

Pyrolysis-Molecular Weight Chromatography: A New On-Line System for Analysis of Polymers. II. Thermal Decomposition of Polyolefins: Polyethylene, Polypropylene, Polyisobutylene

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Synopsis

The thermal decomposition of low-density polyethylene, isotactic polypropylene, and polyisobutylene has been studied in helium at a heating rate of 20°C/min using an experimental system which consists of a programmable pyrolyzer, a thermal conductivity cell, and a mass chromatograph.

For low-density polyethylene, the formation of a homologous series of volatile products corresponding to alkanes and alkenes is interpreted in terms of an intramolecular radical transfer process in the primary macroradicals to the 5th, 9th, 13th, and 17th carbon atoms of the chain.

For isotactic polypropylene, the formation of a homologous series of volatile products corresponding to monomer, dimers, trimers, and higher oligomers is explained also in terms of intramolecular radical transfer processes. Transfers to the 5th, 9th, and 13th carbon atoms in the secondary macroradicals (indexing from the secondary carbon atom at the chain end) and transfers to the 6th, 10th, and 12th carbon atoms in the primary macroradicals are shown to account for the major products of pyrolysis.

For polyisobutylene, in addition to the depolymerization process which accounts for the extensive formation of monomer, intramolecular radical transfer processes in the primary and tertiary macroradicals (the processes proceeding predominantly in the primary macroradicals) are shown to account for the formation of the dimers, trimers, and higher oligomers that occur in the volatile products of decomposition.

INTRODUCTION

The extent of degradation of a polymeric system can, in principle, be followed by monitoring the formation of the decomposition products and/or by measuring changes of properties in the residue. Analysis of the decomposition products and their identification gives detailed information which can be used, for example, as a "fingerprint" for identification,^{1,2} to postulate mechanisms of degradation,³⁻⁵ to elucidate the microstructure of the initial polymer,⁶⁻¹¹ and to determine the composition of polymer blends.^{12,13} Combinations of a pyrolyzer with analytical tools (chromatographic and/or spectrophotometric) are well suited for such applications.^{14,15}

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In the decomposition of polymers, the formation of volatiles is often a consequence of chain reactions involving radical intermediates.^{3,16} Initiation, which can be either random or at specific sites (such as chain ends), leads to the formation of polymer radicals that can depolymerize to give monomer, or undergo intra- and intermolecular transfer reactions to give a number of different decomposition products. It is primarily the nature of the initiation and of the competition between the depropagation (i.e., depolymerization) and the transfer processes which determines the course of decomposition. The relative extents of the competing reactions depend on the structures of the polymers.

The present paper discusses the thermal decomposition behavior of low-density polyethylene, isotactic polypropylene, and polyisobutylene for the purpose of demonstrating the capabilities of a new experimental system.¹⁷⁻¹⁹

EXPERIMENTAL

Description of the System

The details of the instrumental and operational aspects of the experimental system have been described elsewhere.¹⁹ Briefly, the system consists of a programmable pyrolyzer, a thermal conductivity cell, and a mass chromatograph which are coupled in series. The pyrolyzer consists of a quartz tube and an external heater which provides flexibility for either program- or flash-heating to 800°C. The volatile products of pyrolysis are transported by helium through the thermal conductivity cell which monitors their formation. Any desired fraction of the volatile products passing through the thermal conductivity cell can be conveniently selected and analyzed by the mass chromatograph. The mass chromatograph utilizes two independent gas chromatographic systems, with different carrier gases, which are coupled through a common injection port. When a sample is introduced into the instrument, it is split into two approximately equal fractions which are then introduced into the matched chromatographic columns where separation is achieved. As they elute, the constituents are detected by gas density detectors which are situated at the ends of the columns. A gas density detector responds to the difference between the molecular weight of the carrier gas and that of the solute. The instrument provides two simultaneous sets of gas-chromatographic peaks (one from each detector). The ratio of a peak in one set to its counterpart in the other is related to the molecular weight of the constituent which is responsible for the particular peaks through

$$M_x = \frac{(A_1/A_2) KM_{c_2} - M_{c_1}}{(A_1/A_2) K - 1}$$

where M_x , M_{c_1} , and M_{c_2} are the molecular weights of the unknown, carrier gas 1, and carrier gas 2 respectively; A_1 and A_2 are the chromatographic peak areas for the unknown constituent; and K is an instrument constant which is determinable from analyses of samples with known molecular weights.

