On the Cationic Polymerization of Olefins and the Structure of the Product Polymers.[1] 2. Poly-1-butene[2]

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ABSTRACT: Cationic oligomers of 1-butene (PB1) obtained under different conditions showed complicated structure by ^{13}C-NMR investigations. Nine structural units were identified, four of which were previously unknown. At least two other new structural groups may be expected on the basis of the reaction mechanisms involved. A semiquantitative evaluation of the units constituting PB1 was developed from ^{13}C-NMR spectra. Classical 1,2-hydride and methide shifts, hydride transfer, and proton elimination, occurring both during the oligomer synthesis or after its formation, accounted for the structural features observed. The polymerization temperature influenced markedly PB1 composition between −20 and 120 °C; the content of branched alkyl groups increased with the reaction temperature. The features of the cationic oligomerization of 1-butene are discussed with reference to some open problems (tail-to-head or α, ω monomer addition; 1,3-methide shift) concerning the synthesis of cationic polyolefins.

In a previous work[1] we used ^{13}C-NMR spectroscopy to elucidate the structure of cationic poly(4-methyl-1-pentene). We have subsequently extended our studies to linear α-olefins, namely propylene, 1-butene, and 1-pentene. The cationic polymerization of these monomers yields low molecular weight unsaturated products[3,4] whose structural characterization has been carried out mainly through IR spectroscopy.[5-10] These studies showed that the lack of tertiary carbon atoms in linear α-olefin implies a structural complexity greater than in the case of branched olefins because of the absence of prevalent isomerization pathways. In this paper ^{13}C-NMR spectroscopy has been used to improve the knowledge of the structure of poly-1-butene (PB1). The aim of the work was the identification of the structural units constituting cationic PB1 and the mechanistic explanation of their formation in terms of classical cationic rearrangements.

Experimental Section

A. Reagents. 1-Butene (Baker product; purity = 99.29% (VPC), the remaining components being: n-butane = 0.27%, isobutane = 0.22%, isobutylene = 0.15%, propylene = 0.05%, propane = 0.02%) was dried by passing it through two 1-m columns containing P_2O_5 and over activated molecular sieves (4A type). Solvents and components of the catalyst systems were purified and dried as reported elsewhere.[1] i-C_3H_7Cl was pure grade reagent employed after distillation.

B. Procedure. Catalyst handling and polymerization operations were carried out as described in part 1.[1] A stainless steel autoclave, having a capacity of 100 cm^3 and equipped with a magnetic stirrer, control of temperature and pressure, and inlet tubes for the introduction of reagents, was used as the polymerization reactor. The apparatus, dried and maintained under inert atmosphere, was put in a thermostatic bath after having introduced in it solvent and catalyst. A weighed amount of monomer, contained in a stainless steel cylinder, was introduced in the autoclave at the chosen temperature by means of an overpressure of dry N_2. The same procedure was adopted to stop the polymerization with an excess of CH_3OH containing 5% of NH_4OH. The polymer solution was washed with H_2O containing HCl (pH 1) and unreacted monomer was eliminated by distillation at room temperature under reduced pressure. Oligomeric PB1 was recovered as an oily material, after drying overnight under vacuum.

C. Analyses. The number average molecular weight ($\bar{M}_n$) of PB1 was determined with a vapor pressure osmometer (Mechrolab instrument, Model 302) at 37 °C on a toluene solution. The overall content of unsaturation was obtained by bromination, according to the bromide–bromate method.[11] Chlorine present in PB1 was determined by X-ray fluorescence spectrometry.[12]

IR analyses were carried out with a Perkin-Elmer spectrophotometer (Model 225) on neat liquid polymers. Natural abundance ^{13}C-NMR spectra were obtained at 25.14 MHz using a Varian XL-100-15 spectrometer. Spectra were obtained by adding $CDCl_3$ (30%, as internal lock) to liquid PB1. Chemical shifts are reported in ppm from Me_4Si, used as internal reference. For quantitative measurements we used the following FT conditions: SW = 2500 Hz; AT = 1.6 s; PW = 10 μs (90°, PW = 51 μs); NK = 10–20, which assure the complete relaxation of all the methyl carbons investigated. The semiquantitative evaluation of the structural units constituting PB1 was obtained as reported previously.[1]

Results and Discussion

The structural characterization has been carried out first on PB1 obtained at −20 °C since the polymer appeared less irregular. Subsequently we studied PB1 prepared at higher temperatures. The identification of the "structural units"[13] was based on the positions of the signals due to the methyl carbons of different pendant groups and, in some case, also to the methylene carbons situated in the α position relative to methyls. Because of the polymer's complexity no useful information can be obtained from the backbone carbons. The peaks due to methyl carbon atoms are identified by using the selective decoupling technique, by irradiating the protons at 87 Hz from Me_4Si, i.e., at the maximum of the peak due to methyl protons, and at 130 Hz, a frequency typical of methylene and methine protons (the same results were observed in the whole region between 120 and 140 Hz from Me_4Si). The use of the selective decoupling technique for assigning the methyl peaks of the spectrum allows us to conclude that these peaks are due to methyls not directly bonded to unsaturated carbon. The spectra of hydrogenated polymers show all the main peaks present in the corresponding spectra of the original copolymers and hence we have neglected the unsaturations in the identification of the structural units.

A. ^{13}C-NMR Investigations on PB1 Synthesized at −20 °C. Figure 1A shows the ^{13}C-NMR spectrum of PB1 ($\bar{M}_n$ = 1200) obtained in n-pentane at −20 °C in the presence of a typical cationic system, i.e., $AlCl_3$–$(CH_3)_3CCl$ (molar ratio 1:1). In the upfield region of the spectrum weak signals are present between 10 and 12 ppm, typical of the methyl of an ethyl branch (calculated value[14] = 11.36 ppm). This means that the regularly 1,2-enchained unit (named unit A) is present, but its amount is very low. The fine structure of the signal is attributable to the different sequences which unit A belongs to.

