

## COMPOSITION ANALYSIS OF POLYBUTENES\*

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## INTRODUCTION

Polymer pyrolysis may proceed by two paths: (a) chain unzipping to yield monomer and (b) random cleavage. The chain fracture process proceeds by free radical propagation along the polymer chain at thermodynamically weak bonds or sites favoring free radical formation. The random cleavage process proceeds by simultaneous random free radical attack at points along the chain and by multiple thermal homolytic chain cleavage. This latter pyrolysis process gives rise to low monomer yields and an apparently random product distribution. The two processes can operate in competition<sup>1</sup>. The ultrahigh temperature pyrolysis work of BARLOW, LEHRLE AND ROBB<sup>2</sup> has demonstrated that at greater than 900° pyrolysis process *b* supersedes *a*. This has been demonstrated for polymethacrylates, polymethylstyrenes, and several other polymers which can give high monomer yields<sup>2</sup>.

The saturated hydrocarbon polymer "rate of evaporation" studies of WALL AND STRAUS<sup>3</sup> indicate that polyisobutylene and polypropylene decompose principally by random cleavage of the polymer chain. However, the exceptionally high yield of monomer (20%) from polyisobutylene reported in their studies suggests a non-statistical distribution of pyrolysis products.

Information from polymer degradation studies is derived from two sources: (1) rate of pyrolysis studies and (2) an examination of polymer degradation products. The first class of information has provided data for much of the current theoretical work in the field of polyolefin degradation<sup>3-6</sup>.

The techniques and method of pyrolysis/gas chromatography which give the second type of information have been treated by various workers<sup>7-9</sup> but have not found wide application in the field of polymer pyrolysis mechanism studies. This has been due largely to lack of sufficient theoretical information needed to effect more than an empirical relationship between pyrolysis products and polymer structure.

In consideration of this previous work, it is now possible to investigate the pyrolysis behavior of polybutenes by means of pyrolysis product analysis. The polybutenes are currently of great interest to the petroleum industry due to their wide application.

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## EXPERIMENTAL

Polymer samples were prepared by the ionic polymerization of various mixtures of propylene, 1-butene, *cis*- and *trans*-2-butene, and isobutylene. Isobutylene content ranged from 10% to 100%. The nature of the polymerization caused the average molecular weight of the copolymers to depend directly on the isobutylene content of the reaction mixture. These low molecular weight polymers are hereafter referred to as polybutenes.

Two of the polybutene samples, A and C, were segregated into narrow molecular weight range fractions by the solvent-thermal-gradient column methods of BAKER AND WILLIAMS<sup>10</sup> and of CANTOW, PORTER AND JOHNSON<sup>11</sup>. The solvent-nonsolvent system was benzene-acetone, and the thermal gradient was 60–28° down the column. Molecular weights were determined by intrinsic viscometry. Studies were made on polybutene fractions which differed in composition but had the same molecular weight.

Nuclear magnetic resonance (NMR) spectra were determined on the unfractionated polybutene samples diluted to 12.5% with carbon tetrachloride, see Fig. 1.