Operational Conditions

Helium (Matheson, ultrahigh purity grade) was used at a flow rate of 20 ml/min as the carrier gas for the pyrolyzer. Carbon dioxide (Matheson Cole-

man, instrument grade) and monochloropentafluoroethane (Freon-115; du Pont, food grade) were the carrier gases used in the mass chromatograph. The column flow rates were 10 ml/min. The flow rates of the reference gases in the gas density detectors were 41 ml/min for Freon-115 and 122 ml/min for carbon dioxide. The temperatures of the thermal conductivity cell and the gas density detector ovens were maintained at 230° and 242°C, respectively. The transfer line from the pyrolyzer to the mass chromatograph was maintained at 300°C. The gas density detector currents were set at 100 mAmp. The two matched chromatographic columns of the mass chromatograph were stainless steel ($\frac{1}{8}$ in. \times 12 ft) packed with 10% silicone gum SE-30 on 60/80 mesh Chromosorb W-AW.

Calibration of the mass chromatograph was performed by analyzing a synthetic mixture containing 15 known saturated normal hydrocarbons (C_5 to C_{28}). The instrument constant K was evaluated from peak height ratios (Freon-115/ CO_2 response ratios) at column heating conditions which were found to be suitable for separation of the decomposition products.

In addition to the thermal conductivity cell response, thermal history before and during pyrolysis was monitored using a thermogravimetric analyzer (du Pont 950) and a differential thermal analyzer (du Pont 900).

RESULTS AND DISCUSSION

Polyethylene

A 20-mg sample of low-density polyethylene ($\rho = 0.925$, $\bar{M}_w = 140,000$, $\bar{M}_n = 16,000$, 13 methyl groups per 1000 carbon atoms) was pyrolyzed in a flowing helium atmosphere at 20°C/min heating rate from room temperature to 600°C. The thermal conductivity cell response is compared in Figure 1 with the complementary results of thermogravimetric and differential thermal analyses. The products volatilizing between 300° and 600°C were selected for trapping and analysis.

The series of regularly spaced doublet peaks appearing in the mass chromatogram (Fig. 2) is similar to that reported in an earlier investigation involving programmed pyrolysis.²⁰ In contrast, flash pyrolysis experiments have been reported to lead to the formation of triplets corresponding to n -alkanes, n -alkenes, and α,ω -alkadienes.^{10,21-25} The doublets of Figure 2 suggest a homologous series. Indeed, the molecular weights calculated from the response ratios (Table I) compare well with those of C_3 to C_{28} normal hydrocarbons; retention times also compared well with these hydrocarbons. In general, the first peak in each doublet has a molecular weight comparable to that of the alkene, and the second peak to that of the alkane. Close examination of Figure 2 (CO_2 channel) reveals small shoulders just before the alkene peaks of C_9 through C_{15} which may indicate small amounts of alkadienes. Beyond C_{17} (and below C_5), each peak is probably a mixture of saturated and unsaturated hydrocarbons of the indicated C number, but resolution was not obtained under the chromatographic conditions.

