

# <sup>13</sup>C nuclear magnetic resonance study of structure of poly(4-methyl-1-pentene) prepared by cationic polymerization

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The structures of three poly(4-methyl-1-pentene) samples prepared with an AlCl<sub>3</sub> catalyst in C<sub>2</sub>H<sub>5</sub>Cl solvent at -78, -50 and +5°C were studied by <sup>13</sup>C nuclear magnetic resonance spectroscopy. Surprisingly, no detectable amount of the 1,2-unit was observed in these three polymers, meaning that the isomerization reaction takes place much faster than the propagation reaction even at +5°C. The four structural units previously known were confirmed in this work. In addition, a new structural unit, which implies successive hydride, methide and hydride shifts, was found.

(Keywords: <sup>13</sup>C nuclear magnetic resonance; poly(4-methyl-1-pentene); isomerization; cationic polymerization)

## INTRODUCTION

The cationic polymerization of 4-methyl-1-pentene has been studied for nearly three decades<sup>1-7</sup>. This polymer is of particular interest because it involves various structural units produced by the extensive isomerization of the growing carbocation derived from 4-methyl-1-pentene. Over the years, the structure of the polymer has been examined, from which various mechanisms have been proposed<sup>5-7</sup>.

In the present study, we have prepared polymers from this  $\alpha$ -olefin by cationic polymerization with AlCl<sub>3</sub> catalyst in C<sub>2</sub>H<sub>5</sub>Cl solvent and re-examined their structures by high-field <sup>13</sup>C n.m.r. spectroscopy. On the basis of detailed n.m.r. information on the structural units of the polymer, a mechanism that consists of cationic rearrangements involving hydride and methide shifts was proposed.

## EXPERIMENTAL

### Cationic polymerization of 4-methyl-1-pentene

Cationic polymerization of 4-methyl-1-pentene was carried out in C<sub>2</sub>H<sub>5</sub>Cl at the chosen temperatures of -78, -50 and +5°C by AlCl<sub>3</sub> under a dry nitrogen atmosphere. Reaction conditions were as follows: [4-methyl-1-pentene]<sub>0</sub> = 1.0 M; [AlCl<sub>3</sub>]<sub>0</sub> = 10 mM; initial volume of C<sub>2</sub>H<sub>5</sub>Cl = 102 ml; reaction time = 6 h; reaction scale = 500 ml.

For the polymerization, the solvent and the catalyst were 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 monomer charging funnel, then cooled to the desired temperature, followed by stirring for an hour. After that, the monomer solution in n-hexane (1.0 mol/240 cm<sup>3</sup>) was added

slowly and dropwise to this mixture over a period of 6 h so as to initiate polymerization under temperature control. The reaction was terminated with 1 mol of methanol. The quenched polymer solution was washed with hot water to remove the catalyst residue, and the product was recovered by precipitation into precooled methanol and was dried in vacuum.

### <sup>13</sup>C n.m.r. analysis

A polymer solution was prepared by dissolving ~100 mg of a polymer sample at 50°C in deuteriochloroform. <sup>13</sup>C n.m.r. spectra were recorded on a JEOL GX-270 spectrometer operating at 67.8 MHz under proton noise decoupling in Fourier-transform mode. Instrumental conditions were as follows: pulse angle, 45°; pulse repetition time, 5.0 s; spectral width, 5500 Hz; number of scans, 10 000; data points, 64 000. The <sup>1</sup>H decoupling distortionless enhancement by polarization transfer (d.e.p.t.) method was also employed to discriminate among carbon species.

### G.p.c. analysis

The average molecular weight of the polymer sample was determined by g.p.c. (Tosoh Ltd, model HLC-802UR) using G4000H8, G3000H8 and G2000H8 × 2 columns and tetrahydrofuran as solvent at 40°C. The molecular weight was estimated on the basis of a polystyrene standard.