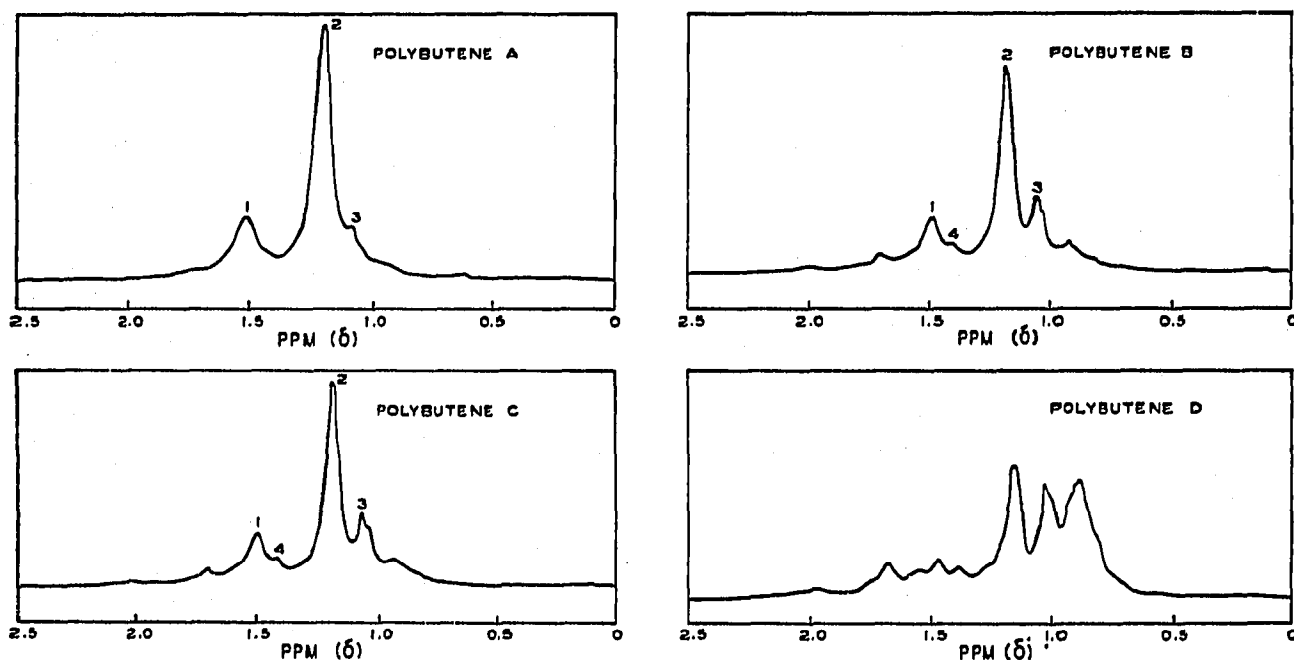


Fig. 1. Nuclear magnetic resonance spectra of polyisobutene containing various amounts of impurities. A = Pure isobutylene feed stock. B = 70% Isobutylene, 20% propylene, 10% butene mixture. C = 58% Isobutylene, 30% propylene, and 12% butene mixture. D = 30% Isobutylene, 40% propylene, and 30% butene mixture. The butene mixture consists of butene-1 and butene-2 in isomeric proportion.

The NMR proton peaks were assigned on the basis of reported resonance values<sup>12</sup> and laboratory working standards. The instrument used was a Varian A-60.

The apparatus used for pyrolysis studies has been described previously<sup>13,14</sup>. The time required for the sample to reach furnace temperature was 15 sec under the conditions used in this study.

The chromatograph was of conventional design using 8000  $\Omega$  (nominal) thermistor

detectors and two columns in series. The first column was a 10-ft. 40/60 mesh Johns-Manville C-22 firebrick column coated with 28.6 % Carbowax 100. The second column was a 50-ft. 40/60 mesh Johns-Manville C-22 firebrick column coated with 23 % propylene carbonate. All columns were constructed from 1/4-in. copper tubing. The Carbowax 100 column was operated at 100° and the propylene carbonate column at 25°. Helium carrier gas flow was maintained at 35 cc/min.

Polymer samples were pretreated for 3 h at 4 mm pressure and 50° after being weighed into pyrolysis cups. Degassing was necessary to effect a relatively complete removal of sorbed oxygen, thus insuring conditions of anaerobic pyrolysis.

The identity of the major components of pyrolysis (propylene, isobutylene, and 2,4,4-trimethylpentene-2) was established by freezing out the gas under the chromatographic peak followed by infrared and mass spectrometric identification. Other components were identified from elution times.

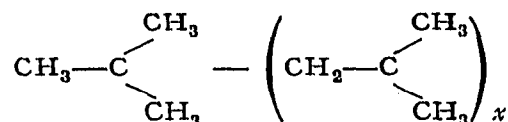
Gas chromatographic response curves were constructed for isobutylene, propylene, and 1-pentene using API standards. These curves were used in the calculation of the weight per cent yields of the principal components.

The amount of chromatographable material produced by the anaerobic pyrolysis of Sample A was determined by trapping all gases leaving the column in a weighed molecular sieve (5A) tube, equipped with stopcocks, similar to that used in carbon-hydrogen analyses. This molecular sieve tube was cooled in boiling liquid nitrogen. At -40° molecular sieve retains all hydrocarbons. On the basis of elution times from the Carbowax column, the sieve contained materials from C<sub>1</sub> to branched chain C<sub>16</sub>. The amount of material on the sieve was obtained from the weight change in the dry, helium-filled sieve before and after pyrolysis. The weighing error, calculated from three blank runs, was ± 0.001 g.