The relative amounts of saturated and unsaturated hydrocarbons produced are dependent upon details of the mechanism of degradation, especially with respect to inter- and intramolecular radical transfer processes.^{5,23,26}

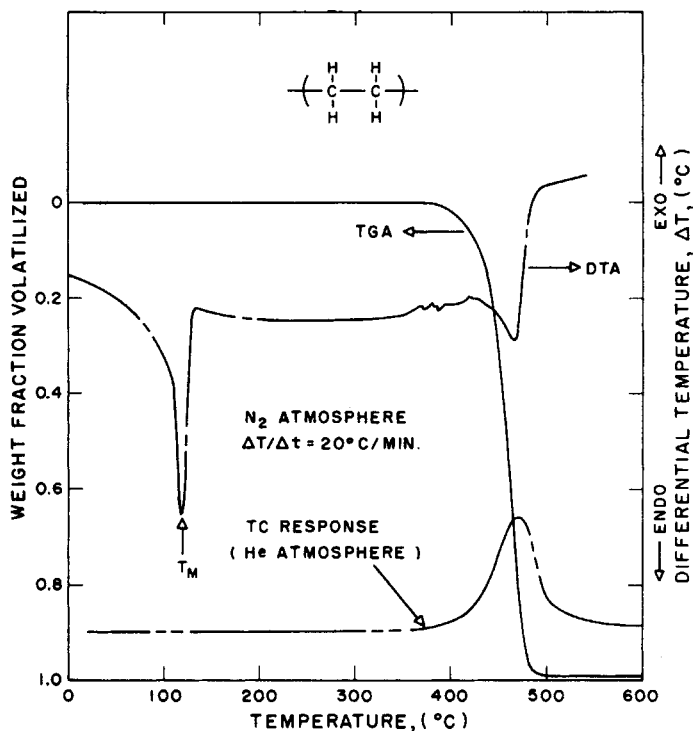
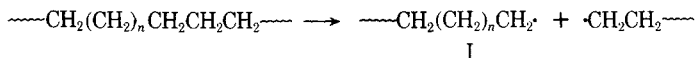


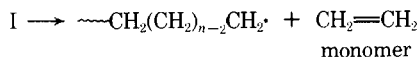
Fig. 1. Thermal history before and during pyrolysis of low-density polyethylene.

According to the free-radical mechanism of degradation, in polyethylene, main-chain scission by thermal energy results in two primary radicals:



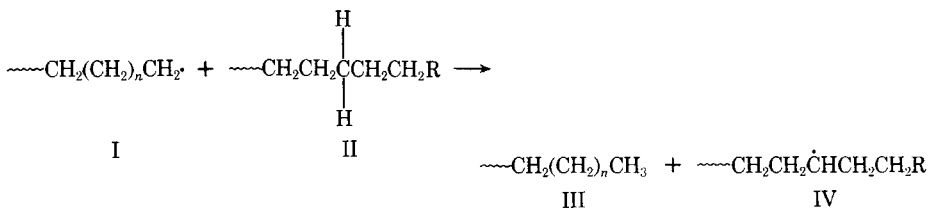
These primary radicals can undergo scission, and intermolecular and intramolecular radical transfer processes.

Decomposition by scission in the β -position to the radical will result in formation of monomer and another primary radical:



Since (in the present investigation) the columns used in the mass chromatograph were not suitable for analysis of ethylene, the formation of ethylene was not detected explicitly.

