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).

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(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".

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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

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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]

An extension of ^{13}C NMR investigations through the synthesis of PP obtained from monomers selectively ^{13}C enriched in positions 1, 2, and 3 allowed us to conclude that the complexity of this polymer is not due to particular rearrangements involving α,ω-monomer addition or "irregular" tail-to-head addition.[1] The existence of long-range methide shifts, favored by the crowding of methyls and perhaps some cooperative conformational effects, seems likely in polypropylene synthesis. In order to complete our investigations on cationic PB1, we have extended the approach of ^{13}C-enriched monomers to this polymer.

Experimental Section

Reagents. 1-Butene, solvents, components of the catalyst systems used, and their purifications have been described previously.[2]

Synthesis of $CH_2{=}CHCH_2{}^{13}CH_3$. The preparation was carried out after testing two possible routes:

$$CH_2{=}CHCH_2Br + Mg \rightarrow CH_2{=}CHCH_2MgBr \xrightarrow[-MgBrI]{^{13}CH_3I} CH_2{=}CHCH_2{}^{13}CH_3 \quad (1)$$

$$^{13}CH_3I + Mg \rightarrow {}^{13}CH_3MgI \xrightarrow{CH_2{=}CHCH_2Br} CH_2{=}CHCH_2{}^{13}CH_3 + MgBrI \quad (2)$$

The second way was found to give a better yield and was followed by using a 1 M solution (20 mL of diethyl ether) of $^{13}CH_3MgI$ ($^{13}CH_3I$ was purchased from Prochem, 90% enrichment). The reaction with allyl bromide was carried out as described in detail for $CH_2{=}CH{-}{}^{13}CH_3$.[1] Also Et_2O, present in the raw reaction product (2.2 mL; 27% 1-butene content according to VPC analysis) was removed by adding $AlEt_3$ as reported previously.[1] The final product was recovered as a solution in *n*-pentane, completely free of Et_2O, which was used for polymerization. ^{13}C NMR analysis confirmed that the product was essentially pure $CH_2{=}CHCH_2{}^{13}CH_3$.

Synthesis of $CH_2{=}CH^{13}CH_2CH_3$. The reaction adopted was

$$CH_2{=}CHBr + Mg \xrightarrow{THF} CH_2{=}CHMgBr \xrightarrow{CH_3{}^{13}CH_2I} CH_2{=}CH^{13}CH_2CH_3 + MgBrI$$

The first step was carried out through the Normant procedure,[3] which yields a solution (in tetrahydrofuran) of vinylmagnesium bromide (2.1 M) after filtration and venting of the excess vinyl bromide. The second step was carried out as described elsewhere[1] by reacting 16 mmol of the solution of vinylmagnesium bromide with 13 mmol of $CH_3{}^{13}CH_2I$ (Prochem product; 90% ^{33}C enrichment) dissolved in 4 mL of THF. After 12 h of reaction (65–75 °C), 0.9 mL of liquid was collected at −78 °C whose composition was (by VPC) 65% 1-butene (by area), 32% THF, 1% C_2H_5I, and 2% C_2H_5Br. ^{13}C NMR analysis confirmed that only $CH_2{=}CH^{13}CH_2CH_3$ was obtained. THF was removed by adding $AlEt_3$ as described.[1] The final product was an *n*-pentane solution, containing also C_2H_5I and C_2H_5Br in the ratio reported above, which was used in polymerization experiments without further purification.

Polymerization. Polymerization runs were carried out at +70 and −20 °C as described for isotopically enriched propylenes.[1] The reaction was terminated by adding an excess of EtOH containing NH_4OH to the reaction mixture which was then washed with H_2O. The polymer was recovered by evaporating the solvent in vacuo. The monomer conversions were always high (80–90%).

Analyses. The polymers obtained were analyzed as described previously.[2] In particular, ^{13}C NMR spectra were recorded with a Varian XL-100-15 instrument equipped with FT.

Results and Discussion

The aim of the work with the monomer ^{13}C enriched in position $-CH_3$ was the confirmation of the structural groups identified in the study with natural-abundance ^{13}C monomer and possibly the identification of the units expected (in particular the isobutyl group) but not verified experimentally in the previous work.[2]