## RESULTS AND DISCUSSION

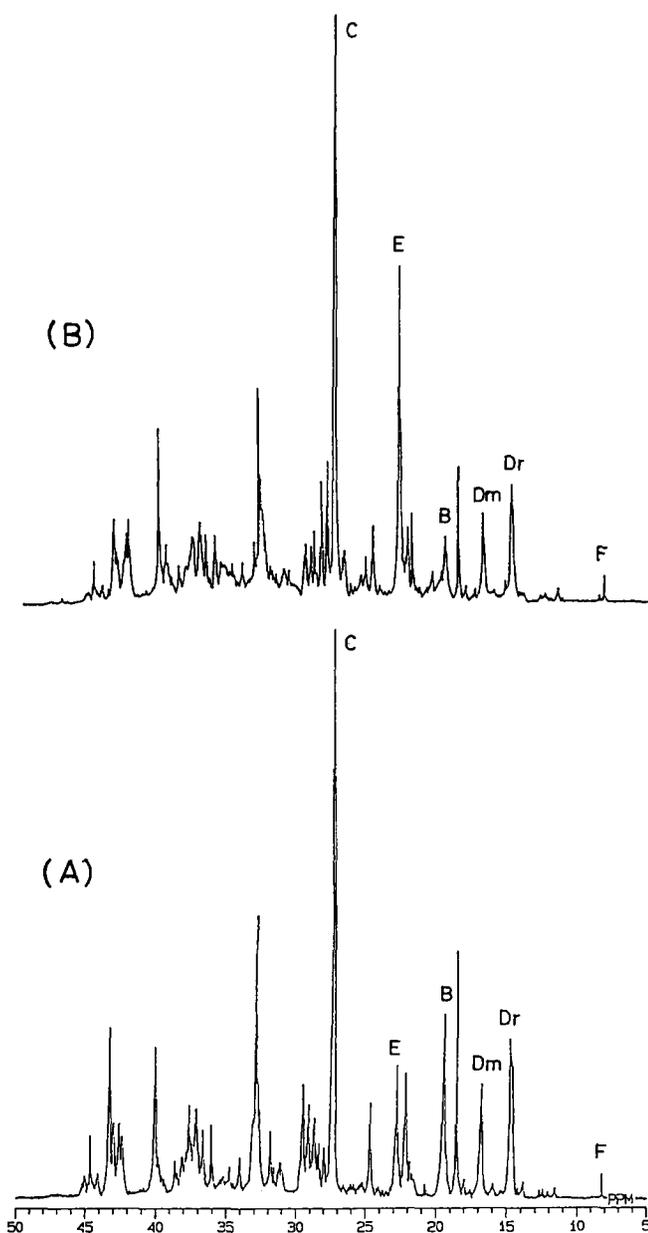
### Structural analysis by <sup>13</sup>C n.m.r.

Cationic polymerizations of 4-methyl-1-pentene were carried out at the temperatures of -78, -50 and +5°C. The results of polymerization are listed in Table 1, showing that the polymer molecular weight depends strongly upon the polymerization temperature in this range, i.e. being high ( $\bar{M}_w = 114 \times 10^3$ ) at -78°C but

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**Table 1** Results of cationic polymerization of 4-methyl-1-pentene

