On the Cationic Polymerization of 4-Methyl-1-pentene and the Structure of the Product Polymer[1]

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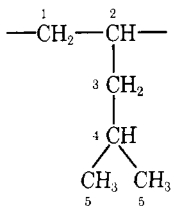
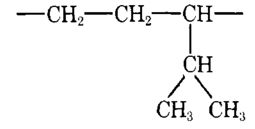
ABSTRACT: ^{13}C NMR investigation of the structure of cationic poly(4-methyl-1-pentene) revealed five structural units. The three previously known were confirmed, while a fourth unit implies successive hydride and methide shifts, still resulting in a 1,4 propagation. A fifth unit arises by hydride shift from C_1 to C_2 of the monomer unit. Reliable quantitative evaluation of these structures was developed from ^{13}C NMR spectra. The influence of the polymerization conditions on the structure of the polymer was investigated; it is mainly dependent on temperature and solvent polarity. In a polar solvent (C_2H_5Cl) the polymer composition was independent of the monomer concentration at −50 °C but slightly dependent at −110 °C. The content of the different structural units, plotted in an Arrrhenius type diagram, showed different slopes in the 0 to −80 and −80 to −130 °C ranges. On the basis of a proposed reaction scheme, the differences between the apparent activation energies for the different isomerization processes and the 1,2-propagation reaction, between 0 and −80 °C, were determined. The results are tentatively explained in terms of different active species existing below and above −80 °C.

I. Introduction

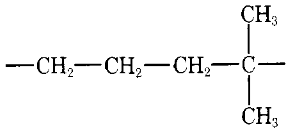
The cationic polymerization of 4-methyl-1-pentene (**1**) was the object of previous studies[2-6] which show three different structural units to be present in the polymer chain, i.e.,



A



B



$$-CH_2-CH_2-CH_2-C(CH_3)_2-$$

C

Unit A originates from the normal 1,2 opening of the double bond of **1**, whereas the units B and C involve intramolecular hydride shifts from positions 3 and 4 of the monomeric unit, respectively. Proof for structures A–C was obtained from IR,[3] ^{1}H NMR[2,4] investigations, and the study of the polymer pyrolyzate.[6] An evaluation of the percentage of the isomerized structures B + C was attempted from IR[3] and 300-MHz NMR spectra.[5,7,8]

The interest in the isomerization polymerization of **1** stems from the possibility of obtaining the alternating ethylene–isobutylene copolymer, otherwise unavailable, if structure C were formed selectively. Therefore, we have reexamined the cationic polymerization of **1** and studied the structure of the resulting polymer through the extensive use of ^{13}C NMR spectroscopy with reference to macromolecular models of the repeat units A, C, and of other new structural units revealed during our investigations. Indeed ^{13}C NMR offered much more insight than other techniques and allowed us to evaluate quantitatively, although with some limitations, the content of all the structural units present in cationic poly(**1**) as functions of the polymerization conditions.

II. Experimental Section

Monomers. 4-Methyl-1-pentene (**1**) (Fluka product) was 95.5 mol % pure with the remaining components 4-methyl-2-*cis*-pentene (3.4%), 3-methyl-1-pentene (1.0%), and 4-methyl-2-*trans*-pentene (0.1%). It was purified by distillation from CaH_2 before use. 2-*cis*-4-*trans*-Hexadiene (**2**) and 4-methyl-1,3-pentadiene (**3**) (purity of both ≥98%) were commercial samples dried over activated molecular sieves 4A and distilled before use.

Solvents. Ethyl chloride was passed from the original container through two 1-m columns containing respectively baked BaO powder and activated molecular sieves (4A type) before condensation into the reaction flask. Ethyl bromide was dried over BaO and distilled before use. Methyl chloride and dichloromethane were purified and dried as reported elsewhere.[9] Toluene and *n*-pentane were washed under the usual procedure and finally refluxed and then distilled from $LiAlH_4$.

Chlorobenzene was dried over anhydrous $MgSO_4$ and then distilled. Propane was a pure grade product and condensed from the container into the reaction vessel, without purification.

Catalysts. $AlCl_3$, $C_2H_5AlCl_2$, $(C_2H_5)_2AlCl$, $AlBr_3$, Cl_2, and $(CH_3)_3CCl$ were treated before use as reported previously.[9] $SnCl_4$ was a pure grade product employed after distillation.

Macromolecular Model Compounds. 1,2-Poly(**1**) was obtained with a coordination catalyst as reported elsewhere[3] and its structure was confirmed through x-ray and ^{1}H NMR analysis.[3] The polymerization of 2-*cis*-4-*trans*-hexadiene (**2**) was done with $C_2H_5AlCl_2$[10] to give selective 2,5 opening of the conjugated double bond system as confirmed by IR and ^{1}H NMR analysis and reported previously.[10] The macromolecular homosequence of the structural unit D was obtained from 2,5-poly(**2**) by hydrogenation (see below). A coordination catalyst ($VOCl_3$ + $(i\text{-}C_4H_9)_3Al$) was used to polymerize 4-methyl-1,3-pentadiene (**3**) through predominant 1,4 opening of the conjugated double bonds system. Conditions: $VOCl_3$ = 0.084 mol/l.; molar ratio Al/V = 2.0; [3] = 1.6 mol/l.; T = −30 °C; time = 3 h. Yield of polymer = 95%, $[\eta]$ = 0.60 dl/g in cyclohexane at 30 °C. ^{1}H NMR analysis (in $CDCl_3$, 25 °C) characterized poly(**3**). The spectrum shows a signal centered at 0.89 ppm from HMDS, attributable to the methyl protons from the 1,4-enchainment of **3**, a doublet centered at 1.92 ppm, due to the protons of the methylene group, and a signal at 5.30 ppm assigned to the unsaturated protons. In the spectrum of poly(**3**) there are also two weak signals at 1.52 and 1.60 ppm due to the methyl groups (magnetically nonequivalent) of the 1,2 units and a peak at 1.21 ppm due to the methylene protons.

A quantitative evaluation based on the methyl proton signals indicates that 86% of **3** polymerized via 1,4 opening, while the rest formed 1,2 units since there is no evidence of the 3,4 unit. 1,4-poly(**3**) was converted into a prevalent homosequence of the structural unit C by hydrogenation, carried out as follows. The polymer was dissolved in cyclohexane (1% w/v) and the same amount of Pd on charcoal (10%) was added to the polymer solution with a small quantity of phenyl-β-naphtylamine. The suspension was introduced into an autoclave and maintained at 60 atm of H_2 at 230 °C for 24 h. After hydrogenation and recovery of the polymer, it was analyzed by ^{1}H NMR to confirm the disappearance of any unsaturation. The hydrogenation step did not involve a significant degradation of the polymer. The same procedure was followed to hydrogenate 2,5-poly(**2**).

Procedure. Polymerization operations, catalyst handling, distillation, storage, and transport of purified solvents were carried out under dry nitrogen atmosphere. The polymerization equipment was

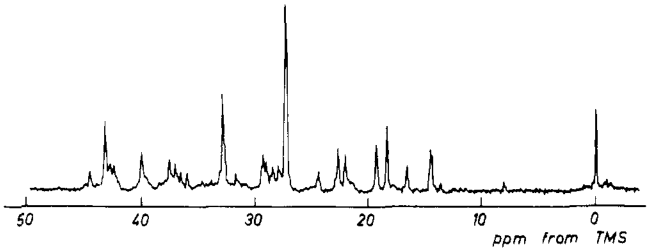


Figure 1. $^{13}C\ \{^1H\}$ NMR spectrum of cationic poly(4-methyl-1-pentene) synthesized in polar solvents.

