

PYROLYSIS-GAS CHROMATOGRAPHY OF
POLY(3-METHYL-1-ALKENES)

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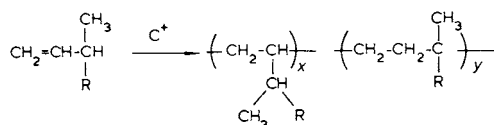
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SUMMARY

The pyrolysis-gas Chromatographic behaviour of poly(3-methyl-1-butenes) and poly(3-methyl-1-pentenenes) with different monomer units was investigated. Both polymers have two different units in their polymer chains, that is, 1, 2- and 1,3-structures. The amounts of the pyrolysis products vary because of the different degradation mechanism of each unit. With poly(3-methyl-1-butenes) the amounts of the two units can be evaluated from the amounts of some of the pyrolysis products.

INTRODUCTION

With cationic catalysts, 3-methyl-1-alkenes polymerize with rearrangement of the propagating carbonium ion from secondary to tertiary [1,2]. This rearrangement proceeds at low polymerization temperatures. Cationically polymerized polymers, therefore, have two units, viz. 1,2- and 1,3-structures.



For poly(3-methyl-1-butenes), the amounts of the two units were evaluated from the near-infrared spectral data [3]. For poly(3-methyl-1-pentenenes), the ratios of the two units were estimated from a comparison of the optical activities between the optically active monomers and their polymers [4]. Pyrolysis-gas Chromatography (Py-GC) is a useful method for the analysis of polymer microstructures, and is especially powerful with insoluble polymers. In previous work, the sequence distributions of some copolymers were investigated by Py-GC [5,6]. In this work, the relationships between the amounts of the two units and the pyrolysis products of cationically polymerized poly(3-methyl-1-butenes) and poly(3-methyl-1-pentenenes) were studied.

EXPERIMENTAL

Each monomer was obtained by dehydration of the corresponding alcohol over activated alumina at 350 °C and was redistilled over sodium metal before use.

The polymerization conditions are given in Table 1.

The ¹³C NMR spectra were obtained by using a 15-MHz high-resolution Fourier transform NMR spectrometer system (JEOL, JNM-FX60) and CDCl₃ or C₆D₆ as solvent.

A Curie-point pyrolyzer (Japan Analytical Industry, JHP-2) was coupled directly to a gas chromatograph (Shimadzu GC-6AM) equipped with dual flame-ionization detectors. Samples of 40-80 μg were pyrolyzed and a stainless-steel column (3 m X 3 mm I.D.) packed with 10% Apiezon L on 60-80 mesh Celite 545 was used. The column temperature was maintained at 60 °C for the first 5 min and increased to 180 °C at a programming rate of 5 min⁻¹. The nitrogen flow-rate was 40 ml min⁻¹ and the hydrogen and air pressures were 0.5 kg cm⁻² and 1.0 kg cm⁻², respectively.

The peak areas were measured by an integrator (Shimadzu Chromatopac-EIA). Identification of the peaks was carried out by comparison with the retention data of known compounds and/or by use of a pyrolysis-gas chromatograph-mass spectrometer system (Shimadzu PYR-10A and GC-MS-7000).

RESULTS AND DISCUSSION

Poly(3-methyl-1-butenes)

Fig. 1 shows the ¹³C NMR spectra of some poly(3-methyl-1-butenes). By comparison of observed and calculated chemical shifts [7,8], it is concluded