Intermolecular radical transfer reactions, i.e.,



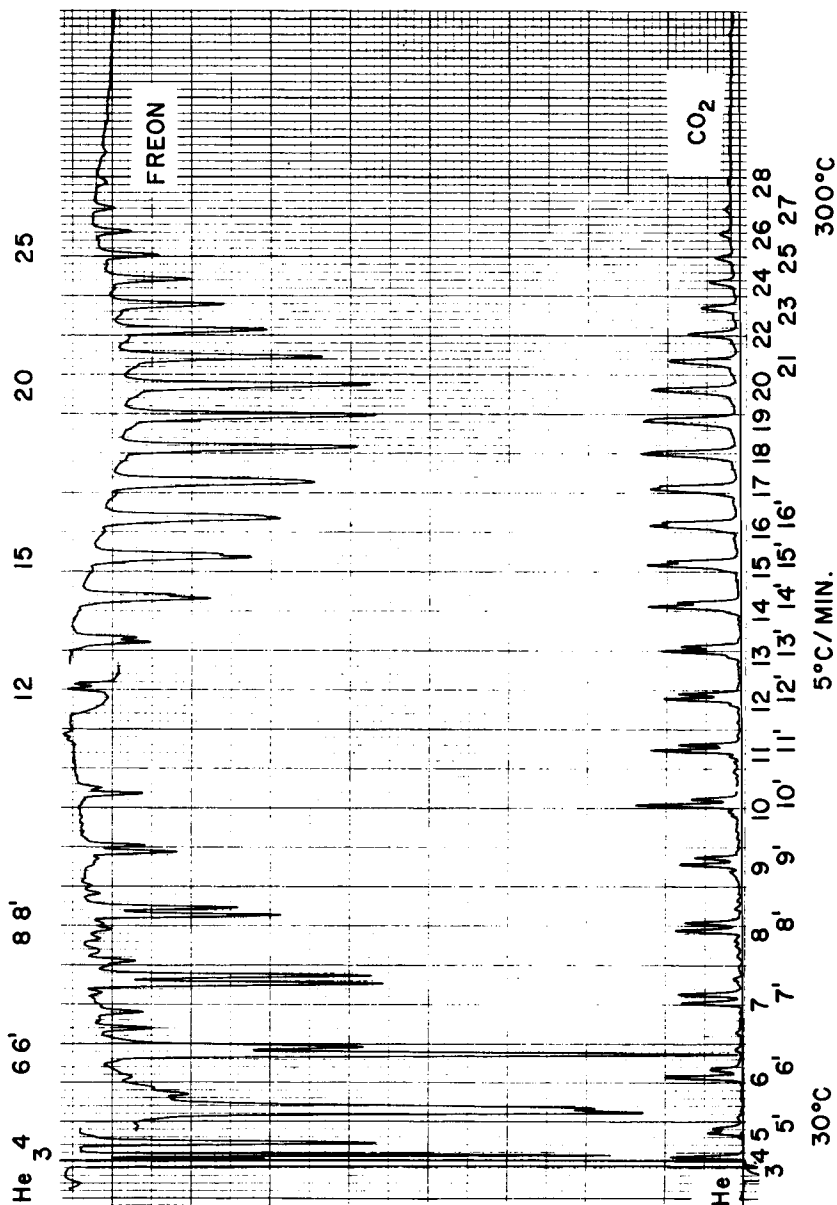
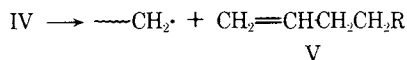


Fig. 2. Mass chromatogram of the pyrolysis products of low-density polyethylene. Columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C and held isothermally at 300°C. The peak attenuations were X8, except for the C₃ and C₄ peaks in the Freon-115 channel for which the settings were X64. After elution of the Freon-115 detector was reversed to produce downward peaks for constituents of higher molecular weight. The molecular weights (calculated from peak height ratios) are tabulated in Table I. The instrument constants were $K = 0.206$ (MW < 154.46) and $K = 0.189$ (MW > 154.46)

result in the formation of a secondary radical (IV). In the process, the primary radical (I) becomes deactivated (III). If the secondary radical thus formed undergoes β -scission to the left of the location of the radical, i.e.,



the lower molecular weight product (V) will be either an alkene or an alkadiene. (The chain end in the smaller fragment symbolized by R may be satu-