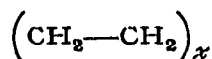
## RESULTS

### *Nuclear magnetic resonance*

The NMR spectra shown in Fig. 1 indicate large differences in the proton types and relative concentrations for four polybutenes. Polybutene A, made from relatively pure isobutylene, exhibits only three proton types in large concentration. Peak 1 is assigned to protons in chain methylene. Peak 2 is due to the side chain methyl protons. Peak 3 is due to terminal protons. The ratio of the areas of Peak 1 to Peak 2 is 2:6. The small size of Peak 3 indicates a relatively high molecular weight polymer. The NMR spectra and methyl-methylene proton ratios indicate a structure which would be expected of a pure, regular head-to-tail polyisobutylene of high molecular weight:



The NMR spectra of polybutenes B and C indicate a composition similar to polybutene A but of lower isobutylene content. Two additional peaks appear in the spectra. Peak 4 is thought to be due to a methylene proton paired with a second methylene:



The split in the terminal methyl proton Peak 3 indicates two types of chain end. The area ratio of Peak 1 to Peak 2 is near 2:6 which indicates that the polymers are essentially polyisobutylene with occasional methylene irregularities.

The NMR spectrum of polybutene D is quite different from polybutenes A, B and C. At least five different types of chain protons are present as well as two types of side chain protons. The terminal proton peak is broadened into a shoulder suggesting a low molecular weight material containing both a large number of terminal protons and proton environments. The number of methyl branches on the chain is low. The assignments above are tentative in view of limited reference compounds available. Further NMR work aimed at verifying these assignments is in progress.

### Pyrolysis

Fig. 2 illustrates the general pyrolysis/gas chromatographic pattern of Sample A. In general, polyisobutylene pyrolyzes in the temperature range 430° to 600° to yield, in varying ratios, methane, ethane, propane, butane, ethylene, propylene, neopentane, 1-butene, isobutylene, *trans*- and *cis*-2-butene, 2-methyl-1-butene, and *trans*- and *cis*-2-pentenes. In addition to these lighter products, the dimer of isobutylene, 2,4,4-trimethyl-2-pentene, is produced. Isobutylene and propylene make up over 30 % of the pyrolysis products and, as such, constitute the principal pyrolysis products. Isobutylene trimer and tetramer materials are also found. In the pyrolysis temperature