TABLE 1
Polymerization conditions of 3-methyl-1-alkenes

Polymer	Catalyst	Solvent	Temperature (°C)
<i>3-Methyl-1-butene</i>			
I	AlCl ₃	C ₂ H ₅ Cl	-78
II	AlCl ₃	C ₂ H ₅ Cl	0
III	AlCl ₃	C ₂ H ₅ Cl	20
IV	AlCl ₃	CCl ₄	77
V	AlCl ₃	CCl ₄	17
VI	AlBr ₃	<i>n</i> -C ₇ H ₁₆	0
VII	Al(<i>i</i> -Bu) ₃ /TiCl ₄	<i>n</i> -C ₇ H ₁₆	15
<i>3-Methyl-1-pentene</i>			
I	AlCl ₃	C ₂ H ₅ Cl	-78
II	AlCl ₃	CCl ₄	0
III	AlCl ₃	CCl ₄	15
IV	AlCl ₃	CCl ₄	77
V	Al(C ₂ H ₅) ₃ /TiCl ₄	<i>n</i> -C ₇ H ₁₆	17

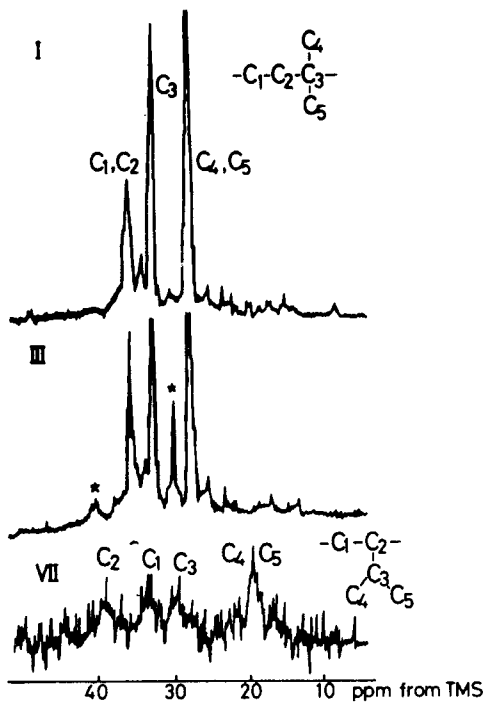


Fig. 1. ^{13}C NMR spectra of poly(3-methyl-1-butenes). I and III, CDCl_3 solutions; VII, C_6D_6 swelling. \star , Signals resulting from the presence of the 1,2-units having 1,3-units with both sides.

that Polymer I is composed of 1,3-units only and that Polymer VII is composed of 1,2-units only. In the ^{13}C spectrum of Polymer I are observed and these signals are attributed to the presence of some 1,2-units among many 1,3-units. The ^{13}C NMR spectra of Polymers II-VI show similar patterns to that of Polymer III. The ratio of the two units could not be obtained by ^{13}C NMR spectrometry owing to the poor solubilities of some of the polymers.

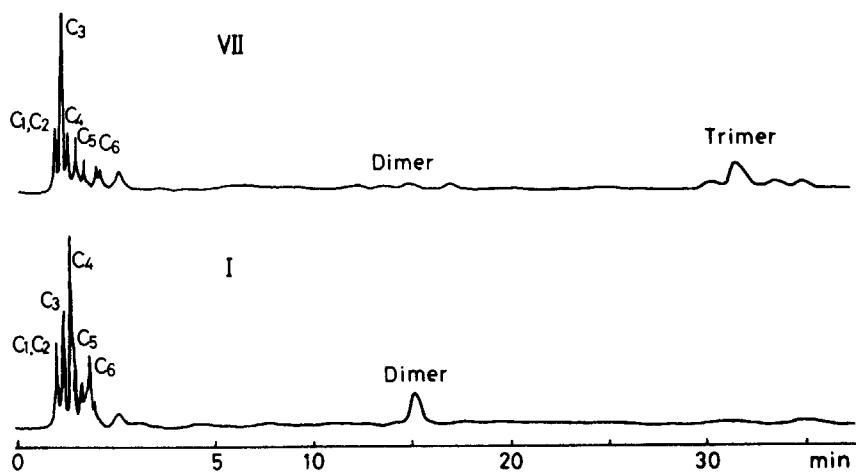
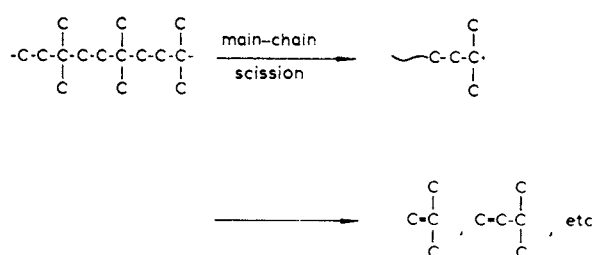


Fig. 2. Pyrograms of poly(3-methyl-1-butenes) at 485°C .