The most intense signals of the spectrum are present at 14.1 and 14.6 ppm. They can be assigned to the methyl carbons of n-butyl and n-propyl groups present in units named C and B, respectively. The calculated chemical shifts are 13.86 and 14.35 ppm. The presence of these units is confirmed by the signals occurring at 21.3 and 23.3 ppm due to methylene carbons situated in the α position relative

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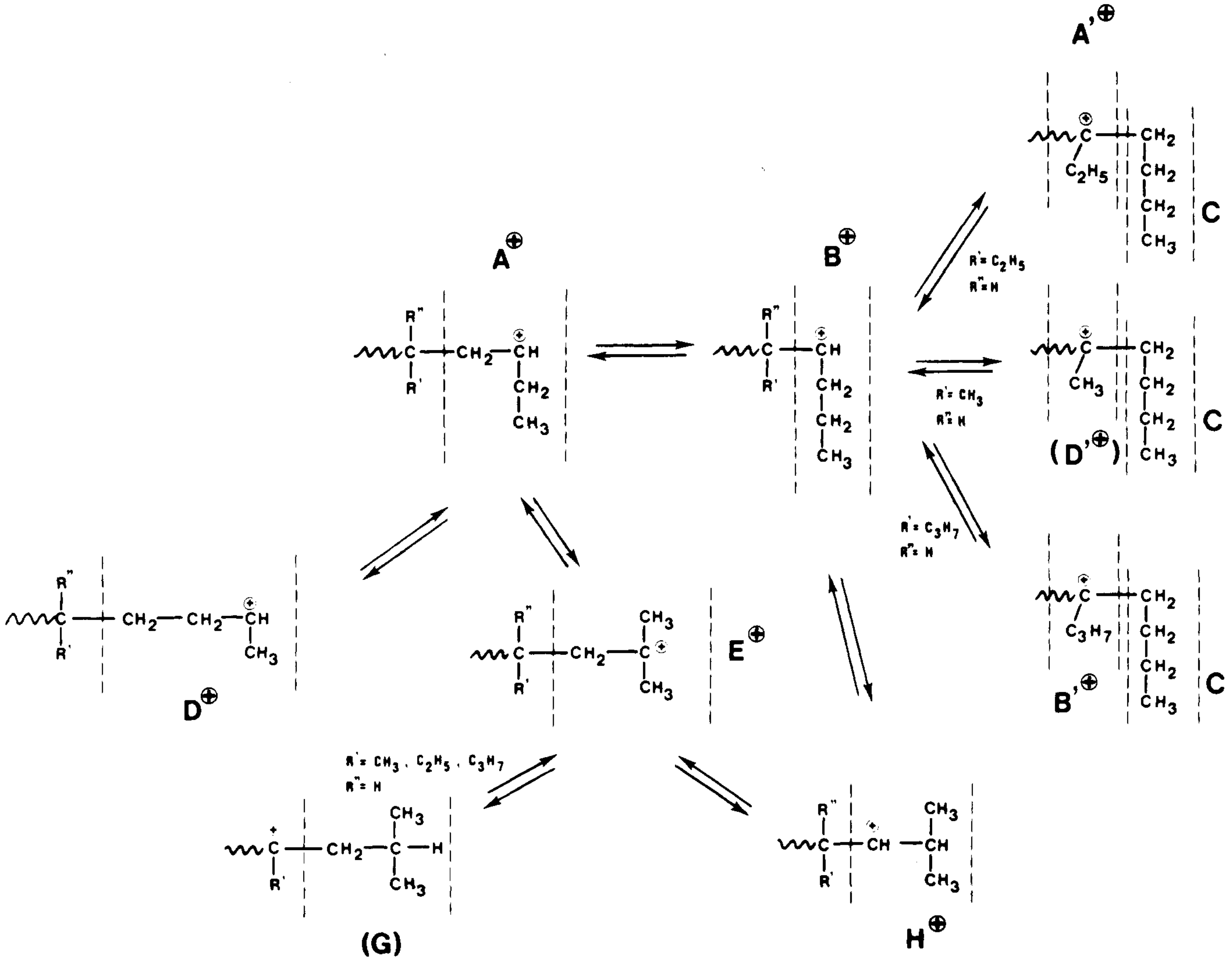
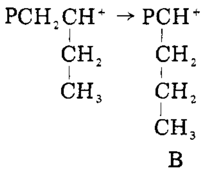
Chart I

Possible Intramolecular Rearrangements Occurring during the Cationic Polymerization of 1-Butene Leading to the Structural Units Identified in This Work. Units Drawn in Parentheses Were not Experimentally Verified



to methyls (calculated values 20.21 and 22.90 ppm, respectively). The peak at 23.3 ppm appears less intense than the corresponding peak due to methyl carbon because it is split into more than one signal. The methylene carbon is nearer to the backbone than the methyl group and is influenced by the different environments. Unit B may originate from an intramolecular hydride shift from C_1 to C_2

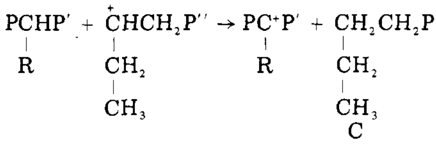

$$\mathrm{PCH_2}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH^+}} \rightarrow \mathrm{P}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\\ \mathrm{B}}}{\mathrm{CH^+}} \qquad (1)$$

which was invoked previously to explain the presence of ethyl branches in cationic polypropylene,[5] and has also been observed in the cationic polymerization of 4-methyl-1-pentene.[1]

Unit C may arise from a double intramolecular 1,2-hydride shift:


$$\mathrm{P}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}\mathrm{CH_2}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH^+}} \rightarrow \mathrm{P}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\\ \mathrm{B}}}{\mathrm{CH^+}} \rightarrow \mathrm{P}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C^+}}\text{—}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\\ \mathrm{C}}}{\mathrm{CH_2}} \qquad (2)$$

(where P = polymer chain; R = alkyl) or from an intermolecular hydride shift (chain transfer to polymer), which originates a terminal *n*-butyl group:


$$\mathrm{P}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}\mathrm{P'} + \underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}}}{\overset{+}{\mathrm{C}}\mathrm{H}}\mathrm{CH_2P''} \rightarrow \mathrm{P}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C^+}}\mathrm{P'} + \underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\\ \mathrm{C}}}{\mathrm{CH_2}}\mathrm{CH_2P''} \qquad (3)$$

In eq 2 the formation of a *n*-butyl branch involves a propagating tertiary-carbenium ion which, in turn, yields a quaternary carbon in the PB1 backbone, carrying a methyl, ethyl, or propyl group. The type of alkyl (R) depends on the type of the penultimate structural unit. We obtain in this case units A′, B′, and D′ (cf. Chart I; unit D descends from the 1,3 enchainment of the monomer: see below).

