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^{13}C NMR STUDY OF STRUCTURES IN 1-HEXENE POLYMER PREPARED WITH $AlCl_3$

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ABSTRACT

The structures of 1-hexene polymer obtained with $AlCl_3$ without solvent at 0°C were studied by ^{13}C NMR spectroscopy. Only negligible amount of sequences of the 1,2-added units were observed in these polymers, signifying that the isomerization reactions take place much faster than the propagation reaction. The most remarkable findings were that longer than normal-hexyl chains and long interior methylene sequences, e.g. $-(CH_2)_6-$, were in abundance. Structures and structural units, which imply rapid reversible successive hydride and alkide shifts, were found.

INTRODUCTION

The straight-chain 1-alkenes have been polymerized by Friedel-Crafts acids for many decades [1-3]. The resulting low-molecular-weight oily liquids, when hydrogenated, have excellent lubricating oil properties [4].

A very complex chemistry is associated with cationic polymerizations of linear 1-alkenes induced by $AlCl_3$, the details of which are not well understood. Many side reactions, or secondary reactions, are known to take place during these cationic polymerizations. For example, carbocation rearrangements by hydride or methide shifts are known to accompany the polymerization; carbon-carbon bond cleavages are well established in certain cases and double-bond isomerizations can occur, etc. Such side reactions are often, in fact, integral parts of the polymerization chain reactions. These reactions appear to be more frequent at higher polymerization temperatures [5-6].

An analysis of the resulting materials presents a challenge for ^{13}C NMR spectroscopy and can help to elucidate structural details of cationically prepared polymers of normal 1-alkenes [6-8].

The ^{13}C NMR investigations of 1-butene [6], 1-pentene [7] and 1-decene [8] polymers obtained with $AlCl_3$ have already been reported. The ^{13}C NMR chemical shifts for isotactic poly(1-hexene) have been also published [9].

In this paper ^{13}C NMR spectroscopy was used to improve the knowledge of the structure of 1-hexene polymer prepared with $AlCl_3$.

EXPERIMENTAL

Materials and Methods

1-Hexene (99%) and $AlCl_3$ (99%) were purchased from Aldrich. The 1-hexene was dried over molecular sieves before use.

The ^1H and ^{13}C NMR spectra were recorded with a Bruker 200 SY spectrometer at ambient temperature in $CDCl_3$. The quantitative NMR spectra were obtained by using the inverse gated mode of decoupling in order to obtain signals without nuclear Overhauser enhancement [10]. When necessary, the assignments were checked by ATP (attached proton test), a method for making distinction between primary and secondary, or between tertiary and quaternary carbon atoms [11]. The chemical shifts are expressed using the solvent $CDCl_3$ absorption $\delta(^{13}C) = 77.0$ ppm as a secondary standard.

GPC analyses were performed with a Waters instrument equipped with RI detector and five Ultrastyragel columns. The calibration curve was constructed with polystyrene standards of narrow molecular weight distribution.

Synthesis

For the polymerization, the monomer 1-hexene (1.00 mol, 84.2 g) was placed in an all-glass apparatus consisting of a 500 ml three-necked round-bottomed flask, fitted with a thermometer, a mechanical stirrer and a charging funnel, then cooled to 0°C. After that, the $AlCl_3$ (5 mmol, 0.667 g) was added to the monomer at once, followed by stirring for 4 hours. The reaction was terminated with water.

The reaction mixture was diluted with *n*-hexane, the organic layer was separated, washed with water several times to remove the inorganic residues, dried with anhydrous $CaCl_2$ and filtered. Residual solvent was removed by evaporation at 100 °C. Yield: 92-96%. The molecular weight was determined by gel permeation chromatography (GPC): $\overline{Mn}$ = 1100, $\overline{Mw}/\overline{Mn}$ = 1.34. The polymerization experiments were reproducible in yield within ± 2 % and in $\overline{Mn}$ within ± 50.

RESULTS AND DISCUSSION

An important feature of ^{13}C NMR is that carbon atoms in two different molecules, which have the same environment within the nearest four carbon atoms, have the same chemical shift within an experimental error of 0.1-0.2 ppm [12].

It is significant to note that different reports on the same structures sometimes gave assignments as far apart as 0.8 ppm. These probably reflected differences in solvents, temperatures, concentrations, shift references, and instrumental setups [13].

The ^{13}C NMR signal assignments were based on the following methods:

(a) A search through the literature was first made to obtain the assignments for hypothesized structures. Many model compounds had been reported in the literature and empirical additivity rules devised [12, 14-17]. Among the prediction formulae the additivity parameters of Carman, Tarpley, Jr., and Goldstein were preferred because they produce more accurate predictions of ^{13}C NMR spectra of branched alkanes. Empirical parameters for calculating the shifts of the olefinic carbon nuclei in alkenes are also available [12, 18]. The parameter system of Brouwer and Stothers allows chemical shifts of olefinic carbons in monoenes to be predicted.