Chart I

	$CDCl_3$ soln	HCB/C_6D_6 soln
SW, Hz	2500	5000
AT, s	1.6	0.8
PD, s	3.4	4.2
PW, μs	20	20 (90°, PW = 51 μs)
NK	5–10	5–10

an all-glass apparatus consisting of a four-necked round-bottom flask, fitted with Teflon taps, thermometer, mechanical stirrer, and refrigerated dropping funnel. The whole apparatus was flushed with dry nitrogen, flamed, and then cooled in a bath at the chosen temperature (Ultra Kryomat K120W, Messgeräte-Werk Lauda). Solvent and monomer were introduced in the flask while the catalyst solution was dropped slowly from the funnel in order to control the reaction temperature. The polymerizations were quenched by adding precooled methanol; the recovered polymer (precipitated from an excess of methanol) was dried overnight under reduced pressure at room temperature.

Analyses. Intrinsic viscosity measurements were done with cyclohexane solutions at 30 °C, with an Ubbelhode viscometer. Number average molecular weight ($\overline{M}_n$) values were obtained with a high-speed membrane osmometer (Mechrolab 502) in toluene at 37 °C.

Natural abundance ^{13}C NMR absorption spectra were obtained at 25.14 MHz by Fourier transform techniques using a Varian XL-100-15 spectrometer. Spectra of cationic poly(1) were obtained from $CDCl_3$ solutions (15 w/v %) at 25 °C. Chemical shifts are reported in ppm from TMS, used as an internal reference. Spectra of 1,2-poly(1) prepared with coordination catalyst and of a sample of cationic poly(1) were obtained from hexachlorobutadiene $(HCB)/C_6D_6$ (70/30 v/v) solutions at 90°C. In this case chemical shifts were measured from C_6D_6 and reported in ppm from TMS, assuming $\delta(C_6D_6) = 128.0$ ppm (cf. ref 11, $\delta(C_6D_6) = 127.96$ ppm).

The FT conditions are listed in Chart I.

The quantitative evaluation of the structural units constituting cationic poly(1) was made by cutting out and weighing each peak area in xero copy of the spectrum. The error involved in this method of intensity evaluation was, in our case, ca. ±10%.

It must be noted that the final composition data of poly(1) are subject to a systematic error, because we have neglected the signals of some diads, as discussed in section III.3. This error can be evaluated for poly(1) prepared in polar solvents as, at the most, 20% of the content of each structural unit.

^1H NMR spectra were recorded from HCB solutions at 110 °C with a Varian HA-100D15 instrument.

A Perkin-Elmer spectrophotometer (model 225) was used for the IR analyzer of polymer films obtained from CS_2 solutions.

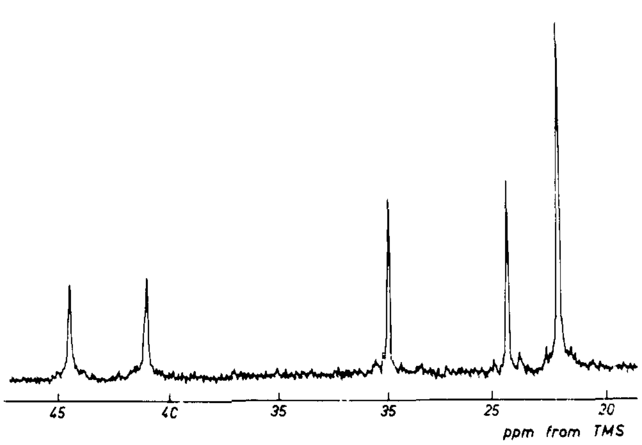


Figure 2. $^{13}C\ \{^1H\}$ NMR spectrum of 1,2-poly(4-methyl-1-pentene).

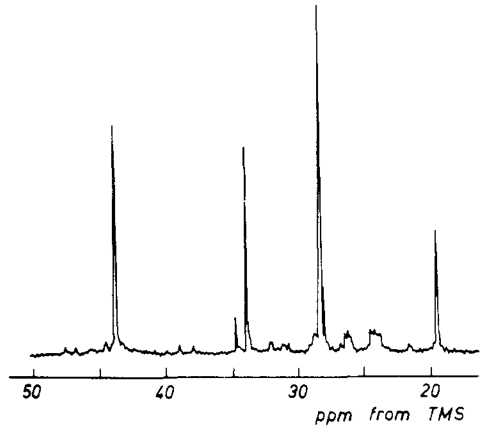
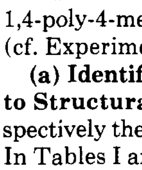


Figure 3. $^{13}C\ \{^1H\}$ NMR spectrum of hydrogenated poly(4-methyl-1,3-pentadiene).

Table I
Experimental and Calculated Chemical Shifts of Carbon Atoms of 1,2-Poly(4-methyl-1-pentene)

Structural unit	Atom	Chemical shift from TMS, ppm	
		Exptl	Calcd
	C_1	41.4	39.98
	C_2	30.3	30.84
	C_3	45.0	44.36
	C_4	24.8	25.92
	C_5	22.4	22.62

III. Results and Discussion

(1) **^{13}C NMR Investigations on Poly(1) Synthesized in Polar Solvents.** Figure 1 shows the ^{13}C NMR spectrum of poly(1) prepared in C_2H_5Cl at −78 °C in the presence of $AlCl_3$. The spectra of poly(1) prepared in other polar solvents (cf. section III) are essentially the same. The interpretation of the complicated spectrum in Figure 1 was first tackled by calculating, according to the rules of Lindeman and Adams,[12] the chemical shifts of the carbon atoms belonging to the homopolymeric sequences of the structural units A–C already identified with the aid of other analytical techniques.[2-6] Second, an experimental comparison was made by examining two model polymers containing respectively the units A and C along the chain. The former was 1,2-poly(1), prepared with coordination catalyst,[3] and the latter was hydrogenated 1,4-poly-4-methyl-1,3-pentadiene which simulates 1,4-poly(1) (cf. Experimental Section).

(a) Identification and Attribution of Signals Referring to Structural Units A, B, and C. Figures 2 and 3 show respectively the ^{13}C NMR spectra of 1,2-poly(1) and 1,4-poly(1). In Tables I and II are compared the results of the calculated with the experimental values of chemical shifts referring respectively to 1,2-poly(1) and 1,4-poly(1). The good agreement between experimental and calculated values allows the assignments of the signals without ambiguity.

Since it was not possible to prepare a macromolecular model containing exclusively the structural unit B, i.e., 1,3-poly(1), we compared (Table III) the calculated values of the chemical

Table II
Experimental and Calculated Chemical Shifts of Carbon Atoms of Hydrogenated 1,4-Poly(4-methyl-1,3-pentadiene)

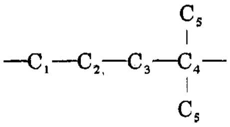
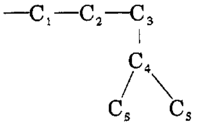
Structural unit	Atom	Chemical shift from TMS, ppm Exptl	Calcd
	C_1C_3	43.3	42.14
	C_2	18.4	19.20
	C_4	33.0	33.65
	C_5	27.3	27.28

Table III
Calculated Chemical Shifts of 1,3-Poly(4-methyl-1-pentene) and Experimental Chemical Shifts of 3-Isopropylpentane[a]

Structural unit	Atom	Chemical shift from TMS, ppm Exptl	Calcd
	C_1, C_2		29.34
	C_3		43.66
	C_4	29.1	30.46
	C_5	19.0	19.63

[a] Carbon atoms of isopropyl group only.

shifts of C_4 and C_5 in structure B with literature values[12] of the corresponding carbon atoms of 3-isopropylpentane. In this case also the experimental values are very close to the calculated data.

In the next step we considered the alternating sequences of the units A–C. It is immediately evident that the calculation of the chemical shifts of the carbon atoms present in the backbone is not useful because of the very high number of possible sequences which should be considered.

On the other hand, it is worth noting that, on the basis of the semiempirical rules, the signals due to the methyl carbons of the units A and B are not influenced by the different types of sequences if constant head-to-tail monomer insertion is assumed. This hypothesis is very likely in the cationic polymerization of olefins.[13] For the structural unit C, a slight shift of the signal can be foreseen due to the C–A dyad with respect to the other two possible dyads C–B and C–C.