Units A′ and B′ can be identified on the basis of the different chemical shift of their methyl carbon atom. In fact, the methyl signal of the $CH_3CH_2C<$ group is shifted upfield (ca. 2.5 ppm) with respect to the methyl signal of unit A, while that of the $CH_3CH_2CH_2C<$ group occurs ca. 0.5 ppm downfield relative to 14.6 ppm (unit B). In Figure 1A a weak signal can be observed at 8.1 ppm, due to the methyl of the ethyl group, while at 15.1 ppm there is a weak but narrow peak which can be assigned to CH_3 of the propyl group, both groups being linked to quaternary carbons.

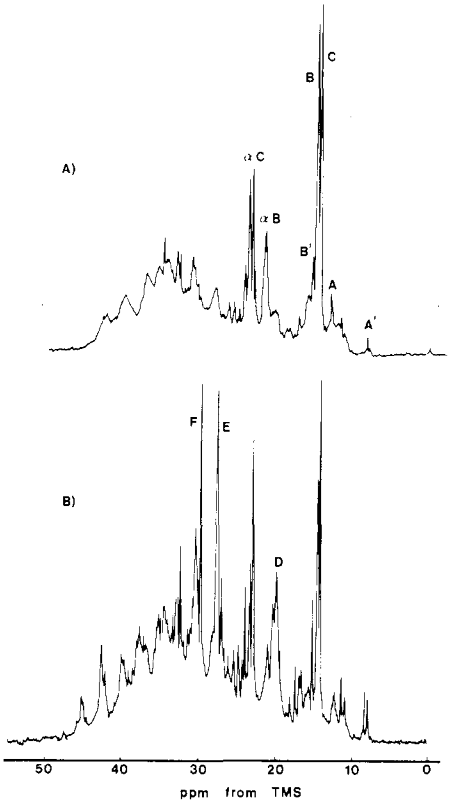
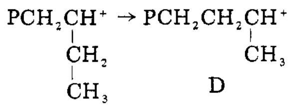


Figure 1. ^{13}C-NMR spectrum of PB1 obtained at −20 °C (A) and at +67 °C (B).

As far as the signal of methyl belonging to the $\mathrm{CH_3C}\!<$ group is concerned, the chemical shift is strongly dependent on the environment of the unit. However, it can be predicted to be in the range between 25 and 30 ppm. In this region there are several signals and one of them can be reasonably assigned to methyls bonded to a quaternary carbon. Therefore, we can conclude that there is experimental evidence for units A′ and B′, but not for unit D′.

B. ^{13}C-NMR Investigation of PB1 Obtained at "High" Temperature. When the polymerization temperature is increased, the resulting PB1 shows noticeable structural modifications relative to the polymer obtained at −20 °C. New structural units have been identified and hence certain polymerization mechanisms are enhanced. Figure 1B shows the ^{13}C-NMR spectrum of PB1 synthesized at 67 °C. In this spectrum three signals due to methyl carbons, namely those occurring at 27.44, 29.53, and 19.8 ppm (the last signal is rather broad), are markedly enhanced. The position of the signal at 19.8 ppm suggests that the carbon responsible for it is directly linked to the chain as occurs in unit D, which may result from the following hydride shift:

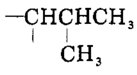


$$\mathrm{PCH_2}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH^+}} \rightarrow \mathrm{PCH_2CH_2}\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{CH^+}} \qquad (4)$$

D

The methyl signal occurs at 19–20 ppm when unit D is followed by a $-\mathrm{CH_2}-$ group, while if a >CH– group follows unit D (D–B dyad) the same signal is shifted upfield (3–5 ppm, depending on the relative orientation of vicinal group).

Weak peaks are present in the region between 15 and 17 ppm and some contribution may be given to the intensity of peaks occurring between 14 and 15 ppm (previously attributed to the methyls of units B′, B, and C) also by vicinal methyl–alkyl groups. The signal occurring at ca. 19 ppm can also be typical of methyls belonging to an isopropyl group joined to the polymer backbone (unit H), i.e.,

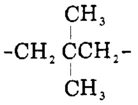


$$-\underset{|}{\mathrm{C}}\mathrm{H}\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}\mathrm{HCH_3}$$

H

We will show in a later section that the presence of unit H is very likely, in particular when PB1 is obtained at high temperature or is left in the presence of cationic initiators.

As far as the two other signals are concerned, the chemical shift at 27.44 ppm is practically coincident with that found (27.33 ppm) in 1,4-poly(4-methyl-1-pentene)[1] and assigned to the *gem*-dimethyl group inserted between two methylenes, i.e.,



$$-\mathrm{CH_2}\overset{\substack{\mathrm{CH_3}\\ |}}{\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}}\mathrm{CH_2}-$$

provided that methylene groups are not linked to two quaternary carbon atoms, as occurs in isobutylene homosequences.[15a] The signal occurring at 29.53 ppm could be attributed to *tert*-butyl groups or to isobutylene dyads. However, if isobutylene sequences were present, a rather intense signal, due to the methylene carbon linked to two *gem*-dimethyls, should appear between 50 and 60 ppm.[15b] In this region of the spectra no signal is evident. Therefore, the signal at 29.53 ppm has to be ascribed to *tert*-butyl groups. This attribution is confirmed by the good agreement with several examples reported by Lindeman and Adams.[14] IR investigations in the region between 1200 and 1600 cm^{-1} (Figure 2) confirmed the presence of