TABLE I
Decomposition Products of Polyethylene

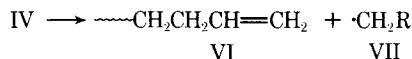
Peak no. (x)	$\left(\frac{A_1}{A_2}\right)^a$	MW calculated	MW saturated x-hydrocarbon ^b	Assignments ^c (n, alkane) (n', alkene)
3	406	42.7	44.09	3 ⁼ , 3
4	-39.1	56.2	58.12	4 ⁼ , 4
5	-14.3	72.0	72.15	5
5'	-15.2	70.7		5 ⁼
6	-8.20	85.1	86.18	6 ⁼
6'	-8.08	85.5		6
7	-4.87	99.2	100.21	7 ⁼
7'	-4.41	101.9		7
8	-3.08	111.6	114.23	8 ⁼
8'	-2.78	114.2		8
9	-1.61	127.0	128.26	9 ⁼
9'	-1.44	129.2		9
10	-0.64	141.6	142.29	10 ⁼
10'	-0.57	142.9		10
11	0.07	156.0	156.31	11 ⁼
11'	0.17	158.2		11
12	0.60	168.6	170.34	12 ⁼
12'	0.66	170.2		12
13	1.00	180.2	184.27	13 ⁼
13'	1.11	183.8		13
14	1.43	195.4	198.40	14 ⁼
14'	1.51	198.6		14
15	1.74	208.6	212.31	15 ⁼
15'	1.86	214.3		15
16	2.02	222.7	226.45	16 ⁼
16'	2.14	229.5		16
17	2.33	241.4	240.35	17 ⁼ , 17
18	2.49	252.6	254.50	18 ⁼ , 18
19	2.72	267.1	268.39	19 ⁼ , 19
20	2.89	287.4	282.56	20 ⁼ , 20
21	2.96	294.7	296.43	21 ⁼ , 21
22	3.08	308	310.59	22 ⁼ , 22
23	3.17	320	324.47	23 ⁼ , 23
24	3.29	336	338.66	24 ⁼ , 24
25	3.38	350	352.51	25 ⁼ , 25
26	3.50	370	366.72	26 ⁼ , 26
27	3.55	379	380.55	27 ⁼ , 27
28	3.65	400	394.77	28 ⁼ , 28

^a Response ratio, Freon-115/CO₂.

^b CRC Handbook of Chemistry and Physics, 48th ed.

^c C—Number.

rated or unsaturated.) If the secondary radical (IV) undergoes β -scission to the right of the location of the radical, i.e.,

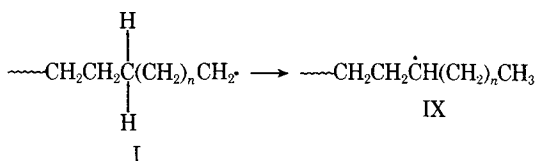


the newly formed radical (VII) can abstract a hydrogen atom from another molecule and form

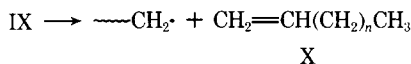


which is either an alkane or an alkene (depending upon whether R is saturated or unsaturated). It is apparent from structures III and VI that saturated and unsaturated chain ends (even if not initially present) can form during the course of decomposition. The smaller fragments (V and VIII) formed by intermolecular transfer reactions are, therefore, alkenes, alkadienes, and alkanes. It follows from the foregoing mechanism that, irrespective of the nature of the initial chain ends, in the later stages of degradation the extent of formation of alkenes is expected to be more than that of alkadiene and alkane since structures V and VIII both can be alkenes, whereas alkadiene is predicted only by structure V and alkane only by structure VIII.

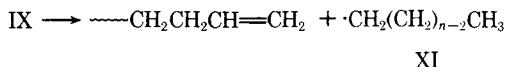
A primary radical can undergo intramolecular radical transfer reaction and form a secondary radical:



If the secondary radical (IX) thus formed undergoes β -scission to the left of the radical, i.e.,



the lower molecular weight product (X) that is formed will be an alkene. If the secondary radical undergoes β -scission to the right of the radical, i.e.,



a primary radical (XI) is formed which can abstract a hydrogen atom from another molecule and form $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$ (XII), which is a low molecular weight volatile alkane ($\text{XI} + \text{II} \rightarrow \text{XII} + \text{IV}$). The alkadienes which would be produced in consequence of this intermolecular step ($\text{IV} \rightarrow \text{V}$) would be the same as described earlier for more direct intermolecular transfer reactions; however, they are barely observed.

The observation that very little alkadiene is produced during pyrolysis of polyethylene at the heating rate of 20°C/min suggests that intramolecular radical transfer dominates since alkadiene is a more direct product for the intermolecular than for the intramolecular process. Studies with 1 to 1 mixtures of polyethylene and poly(tetradecuteroethylene)²⁷ provide additional evidence for the proposition that under mild conditions degradation of polyeth-

ylene must be proceeding through a predominantly intramolecular transfer mechanism.