According to the tables of Lindeman and Adams[12] the value of this shift is 0.49 ppm. Therefore, only four signals due to methyl carbons should be taken into account when only three structural units, i.e., A, B, and C, were present in cationic poly(1) and when all the possible dyads were considered.

The signals of Table II are all clearly evident in Figure 1, in particular the large peak at 27.3 ppm, thus indicating the prevalence of structure C over the other units.

Analogously, the signals of Table I due to the carbon atoms of the branch of structure A are present in Figure 1, but their intensity is lower than that of the signals due to structure C. Their shifts are observed as follows: C_5 at 22.1 ppm, C_4 at 24.5 ppm, and C_3 at 44.6 ppm, i.e., they are shifted upfield (0.3 ppm) with respect to the values of Table I. Such a constant deviation was attributed to the different conditions under which the spectrum of 1,2-poly(1) was recorded and to the different internal reference from which chemical shifts were measured.

In fact, when the spectrum of Figure 1 was recorded under the same conditions of Table I, i.e., in hexachlorobutadiene (HCB) at 90 °C, the chemical shifts of C_5, C_4, and C_3 occurred respectively at 22.4, 24.8 and 45.0 ppm.

Finally, in Figure 1, the signal at 19.3 ppm due to the methyl carbons of the unit B is also seen, as expected on the basis of the calculation reported in Table III. Therefore, ^{13}C NMR investigations have confirmed the presence of the structural units A–C previously identified.[15]

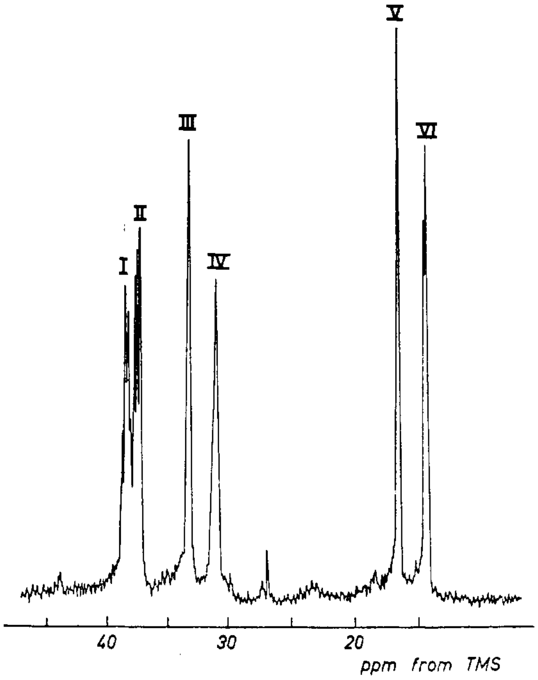
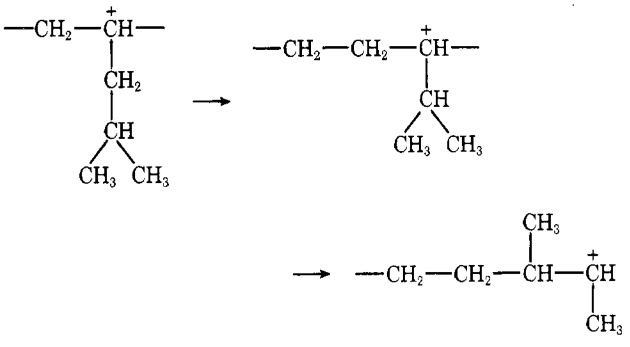


Figure 4. ^{13}C $\{^1H\}$ NMR spectrum of hydrogenated 2,5-poly(2,4-hexadiene).

(b) Identification and Assignment of Signals Due to a New Structural Unit D Involving a Methide Shift. Figure 1 shows signals which cannot be explained on the basis of structures A–C only. For instance, the peaks observed at 14.6 and 16.3 ppm belong to methyl carbons, as can be inferred from their position and demonstrated through off-resonance decoupling measurements. However, they cannot be assigned to units A–C, even if one supposes head-to-head or tail-to-tail enchainments. We assumed as a working hypothesis (which was later confirmed) that a new structural unit D could be formed by a methide shift from position 4 to the carbenium ion in position 3 of the last monomeric unit, following a previous hydride shift from C_3 to C_2, i.e.,



D

Such a rearrangement is possible in the cationic polymerization of olefins.[16,17] The experimental evidence comes from the ^{13}C NMR spectrum of hydrogenated 2,5-poly(2,4-hexadiene) (cf. Experimental Section) and its comparison with Figure 1. Such a model polymer has structure D as the repeat unit and in its spectrum (Figure 4) there are six main bands, two of which (I and II) contain fine structure, and they can be attributed to methine carbon atoms. The other four signals (at 14.5, 16.3, 31.0, and 33.1 ppm from TMS) can be attributed as pairs respectively to methyl and methylene carbons. Their doublet character stems from the reciprocal orientation of the two vicinal methyl groups, i.e., erythro or threo. The signals

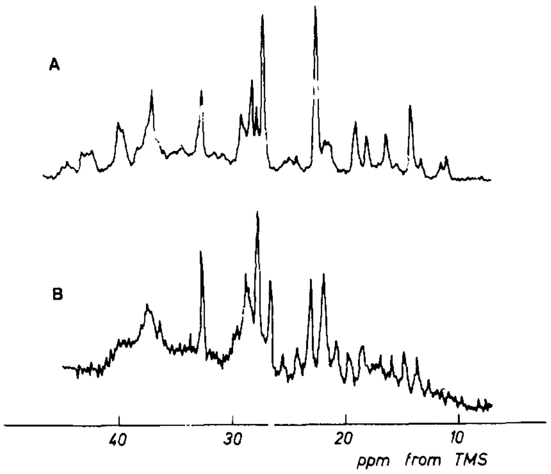


Figure 5. ^{13}C NMR spectrum of cationic poly(4-methyl-1-pentene) synthesized in nonpolar solvents: (A) proton noise decoupled, (B) off-resonance coupled.

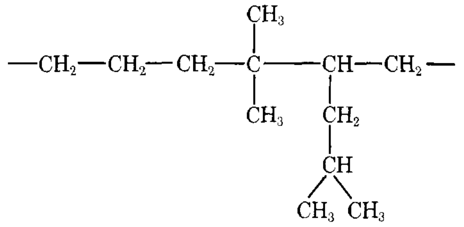
due to the methyl carbons of D are found exactly in the same position of the spectrum of cationic poly(1), i.e., at 14.6 and 16.3 ppm in Figure 1. Considerations similar to those in the previous section suggest that the chemical shifts of the methyl carbons belonging to the different alternating dyads will not change with respect to the homosequence, except for a slight modification (calculated 0.49 ppm) of the chemical shift of the second methyl in the dyad D–A.

(2) ^{13}C NMR Investigations of Poly(*1*) Synthesized in Nonpolar Solvents. Relevant differences were found in the ^{13}C NMR spectra of poly(1) synthesized in a nonpolar solvent, e.g., *n*-pentane or propane (Figure 5 and cf. Figure 1). In fact, the signal of Figure 5 at 22.7 ppm is noticeably increased with respect to the corresponding peak of Figure 1. Similarly, the signals at 28.4 and 37.1 ppm appear more intense in Figure 5.

Off-resonance decoupling experiments showed that the signal at 22.7 ppm should be assigned to methyl carbons. Even though it is very close to the signal due to the methyl carbons of structural unit A, there is no doubt that it cannot be attributed to unit A, since in Figure 5 the signal at 24.5 of the methine carbon atom of unit A branch in all the sequences does not show a correspondent increase of intensity.

Two hypotheses were advanced to explain the intense signal at 22.7 ppm: (a) irregularities of enchainment (tail-to-tail), and (b) a reaction scheme, represented in Figure 6, which is responsible for a new structural unit, E, originated by a hydride shift from position 1 of the last monomeric unit.