(b) In some cases, however, when two or more lines in the spectrum fall within approximately 1 ppm of each other, the prediction formulae are no longer suitable for making unambiguous assignments, since the effect of concentration and solvent can significantly influence the chemical shifts. Chemical shifts obtained from selected model compounds, or if not available, compounds with similar structure or sub-structure tend to be of greater predictive value than empirical formulae. The procedure, which can be recommended, is to choose the nearest structurally similar structure or sub-structure to the structure for which shifts are required, and then to modify the observed shifts of the carbons of this model by the well-tested additivity parameters.

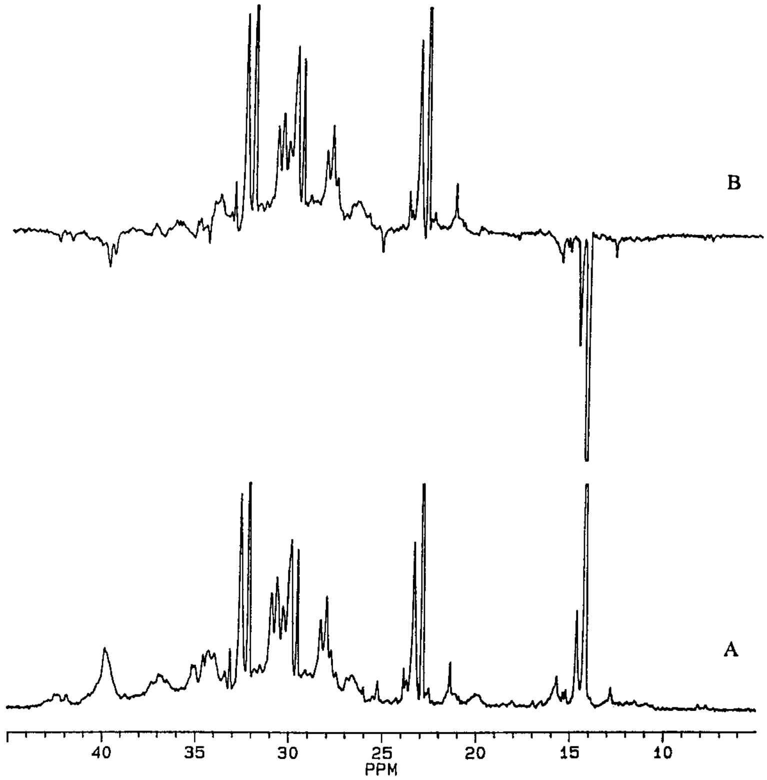


Figure 1. (A) ^{13}C NMR and (B) ^{13}C APT NMR spectra of 1-hexene polymer prepared by $AlCl_3$

(c) The assignments were correlated with the ^{13}C APT NMR spectrum.

(d) Finally the assignments reported for other polymers and copolymers were also of considerable help [6-9, 13, 19-21].

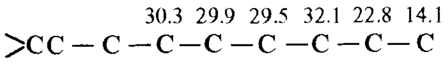
The observed ^{13}C APT spectrum is presented together with the ordinary ^{13}C NMR spectrum in Figure 1. The ^{13}C APT NMR spectrum gives signals whose phase is positive for secondary and quaternary carbon atoms, and negative for primary and tertiary carbon atoms. Where there is confusion between CH/CH_3 and CH_2/quaternary carbon resonances, resonances can be assigned by taking into consideration other additional evidence, i.e. the signals of neighbouring carbons in a hypothesized structure must also be found if they are not overlapped.

The ^{13}C NMR spectral features of the sample (Figure 1) are fundamentally different from those shown in the literature for poly(1-hexene) containing 1,2-added units [9]. This indicates that the polymers prepared in this work by $AlCl_3$ do not have the regular -[CH$_2$CH(CH$_4$H$_9$)]$_n$ skeleton. In contrast, other structures occur in abundance.

The ^{13}C NMR spectra of 1-hexene polymer consist of well-defined, relatively sharp signals together with a multitude of other broader and weak ones. The relatively sharp resonances correspond to carbons three single bond lengths away from the branching points in the main chain, which are little effected by backbone microstructure. The resonances corresponding to carbons one and two single bond lengths away from the main chain branching points are influenced by the different structural environments in the backbone. Therefore, they are split into more than one signal and the corresponding peak appears less intense and broad. The least narrow linewidth resonances are associated with structural moieties from interior sequences of the polymer chain.

The peak at 14.1 ppm is assigned to end-standing methyl carbons in *n*-butyl and longer normal chains. The related methylene carbon resonances are observed at 22.8, 23.3, 29.5, 29.9, 30.3, 32.1, and 32.5 ppm. Surprising spectral features are the presence of resonances at 29.5 and 29.9 ppm, which are characteristic methylene carbon resonances of longer than *n*-hexyl linear chains. Among the methyl resonances, the second most intense resonance appears at 14.6 ppm which is associated with methyl terminals of *n*-propyl branches.

The normal chain ends identified are shown in Structures **1-6**. The numbers on the structures are observed chemical shifts and the numbers in parenthesis indicate predicted chemical shifts of resonances which are thought to be overlapped by other signals.