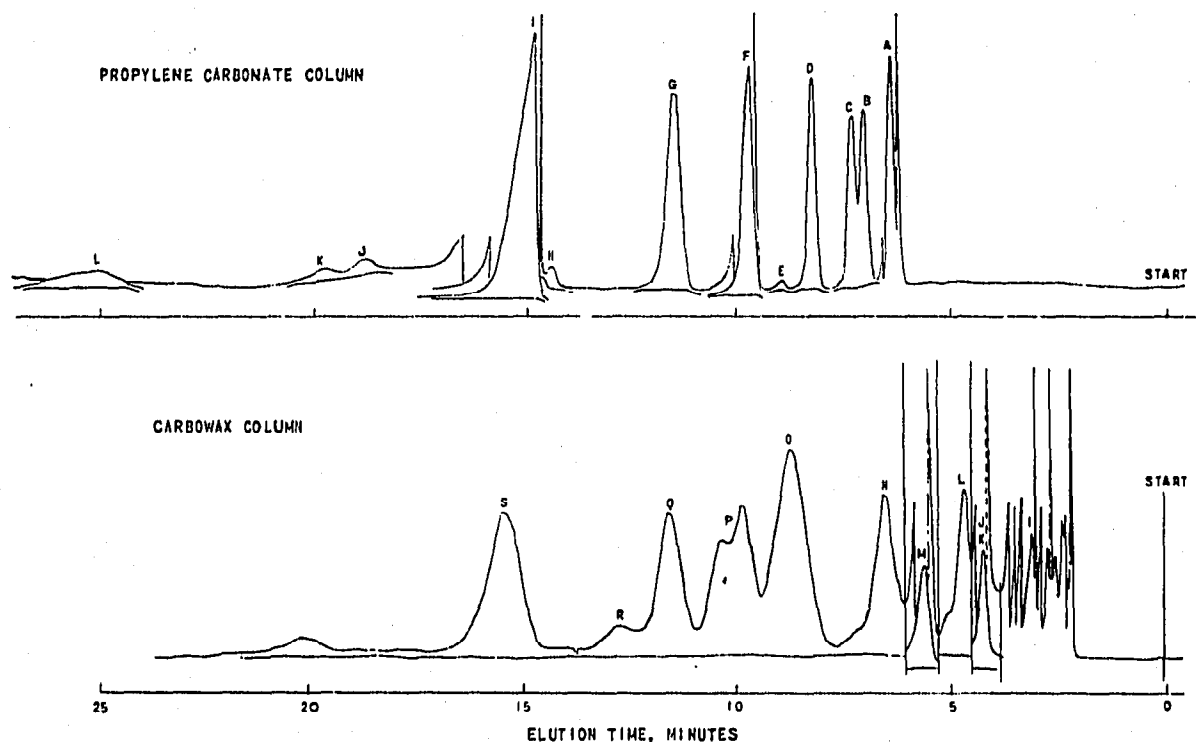


Fig. 2. Pyrolysis/gas chromatograms of polyisobutylene A. A sample equivalent to 0.0198 g of polymer was pyrolyzed at 485° in a 35 cc/min helium carrier gas stream. The Carbowax column record was recorded at four times the base sensitivity of the propylene carbonate column. The chromatographic peaks are identified as follows: A = Air and methane. B = Ethane. C = Ethylene. D = Propane. E = Butane. F = Propene. G = Isobutane. H = Butene-1. I = Isobutylene. J = *trans*-2-Butene. K = *cis*-2-Butene. L = 2-Methyl-1-butene. M = 2,2,4-Trimethyl-2-pentene. N, O = Dimer olefins. P, Q, R = Trimer olefins. S = Tetramer olefin.

range 400° to 500°, 80–86 % of the polymer sample is pyrolyzed to materials in the carbon range C<sub>1</sub> to C<sub>16</sub>. The remaining 14–20 % is not found in the pyrolysis cup and is, therefore, trapped on the column. This non-chromatographable material must be relatively long polymer chain fragments which are swept from the pyrolysis chamber before further pyrolytic cleavage occurs. The reproducibility of pyrolysis product yields is  $\pm 5\%$  as is shown in Table I.

TABLE I  
PRINCIPAL PRODUCT YIELD OF POLYBUTENES PYROLYZED AT 525°

Sample	Average molecular weight	Weight % propylene*	Weight % isobutylene*	Weight % 2,4,4-trimethyl-2-pentene*	Weight % trimers and tetramers*
A	5300	6.61	30.9	2.37	25.9
		6.52	31.0	2.20	24.6
B	1400	6.35	26.3	2.77	30.0
		6.05	24.8	2.40	31.0
C	1200	5.84	23.4	2.80	32.0
		5.63	21.0	2.75	31.8
D	450	3.93	13.8	3.09	30.0
		3.50	13.6	2.89	29.6

\* Weight % based on initial sample weight.

In order to isolate the variables present in any detailed pyrolytic study, experiments were performed on the effects of temperature, flow rate, and sample size on pyrolysis results. The rate of decomposition of polyisobutylene below 420° is too slow to give chromatograms with properly resolved peaks. For all polybutene samples, the production of isobutylene and propylene rises sharply from 420° to 485° and then decreases slowly from 485° to 550°. The point of maximum production of isobutylene was unique for each of the four polybutenes as shown in Fig. 3.

The temperature of initial pyrolysis as well as the temperature at which maximum isobutylene production occurred was found to increase with increasing molecular weight and increasing degree of polymer chain homogeneity. The polybutene samples show an increasing yield of isobutylene in the order A, B, C, D.

Isobutylene production was found to increase by 15 % when the helium flow rate was decreased from 35 cc to 20 cc/min at 550°. Production of the dimer, 2,4,4-trimethyl-2-pentene, decreased under the same conditions as did the peaks due to higher molecular weight chain fragments. This indicates that the decomposition of polymer under the dynamic conditions of pyrolysis/gas chromatography is incomplete and that a higher isobutylene yield can be effected by further action on high molecular weight fragments. With careful control of carrier gas flow rate, isobutylene yield is kept within  $\pm 5\%$ .