Although the first hypothesis is not supported in the literature concerning the cationic polymerization of olefins,[13] if one supposes the existence of a tail-to-tail enchainment between a unit A and another unit, e.g., C, the following situation would result:



E

In this hypothetical structure the chemical shifts due to the methyl and methine carbons are coincident with the corresponding chemical shifts of structure A. Therefore, when the intensity of the peak at 22.7 ppm (methyl carbon) increases, a correspondent increase of the peak at 24.5 ppm (methine carbon) should be expected. But this does not occur, as mentioned above.

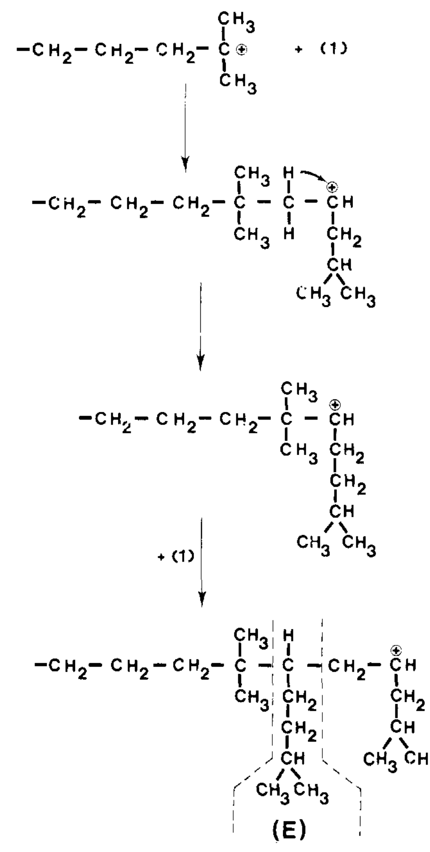
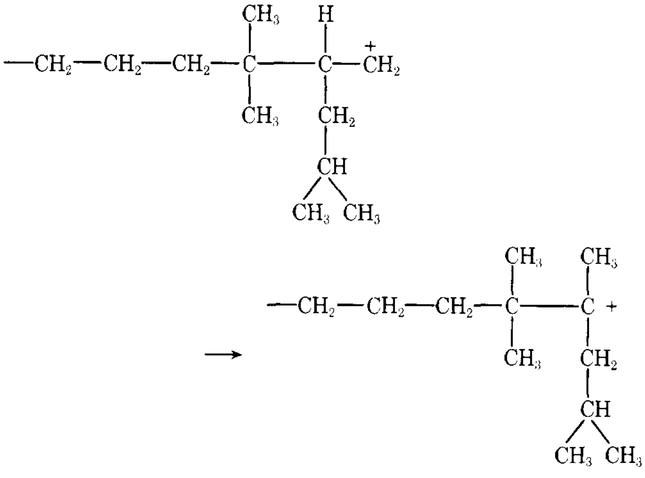


Figure 6. Reaction scheme for the formation of unit E.

However, from a tail-to-tail insertion of the last unit in the growing chain end, another structural unit might derive from a hydride shift, i.e.,



In this structure the chemical shift due to the two equivalent methyl carbons is shifted downfield (calculated 0.49 ppm) with respect to the corresponding atoms of structure A, because of the presence of three carbon atoms in the δ position. Furthermore, an increase of the intensity of the signal at 24.5 ppm (methine carbon) is not compatible with the supposed structure, since the presence of a carbon atom in the γ position shifts the peak from 24.5 to ca. 22 ppm. Unfortunately, in this region of the spectrum there are other signals and, therefore, this hypothetical mechanism cannot be excluded "a priori" on the basis of the spectroscopic evidence. However, this mechanism requires, since the signal at 22.7 ppm is so large,

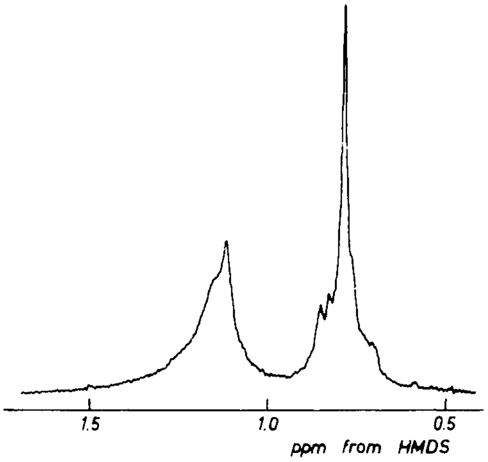


Figure 7. ^{1}H NMR spectrum at 100 MHz of cationic poly(4-methyl-1-pentene) synthesized in polar solvents. Solution (5%) in hexachlorobutadiene at 110 °C.

that one must make the unlikely assumption of a correspondingly large number of irregular monomer insertions during the cationic polymerization of the olefin.[13] Furthermore, this structure involves two adjacent tetrasubstituted carbon atoms which are unfavorable from a thermodynamic and steric point of view.

The second hypothesis, (b), seems to us more consistent with the analysis of the spectrum reported in Figure 5. In fact, the chemical shifts calculated for the carbon atoms C_5, C_4, and C_3 of the structural unit E (cf. Figure 6) are respectively 22.13, 27.99, and 37.16 ppm, in good agreement with the experimental values of those three signals in Figure 5 (respectively at 22.7, 28.4, and 37.1 ppm). These are noticeably more intense than all the others.

It was not possible to demonstrate with off resonance decoupling measurements that the signal occurring at 28.4 ppm was due to a tertiary carbon atom, but the same technique allowed us to conclude that the peak at 37.1 ppm was really due to a methylene carbon, as required by the structural unit E.

As further and partial support to our conclusion, the IR analysis of cationic poly(1) prepared in a nonpolar solvent shows a marked increase in the absorption bands at 1364 and 1383 cm^{-1} (isopropyl group) when compared with those of poly(1) prepared in a polar solvent.

In conclusion, the polymerization mechanism represented in Figure 6 seems very likely in the light of our present knowledge and is mainly supported by ^{13}C NMR analysis.

(3) Quantitative Evaluation of the Structural Units Present in Cationic Poly(1). We have used ^{13}C NMR integral spectra to obtain quantitative structural information on cationic poly(1). Even though we have encountered some well-defined limitations (see below), ^{13}C NMR spectroscopy offers, at present, the best approach for defining the composition of cationic poly(1).

In fact, the structural complexity of cationic poly(1), as revealed by ^{13}C NMR spectroscopy, shows that ^{1}H NMR is not adequate as a structure probe. In our early investigations, we obtained a poorly resolved ^{1}H NMR spectrum of poly(1) at 100 MHz (Figure 7).

The spectrum contains a signal at 0.79 ppm, due to the methyl protons of the unit C, with two upfield shoulders at 0.75 and 0.70 ppm, while two other signals, in the region of methyl resonances, are present at 0.83 and 0.85 ppm. Quantitative evaluations are practically impossible with the 100 MHz spectrum, but it is known from the literature[7] that two well-resolved signals appear at 0.740 and 0.709 ppm when the spectrum is recorded at 300 MHz. They have been attributed to the methyl protons of the unit A and were utilized for the quantitative evaluation of this structural unit in cationic poly(1). However, the following considerations do not support this conclusion:

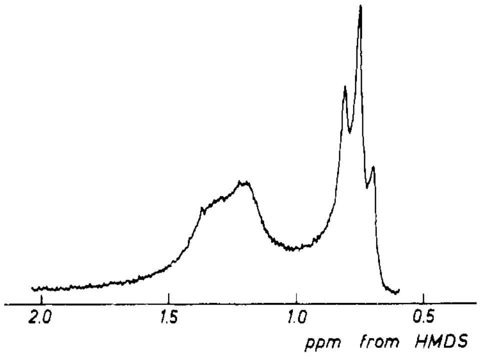


Figure 8. ^{1}H NMR spectrum at 100 MHz of hydrogenated 2,5-poly-(2,4-hexadiene). Conditions: as in Figure 7.