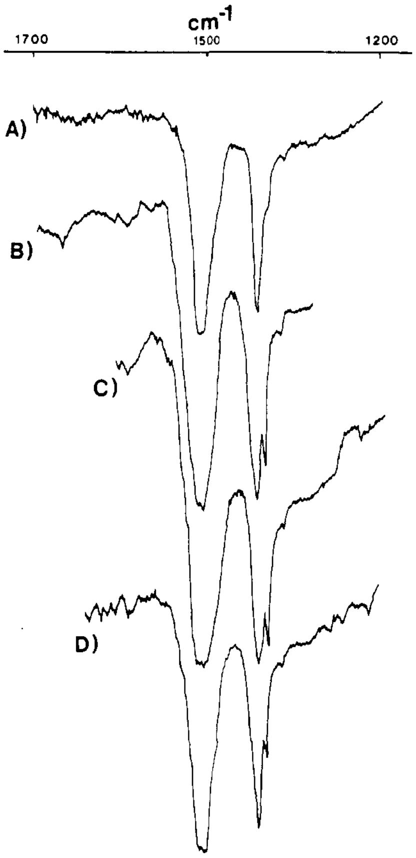
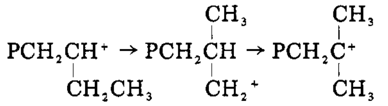


Figure 2. IR spectrum between 1200 and 1600 cm^{-1} of PB1 obtained at −20 °C (A), 20 °C (B), 67 °C (C), and 123 °C (D).

gem-dimethyl and *tert*-butyl groups. In fact, by increasing the polymerization temperature the presence of a band at 1365 cm^{-1} characteristic of these groups becomes evident at the side of the band at 1380 cm^{-1} due to symmetric C–H bending of all the types of C–CH_3 groups. The trend of the intensity of the band at 1365 cm^{-1} is similar to that obtained by ^{13}C-NMR data, showing a maximum for the sample prepared at 67 °C.

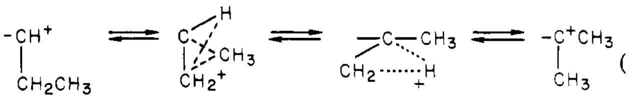
The formation of *gem*-dimethyl groups is very likely originated by a rearrangement mechanism, since the preliminary isomerization of 1-butene to isobutylene is known to occur under conditions more drastic[16,17] than those adopted in our polymerization runs. The rearrangement which may be suggested to account for *gem*-dimethyl group formation implies a methide shift:



$$\mathrm{PCH_2\underset{\displaystyle CH_2CH_3}{CH^+}} \rightarrow \mathrm{PCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2{}^+}{CH}}} \rightarrow \mathrm{PCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}}} \qquad (5)$$

Such a possibility was verified in previous works devoted to the cationic polymerization of 4-methyl-1-pentene,[1] 3,3-dimethyl-1-butene,[18] and 4,4-dimethyl-1-pentene.[19] However, the case of PB1 is substantially different, since the first step of eq 5 is energetically unfavored, while the second step is very likely. Therefore, it is necessary to invoke an almost simultaneous concerted exchange of methide and hydride ion which leads to a final tertiary carbenium ion, more stable than the initial secondary ion.

An isomerization mechanism analogous to eq 5 was suggested[20] to explain the isomerization of *n*-paraffins to isoparaffins in the presence of Lewis acids. In reality, eq 5 may be rationalized in terms of protonated cyclopropane

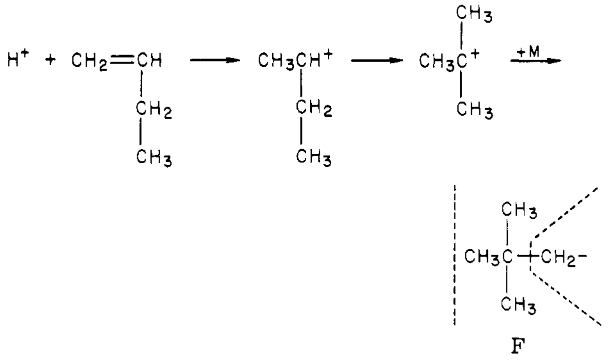


(6)

as suggested in the case of cycloalkane isomerization.[21] This mechanism obviates the necessity of a primary carbenium ion intermediate and involves the existence of equilibria between tertiary and secondary carbenium ions.

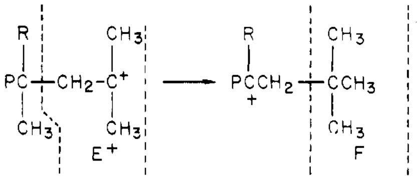
As far as the presence of the *tert*-butyl group (named unit F) is concerned, it is not attributable to the catalyst fragments. In fact, when the type of catalyst is changed, the resulting oligomers display the same ^{13}C-NMR spectrum. The mechanism which could give rise to a *tert*-butyl group in PB1, according to classical 1,2-hydride and/or methide shift, required the presence of a methyl in the α position to an isopropyl carbenium ion. Such a situation hardly can be foreseen on the basis of the rearrangements taken into account in this work.

Indeed the content of unit F in PB1 obtained at low conversion is very low (≤1%) up to 60 °C. Only when the reaction conditions become more severe ($T \geq 80$ °C, high catalytst concentration or long reaction time) does the amount of the *tert*-butyl unit increase significantly. In particular, when the polymerization temperature increases, also the unsaturation content of PB1 increases, whereas $\bar{M}_n$ decreases (Table II), as expected. Since chain-breaking reactions occurring during the cationic polymerization of olefins take place mainly through proton elimination,[22–24] we are inclined to believe that the *tert*-butyl group is mainly formed during the initiation reaction induced by a proton (eq 7) and followed by the rearrangement described above by eq 6. The overall scheme would be:



(7)

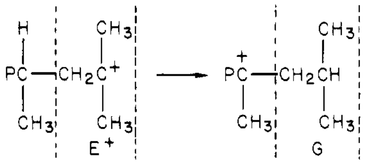
Another rearrangement might be invoked to explain the formation of unit F, i.e., the 1,3-methide shift (eq 8):



(8)

which has been proposed by Puskas et al.[24] to account for the presence of the neopentyl group in polyisobutylene.