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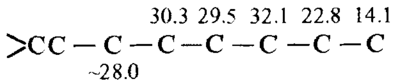

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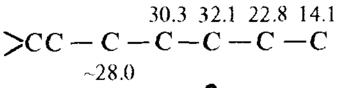

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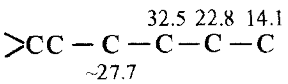

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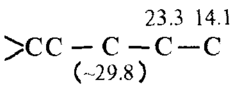

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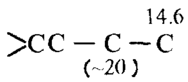
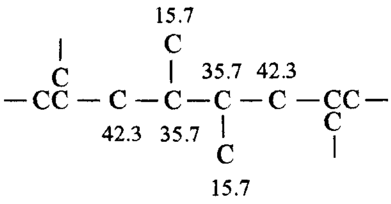
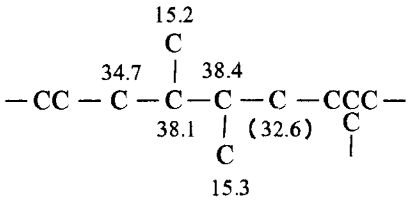


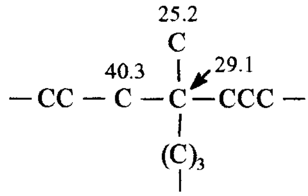
6


$-CC-C-C-C-C-CC-$

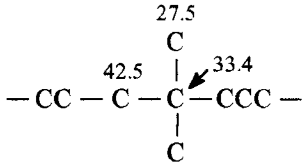
7


$-CC-C-C-C-C-CCC-$

8


$-CC-C-C-CCC-$

9


$-CC-C-C-CCC-$

10

The observed methylene carbon resonances are also consistent with the presence of longer than n-octyl chains, but their presence is less likely. These assignments are in good agreement with those reported for linear alkane chain ends in the literature [12-14, 19-21]. We cannot distinguish between the pendant alkyl groups of the inner monomeric units and the alkyls at the end of the molecules. Most likely, the longer than *n*-butyl chains are end groups. The presence of very weak resonances in the range 10.5-11.5 indicates the presence of very small amounts of methyl terminals of ethyl branches. The amounts are near the detection limits for ^{13}C NMR.

The methyl resonances appearing in the range from 15.0 to 16.0 ppm can be assigned to methyl carbons in structures **7** and **8**. These assignments correspond closely to the methyl resonances observed for similar structures in model compounds [22] and in regioirregular structures of poly(propylene) [23].

A certain degree of ambiguity remains for some methyl carbons of this type having very similar shifts. Depending on various structural environments, resonances of methyl carbons in $-CH(CH_3)CH(CH_3)-$ structure can also appear and overlapped in the range 14.2-14.6 ppm. Weak methyl resonances can appear also in the range 11.5-19.0 ppm from methyl terminals of alkyls attached to olefinic carbons.

The lowest field methyl resonances appear at 25.2 ppm and 27.5 ppm and have been assigned [6, 8] to methyl carbons attached to quaternary carbons as shown in Structures **9** and **10**.

The weak signal appearing near 20.0 ppm consists of several resonances, the one type is the methyl group resonances from isolated methyl branches attached to tertiary carbons and the other type is associated with C-2 methylene of propyl branches.

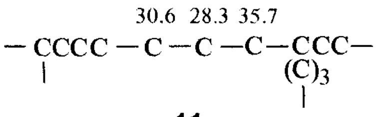
Striking features of the spectra are the peaks appearing at 30.6 and 30.9 ppm, which are characteristic of long interior methylene sequences [15, 19]. The observed signals correspond to several interior methylene sequences as shown in structures **11**-**16**.

Based on the observed methylene carbon resonances, the presence of longer than -$(CH_2)_6$- interior methylene sequences cannot be ruled out, but their presence is less likely. The resonances of methylene carbons from backbone and the methylene carbons of side chains one and two single bond lengths away from the branching points are highly overlapped. The broad appearance of the signals is attributable to the diversity of structural environments which surrounds the carbon atom in question.

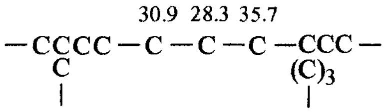
It may be of interest to find out whether sequences of the unrearranged -$CH_2CH(C_4H_9)$- units are present at all in these cationic 1-hexene polymers. The fact is, that characteristic resonances of these structures, which can give supporting evidence, are overlapped with other signals. The methine and methylene carbon resonances of regularly 1,2-enchained units of poly(1-hexene) are at 33.5 and 41.5 ppm, respectively. If sequences of the regularly 1,2-enchained units are present in these 1-hexene polymer, their amount can be very low.

Of particular interest are resonances for the methine carbons, which are located at branch points. In the range 33.2-39.2 ppm the strong methylene resonances tend to obscure a positive identification of the methine resonances from branch points. In the range from 39.5 to 43.2 ppm the methine resonances are more intense. A complete interpretation of all resonances is difficult because of the many overlapping resonances. But, by the comparison of the overall observed resonance patterns in ^{13}C NMR and ^{13}C APT NMR spectra, we were able to devise an interpretation of the methine resonances from branch points. The methine resonance of isolated methyl branches -$(CH_2)_3CH_9CH_3)(CH_2)_3$- should be visible near 33 ppm but this is obscured by the methylene resonances. The chemical shifts of main type of methine carbons together with chemical shifts associated with neighboring methylene carbons are shown in Structures **17**-**21**.