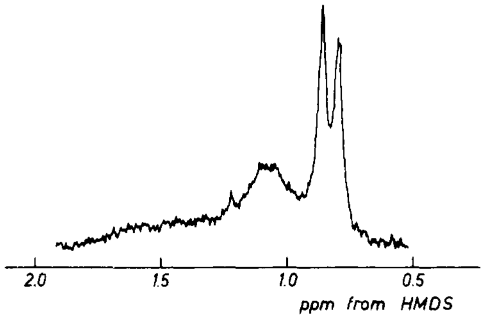


Figure 9. ^{1}H NMR spectrum at 100 MHz of 1,2-poly(4-methyl-1-pentene). Conditions: as in Figure 7.

(a) Figure 8 shows the 100 MHz ^{1}H NMR spectrum of a solution of hydrogenated 2,5-poly(2,4-hexadiene). There are three peaks at 0.69, 0.75, and 0.81 ppm in the region of methyl resonances, which derive from the overlap of two doublets centered at 0.72 and 0.78 ppm, assigned to the erythro and threo configurations of the vicinal methyls. Therefore, the 0.725 ppm doublet reported in the literature[7] probably overlaps both the signals of unit A and those of unit D.

(b) Figure 9 shows the ^{1}H NMR spectrum of a solution of 1,2-poly(1). A doublet centered at 0.82 ppm ($J_{\text{H-CH}_3}$ = 6 Hz) indicates that the signals due to the methyls of the homopolymeric sequences of unit A are present at 0.79 and 0.85 ppm and not as a doublet centered at 0.725 ppm. Even though we cannot rule out at present the possibility that some heterosequences of unit A may give methyl signals near 0.725 ppm, it is evident from our data that the doublet at 0.725 ppm is not due simply to unit A; furthermore more signals due to unit A appear relatively distant from 0.725 ppm.

Nothing can be said at present about the chemical shifts of the methyl protons of unit E. We have encountered some limitations in performing quantitative measurements, as discussed below.

We have considered only the signals due to the methyl carbons of the different structural units to obtain quantitative information. The experimental signals for structures A–D are:

(1) at 22.1 ppm, due to unit A in all the sequences;
(2) at 19.3 ppm, due to unit B in all the sequences;
(3) at 27.3 ppm, due to unit C in the dyads C–C, C–B, and C–D;
(4) at ca. 27.8 ppm, due to unit C in the dyad C–A; and
(5) at 16.3 and 14.6 ppm, due to unit D in the dyads D–D,

Table IV
Polymerization of 4-Methyl-1-pentene (1) in Polar Solvents[f]

Run	Solvent Type	Solvent Dielectric constant[a]	$AlCl_3$, mol/l. × 10^2	Time, h	Conversion, %	[η], dl./g	Structural units, % A	B	C	D	E
1[b]	EtCl	9.45[c]	1.50	1	100	3.25	8.4	13.3	48.5	20.0	9.7
2	EtBr	9.39[c]	2.20	3	55.0	0.59	9.1	10.8	49.8	20.1	10.4
3	MeCl	12.60[d]	0.76	0.25	32.5	0.39	8.8	11.7	50.7	19.4	9.5
4	CH_2Cl_2	8.93[e]	0.66	0.50	43.0	0.43	8.6	11.6	44.2	17.1	18.5
5	Clorobenzene	5.62[e]	2.95	6	35.9	0.45	10.2	12.8	41.9	23.9	11.1

[a] According to ref 28. [b] [1] = 1.58 mol/l. [c] At +20 °C. [d] At −20 °C. [e] At +25 °C. [f] Conditions: [1] = 2.37 mol/l.; $T = -78$ °C.

Table V
Polymerization of 4-Methyl-1-pentene (1) with Different Catalyst Systems[b]

Run	Catalyst Type	Catalyst mol/l. × 10^2	Cocatalyst Type	Cocatalyst mol/l. × 10^2	Time, h	Conv, %	[η], dl./g	$\overline{M}_n \times 10^{-5}$	Structural units, % A	B	C	D	E
1[a]	$AlCl_3$	1.50			1	100	3.25	2.70	8.4	13.3	48.5	20.0	9.7
2	$AlBr_3$	0.90			6	28.1	0.80	0.64	7.4	12.3	46.8	19.0	14.5
3	$AlEtCl_2$	10.00			8	19.3	0.63	0.36	9.1	13.4	47.0	18.7	11.8
4	$AlEtCl_2$	4.00	$(CH_3)_3CCl$	1.00	1	95.3	0.71	n.d.	9.3	12.0	45.0	20.5	13.1
5	$AlEtCl_2$	4.00	Cl_2	4.00	0.2	22.5	2.28	1.85	7.3	12.3	50.0	20.0	10.4
6	$AlEt_2Cl$	2.00	$(CH_3)_3CCl$	1.20	6	66.8	0.38	0.15	8.0	10.8	49.9	18.6	12.7
7	$AlEt_2Cl$	2.00	$SnCl_4$	2.00	6	35.0	0.57	n.d.	9.1	12.5	47.1	19.1	12.1

[a] [1] = 1.58 mol/l. [b] Conditions: solvent = C_2H_5Cl; [1] = 2.37 mol/l.; $T = -78$ °C.

D–C, and D–B. Also, the signal of the first methyl of unit D present in the dyad D–A is overlapped by the signals at 16.3 and 14.6 ppm, and two other peaks at 16.8 and 15.1 ppm, due to the second methyl of unit D in the dyad D–A, should be expected and considered to evaluate this unit. But these peaks are not evident in the spectrum.

Because of the low concentration (i.e., less than 10%) of unit A in the polymer and also because the last two signals are due to a single carbon atom, the absence of the peaks at 16.8 and 15.1 ppm is reasonable. Therefore, an evaluation of the areas of the six signals listed above gives a quantitative measurement of structures A–D.

More complicated is the assignment of signals due to the dyads involving unit E. In fact this unit has a single carbon atom belonging to the backbone from which the branch initiates.

Therefore, there is an additional $\gamma + \delta$ effect for the methyl carbons of unit C and the second methyl of unit D, respectively, in the dyads C–E and D–E, while there is only a δ effect for the methyl of unit B in the dyad B–E. The identification of these additional signals does not appear possible even though, when poly(1) contains abundant amounts of structure E, there are signals which might be attributed to the dyads under discussion. These signals are shifted upfield by the value of γ negative, i.e., 2.5–3 ppm, from 27.3, 16.3, and 14.6 ppm.

Lacking direct evidence for these assignments, we have neglected the dyads B–E, C–E, and D–E and our calculations of the structural composition of poly(1) have been done by computing the areas of the peaks listed above unit (1)–(5) plus that of the peak at 22.7 ppm for unit E.

It is evident that the composition of poly(1), calculated in this manner, underestimates units B, C, and D and overestimates units A and E. This systematic error is proportional to the content of unit E. However, despite the lack of precision in determining the absolute concentration of the structural units of poly(1), the method here proposed can be considered reliable, within the limits of error given in the Experimental Section, when it is applied to the evaluation of the parameters regulating the structure of poly(1).

(4) Influence of the Polymerization Conditions on the Structure of Poly(1). Since altering the experimental conditions during the cationic polymerization of 1 causes significant changes in the ^{13}C NMR spectra of the resulting polymer, we have investigated the influence of certain parameters of the polymerization process.

Two main groups of results have been obtained: the first refers to polymers prepared in polar solvents, the second to polymerization experiments performed in nonpolar media. Despite the relevant difference between the structures of poly(1) prepared in polar and nonpolar solvents, the relative modification of the intensity of the signals is rather modest within each group of results. Furthermore, poly(1) prepared in polar solvents contains less than 20% of unit E, which means that the systematic error involved in determining the percentage of all the structural units is relatively small and thus allows a reliable quantitative evaluation of the influence of the polymerization conditions (cf. section III.3).

