinguish between "head-to-head" and "tail-to-tail" addition.

(19) It was estimated that in a strongly solvating solvent *tert*-butyl cation is about 33 kcal/mol more stable and isopropyl cation is about 22 kcal/mol more stable than ethyl cation.[20] In the gas phase the differences in stability are even greater, 55 and 32 kcal/mol, respectively.[21] These figures account for the high tendency of primary carbenium ions to rearrange quickly to more stable species instead of giving rise to bimolecular reactions. Also secondary and tertiary carbenium ions give rise to similar rearrangements,[17] whose rates are, very likely, lower than those of primary ions.

(20) A. G. Evans, "The Reactions of Organic Halides in Solution", Manchester University Press, 1946, p 15.

(21) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, p 42.

(22) C. M. Fontana[23] mentioned that "evidence has been found to favor the longer range shifts, i.e., 1,3- and 1,4-methide shifts, under mild conditions", but the corresponding results supporting this conclusion were not published.

(23) C. M. Fontana, "The Chemistry of Cationic Polymerization", P. H. Plesch, Ed., Pergamon Press, Oxford, 1963, p 211.

(24) For instance, the apparent 1,3-methide shift proposed for the cleavage of isopentane to isobutane may occur, but at least two other alternative explanations may be put forward.[25]

(25) C. D. Nenitzescu, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Eds., Wiley, New York, 1970, p 499.

(26) Several years ago it was proposed[27] that "almost any conceivable rearrangement can be represented by means of a series of 1,2 shifts of alkyl groups or hydrogen in carbenium ion intermediates". This conclusion appears rather unlikely from an energetic point of view if alkyl groups heavier than methyl are taken into account. Furthermore, every 1,2-methide shift is not permitted "a priori".

(27) F. E. Condon, "Catalysis", Vol. VI, P. H. Emmett, Ed., Reinhold, New York, 1958, p 43.

On the Cationic Polymerization of Olefins and the Structure of the Product Polymers. 4. 1-Butene Selectively ^{13}C Enriched in Positions 3 and 4

A. Priola, C. Corno, and S. Cesca*

Assoreni, Polymer Research Laboratories, San Donato Milanese, 20097 Italy.

Received November 6, 1979

ABSTRACT: 1-Butene selectively ^{13}C enriched in positions 3 and 4 was polymerized with cationic systems in order to confirm previous results concerning the structure and oligomerization mechanisms studied with natural-abundance ^{13}C monomer. Two other structural groups were identified, and the presence of appreciable amounts of α,ω enchainment was ruled out. Branched structural groups arise from a concerted exchange of methide and hydride ion, but at relatively high temperatures other mechanisms are operating.

Recently, we studied by ^{13}C NMR spectroscopy the structure of cationic polymers of two linear α olefins: propylene[1] and 1-butene.[2] The substantial number of branches and the relatively small proportion of regular 1,2 enchainment of the monomers allowed us to conclude that structural order is lacking in these polymers. The same structural features were present in both polymers, although in different degrees. In particular, the greater abundance of methyls in polypropylene (PP) compared to poly(1-butene) (PB1) accounts for the formation in the former of structural groups with crowded methyls, i.e., *tert*-butyl, *gem*-dimethyl, isopropyl, and isobutyl groups, even at low temperature. The structural complexity of both polymers studied could be explained only in part in terms of classical cationic rearrangements, i.e., hydride and methide shifts to vicinal carbons. The difficulty of rationalizing is particularly worth noting in the case of structural branched groups.[1,2]

0024-9297/80/2213-1110$01.00/0