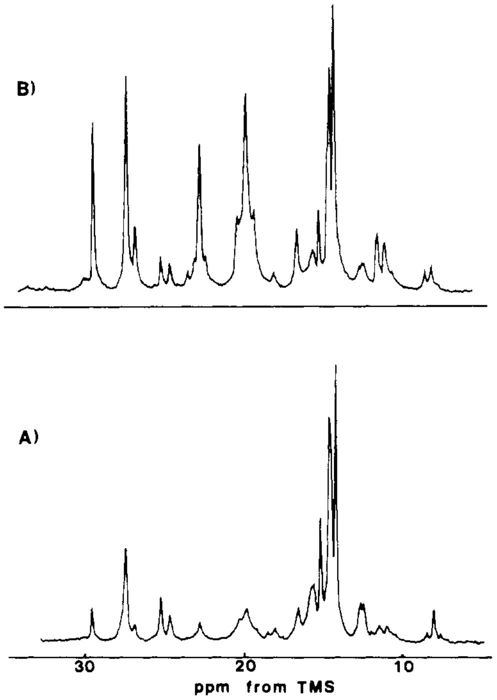


Figure 1. ^{13}C NMR spectra of cationic PB1 obtained from monomer ^{13}C enriched at the methyl carbon: (A) synthesized at −20 °C; (B) synthesized at +70 °C.

The investigations with the monomer enriched in position $-{}^{13}CH_2-$ were planned to confirm some intramolecular rearrangements suggested earlier[2] for explaining the formation of branched structural groups.

$CH_2{=}CH{-}CH_2{-}{}^{13}CH_3$. Figure 1 shows the ^{13}C NMR spectra of cationic poly(1-butene) synthesized at −20 and +70 °C (catalyst system $EtAlCl_2$ + *i*-C_3H_7Cl (1:1 mole ratio) in *n*-pentane). The spectrum is much simpler than that of the polymer obtained from natural-abundance monomer[2] and is rather similar to that observed in PP synthesized from $CH_2{=}CH^{13}CH_3$.[1] Selective decoupling experiments, analogous to those performed with PP,[1] confirmed that all the signals of both spectra of Figure 1 were assignable to methyl carbons. Therefore, also in the case of PB1 no evidence of the α,ω enchainment of the monomer was obtained.

As far as the structural groups are concerned, both spectra of Figure 1 show, with different intensity, the same peaks identified in the polymer samples obtained from natural-abundance ^{13}C monomer. Besides these signals, the peak occurring at 22.69 ppm is particularly evident in Figure 1B. It is assigned to the methyls of the isobutyl group. Figure 1B also shows two weak signals at 24.62 and 25.18 ppm which can be assigned to isolated methyls linked to quaternary carbons, i.e., the structural group designated D′ in the previous work.[2]

One should note in Figure 1 the difference in intensity of the signals at 19.76, 22.69, 27.37, and 29.47 ppm assigned to the four branched structural groups, i.e., isopropyl, isobutyl, *gem*-dimethyl, and *tert*-butyl groups, respectively. The amount of these branched groups increases when the polymerization temperature increases. Also, the signal observed at 19.76 ppm in the spectrum of Figure 1A is rather weak and broad and is thus assignable to an isolated methyl (unit D of PB1) because it is markedly influenced by the structural environment of the backbone. The situation is reversed in Figure 1B, where the peak appears sharp and strong owing to the predominant contribution of the isopropyl group (unit H). The quantitative aspects will be discussed below.

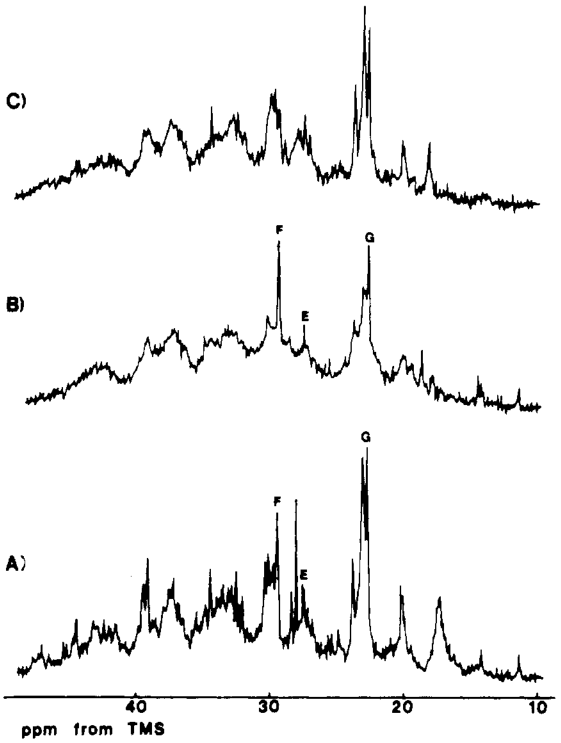
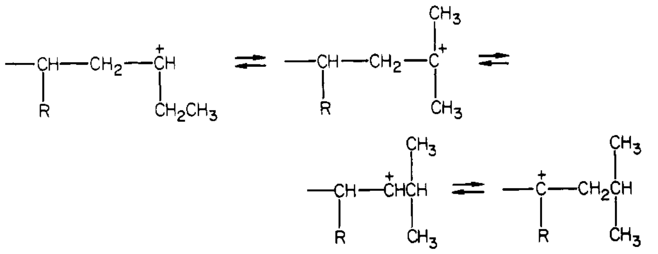