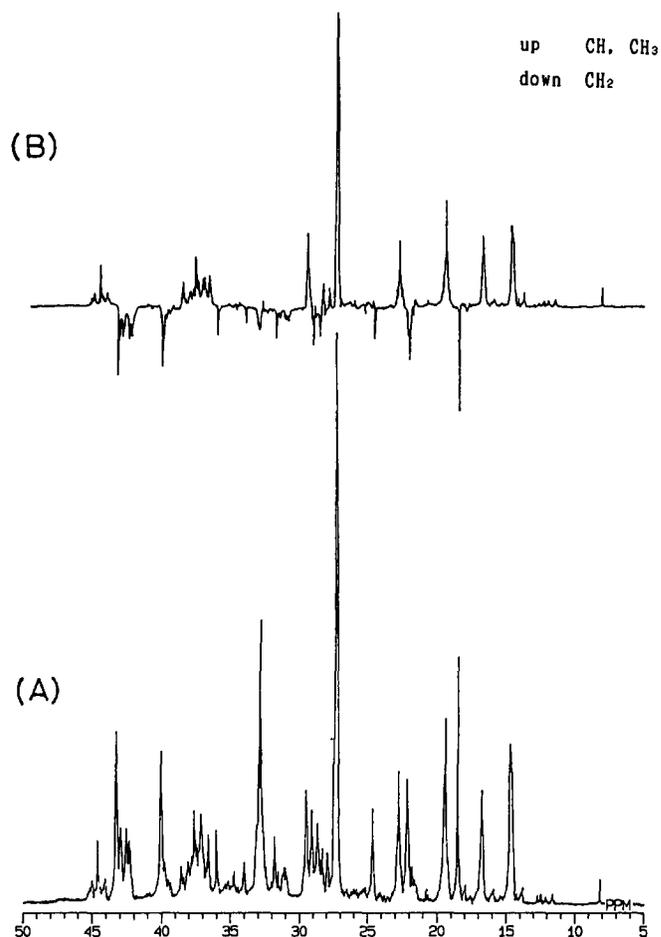
Run no.	Temperature (°C)	Yield (%)	Molecular weight		
			$\bar{M}_n (\times 10^{-3})$	$\bar{M}_w (\times 10^{-3})$	$\bar{M}_w/\bar{M}_n$
1	-78	92	41.5	114	2.76
2	-50	99	14.0	40	2.85
3	+5	100	1.5	6	4.11



**Figure 1** The 67.8 MHz <sup>13</sup>C n.m.r. spectra of cationic polymerized poly(4-methyl-1-pentene) observed in CDCl<sub>3</sub> at 50°C. (A) Polymer prepared at -78°C. (B) Polymer prepared at +5°C. The peaks B, C, Dm, Dr, E and F show the methyl resonances of respective structural units, which are used for the quantitative evaluation

low ( $\bar{M}_w = 6 \times 10^3$ ) at +5°C, as reported in the literature<sup>7</sup>.

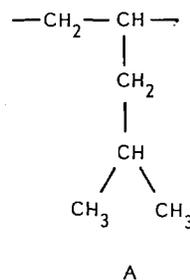
The structures of the polymers were investigated by <sup>13</sup>C n.m.r. spectroscopy. The observed spectra of two samples prepared at -78 and +5°C are shown in Figure 1. The <sup>13</sup>C spectral features of the sample prepared at -50°C are almost the same as those of the other one prepared at -78°C. Also, these two <sup>13</sup>C spectra are essentially the same as those shown in the literature<sup>6,7</sup>.



**Figure 2** (A) <sup>13</sup>C n.m.r. and (B) <sup>1</sup>H-decoupled <sup>13</sup>C d.e.p.t. spectra of poly(4-methyl-1-pentene) prepared at -78°C

This indicates that the polymers prepared at -50 and -78°C in this work are fundamentally the same as those polymerized in C<sub>2</sub>H<sub>5</sub>Cl in this temperature range in the previously reported studies, although our polymerization procedure is exactly the opposite to that adopted by Ferraris *et al.*<sup>7</sup>, where a catalyst solution (AlCl<sub>3</sub> in C<sub>2</sub>H<sub>5</sub>Cl) was added to a monomer solution.

For the structural analysis of the polymer, first of all the <sup>13</sup>C n.m.r. spectrum of the polymer obtained at -78°C was also measured by the d.e.p.t. mode in order to distinguish the types of carbon species. The observed d.e.p.t. spectrum is presented together with the ordinary spectrum in Figure 2. It is noticeable that the two peaks at 22.1 and 24.7 ppm, both of which had been assigned to the methyl and methine groups of the 1,2-added 4-methyl-1-pentene unit, respectively<sup>6,7</sup>, were assigned to methylene groups by the measurement using d.e.p.t. pulse sequence. This result is particularly surprising, because it indicates that the 1,2-added 4-methyl-1-pentene unit (A) is not present in these polymers.