The intramolecular radical transfer mechanism also provides an explanation for the shape of the chromatogram in Figure 2 in terms of the relative amounts of the different hydrocarbons produced.

The facility of radical transfer to different atoms of the chain depends on the flexibility of the chain, and the specific carbon to which the transfer takes place is governed by geometric (i.e., steric) factors. Since the coiling (or backbiting) process involves pseudocyclization steps, highly strained configurations are not permitted. It has been argued that intramolecular radical transfer involves the fifth carbon atom through a pseudosix-membered ring intermediate. If subsequent repetitive intramolecular transfer follows before chain scission,^{5,26} the consequence of preferential radical transfer to the 5th, 9th, 13th, 17th, and 21st, . . . etc. C atoms is the preferential formation of C₆, C₁₀, C₁₄, C₁₈, C₂₂, . . . alkenes (reaction IX → X) and C₃ (see Freon 115 channel), C₇, C₁₁, C₁₅, C₁₉, . . . alkanes (reaction IX → XI → XII), respectively. An examination of Figure 2 (CO₂ channel) shows that the chromatogram has minima and maxima, and that the maxima indeed correspond to C₆, C₁₀, C₁₄, and C₁₈ alkenes and C₃, C₇, C₁₁, and C₁₅ alkanes.

The probability of sequential migration of the free radical along the chain without undergoing β -scission reactions from C₁ to C₅ to C₉ to C₁₃ to C₁₇ to C₂₁ . . . carbon atoms would be expected to decrease as the number of transfer steps increases. Figure 2 indicates that, since C₂₂ alkene does not correspond to a local maximum, more than four consecutive transfers along the backbone chain is apparently not favored in low-density polyethylene, or else the recovery of the high molecular weight constituents such as C₂₂ from the traps is not complete. (In polymethylene, i.e., polyethylene without branches, additional transfers along the chain may be more probable.)

One- and two-step transfer processes should be most dominant. Figure 2 is in agreement with this expectation also, since, among alkenes, C₆ and C₁₀, and among alkanes, C₃ and C₇ represent major products of decomposition and are products of intramolecular radical transfers to the 5th and 9th carbon atoms of the chain.

Intramolecular coiling processes involving pseudosix-membered ring intermediates will not predict formation of the C₅, C₈, C₉, C₁₂, C₁₃, and C₁₆ hydrocarbons which are in fact observed (Fig. 2).

A further observation with respect to Figure 2 is that in view of a search of the literature related to the identification of the decomposition products of polyethylene,^{1,5,10,14,15,20-34} it represents the widest range of assigned molecular weights thus far published for a single pyrogram of polyethylene.

Polypropylene

The second member of the three polyolefins studied in this investigation was isotactic polypropylene (~100% isotactic, $\bar{M}_w = 284,000$ and $\bar{M}_w/\bar{M}_n = 2.98$). A 10-mg sample was pyrolyzed by program heating at 20°C/min in helium from room temperature. The response of the thermal conductivity cell during pyrolysis was compared with the results of thermogravimetric and differential thermal analyses (Fig. 3). The fraction between 300° and 600°C was trapped and analyzed by the mass chromatograph (Fig. 4).