The case of PB1 is clearly different and we think that eq 8 is not mainly responsible for the formation of unit F. More likely is a 1,3-hydride shift which would generate an isobutyl group, eq 9

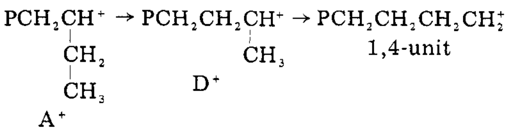


(9)

since the migrating tendency of the hydride ion is more favored than that of the methide ion.[1] However, the signal of unit G is expected in a region of the ^{13}C-NMR spectrum (22–23 ppm) which contains other signals, and thus no experimental evidence can be obtained.

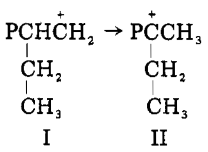
C. Influence of the Polymerization Mechanism upon the Polyolefin Structure: Some Open Problems. The results discussed in the previous sections have been interpreted on the basis of classical cationic rearrangements, i.e., hydride and methide shift, and assuming a regular head-to-tail addition of the monomer. Very recently the possibility of abundant tail-to-tail addition was invoked to explain the presence of tetra-substituted unsaturation in low molecular weight polyisobutylene,[24] cationic polypropylene, and poly-1-butene.[9]

Another source of structural irregularity in polyolefins is the α,ω-enchainment of the monomer[25] which in the case of cationic poly-1-butene may arise from a double hydride shift occurring along the adjacent carbon atoms of unit A^+ and formally corresponding to a 1,4-enchainment of the monomer:



$$\underset{\displaystyle A^+}{\mathrm{PCH_2\underset{\displaystyle \underset{\displaystyle CH_3}{CH_2}}{CH^+}}} \rightarrow \underset{\displaystyle D^+}{\mathrm{PCH_2CH_2\underset{\displaystyle CH_3}{CH^+}}} \rightarrow \underset{\text{1,4-unit}}{\mathrm{PCH_2CH_2CH_2CH_2^+}} \qquad (10)$$

As far as our results are concerned, the occurrence of the tail-to-head monomer addition may yield two structural units I and II:



$$\begin{array}{ccc} PCH\overset{+}{C}H_2 & \rightarrow & P\overset{+}{C}CH_3 \\ | & & | \\ CH_2 & & CH_2 \\ | & & | \\ CH_3 & & CH_3 \\ \text{I} & & \text{II} \end{array} \qquad (11)$$

the second of which arises from the previous one through an energetically favored hydride shift. It is evident that unit I cannot be distinguished from unit A if it is identified, as in our case, through the signal of the methyl carbon. For unit II the chemical shift of the methyl of the ethyl group is practically coincident with that of unit A′, while the methyl bonded to the quaternary carbon gives rise to a signal strongly dependent on its environment and which therefore cannot be predicted. Therefore, eventual tail-to-head 1-butene addition may yield structural units whose chemical shifts are practically coincident with those of units A and A′. Since the abundance of these units in PB1 is relatively low (see Figure 5), it can be concluded that the irregular enchainment of the olefin is a relatively modest phenomenon on the basis of the results presented in this work.

As far as α,ω monomer arrangement is concerned, in previous work[7,25] IR spectroscopy was used to check this possibility. The analysis was based on the absorption band at 720 cm^{-1} typical of the methylene sequence, i.e., $-(CH_2)_n-$ where $n > 3$. However, it must be noted that even though ion $PCH_2CH_2CH_2CH_2^+$ was formed, further rearrangements might occur as a consequence of the attack of another monomer molecule. Thus, the sequence $-(CH_2)_4-$ could not exist actually, despite the real occurrence of the rearrangements described by eq 10. We think that the possibility of the mechanisms described by eq 10 and 11 can be checked by ^{13}C-NMR studies on polyolefins obtained from monomers containing the ^{13}C-enriched methyl group. In fact, the latter would be transformed into a methylene group if the α,ω-propagation were operative. This approach has been adopted by us in the case of propylene oligomerization.[27]

D. Quantitative Evaluation of the Structural Units Present in Cationic PB1. The complexity of the ^{13}C-NMR spectra discussed above limits the precision of the quantitative evaluation of the amount of structural units constituting PB1 which can be obtained by measuring the area of the methyl signals present in the spectrum. Even though these limitations have induced us to conclude that our analysis can be only semiquantitative (see below), the interest for this evaluation stems from the possibility of investigating some relevant aspects of PB1 synthesis identifying some unequivocal trends. The limitations of the quantitative establishment of PB1 composition stem from three types of difficulties. First, some of the eight signals discussed above may be influenced by other structural units or by their relative position in the spectrum. In fact: (i) both the signals occurring between 7 and 9 and 10 and 12 ppm (units A′ and A, respectively) may receive some contribution from the tail-to-head enchainment of the monomer (units II and I of eq 11, respectively); (ii) the signals at 14.1, 14.6, and 15.1 ppm may receive some contribution from a methyl linked to the backbone and vicinal to an alkyl group, as discussed previously; (iii) the signal at 19.8 ppm is due to unit D and also to the isopropyl group linked to the backbone (unit H); and (iv) both signals at 27.44 and 29.53 ppm are situated on a trace which is not linear, because of the contribution of the backbone carbons (the base line used for their evaluation follows the trace profile). Second, there is lack of experimental evidence for some possible structural units (D′, G, and H), possible dyads involving unit D and possible structural groups constituted by *gem*-dimethyl or *tert*-butyl linked to secondary carbons.