Sample sizes from 0.01 to 0.05 g showed a small, 4.8 %, variation in the weight per cent of isobutylene and propylene produced. This variation is within the observed reproducibility of 5 % and was not considered further.

The effect of molecular weight on the weight per cent yield of isobutylene was

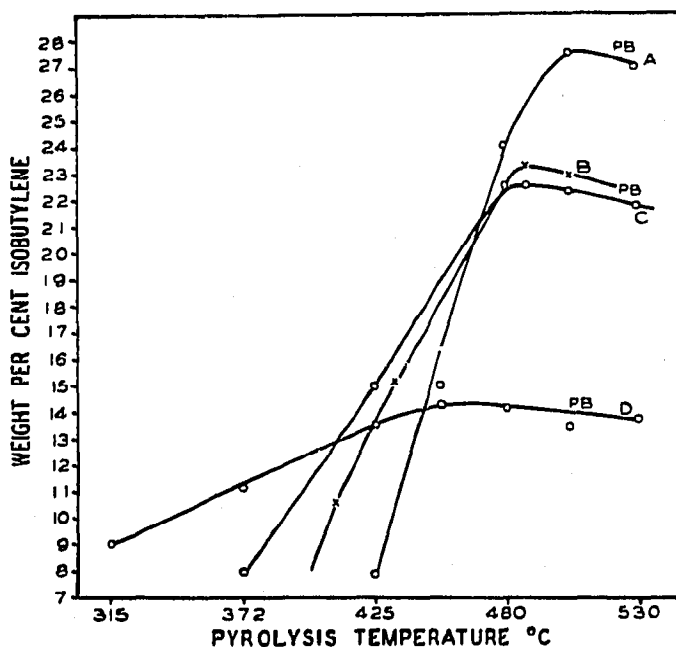


Fig. 3. Isobutylene yield at various pyrolysis temperatures.

studied under uniform conditions of flow (35 cc/min), sample size (0.02 g), and temperature 485°. The weight per cent yield of isobutylene increased with increasing molecular weight as shown in Fig. 4. However, the data from Samples A and C formed two experimental groups. The increase of isobutylene production with increasing molecular weight fractions of pure polyisobutylene, Sample A, was small. Conversely, the increase in isobutylene production from Sample C was large with the increasing molecular weight of the fraction.

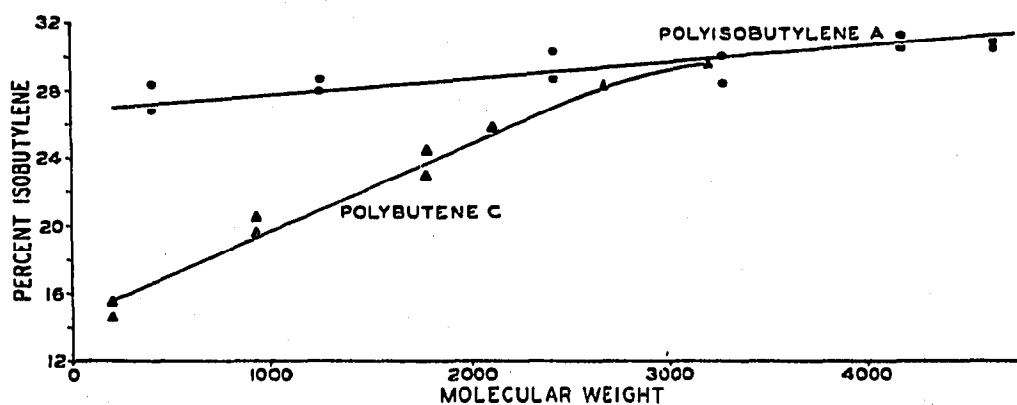


Fig. 4. Isobutylene yield of polybutenes A and C at different molecular weights.

#### DISCUSSION

The 80% to 86% yield of chromatographable material indicates that the degree and rate of degradation are high for polyisobutylene under the conditions used in this study. The 22% to 27% average yield of isobutylene from Sample A agrees well with

the mass spectrometric data of WALL AND STRAUS<sup>3</sup> and is comparable, therefore with other experimental studies done by the "rate of evaporation" techniques.