(a) Polar Solvents. Table IV shows the results obtained polymerizing 1 at −78 °C in different solvents with a dielectric constant ranging from 5 to 12, in the presence of $AlCl_3$ as catalyst.

The structure of the resulting polymers is practically independent of the type of solvent used, although there is some scattering of the data in CH_2Cl_2 and chlorobenzene. The same result was seen when different types of catalysts were employed in the same solvent, i.e., C_2H_5Cl (cf. Table V), even though different yields and molecular weights were observed. Also the percent conversion to polymer (from 5 to 95%) did not influence the structure of macromolecules obtained at −78 °C with the catalyst system $(C_2H_5)AlCl_2 + (CH_3)_3CCl$ (Table VI). Similar results have been obtained by Kennedy et al.[7] (at −50 °C with $(C_2H_5)AlCl_2$ as catalyst) by evaluating the repeat units A, B, and C from 300 MHz ^1H NMR. The influence of the temperature of polymerization is reported in Table VII for the system $AlCl_3$–C_2H_5Cl. The structure of the polymer, synthesized between 0 and −128 °C, varies as follows: (a) The content of structures A, B, D, and E decreases slightly between 0 and −80 °C within the limits of the experimental errors; this is most evident in the case of unit E, whose percentage varies from 11 to 9%. (b) The content of unit C increases continuously from 45% at 0 °C to 50% at −80 °C; then it remains

Table VI
Influence of the Conversion on Structure of Poly(4-methyl-1-pentene)[a]

Run	Conversion, %	Time, min	[η], dl./g	Structural units, % A	B	C	D	E
1	5.4	12	n.d.	8.4	12.0	49.7	17.7	12.2
2	27.0	20	0.19	8.8	12.5	46.9	19.2	12.5
3	54.9	50	0.43	8.7	12.1	48.2	19.8	11.2
4[b]	95.3	60	0.71	9.3	12.0	46.0	20.5	12.1

[a] Conditions: solvent = EtCl; T = −78 °C; [EtAlCl$_2$] = 1.2 × 10^{-2} mol/l.; [(CH$_3$)$_3$CCl] = 0.48 × 10^{-2} mol/l.; [1] = 2.37 mol/l. [b] [AlEtCl$_2$] = 4.0 × 10^{-2} mol/l.; [(CH$_3$)$_3$CCl] = 1.0 × 10^{-2} mol/l.

Table VII
Influence of the Polymerization Temperature on Structure of Poly(4-methyl-1-pentene)[a]

Run	T, °C	[η], dl./g	Structural units, % A	B	C	D	E
1	0	0.60	9.1	13.4	44.5	22.0	11.0
2	−6	n.d.	9.3	11.7	46.7	21.1	11.1
3	−30	n.d.	8.2	13.6	47.7	19.3	11.2
4	−30	0.71	8.8	11.9	48.3	20.4	10.6
5	−50	0.84	9.4	13.7	49.6	18.2	9.1
6	−64	1.84	9.3	10.5	49.7	19.4	11.1
7[b]	−78	3.25	8.4	13.3	48.5	20.0	9.7
8	−78	1.24	8.6	12.2	49.0	21.1	9.1
9	−90	n.d.	8.4	11.6	49.4	21.2	9.4
10	−110	1.09	8.0	10.2	49.6	16.9	15.3
11	−116	n.d.	7.6	10.7	50.0	16.3	15.4
12	−128	1.05	7.0	9.8	49.8	14.2	19.2

[a] Conditions: solvent = C$_2$H$_5$Cl; [1] = 2.37 mol/l.; catalyst [AlCl$_3$] = 0.22 to 4.70 × 10^{-2} mol/l. [b] [1] = 1.58 mol/l.

constant. (c) Between −80 and −128 °C a relatively sharp increase of the percentage of unit E is observed (from 9 to 20%). The opposite trend is shown by unit D (from 21 to 14%), and the content of units A and B also decreases slightly (from 9 to 7% and from 13 to 10%).

The most interesting result from Table VII (particularly intriguing in terms of polymerization mechanism) is the sharp change of composition of poly(1) which occurs near −80 °C. An analogous result was observed at −100 °C in the polymerization with hydride shift of 3-methyl-1-butene.[19]

These facts might suggest that different polymerization mechanisms are operating below and above the temperature of the abrupt change of composition of the polymer. Such a hypothesis may be supported in our case by the results in Table VIII, which show that at T = −50 °C the polymer structure is independent of the monomer concentration, whereas at T = −110 °C it is dependent of it.

Therefore it can be assumed that between 0 and −80 °C the previously suggested[19] polymerization mechanism holds, whereas other hypotheses must be invoked to account for the experimental data obtained at $T < -80$ °C. For instance, monomer diffusion control could be operating at temperatures below −80 °C as suggested previously[19] in the case of poly(3-methyl-1-butene). Indeed, we observed that typical samples of cationic poly(1) separated massively at ca. −80 °C from the polymerization mixtures containing both C$_2$H$_5$Cl and unreacted 1.[20]

However, this experimental evidence does not account for all the data of Table VII since the content of some isomerized structures increases below −80 °C, e.g., unit E, whereas other repeat units, e.g., B and D, decrease from −80 to −128 °C.

Therefore, it seems likely to assume that, in addition the diffusion monomer control and, perhaps as a consequence of this new situation occurring at $T < -80$ °C, the catalyst species are different from those operating at $T > -80$ °C.

For instance, the monomer might not enter as a third component in the complex involving the cation of the end growing chain and the counterion.[7,21] According to this new situation some isomerization process might be favored with respect to other reactions. Their relative extent will be regulated by the value of the corresponding rate constants, which can be evaluated from the composition data. In fact, according to the scheme of Figure 10 which describes the formation of the isomerized structures arising from intramolecular methide or hydride shifts, it is evident that: $R_A = k_A[A^+]$, $R_B = k_B[A^+] - (k_D + k_C)[B^+]$, $R_C = k_C[B^+]$, $R_D = k_D[B^+]$, and $R_E = k_E[A^+]$, where R_A, R_B, etc., are the rates of formation of the structural units A, B, etc., k_A, k_B, etc., are the rate constants, and $[A^+]$, $[B^+]$, etc., are the concentrations of the different cationic species from which the structural units arise.

The key assumption of the scheme of Figure 10 is that each structural unit derives from ternary complexes (see above and ref 7 and 21) through monomolecular processes. Experimental support for this assumption was found by Fontana et al.[21] and more recently by Kennedy et al.[7] The data of Table VIII at $T > -80$ °C also support the validity of the scheme. On the other hand, at $T < -80$ °C, the dependence of the polymer composition on the monomer concentration cannot be explained by monomolecular processes only. In fact, the formation of structure unit A occurs through a bimolecular process.

Therefore, between 0 and −80 °C the following equations hold: $k_A/k_E = [A]/[E]$, $k_B/k_E = ([B] + [C] + [D])/[E]$, $k_B/k_A = ([B] + [C] + [D])/[A]$, $(k_B + k_E)/k_A = ([B] + [C] + [D] + [E])/[A]$, and $k_C/k_D = [C]/[D]$; while at $T < -80$ °C only the second and the last equations are consistent with the previous discussion.

The Arrhenius plots of the ratios of the rate constants are represented in Figures 11 and 12, respectively, for the range of temperature 0 to −80 °C and −80 to −128 °C. By the least-squares method, the differences in the apparent activation energies for the formation of certain structural units were calculated (Table IX).