Finally, there is partial overlapping of signals, and this limits the precision of the analysis. However, it is worth noting that the quantitative evaluation of all the signals assigned by us to methyls is near (±10%) to the expected value, i.e., 25% of the overall area of the spectrum.

E. Influence of the Experimental Conditions. Table I collects some results obtained in the polymerization of 1-butene with initiators based on Al halides and different cocatalysts. Et_2AlCl and $EtAlCl_2$ alone are not active in our conditions, whereas $AlCl_3$ gives PB1 with low yield. When Et_2AlCl or $EtAlCl_2$ are used, a molar excess of the cocatalyst is necessary to obtain PB1 in high yields. In these conditions probably $AlCl_3$ is formed "in situ"[28] through exchange reactions and is solubilized in the reaction system. It can be noted that the $\bar{M}_n$ of the obtained products is always low and the MWD rather broad; for example, a sample having $\bar{M}_n = 550$ contained 10% of trimers, tetramers, and pentamers and 15% of a fraction with $\bar{M}_n = 1000$.[29] The composition data for the samples obtained at 20 °C are very similar and show no clear influence of the catalyst system employed. Structural units B and C are prevalent, their content being almost equivalent (20–25%). This means that intramolecular hydride shifts are very favored in the cationic polymerization of 1-butene at room temperature with respect to the normal 1,2-propagation (~20%) and to the methide shifts (units E and F, 6–17%). The polymer composition apparently (Table II) is not affected by the polarity of the solvent. This fact is surprising taking into account the fact that, in the case of 4-methyl-1-pentene polymerization,[1] there was a strong effect of the solvent on the polymer structure.

As far as the monomer concentration is concerned (Table II), the content of units A and C increases when the monomer concentration increases, while the trend is reversed for units D + H and E. The reason for such a result remains obscure but it seems to indicate that the cationic polymerization of 1-butene cannot be described according to the Fontana's assumption[30] which implies a lack of dependence of the polymer composition on the monomer concentration.

The polymerization temperature is the main parameter which influences PB1 composition. The results are given by the third set of experiments of Table I and are plotted in Figure 3. The existence of a maximum or a minimum in some diagram of Figure 3 suggests that the reversed tendency in the content of some group occurring at higher temperature could depend on postmodification reactions involving the oligomer already formed.

Indeed, a PB1 sample in the presence of a cationic system does not change its molecular weight significantly ($\bar{M}_n$ value is 1050 and 1150 before and after the treatment, respectively), whereas the structural composition (Figure 4) is markedly modified. In particular, the content of groups A, B, and C decreases, whereas that of E, F, and D + H increases. In other words the content of branched groups increases at the expense of linear structures. This fact is an index of rearrangements involving secondary carbenium ions which evolve toward thermodynamically more stable branched groups.[20] We believe that the presence of unsaturations (Tables I and II) and of chlorine atoms (200–600 ppm of chlorine are present in PB1 depending on the polymerization conditions) favors the attack by electrophilic species, from which structural modifications arise. In fact, hydrogenated and dechlorinated PB1 samples,[31] left in the presence of the same

Table I
Oligomerization of 1-Butene with Different Catalyst Systems and at Different Temperatures[a]

run no.	catalyst type	catalyst mol/L × 10^{-2}	cocatalyst type	cocatalyst mol/L × 10^{-2}	T °C	yield, %	$\bar{M}_n$	Br. no., g/100 g of polym
1	Et_2AlCl	2.22	$(CH_3)_2CHCl$	6.67	20	11.4	600	28
2	$EtAlCl_2$	2.22	$SnCl_4$	4.44	20	97.2	800	27
3	$EtAlCl_2$	2.22	ICl	4.44	20	92.8	820	28
4	$EtAlCl_2$	1.11	$(CH_3)_3CCl$	2.22	20	89.3	620	31
5	$AlCl_3$	2.29			20	31.2	910	18
6	$AlCl_3$	2.29	$(CH_3)_3CCl$	2.22	20	85.7	890	20
7	$AlCl_3$	2.38	$TiCl_4$	2.22	20	60.0	800	20
8	$AlCl_3$	2.13	$(CH_3)_2CHCl$	2.22	20	70.9	770	19
9	$AlCl_3$	2.20	$(CH_3)_2CHCl$	2.22	67	75.0	490	41
10	$AlCl_3$	2.20	$(CH_3)_2CHCl$	2.22	123	71.6	360	60

[a] Conditions: solvent = *n*-pentane; [1-butene] = 2.78 M; time = 60 min.

Table II
Influence of the Solvent and Monomer Concentration on PB1 Structure[a]

run no.	solvent	[1-butene], mol/L	*T*, °C	yield, %	$\bar{M}_n$	Br., no., g/100 g of polym	structural units, % A	A′	B	B′	C	D + H	E	F
1	*n*-pentane	2.78	−20	37.9	1190	10	20	4	26	7	23	11	7	2
2	CH_2Cl_2	2.78	−20	86.8	1220	14	18	4	24	8	29	9	7	1
3	CH_2Cl_2	2.78	+20	69.3	780	21	14	5	22	8	25	14	10	2
4	*n*-pentane	4.55	+20	87.4	850	18	17	4	19	8	29	14	8	1
5	*n*-pentane	1.13	+20	95.8	675	13	14	4	19	8	24	17	11	3
6	*n*-pentane	0.50	+20	89.6	n.d.	13	12	4	18	8	19	20	15	4

[a] Conditions: catalyst system = $AlCl_3$-$(CH_3)_2CHCl$ (1/1 by mol; 0.022 mol/L); time = 60 min.