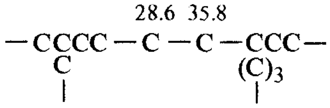
Chemical shifts of methine carbons in Structures **7** and **8** have already been presented. The methine resonances appearing in the range 39.5-41.0 ppm are assigned to the methine carbons in structures **22**-**24**.


$$-\underset{|}{C}CCC-\overset{30.6}{C}-\overset{28.3}{C}-\overset{35.7}{C}-\underset{\underset{|}{(C)_3}}{C}CC-$$

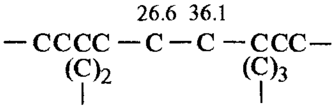
11


$$-\underset{\underset{|}{C}}{C}CCC-\overset{30.9}{C}-\overset{28.3}{C}-\overset{35.7}{C}-\underset{\underset{|}{(C)_3}}{C}CC-$$

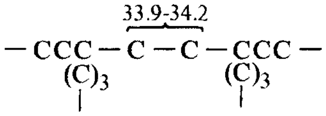
12


$$-\underset{\underset{|}{C}}{C}CCC-\overset{28.6}{C}-\overset{35.8}{C}-\underset{\underset{|}{(C)_3}}{C}CC-$$

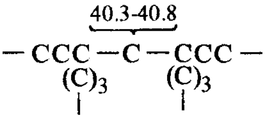
13


$$-\underset{\underset{|}{(C)_2}}{C}CCC-\overset{26.6}{C}-\overset{36.1}{C}-\underset{\underset{|}{(C)_3}}{C}CC-$$

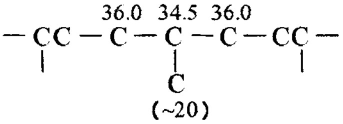
14


$$-\underset{\underset{|}{(C)_3}}{C}CC-\overbrace{C-C}^{33.9\text{-}34.2}-\underset{\underset{|}{(C)_3}}{C}CC-$$

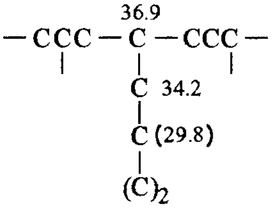
15


$$-\underset{\underset{|}{(C)_3}}{C}CC-\overbrace{C}^{40.3\text{-}40.8}-\underset{\underset{|}{(C)_3}}{C}CC-$$

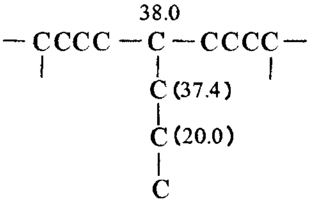
16


$$-\underset{|}{C}C-\overset{36.0}{C}-\underset{\underset{\underset{(\sim 20)}{C}}{|}}{\overset{34.5}{C}}-\overset{36.0}{C}-C\underset{|}{C}-$$

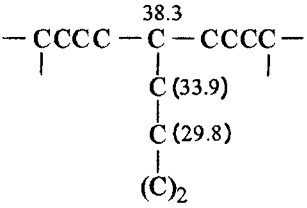
17


$$-C\underset{|}{C}C-\underset{\underset{\underset{\underset{\underset{\underset{(C)_2}{|}}{C\,(29.8)}}{|}}{C\;34.2}}{|}}{\overset{36.9}{C}}-CC\underset{|}{C}-$$

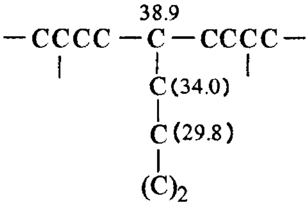
18


$$-\underset{|}{C}CCC-\underset{\underset{\underset{\underset{\underset{\underset{C}{|}}{C\,(20.0)}}{|}}{C\,(37.4)}}{|}}{\overset{38.0}{C}}-CCC\underset{|}{C}-$$

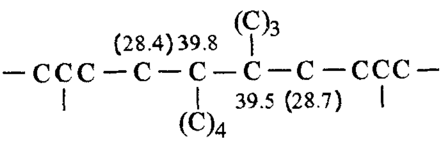
19


$$-\underset{|}{C}CCC-\underset{\underset{\underset{\underset{\underset{\underset{(C)_2}{|}}{C\,(29.8)}}{|}}{C\,(33.9)}}{|}}{\overset{38.3}{C}}-CCC\underset{|}{C}-$$

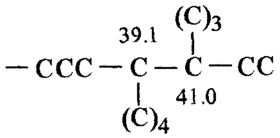
20


$$-\underset{|}{C}CCC-\underset{\underset{\underset{\underset{\underset{\underset{(C)_2}{|}}{C\,(29.8)}}{|}}{C\,(34.0)}}{|}}{\overset{38.9}{C}}-CCC\underset{|}{C}-$$

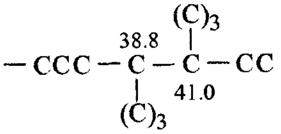
21



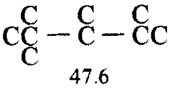
22



23



24



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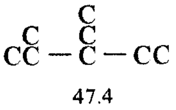
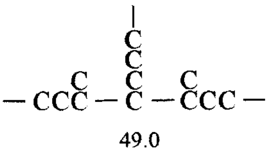


26



27

These assignments are obtained by modification of known assignments of similar sub-structures [24] and model compounds [14].