Figure 2. ^{13}C NMR spectra of cationic PB1 obtained at −20 °C from monomer ^{13}C enriched at position 3: (A) noise decoupled; (B) decoupling at 87 Hz; (C) decoupling at 130 Hz.

$CH_2{=}CH{-}^{13}CH_2CH_3$. In previous work on PB1,[2] we proposed some possible intramolecular rearrangements to account for the formation of branched groups which involved some methide shifts. Two possible general isomerization processes can be taken into account:

(1) Methyl groups can migrate to an adjacent carbon atom and the primary carbenium ion, formed from the removal of the methide ion, simultaneously acquires a hydride ion and becomes a methyl group.[2] The result is formation of a *gem*-dimethyl or isopropyl group, depending on whether tertiary or secondary carbenium ion, respectively,[4] is formed; i.e.



$$-\underset{R}{CH}-CH_2-\overset{+}{\underset{CH_2CH_3}{CH}} \rightleftharpoons -\underset{R}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C^{+}}} \rightleftharpoons$$

$$-\underset{R}{CH}-\overset{+}{C}H\overset{CH_3}{\underset{CH_3}{CH}} \rightleftharpoons -\underset{R}{\overset{+}{C}}-CH_2\overset{CH_3}{\underset{CH_3}{CH}}$$

(2) A methide shift can involve distant carbons.[6] Apart from the mechanism of long-range shifts,[7] methide migration can give rise to isopropyl (or isobutyl) and *gem*-dimethyl groups, depending on the type of carbenium ion involved, i.e., secondary or tertiary, respectively, which must carry at least one methyl group. These groups are required in the eventual formation of the *tert*-butyl group.

According to the first hypothesis, when the monomer is labeled in position —CH_2—, the resulting branched groups contain one labeled methyl carbon. In the second hypothesis, the primary carbenium ion formed after the removal of the methide ion may undergo different transformations. If we consider, for the sake of simplicity, the transformation of the —CH_2^+ ion into a methyl group, the latter may belong to linear or branched final structures. Therefore, several signals (in practice, all those possible for methyl groups) of weak intensity are to be expected.

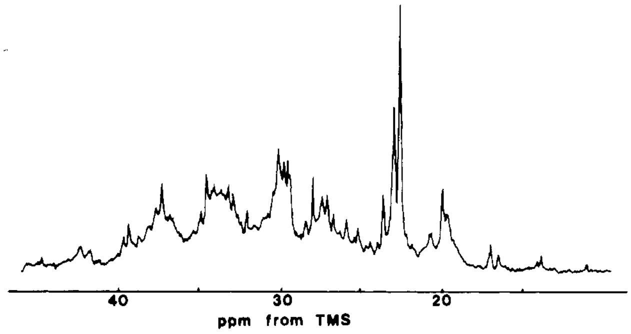


Figure 3. ^{13}C NMR spectrum of cationic PB1 obtained at +70 °C from monomer ^{13}C enriched at position 3.

Table I
^{13}C NMR Assignments and Composition of Two PB1's Prepared at −20 °C and +70 °C

structure	unit	chem shift, ppm	composition, % −20 °C	composition, % +70 °C
$>C-CH_2-CH_3$	A′	7-9	2.9	1.9
$>CH-CH_2-CH_3$	A	10-12	10.7	9.2
$-CH_2-CH_2-CH_2-CH_3$	C	14.1	17.2	12.9
$>CH-CH_2-CH_2-CH_3$	B	14.6	18.0	9.5
$>C-CH_2-CH_2-CH_3$	B′	15.1	3.8	1.5
$-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-\underset{\mid}{CH}-$	D	15-17	15.8	8.2
$-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-$	D	19-20	9.5	23.4
$>CH-CH\langle^{CH_3}_{CH_3}$	H	19.6		
$-CH_2-CH\langle^{CH_3}_{CH_3}$	G	22.6	3.0	9.8
$-\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}-$	D′	24-25	6.7	3.1
$-CH_2-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-CH_2-$	E	27.4	10.2	12.9
$CH_3-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-CH_2-$	F	29.5	2.2	7.4

Figures 2A and 3 show the spectra of two polymers obtained from $CH_2{=}CH^{13}CH_2CH_3$ and synthesized at −20 and 70 °C, respectively. It is evident that the spectra are more complicated than those reported in Figure 1.