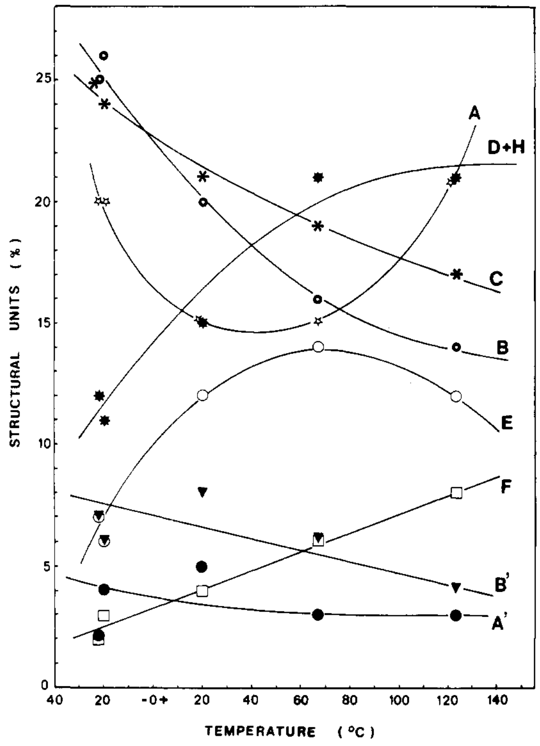


Figure 3. Influence of the temperature of oligomerization upon the composition of PB1 obtained at high conversion.

cationic system and under the same conditions of Figure 4, do not show any change in the ^{13}C-NMR spectra obtained before and after the treatment.

Significant structural differences were observed when PB1 was obtained at low conversion compared to high conversion (Figure 5). The polymer obtained under the mildest conditions (low temperature and low conversion) shows a composition 95% of which is accounted for by six structural units. When the polymerization temperature increases, the concentration of units A′ and A appears almost constant and the content of C increases slowly. The dramatic increase of the signal at 19.8 ppm apparently occurs at the expense of units B and B′. Therefore we are forced to postulate other rearrangements which might arise from units B and B′. For instance isopropyl groups linked

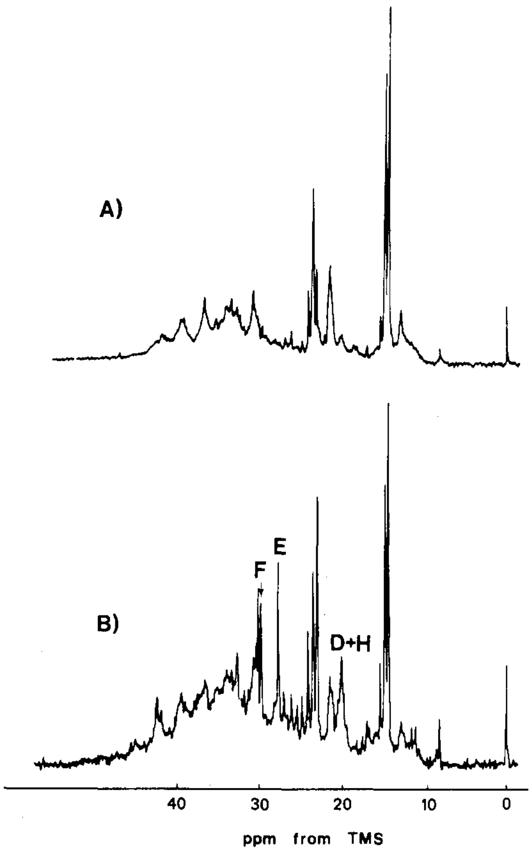
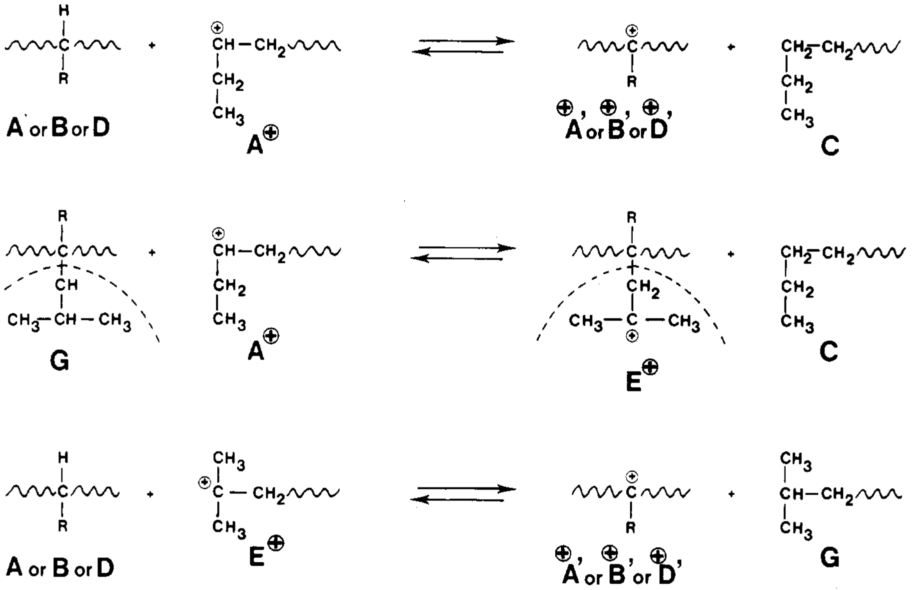
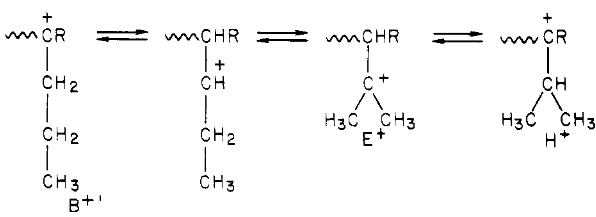


Figure 4. ^{13}C-NMR spectrum of PB1 obtained at −20 °C (A) and after treatment for 2 h at +20 °C with $AlCl_3$ + $(CH_3)_2CHCl$ (B). The content of some structural groups before and after the treatment is: (D + H) = 9 and 24%; E = 1 and 7%; F = 0.6 and 3%.

Chart II
Possible Intermolecular Rearrangements Occurring during PB1 Synthesis



directly to the backbone (unit H) might derive from units B′ through hydride and methide shifts (eq 12), in analogy with the mechanism described by eq 6.