An analysis of a lower molecular weight fraction obtained by vacuum distillation indicates that additional CH resonances appear at 47.4, 47.6, and 49.0 ppm. The presence of CH resonances at 47.4, 47.6, and 49.0 ppm suggests highly branched very crowded structures to be present as in structures **25**-**27**.

Figure 2 shows the ^{13}C NMR spectrum of double bond region of 1-hexene polymer obtained with $AlCl_3$. The resonances in double bond region are very weak, thus concentrated solutions (~45%) were used in measurements detecting olefinic carbon resonances. Figure 3 presents the ^{13}C APT spectrum of olefinic region.

No detectable amount of olefinic methylene carbons ($=CH_2$) can be observed in these samples, which would appear in the range 105-117 ppm. Only chemical shifts of olefinic carbons in internal double bonds can be observed. The 124-145 ppm region of the ^{13}C NMR spectrum indicates the presence of several type of double bonds. The observed poorly resolved signals are probably associated with carbons in structures **28**-**38**.

In certain cases, further support for the presence of these structures came from the ^{13}C NMR single bond region. As can be seen from chemical shift values,

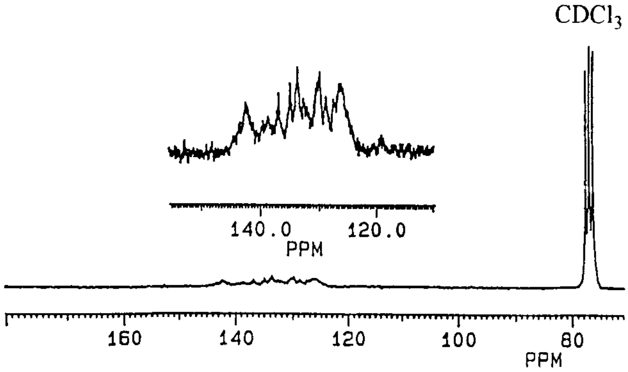


Figure 2. ^{13}C NMR spectrum of double bond region of 1-hexene polymer obtained with $AlCl_3$

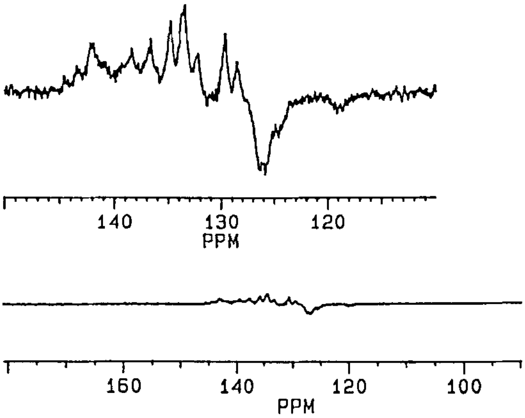


Figure 3. ^{13}C APT NMR spectrum of double bond region of 1-hexene polymer obtained with $AlCl_3$

in some cases, weak methyl resonances are overlapped in the range 14.0-16.0 ppm from methyls and methyl terminals of alkyls attached to olefinic carbons. E and Z refer to trans end cis placements, respectively, of the larger alkyl groups on each of the carbons of the double bond. Both E and Z isomers are assumed to be present but in some cases not observed due to the overlapping of signals.

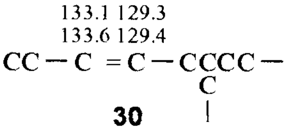
The chemical shifts of conjugated dienes and polyenes are not significantly different from those of the monoenes. Resonances of tetrasubstituted double bonds, conjugated dienes and polyenes may also be present in the region 124-137 ppm, but

12.7 123.8 131.1 cis (Z)
18.0 124.7 131.8 trans (E)
C — C = C — CCC —

28

(14.5) 21.0 131.8 129.6 cis (Z)
(14.1) 25.9 132.3 129.7 trans (E)
C — C — C = C — CCC —

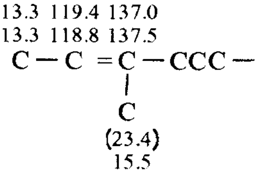
29


133.1 129.3 cis (Z)
133.6 129.4 trans (E)
$CC-C=C-C\underset{\underset{|}{C}}{C}CC-$

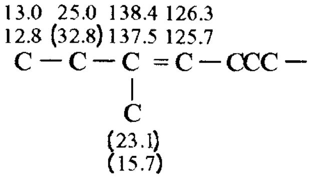
30

14.0 23.5 (29.9) 130.5 129.9 cis (Z)
13.8 23.4 35.4 131.0 130.5 trans (E)
C — C — C — C = C — CCC —