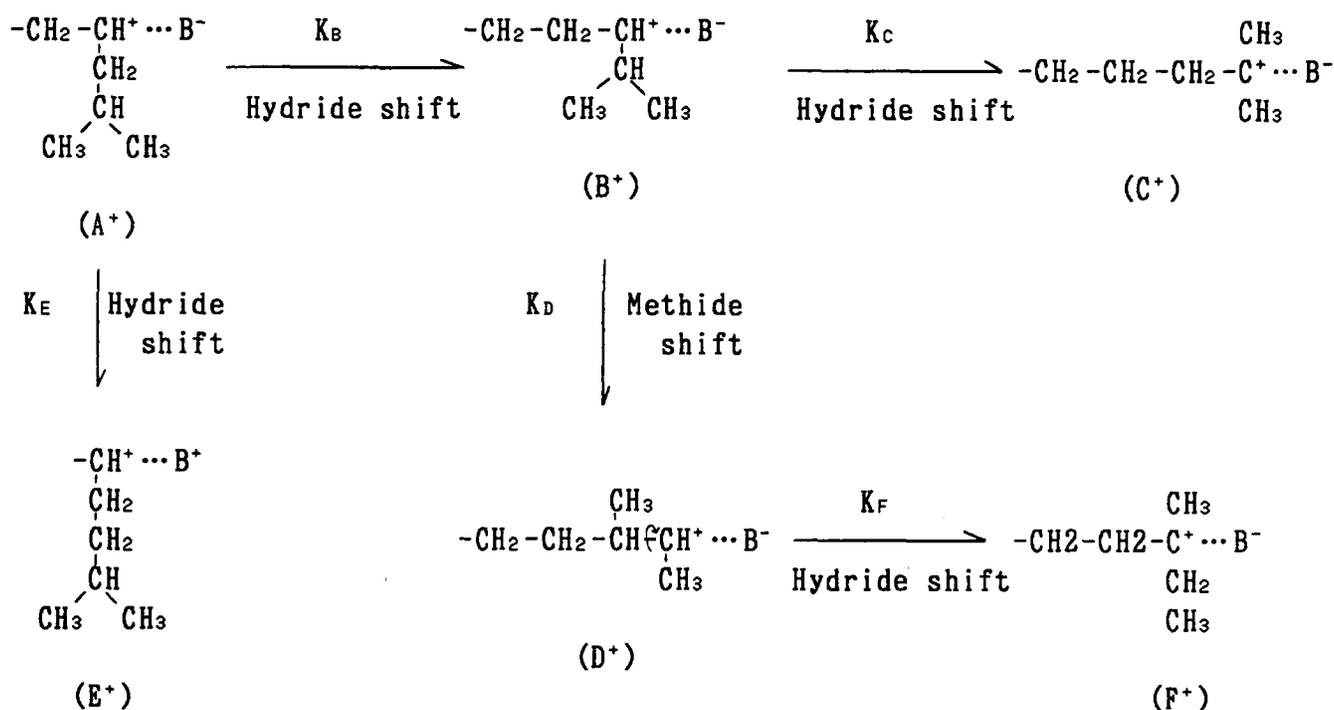
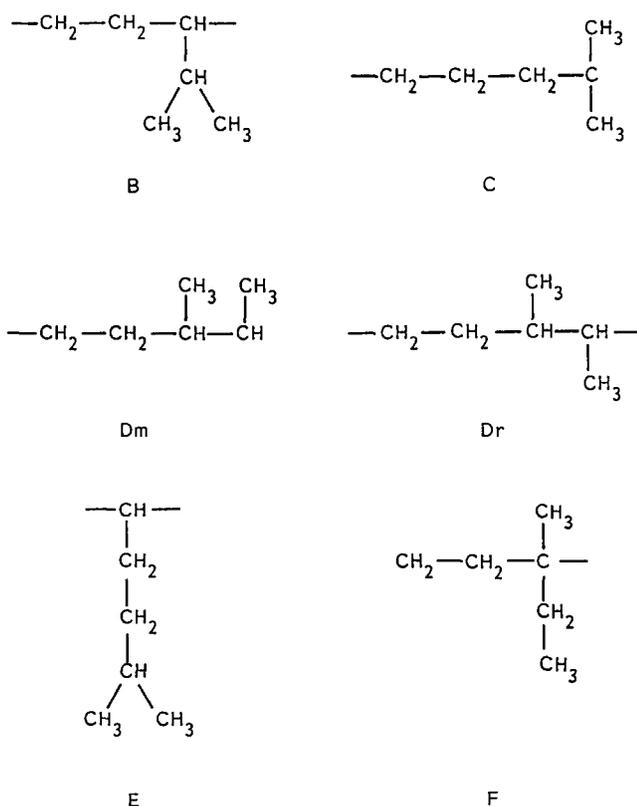