The evaluation of the ratio of the two units by Py-GC is discussed below.

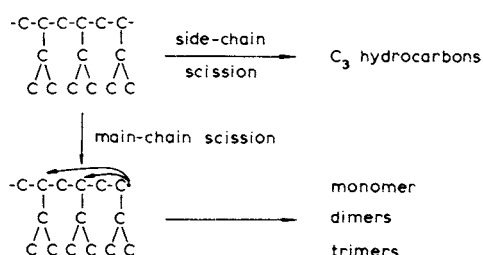
The pyrograms of Polymers I and VII are shown in Fig. 2. Large differences between the two polymers are observed. In the region of the pyrolysis products with lower boiling points, Polymer I gives more C₄ and C₅ hydrocarbons, and Polymer VII gives more C₃ than other hydrocarbons. Moreover, a relatively large peak is observed in the dimer region on the pyrogram of Polymer I, while a large peak is observed in the trimer region on the pyrogram of Polymer VII. These differences can be explained by the degradation mechanisms of 1,2- and 1,3-structures. In the degradation of Polymer I, composed of 1,3-units only, scissions at the main chains to produce tertiary radicals are most probable:



Hence, isobutylene (C₄), 3-methyl-1-butene monomer (C₅) and other C₄ and C₅ compounds are easily produced. The dimer (3,3,6-trimethyl-1-heptene) may be produced by β -scission after the intramolecular radical transfer via the six-membered ring [9] :



On the other hand, with Polymer VII, composed of 1,2-units only, scissions at the side-chains are as probable as those at the main chains. Therefore, a large amount of C₃ hydrocarbons are produced by scissions at the side-chains, as observed on the pyrogram. Scissions at the main chains produce monomer (C₅), dimers and trimers (mainly 7-methyl-2,4-diisopropyl-1-octene) by scissions after "back-biting":



By considering the degradation mechanism of the two units stated above, the amounts of the two units were evaluated. Table 2 shows the relative peak-area ratios of the major pyrolysis products of Polymers I and VII. Polymers II-VI have small amounts of 1,2-units as judged by the ¹³C NMR spectra. Because these polymers have few 1,2-continuous units, dimer or

TABLE 2
Relative peak-area ratios of major pyrolysis products

Polymer	Pyrolysis products				
	C ₁ , C ₂ *	C ₃	C ₄	C ₅ , C ₆ *	D **
I	0.72	1.0	3.32	3.13	1.50
VII	0.51	1.0	0.54	1.35	

* Total peak area.
** Dimer.

trimer formation from such units can be neglected in the following discussion. In Table 2, therefore, the ratios of dimer and trimer produced from Polymer VII have been omitted.

In the pyrolysis of Polymers II-VI, it is assumed that the peak areas of the major pyrolysis products can be described as follows: the sum of the peak areas comes from both 1,2- and 1,3-units:

$$A(C_1, C_2) = k_1 N(1, 3) + k'_1 N(1, 2)$$

$$A(C_3) = k_2 N(1, 3) + k'_2 N(1, 2)$$

$$A(C_4) = k_3 N(1, 3) + k'_3 N(1, 2)$$

$$A(C_5, C_6) = k_4 N(1, 3) + k'_4 N(1, 2)$$

$$A(D) = k_5 N(1, 3)$$

where A is the peak area, $N(1,3)$ and $N(1,2)$ are the amounts of 1,3- and 1,2-units in the sample, respectively, and h is a constant containing the formation constant of each pyrolysis product and the sensitivity to the flame-ionization detector as well as h'. In the peak area of dimer, the contribution of the 1,2-unit has been omitted for the reason given above.