(12)

The ionic species which can be postulated to be present during the synthesis of PB1 on the basis of the composition of the oligomer formed at low conversion arise from equilibrium reactions, similar to those observed in cationic rearrangements of *n*-alkanes, alkyl halides, and olefins.[20] They are drawn in Charts I and II; the schemes are intended to be only indicative of the possibilities of reaction which carbenium ions derived from 1-butene can undergo. Finally, Figure 5 shows clearly that the formation of units E, F, and H, involving methide jumping, is enhanced by the temperature increase, suggesting that the activation energies of these processes are higher than those involving hydride shifts.[1]

Conclusions

The structural investigation of cationic poly-1-butene, performed mainly through ^{13}C-NMR spectroscopy, has revealed a great complexity in the oligomers obtainable under different experimental conditions. Nine structural units were ascertained, four of which (units B′, E, F, and H) were unknown before our study. At least two other structural groups, i.e., D′ and G, may be expected on the basis of the reaction mechanisms involved, but their experimental identification was impossible.

The elevated number of branches and the low amount (ca. 20%) of unit A, i.e., the regular 1,2-enchainment of the monomer, allow the conclusion that a constitutional order is lacking in this polymer of 1-butene. The structure observed can be accounted for by rearrangements which take place both during the oligomer synthesis and as postmodification reactions, when the oligomer is left in the presence of cationic systems. The isomerization processes are favored by the presence of unsaturations and chlorine atoms in the chains. As a result of these rearrangements, thermodynamically more stable branched groups, i.e., *tert*-butyl, isopropyl, and *gem*-dimethyl, are formed.

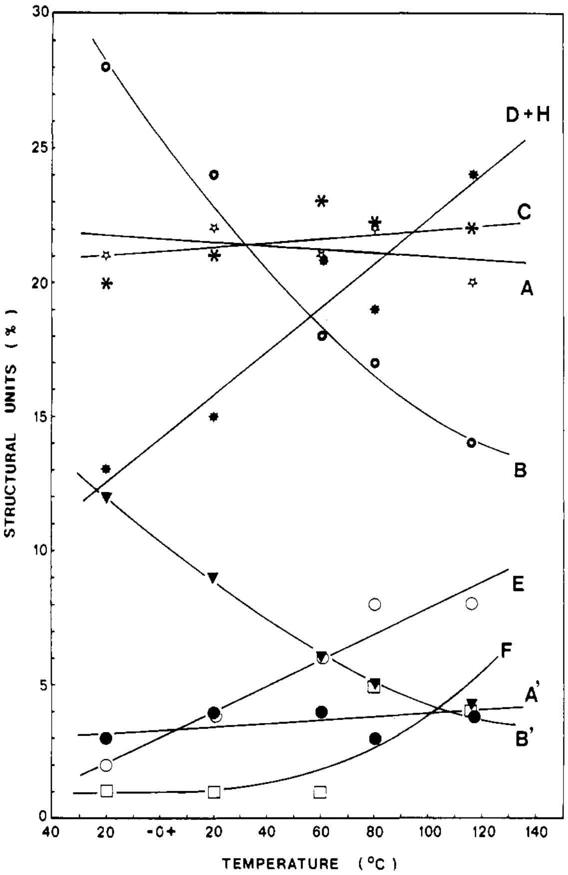


Figure 5. Influence of the temperature of oligomerization upon the composition of PB1 obtained at low conversion (10%).

As fas as the influence of the polymerization conditions is concerned, PB1 structure is mainly governed by the polymerization temperature, while the influence of other parameters, e.g., type of solvent, Al compound, cocatalyst, is almost negligible.

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Cationic Copolymers of Isobutylene. 1. Nuclear Magnetic Resonance Investigation of the Structure and Monomer Distribution in Isobutylene–Butadiene Copolymer

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ABSTRACT: The structure of isobutylene (I)–butadiene (B) copolymers, obtained with a cationic catalyst, has been examined by ^{1}H and ^{13}C NMR spectroscopy. The spectra of these copolymers and their hydrogenated derivatives were investigated. From the assignment of these spectra, a detailed description has emerged of the sequence distribution of isobutylene and *trans*-1,4- and 1,2-butadiene units in the chain. The data for the triad fractions centered on isobutylene and *trans*-1,4-butadiene units show that the monomeric units are distributed in an essentially block manner. The great complexity of the I–B system does not allow us to describe it by the two-component copolymerization model.

New isobutylene copolymers have been synthesized recently in our laboratories. By means of coordination catalysts, we obtained isobutylene–butadiene copolymers which showed peculiar structural features.[1] Moreover, we studied the copolymerization of particular trienes (e.g., 1,3,5-hexatriene or 2,4,6-octatriene) with isobutylene in the presence of cationic initiators, obtaining macromolecules which contain conjugated double bonds.[2,3]

The structural characterization of these copolymers prompted us to study also the structure of isobutylene–butadiene (I–B) copolymers obtained in the presence of cationic catalysts. Their preparation has been known for a long time,[4] but their structural characterization is rather poor, since the resulting copolymers have mainly been studied from a technological point of view.[4]

The most recent studies on cationic I–B copolymers can be summarized as follows:[5] (1) Butadiene enters the copolymer chain mainly as the trans-1,4 unit; minor amounts (20–25%) of 1,2 units are also present. (2) The reactivity of butadiene is higher in an apolar, homogeneous medium than under polar, heterogeneous conditions. (3) The reactivity of butadiene with respect to isobutylene increases with the temperature. (4) At low temperature, the reactivity of butadiene (B) is extremely low compared to that of isobutylene (I). For instance, the reactivity ratios obtained for their copolymerization at −100 °C in CH_3Cl and in the presence of $EtAlCl_2$ were (Finemann and Ross method) $r_I = 43$ and $r_B \simeq 0$. (5) A random distribution of the monomeric units appears very likely and long sequences of butadiene units seem unlikely.

On the other hand, a critical examination of the data so far published indicates the great complexity of the I–B system. For instance, the content of 1,2-butadiene units (ca. 20%) suggests that the I–B copolymer is actually a terpolymer. The two-component copolymerization model cannot describe the copolymerization reaction and the

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