Figure 3 The scheme of isomerization reactions in cationic polymerization of 4-methyl-1-pentene with AlCl<sub>3</sub> catalyst in C<sub>2</sub>H<sub>5</sub>Cl solvent, where K<sub>B</sub>, K<sub>C</sub>, etc. are rate constants and B<sup>-</sup> is a counteranion

Table 2 Composition of structural units in poly(4-methyl-1-pentene) prepared at various polymerization temperatures

Run no.	Temperature (°C)	Structural unit <sup>a</sup> (%)					
		B	C	Dm	Dr	E	F
1	-78	16	47	10	16	10	1
2	-50	15	47	10	16	10	2
3	+5	7	44	8	13	26	2

<sup>a</sup>The structural units are shown below:



These methylene peak assignments strongly support our conclusion because the polymer must have some methylene carbons resonating in the relatively high-field range as discussed above from the viewpoint of the chemical structure.

In addition, Ferraris *et al.* reported that the methyl peak of unit A resonates as 22.1 ppm, while the corresponding one of unit E resonates at 22.7 ppm. However, these n.m.r. data are in conflict with the chemical-shift calculation because the methyl group of the former unit with two δ-carbons resonates at lower field than that of the latter unit having one δ-carbon by 0.49 ppm, according to the table of Lindeman and Adams<sup>10</sup>. Since unit E has been confirmed as previously mentioned, the n.m.r. assignment of unit A is wrong. This result also reinforces our conclusion that the initially formed 1,2-type growing carbocation completely isomerizes to other carbocations leading to the unit structures B-F.

The contents of the units B-F were determined from the relative peak areas of methyl groups according to the method proposed by Ferraris *et al.*<sup>7</sup>. The results are summarized in Table 2. As shown, the polymers prepared at -50 and -78°C have nearly the same composition, while the polymer at +5°C possesses a relatively higher content of unit E and lower content of unit B, which implies that the isomerization reaction is affected by temperature in the range between +5°C and -50°C.

#### Reaction mechanism

The present n.m.r. data show that the isomerization reaction takes place much faster than the propagation reaction even at 5°C and as a result no detectable amount of 1,2-added 4-methyl-1-pentene unit is formed.

In Figure 3 is shown the scheme of the isomerization reactions in the cationic polymerization of 4-methyl-1-pentene. The carbocation structure (A<sup>+</sup>), which

possesses a secondary ion bonding to two methylene groups, is the most unstable among the carbocation structures (A<sup>+</sup>)-(F<sup>+</sup>) in Figure 3, resulting in the rapid isomerization to (B<sup>+</sup>) and (E<sup>+</sup>).

Moreover, the present n.m.r. data show that the rate constant ratio  $K_E/K_B$  in Figure 3 becomes higher as the reaction temperature rises above -50°C, because the E unit increases in the polymer produced at 5°C as shown in Table 2. After attacking the carbocation (D<sup>+</sup>) on a 4-methyl-1-pentene monomer, the Dr unit structure is formed more favourably than the Dm one owing to less steric hindrance of two neighbouring methyl groups, leading to *meso*/racemic placements in a 2/3 ratio.

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