Other pyrolysis products are hardly produced and can be neglected. The ratio of the relative peak-area ratio for each pyrolysis product to the sum of the peak-area ratios in Polymer I can be considered to show the portion of the peak area of the corresponding pyrolysis product from the 1,3-unit in Polymers II-VI, i.e., each value of h in the above equations. Similarly, values

TABLE 3
k and k' values

1,3-unit	1,2-unit
$k_1 = 0.074$	$k'_1 = 0.15$
$k_2 = 0.10$	$k'_2 = 0.29$
$k_3 = 0.34$	$k'_3 = 0.16$
$k_4 = 0.32$	$k'_4 = 0.40$
$k_5 = 0.16$	

TABLE 4
Q and x values

Polymer	Q ⁻¹ *	x × 100
II	2.86–2.97	5.8– 7.5
III	2.60–2.88	7.2–11.9
IV	2.56–2.72	9.8–12.6
V	2.57–2.65	11.0–12.4
VI	2.20–2.46	14.5–20.1

* Each polymer was pyrolyzed six times.

of *k'* are obtained from the ratio of the relative peak-area ratio for each pyrolysis product in Polymer VII. Values of *h* and *k'* are given in Table 3. The most remarkable difference in the degradation of the two units is observed in the formation of C3 and C4 hydrocarbons, as shown in Fig. 2. The amounts of the two units were evaluated by the use of these compounds.

The ratio of the peak areas of C3 and C4 hydrocarbons can be described as follows:

$$\frac{A(C_3)}{A(C_4)} = \frac{k_2 N(1, 3) + k'_2 N(1, 2)}{k_3 N(1, 3) + k'_3 N(1, 2)} = \frac{k_2(1-x) + k'_2 x}{k_3(1-x) + k'_3 x}$$

where

$$x = \frac{N(1, 2)}{N(1, 2) + N(1, 3)}$$

By the use of the value of $Q = A(C_3)/A(C_4)$ Obtained from the pyrogram

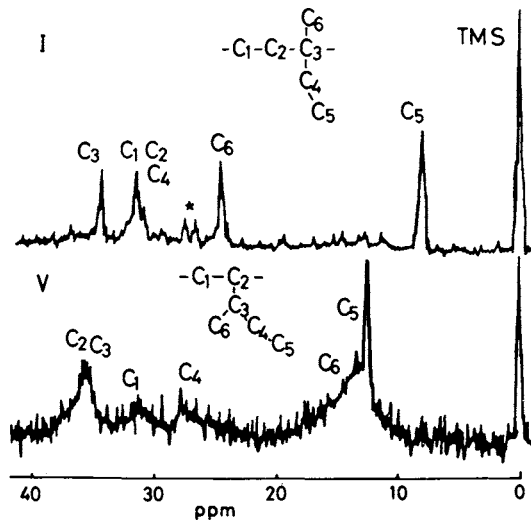


Fig. 3. ¹³C NMR spectra of poly(3-methyl-1-pentenes). I, CDCl₃ solution; V, C₆D₆ swelling. ★, Signals resulting from the presence of the 1,2-units having 1,3-units with both sides.

and the values of k_2 , k'_2 , k_3 and k'_3 , the proportion of the 1,2-unit, x , can be calculated. The values of Q and x thus obtained are given in Table 4. The change in the value of x with variations in the polymerization temperature and solvent used is similar to the values obtained by Kennedy *et al.* [3] by using near-infrared spectrometry.