In Figure 11 all the plots indicate that very slight activation energy differences exist between 0 and −80 °C for the isomerization process related both to the propagation reaction and reciprocally when they are concurrent. The energetic situation is substantially similar in the range −80 to −128 °C (Figure 12) even though it is clearly different from that of Figure 11,

Table VIII
Influence of the Monomer Concentration on Structure of Poly(4-methyl-1-pentene) in C$_2$H$_5$Cl

Run	[1], mol/l.	AlCl , mol/l. × 10^2	T, °C	Time, h	Conversion, %	[η], dl./g	Structural units, % A	B	C	D	E
1	0.632	0.72	−50	3	87.2	0.48	8.5	12.5	50.7	18.4	9.7
2	1.184	0.75	−50	4	10.4	n.d.	9.1	11.9	50.1	19.2	9.6
3	2.370	0.65	−50	0.4	50.0	0.84	9.4	13.7	49.6	18.2	9.1
4	0.632	2.1	−110	8.5	89.5	1.45	9.3	10.3	52.6	18.1	9.7
5	1.264	2.1	−110	9	39.5	1.41	8.4	10.5	50.5	17.4	13.2
6	2.370	3.0	−110	21	100	1.09	8.0	10.2	49.6	16.9	15.3

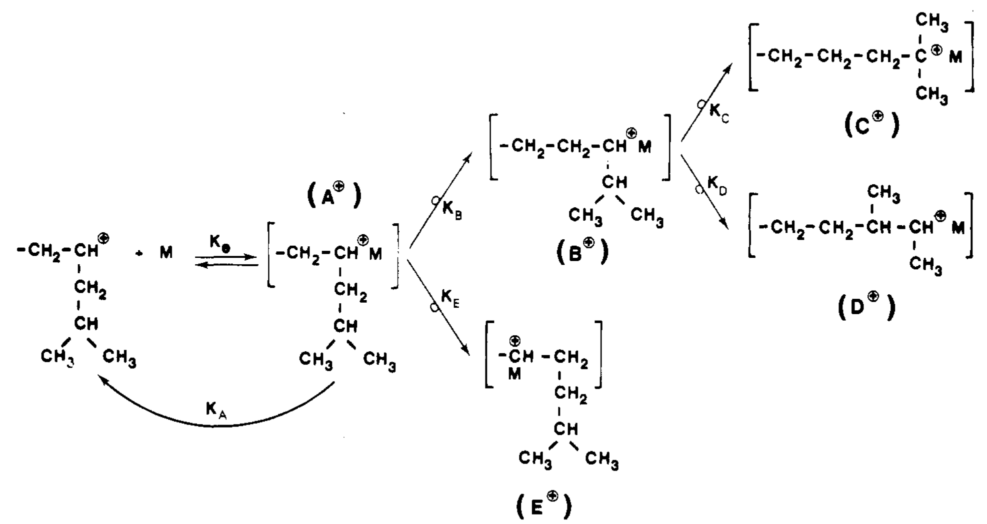


Figure 10. Reaction scheme for the formation of all the structural units identified in cationic poly(4-methyl-1-pentene); M = monomer.

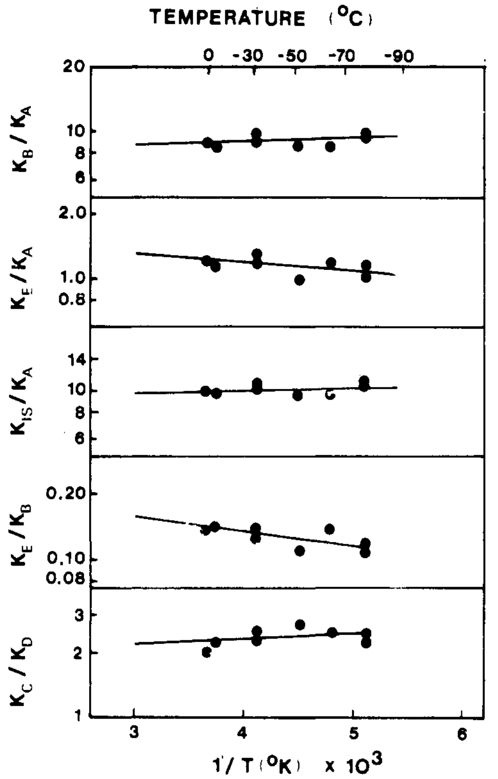


Figure 11. Arrhenius plots of different rate constant ratios measured between 0 and −80 °C.

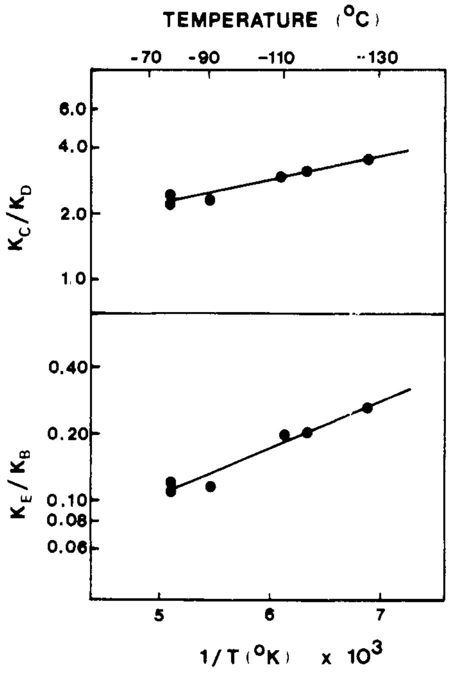


Figure 12. Arrhenius plots of some rate constant ratios measured between −80 and −126 °C.

as discussed below. These results account for the difficulty in obtaining, with cationic catalysts, poly(1) with a unique structural unit.

From Table IX it is evident that both the overall isomerization process and that leading to units B, C, and D are very slightly favored with respect to the propagation reaction by 0.06 and 0.07 kcal/mol, respectively, in the range from 0 to −80 °C.

In contrast, the isomerization process leading to unit E is unfavored by 0.15 kcal/mol.

For the concurrent monomolecular rearrangements leading to structural units E and B, C, D we have observed the most striking results. Above −80 °C the isomerization leading to unit E is unfavorable with respect to that leading to units B, C, D by 0.24 kcal/mol, whereas below −80 °C the situation is reversed (cf. Figures 11 and 12) and the formation of the unit

Table IX

Differences between the Apparent Activation Energies of the Isomerization Reactions and the Propagation Reaction in the Cationic Polymerization of 4-Methyl-1-pentene in C_2H_5Cl[a]

Polymerization temp, °C	$E_B - E_A$, kcal/mol	$E_E - E_A$, kcal/mol	E_{IS}[b] $- E_A$, kcal/mol	$E_E - E_B$, kcal/mol	$E_C - E_D$, kcal/mol
0 to −80	−0.07 ± 0.03	0.15 ± 0.04	−0.06 ± 0.02	0.24 ± 0.03	−0.16 ± 0.03
−80 to −128				0.96 ± 0.05	−0.46 ± 0.02

[a] Values calculated within 66% confidence limits. [b] Activation energy of all the isomerization processes.

Table X
Polymerization of 4-Methyl-1-pentene in Different Nonpolar Solvents

Run	Solvent		$EtAlCl_2$ mol/l. × 10^2	Conversion, %	[η], dl./g	Structural units, %				
	Type	Dielectric constant[a]				A	B	C	D	E
1	*n*-Pentane	1.844[b]	25.0	6.0	0.53	8.1	11.9	29.8	20.6	29.6
2	Propane	1.61[c]	20.0	89.0	0.70	11.4	17.4	24.1	24.0	23.1
3	Toluene	2.379[d]	*e*	12.1	n.d.	9.9	15.6	28.1	27.5	19.1
4	C_2H_5Cl	9.45[b]	10.0	19.3	0.63	9.1	13.4	47.0	18.7	11.8

[a] Cf. ref 28. [b] At 20 °C. [c] At 0 °C. [d] At 25 °C. [e] [Et_2AlCl] = 0.04 mol/l.; [$(CH_3)_3CCl$] = 0.04 mol/l. [f] Conditions: [1] = 2.37 mol/l.; $T = -78$ °C.