TABLE II
 Decomposition Products of Polypropylene

Peak no.	$\left(\frac{A_1}{A_2}\right)^a$	MW calculated	Compound with Comparable MW Structure (MW)
1	-163	40.8	propylene (42); propane (44)
2	-40.9	55.0	isobutylene (56)
3	-10.6	77.0	pentane (72)
4	-7.76	84.7	2-methyl-1-pentene (84)
5	-7.39	86.0	2-methylpentane (86)
6	-5.13	95.8	2,4-dimethyl-1-pentene (98)
7	-2.85	111.9	2-methyl-1-heptene (112)
8	-2.72	113.0	4-methylheptane (114)
9	-1.67	124.7	2,4-dimethyl-1-heptene (126)
10	0.0	154.4	4,6-dimethylnonane (156)
11	0.64	171.0	2,4,6-trimethylnonane (170)
12	1.66	210.7	2,4,6,8-tetramethyl-1-hendecene (210)
13	1.69	212.5	2,4,6,8-tetramethylhendecane (212)
14	2.26	248.9	2,4,6,8,10-pentamethyl-1-tridecene (252)
15	2.38	258.6	2,4,6,8,10-pentamethyltridecane (254)
16	2.51	270.4	2,4,6,8,10,12-hexamethyl-1-tridecene (266)
17	2.67	286.6	2,4,6,8,10,12-hexamethyl-1-pentadecene (294)
18	2.86	309	2,4,6,8,10,12,14-heptamethyl-1-pentadecene (308)
19	3.0	329	4,6,8,10,12,14-hexamethylheptadecane (324)
20	3.37	397	2,4,6,8,10,12,14,16,18-nonamethyl-1-nonadecene (392)
21	3.45	417	2,4,6,8,10,12,14,16,18-nonamethyl-1-uncosene (420)
22	3.71	498	2,4,6,8,10,12,14,16,18,20-undecamethyl-1-tricosene (462)

^a Response ratio, Freon-115/CO₂.

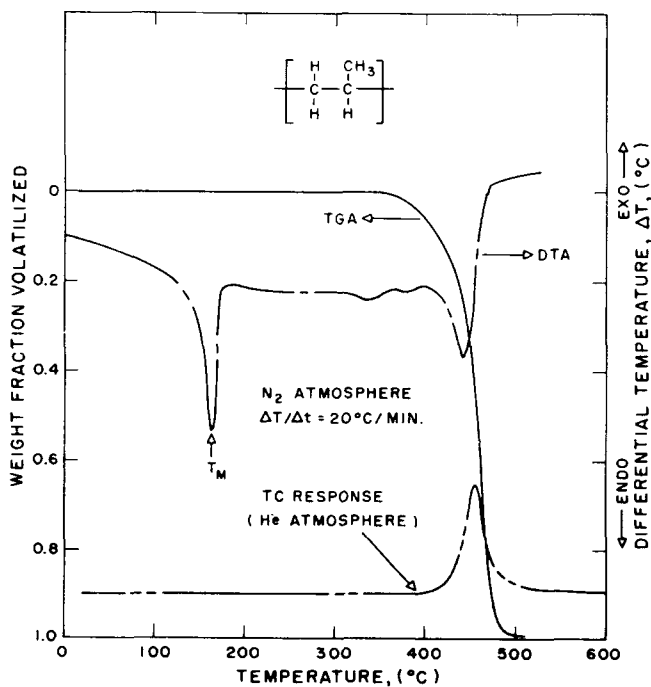


Fig. 3. Thermal history before and during pyrolysis of isotactic polypropylene.