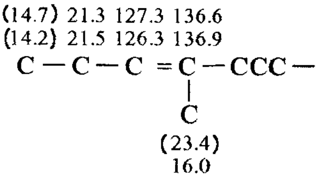
31


13.3 119.4 137.0 cis (Z)
13.3 118.8 137.5 trans (E)
$C-C=\underset{\underset{C}{|}}{C}-CCC-$
(23.4)
15.5

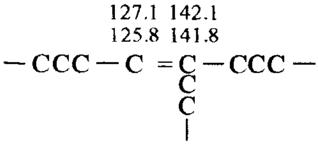
32


13.0 25.0 138.4 126.3 cis (Z)
12.8 (32.8) 137.5 125.7 trans (E)
$C-C-\underset{\underset{C}{|}}{C}=C-CCC-$
(23.1)
(15.7)

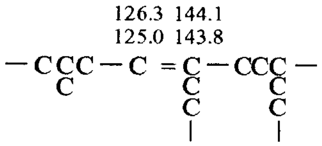
33


(14.7) 21.3 127.3 136.6 cis (Z)
(14.2) 21.5 126.3 136.9 trans (E)
$C-C-C=\underset{\underset{C}{|}}{C}-CCC-$
(23.4)
16.0

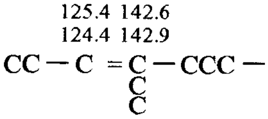
34


127.1 142.1 cis (Z)
125.8 141.8 trans (E)
$-CCC-C=\underset{\underset{\underset{|}{C}}{C}}{C}-CCC-$

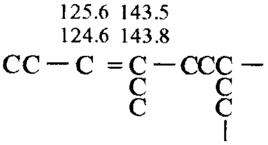
35


126.3 144.1 cis (Z)
125.0 143.8 trans (E)
$-C\underset{C}{C}C-C=\underset{\underset{\underset{|}{C}}{C}}{C}-CC\underset{\underset{\underset{|}{C}}{C}}{C}-$

36


125.4 142.6 cis (Z)
124.4 142.9 trans (E)
$CC-C=\underset{\underset{C}{C}}{C}-CCC-$

37


125.6 143.5 cis (Z)
124.6 143.8 trans (E)
$CC-C=\underset{\underset{C}{C}}{C}-CC\underset{\underset{\underset{|}{C}}{C}}{C}-$

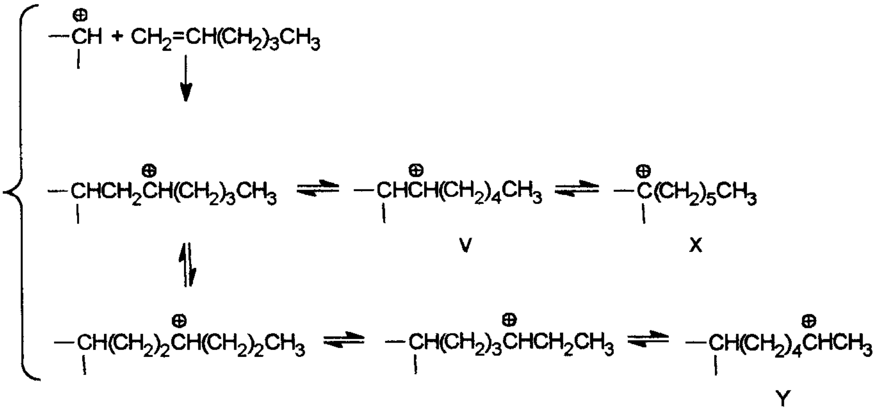
38

the ^{13}C NMR data do not provide definitive evidence to indicate their presence or absence, because the chemical shift values of these structures are practically coincident with those found in this region.

Most reaction mechanism of cationic polymerization is derived from product analysis, that is from circumstantial evidence. Bearing in mind that just because the mechanism chosen fits the products, this does not assure that the proposed mechanism is true [25]; the significant features of the polymerization of 1-hexene may be summarized in the following paragraphs.

There has been general recognition that rapid reversible hydride shifts occur as an intrinsic part of the cationic polymerization reaction of normal 1-alkenes [1-3, 5-6]. The propagation takes place through a secondary carbocation (e.g. carbocation Y) which had been generated from another secondary cation by hydride shift. The hydride shift reactions are thought to be faster than the propagation reaction. The carbocations which can be postulated to be present by successive hydride shifts are shown below:

1



Carbocations are written as if standing alone. Omission of the counterion is for the sake of simplicity and does not imply that the nature of the anion has no effect on the reactivity of the cation.