Table XI
Influence of the Polymerization Temperature on the Structure of Poly(4-methyl-1-pentene) Obtained in Nonpolar Solvents[a]

Run	Solvent	Catalyst system		T, °C	[η], dl./g	$\overline{M}_n \times 10^{-4}$	Structural units, %				
		Type	mol/l.				A	B	C	D	E
1	*n*-Pentane	$EtAlCl_2$	0.08	+20	n.d.	n.d.	8.0	16.0	32.3	25.1	18.7
2	*n*-Pentane	$EtAlCl_2$	0.12	0	0.30	3.05	7.7	15.3	32.5	26.0	18.6
3	*n*-Pentane	$EtAlCl_2$	0.20	−40	0.28	n.d.	9.6	16.0	30.8	21.4	22.3
4	*n*-Pentane	$EtAlCl_2$	0.25	−78	0.53	n.d.	8.1	11.9	29.8	20.6	29.6
5	Propane	$EtAlCl_2$	0.20	−78	0.70	6.50	11.4	17.4	24.1	24.0	23.1
6	Propane	$EtAlCl_2$	0.80	−110	0.18	1.60	8.0	17.2	30.0	23.0	21.9
7[b]	Propane	*c*	0.17	−160	n.d.	n.d.	6.0	13.5	36.1	19.8	24.6
8[b]	Propane	*c*	0.15	−160	n.d.	n.d.	9.3	12.0	33.2	19.7	25.8

[a] [1] = 2.37 mol/l. [b] [1] = 1.18 mol/l. [c] Catalyst complex $AlCl_3 \cdot (CH_3)_3CCl$ prepared according to ref 29.

E is energetically more probable by 0.96 kcal/mol. We assume that change in the structure of the catalytic species promoting the cationic polymerization of 1, and discussed above, accounts for the abrupt change in the plot of k_E/k_B as a function of temperature at about −80 °C.

Finally, the hydride shift reaction leading to unit C is always more probable (Figures 11 and 12), over the entire temperature range investigated, than the methide shift reaction leading to unit D.

(b) Nonpolar Solvents. The results of typical polymerizations of 1 in nonpolar solvents such as propane, *n*-pentane, or toluene, whose dielectric constant is ca. 2, are collected in Table X. For comparison, in the same table are the results of a typical polymerization carried out in a polar solvent (C_2H_5Cl).

As was noted in section III.2, poly(1) obtained in nonpolar solvents contains more of unit E than is observed in samples prepared in polar solvents. The amount of structural unit C, resulting from a double hydride shift, correspondingly decreases, while the content of all the other repeat units remains practically unchanged.

A possible explanation for the difference in structure of poly(1) obtained in polar and nonpolar solvents may be connected to the existence of the chain propagating centers as paired ions.[22] Intimate contact of the counterion with the growing carbenium ion might hinder the double hydride shift necessary to form the structural unit C. However, the quantitative evaluation of all the structural units of poly(1) containing abundant amounts of unit E is markedly affected by the difficulty in computing the signals in the ^{13}C NMR spectra due to the E–C and E–D dyads, as discussed in section III.3.

Therefore, it is practically impossible to study the influence of the experimental conditions on the structure of the polymer prepared in nonpolar solvents. Only to a first approximation have we attempted to investigate the influence of the polymerization temperature on the composition of the polymer. The results are reported in Table XI and they indicate that there is a different trend in the composition of poly(1) than that observed in polar solvents. In fact, poly(1) prepared in *n*-pentane between +20 and −80 °C shows a significant increase in the unit E content, whereas between −80 and −160 °C in propane a noticeable increase of the unit C content results.

IV. Conclusions

The detailed investigation of the structure of cationic poly(1), performed essentially through ^{13}C NMR, has allowed us to identify two new structural units: (a) one formed from a hydride shift followed by a methide shift, thus resulting in a 1,4-propagation (unit D); (b) the other arising from a hydride shift from C_1 to C_2 of the monomer (unit E).

The previously known[7] structural units, i.e., resulting from 1,2, 1,3, and 1,4 propagations, were confirmed.

For unit D it is worthwhile to observe that a methide shift in cationic polymerization was first observed during the polymerization of 3,3-dimethyl-1-butene.[16] Another interesting example of a methyl shift is the cationic polymerization at low temperature of 4,4-dimethyl-1-pentene,[17] which involves selectivity, at $T \leq -78$ °C, the successive shift of a hydride and then of a methyl group, just as they occur during the formation of unit D.

There are no examples in the literature of competition between hydride and methide shift during polymerization reactions. However, cationic rearrangements involving migrations of hydrogen and methyl groups are known for alkyl halides in the presence of Lewis acids.[23,24]

The "driving force" for the formation of structural unit E could be the stabilization of the carbenium ion on C_1 by the methyl and alkyl groups adjacent to or bonded to C_1.[25]

All the activation energy differences obtained for the isomerization and propagation reactions (cf. Table IX) are small (always less than 1 kcal/mol), indicating that there is no process clearly favored from an energetic point of view. Similar results were obtained for the polymerization[19] of 3-methyl-1-butene in the range +10 to −100 °C. The difference between the activation energy for hydride and methide shifts (always negative in the range 0 to −128 °C) indicates a lower mobility of the methyl group with respect to the hydrogen atom.

It it also interesting that poly(1), prepared in polar solvents, shows an increase of the ratio of structural units E/(B + C + D) with a decrease of temperature from −80 to −128 °C. The activation energy leading to unit E is 0.96 kcal/mol lower than that corresponding to the formation of units B + C and D.

The important parameters responsible for the structure of poly(1) are the polarity of the solvent plus the polymerization temperature.

The influence of the reaction medium on cationic isomerizations was discussed elsewhere.[25] The tendency for rearrangement to a more stable cation is lower in better solvating solvents. On the other hand, there are examples in which rearrangement is greater in less nucleophilic solvents, and still others in which nucleophilic solvation of the more exposed hydrogen seems to aid its migration.[26] At the present time we are unable to account for these opposite trends in hydrogen and carbon participation in rearrangements.[27] Perhaps this lack of fundamental knowledge of the chemistry of carbenium ions may explain why we are unable to find experimental conditions under which poly(1) containing a unique type of structural unit is formed.

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Interaction of Univalent and Divalent Cations with Carrageenans in Aqueous Solution

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ABSTRACT: The activity coefficients of sodium, potassium, and calcium counterions have been determined for κ-, ι- and λ-carrageenans. Electromotive force measurements were made at 25 °C in aqueous solutions containing sodium, potassium, and calcium carrageenans, with and without added simple electrolyte. In the absence of added salt the activity coefficients increased with increasing dilution, and at a given concentration the observed order is $\gamma_{\mathrm{Na}} > \gamma_{\mathrm{K}} > \gamma_{\mathrm{Ca}}$. The experimental ratio $\gamma_{\mathrm{Na}}/\gamma_{\mathrm{Ca}}$ is in agreement with values predicted from Manning's theory. The activity coefficients of the sodium and potassium counterions increase with increasing concentration of added simple electrolyte. The behavior of the sodium counterion agrees more closely than the potassium counterion with the theoretical predictions. The activity coefficients of the counterions were found to depend upon the degree of substitution, and hence on the charge of the polyanion, in agreement with the theory.

The interaction between cations and polyanions has been extensively studied with particular reference to the relative order of cation binding strength and the effect of the anionic substituents in the macromolecule. The condensation of the cations on to the polyanion and the electrostatic interaction of the uncondensed cations with the polyanion have been considered theoretically in terms of the influence of the charge density of the polyanion.[1,2] The theoretical treatment has been applied to the interaction of counterions with a variety of polyanions including polyanionic polysaccharides.[3-11] Although in general satisfactory agreement with the theory is reported, the relative order of activity coefficients $\mathrm{Na}^+ < \mathrm{K}^+$ found for κ- and λ-carrageenans[5] is the opposite of reported values for sulfated polyanions.[6,7]

We have now investigated the interactions of sodium, potassium, and calcium counterions with κ-, ι-, and λ-carra-