The main signals occur in the region between 22 and 23 ppm, which are assigned to α-methylene carbons of the *n*-butyl branch (unit C). Due to the distance of the labeled methylene of unit C from the backbone, its signals appear sharp. Other strong bands, occurring at ca. 20, 27, 30, 33, and 37 ppm, are rather broad. For the purposes of our discussion, the bands at ca. 20, 23, 27, and 30 ppm are of interest since they should include, together with other peaks, the signals due to the isopropyl, isobutyl, *gem*-dimethyl, and *tert*-butyl groups, respectively. The aim of the selective decoupling experiments was, therefore, the identification of the methyl peaks due to the four branched structures mentioned above and resulting from the transformation of —CH_2^+ into —CH_3. Figures 2B and 2C show the spectra obtained from selective decoupling experiments with the sample prepared at −20 °C. The figures show in the regions between 29 and 30 and between 22 and 23 ppm two strong peaks (at 29.58 and 22.78) which can be confidently assigned to methyl groups, while only a weak signal in the region between 27 and 28 ppm can be attributed to methyl carbons (that observed at 27.50 ppm). Therefore, there are more *tert*-butyl and isobutyl groups than *gem*-dimethyl groups among the expected structures, while the isopropyl group is practically absent.

It is surprising that the intensity of the two main signals attributed to the methyl carbons is stronger in the sample prepared at lower temperature (compare Figure 2A,B). In fact the trend observed in PB1 prepared with both natural-abundance ^{13}C monomer[2] and monomer enriched with ^{13}C in position —CH_3 (see below) is reversed. It can be concluded that two mechanisms are involved in the formation of branched groups. The former transforms —$^{13}CH_2$— into —$^{13}CH_3$, as discussed previously;[2] the latter involves essentially $^{13}CH_3$ migration and might occur through long-range methide shifts. The two rearrangements show opposite trends when the reaction temperature increases.

Quantitative Evaluation. As in the case of PP, the ^{13}C NMR spectrum of PB1 synthesized from the monomer ^{13}C enriched in position —CH_3 allowed us to obtained more precise compositional data than obtainable from the natural-abundance polymer. The results, listed in Table I, are given in terms of methyl content and not as absolute percentages because of the reasons discussed previously.[1] The data show the systematic increase of the content of branched groups compared to that of the linear groups when the reaction temperature increases from −20 to +70 °C. In particular, one should note the accompanying modification of the sharp signal at 19.6 ppm assigned to structure H and that of the peak of unit F.

Conclusions

The use of ^{13}C-enriched monomers in the cationic polymerization of 1-butene has elucidated some questions encountered in previous work carried out with natural-abundance ^{13}C monomer.[2] First, signals assignable to two structural units (D′ and G), expected but not experimentally verified, have been identified. Second, the absence of the α,ω enchainment of the monomer is confirmed, as observed in the case of polypropylene.[1] Third, it is found that branched structural groups can arise from a concerted exchange of methide and hydride ion, as proposed previously,[2] but at high temperature other rearrangements are dominant. In fact, the dependence of the former rearrangement on the reaction temperature is reversed compared to the latter mechanisms, which might involve long-range methide shifts having higher activation energy than hydride shifts.[8] Samples of poly(1-butene) prepared under different conditions and over a broad range of temperatures consistently show the presence of all 11 structural groups identified, none of which reaches a percentage higher than 25%. Therefore, no preferential isomerization pathway is evident.

References and Notes

(1) G. Ferraris, C. Corno, A. Priola, and S. Cesca, preceding paper in this issue.
(2) C. Corno, G. Ferraris, A. Priola, and S. Cesca, *Macromolecules*, **12**, 404 (1979).
(3) H. Normant, *C. R. Hebd. Seances Acad. Sci.*, **239**, 1510, 1811 (1954).
(4) The existence of equilibria between tertiary and secondary carbenium ions is usually admitted in cationic rearrangements (energy difference = 11 kcal/mol).[5]
(5) J. L. Fry and G. J. Karabatsos, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Eds., Wiley, New York, 1970, p 521.
(6) As far as this possibility is concerned, see notes 22 and 23 of ref 1.
(7) C. D. Nenitzescu, "Carbenium Ions", Vol. I, G. A. Olah and P. v. R. Schleyer, Eds., Wiley, New York, 1970, p 499.
(8) G. Ferraris, C. Corno, A. Priola, and S. Cesca, *Macromolecules*, **10**, 188 (1977).