Poly(3-methyl-1-pentenes)

Fig. 3 shows the ^{13}C NMR spectra of two poly(3-methyl-1-pentenes). In spite of the low polymerization temperature of -78°C , Polymer I shows some signals resulting from the presence of a small amount of 1,2-units, as judged from the calculated chemical shifts. The patterns of the ^{13}C NMR spectra of Polymers II-IV are similar to that of Polymer I. Polymer V is composed of 1,2-units only. Because of the lack of a polymer composed completely of 1,3-units, the amounts of two units could not be evaluated. On pyrolysis, however, a degradation mechanism similar to that of poly(3-methyl-1-butene) was observed, i.e., the difference in the mechanism of formation of products for 1,2- and 1,3-units is clear.

Fig. 4 shows the pyrograms of Polymer I, Polymer V and poly(4-methyl-1-pentene) polymerized with a Ziegler-Natta type of catalyst. Polymer I, the 1,3-unit-rich polymer, produces more C_5 and C_6 compounds and Polymer V more C_4 compounds than other hydrocarbons. poly(4-methyl-1-pentene), composed of 1,2-units only, produces more C_3 and C_4 hydrocarbons. Moreover, the pyrogram of Polymer I has a relatively large peak in the dimer region, whereas those of Polymer V and poly(4-methyl-1-pentene) have large peaks in the trimer region.

Table 5 lists the relative peak-area ratios of hydrocarbons with lower boiling points for poly(3-methyl-1-pentenes) and poly(4-methyl-1-pentene).

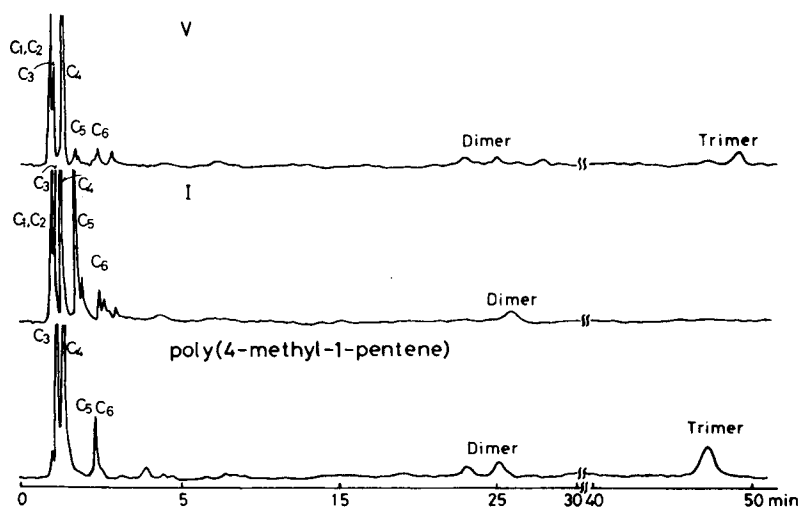
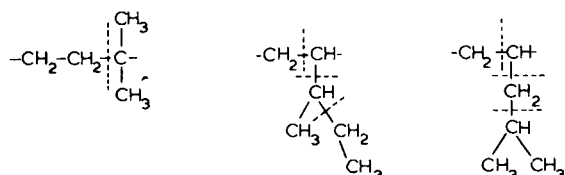


Fig. 4. Pyrograms of poly(3-methyl-1-pentenes) and poly(4-methyl-1-pentene) at 485°C .

TABLE 5
Relative peak-area ratios of major pyrolysis products of poly(methylpentenes)

Polymer	C ₁ , C ₂	C ₃	C ₄	C ₅ , C ₆
I	0.80	0.47	1.0	1.7
II	0.76	0.42	1.0	2.0
III	0.86	0.55	1.0	1.8
IV	0.76	0.62	1.0	1.4
V	0.24	0.16	1.0	0.32
Poly(4-methyl-1-pentene)	0.031	0.31	1.0	0.25



As discussed above, the difference in the degradation mechanism of each unit is clear. Hence, evaluation of the amounts of the two units in the polymers is possible, if the polymer composed of 1,3-units only is obtained for poly(3-methyl-1-pentene).

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