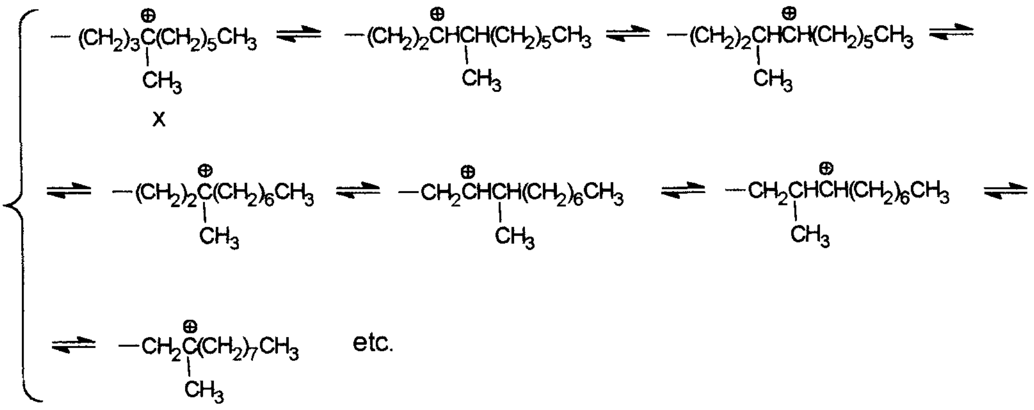
It is customary to represent carbocation rearrangements as taking place in a direction which leads to a more stable cation, that is, primary →secondary→tertiary carbocation, with suitable modification for special steric effects. This commonly used generalization is probably an oversimplification [26]. In some instances, reaction products seem to indicate that rearrangement of the intermediate carbocation occurs in the direction of the less stable cation [25, 27-29]. For example, a reversible rearrangement between intermediate secondary and tertiary carbocations has been demonstrated, by a combination of rapid reversible hydride and methide shifts [29].

Steric factors in the intermediate polymer cations may play an important role, for instance, by hindering propagation through steric blocking of the ionic site. In certain cases, (e.g. carbocations X and V) the steric blocking may be sufficient to decrease the chances for propagation, thus increasing the likelyhood of other reaction paths (alkide shifts, proton loss, fragmentation, hydride abstraction) to compete with propagation [5].

Rapid reversible successive hydride and alkide shifts along the chain are proposed to explain the observed structures in this study. Alkide shifts in carbocations are generally slower than hydride shifts. The most common alkide shift in the acyclic series of hydrocarbons is the methide shift.

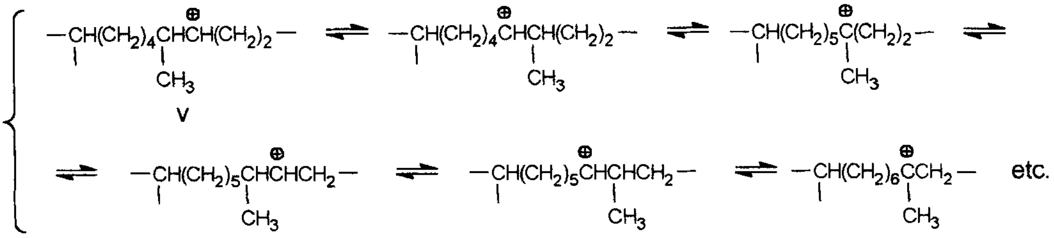
The longer than *n*-hexyl linear chains and long interior methylene sequences may originate from rearrangements presented in Equations 2 and 3.

2



$$\begin{aligned}
&-(CH_2)_3\underset{\underset{\displaystyle X}{CH_3}}{\overset{\oplus}{C}}(CH_2)_5CH_3 \rightleftharpoons -(CH_2)_2\overset{\oplus}{C}H\underset{CH_3}{C}H(CH_2)_5CH_3 \rightleftharpoons -(CH_2)_2\underset{CH_3}{C}H\overset{\oplus}{C}H(CH_2)_5CH_3 \rightleftharpoons \\
&\rightleftharpoons -(CH_2)_2\underset{CH_3}{\overset{\oplus}{C}}(CH_2)_6CH_3 \rightleftharpoons -CH_2\overset{\oplus}{C}H\underset{CH_3}{C}H(CH_2)_6CH_3 \rightleftharpoons -CH_2\underset{CH_3}{C}H\overset{\oplus}{C}H(CH_2)_6CH_3 \rightleftharpoons \\
&\rightleftharpoons -CH_2\underset{CH_3}{\overset{\oplus}{C}}(CH_2)_7CH_3 \quad \text{etc.}
\end{aligned}$$