The high monomer yield from pure polyisobutylene is unusual for the pyrolysis of polyolefins. The 5 % yield of propylene and 13 % yield of 2,4,4-trimethyl-2-pentene also do not fit with the expected statistical product distribution of a system undergoing random cleavage. SIMHA's general theory<sup>6</sup> predicts a wider distribution of products. Since all kinetic data<sup>3,6</sup> indicate that the thermal decomposition proceeds by the simultaneous cleavage of the chain at many locations, the polymer chains must contain weak points at relatively even intervals which gives rise to the restricted product distribution.

This weak bond, at a quaternary carbon atom, agrees with the work of GRANT AND GRASSIE<sup>15</sup> and GRASSIE<sup>16</sup> who noted that polymethacrylic acid produced large amounts of monomer whereas polyacrylic acid did not. Polypropylene has a structure equivalent to polyisobutylene but lacking a quaternary carbon atom. Correspondingly, the pyrolysis product distribution of polypropylene is large; and the monomer yield, 2 %, is low<sup>17</sup>. The higher decomposition temperature of polypropylene, as opposed to polyisobutylene, 380° and 340°, respectively<sup>18</sup>, further indicates a large difference in chain stability towards thermal cleavage.

The pyrolysis temperature of maximum isobutylene production increases with increasing isobutylene content, see Fig. 3. This is probably caused by the addition of new but uncharacterized weak bond sites present in polymers B, C and D. This decrease in thermal stability of a polymer chain with increase in number of pendent groups is consistent with other pyrolysis studies<sup>17</sup>.

The increase of the isobutylene yield and the decrease in dimer yield with decreased flow rate indicate incomplete decomposition of dimer fragments at higher flow rates; *i.e.*, shorter residence time in the pyrolysis chamber. This effect necessitates accounting for the dimer production when considering monomer yield.

The molecular weight effects observed with fractionated polyisobutylenes is in agreement with the statements of SIMHA<sup>19</sup> and WALL<sup>3</sup> concerning the role of molecular weight in a randomly cleaved system. Molecular weight has very little effect on monomer yield. A large effect is noted, Sample B, when the final molecular weight of the polymer is determined by the initial isobutylene content of the reactants. The distribution of fragments above the dimer, 2,4,4-trimethyl-2-pentene, follows a decreasing exponential curve which is further evidence of a random cleavage of the chain<sup>17</sup>. If unzipping via radical propagation down the length of the chain were operating to any extent, a sharp cutoff of pyrolysis fragments would have been observed<sup>6</sup>.

#### CONCLUSION

This work confirms that polyisobutylene decomposes primarily by a random cleavage of the polymer chain. Due to the instability of the quaternary carbon atom in the chain, cleavage at these sites is favored. The high thermal stability of the isobutylene fragment over that of possible higher cleavage products favors the apparent high monomer yield. The effect of impurities in the polyisobutylene chain is to lower the thermal stability of the material by the introduction of irregular chain branching. These additional branched sites result in cleavage products other than isobutylene or 2,4,4-trimethyl-2-pentene.

The structure of polybutenes is defined by combined pyrolysis/gas chromatography and NMR. The pyrolysis chromatograms give a direct analysis of polybutene type, and NMR spectra define chain structure according to branching. The approximate molecular weight of the polymer is also reflected by NMR spectra and pyrolysis chromatograms where original reactant composition controls the product molecular weight.

#### SUMMARY

The structure and composition of polyolefins made from pure isobutylene and from isobutylene diluted with various amounts of other light olefins have been investigated. The techniques used were nuclear magnetic resonance and combined anaerobic pyrolysis and gas chromatography. Nuclear magnetic resonance gave a measure of molecular weight and of isobutylene polymerized into the polymers. Pyrolysis chromatograms of pure polyisobutylene indicated a broad range of volatile hydrocarbon products, principal of which were propylene and isobutylene. For three mixed olefin polymers, the yields of propylene and isobutylene were directly proportional to the amount of isobutylene polymerized into the copolymer. Each polymer composition exhibited a pyrolysis temperature for maximum isobutylene yield. This temperature increased with the isobutylene content of the polymer.

Pyrolysis chromatograms were found to be virtually identical for a molecular weight series of pure polyisobutylenes. Fractionated olefin copolymers did show a distinct increase in isobutylene production from pyrolysis with increasing molecular weight. This is because the molecular weight of butene copolymers generally increases with the isobutylene content of the copolymerized mixture.

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