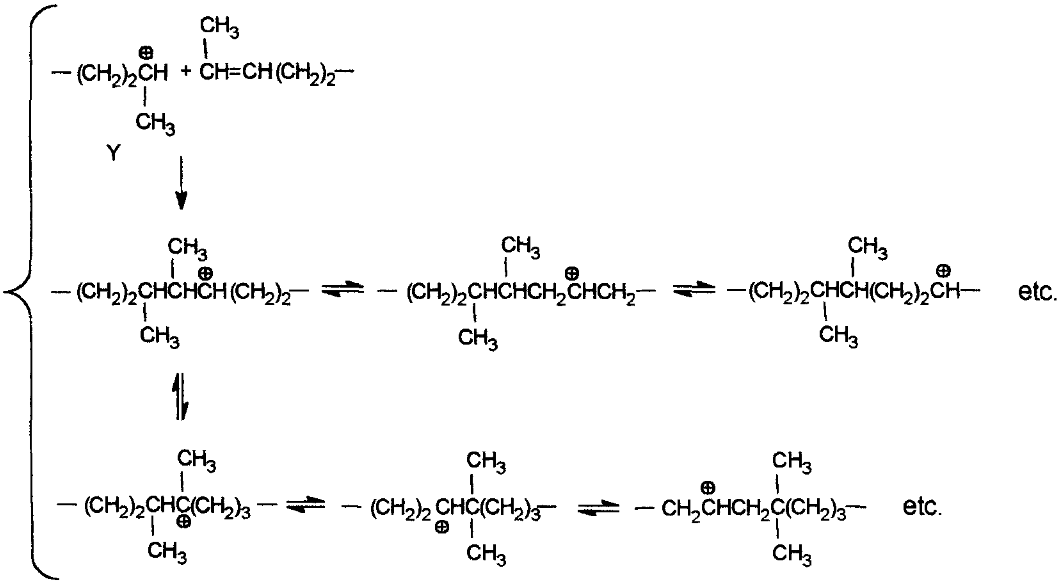
3



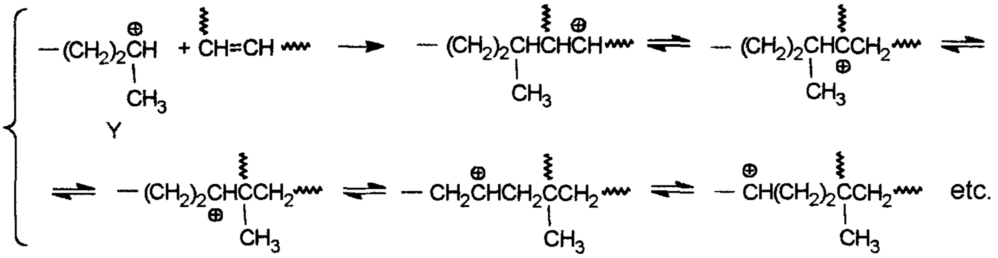
$$\begin{aligned}
&-\underset{|}{C}H(CH_2)_4\underset{CH_3}{C}H\overset{\oplus}{C}H(CH_2)_2- \rightleftharpoons -\underset{|}{C}H(CH_2)_4\overset{\oplus}{C}H\underset{CH_3}{C}H(CH_2)_2- \rightleftharpoons -\underset{|}{C}H(CH_2)_5\underset{CH_3}{\overset{\oplus}{C}}(CH_2)_2- \rightleftharpoons \\
&\qquad V \\
&\rightleftharpoons -\underset{|}{C}H(CH_2)_5\underset{CH_3}{C}H\overset{\oplus}{C}HCH_2- \rightleftharpoons -\underset{|}{C}H(CH_2)_5\overset{\oplus}{C}H\underset{CH_3}{C}HCH_2- \rightleftharpoons -\underset{|}{C}H(CH_2)_6\underset{CH_3}{\overset{\oplus}{C}}CH_2- \quad \text{etc.}
\end{aligned}$$

Double bond isomerization is possible at the monomer stage. Beyond this reaction, many transfer processes leave the polymer with an internal double bond. Because of this, there is always the possibility that this bond may take part in the growth of another chain. Presumably, this possibility increases with extent of conversion. The minor structures of **7**-**10** can be explained as the result of chain growth from such internal double bonds (Equations 4 and 5).

4

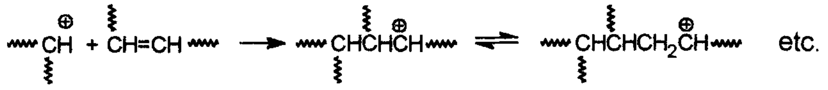


5



The structures **22**-**24** can be explained as the result of rearrangements presented in Equation 6.

6



The solubility of $AlCl_3$ in alkenes is low, thus the reaction mixture in our experiments is a heterogeneous system. The actual polymerization can occur either on the $AlCl_3$ surface or in the interior of liquid phase. We think that polymerization takes place in the layer surrounding $AlCl_3$ particles and less likely inside of the liquid phase. Presumably active sites produce noncrystallizing macromolecules (polymer soluble in continuous phase) and at some stage of the chain growth the increasing thermal fluctuations due to local heat evolution is sufficient to detach the chains from the $AlCl_3$ surface.

To account for the formation of longer than hexyl straight chains, the possible existence of transient primary carbocations should also be considered. Transient primary carbocations from monomer, which have low intrinsic stability and therefore show high reactivity, may exist and propagate in the form of adsorbed tight ion pairs on $AlCl_3$ surface. The resulting entity is a linear propagating dodecyl cation.

Other side reactions not part of the propagation step, such as the formation of saturated hydrocarbons in reversible intermolecular hydride transfer reaction, may also be important [1, 5, 6]. Most likely, the hydride ions are supplied by tertiary carbons or allylic carbons of an alkene (e.g. 1-hexene monomer).

Highly unsaturated hydrocarbons are believed to be present 1,3 in these products. Presumably, these highly unsaturated hydrocarbons (conjugated polyenes) show themself in strong UV absorbance in the range 310-380 nm. The highly unsaturated hydrocarbons probably arise from successive abstraction of allylic hydride ions from an alkene. Abstraction of the hydride ion from an allylic carbon atom of the alken occurs quite readily because of the resonance stabilization of the resulting carbocation. Further abstraction reactions result in the formation of polyunsaturated hydrocarbons [1, 3].

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