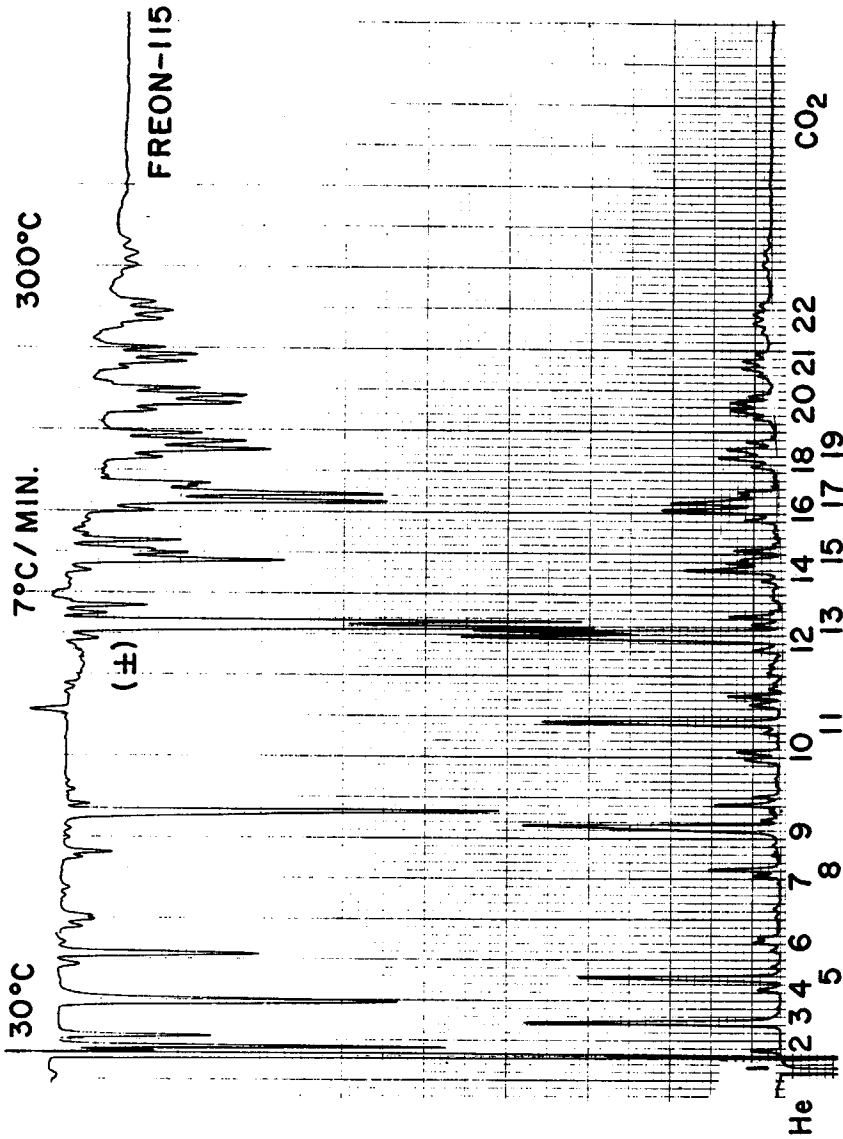
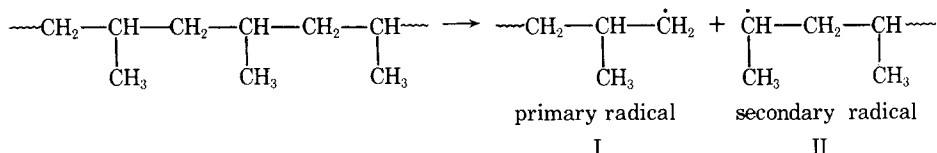


Fig. 4. Mass chromatogram of the pyrolysis products of isotactic polypropylene. Columns (SE-30) were program heated (at 7°C/min) from 30° to 300°C and held isothermally at 300°C. In the CO₂ channel, the peak attenuations were X8, except for peak 9 (a major product) for which the setting was X32. In the Freon-115 channel, the peak attenuations were X128 (peak 1), X64 (peaks 2 through 5), X32 (peaks 6 through 11), and X8 thereafter. Peaks 20, 21 and 22 refer to the third peak in the multiplets. The symbol ± indicates the location at which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table II. The instrument constants were $K = 0.221$ (MW < 154.46) and $K = 0.204$ (MW > 154.46); in the calibration experiment, columns were also heated at 7°C/min.

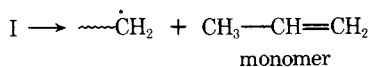
The chromatogram is again suggestive of a homologous series of products. The molecular weights have been calculated from the response ratios based on peak heights and are tabulated in Table II. These show that the peaks in the chromatogram have molecular weights corresponding approximately to those of monomer, dimers, trimers, and higher oligomers.

As in the case of polyethylene, the formation of the products of pyrolysis of polypropylene can be explained in terms of a free-radical mechanism.

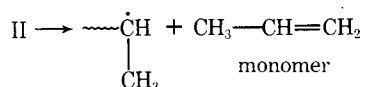
For polypropylene, initiation by chain scission will result in primary and secondary radicals:



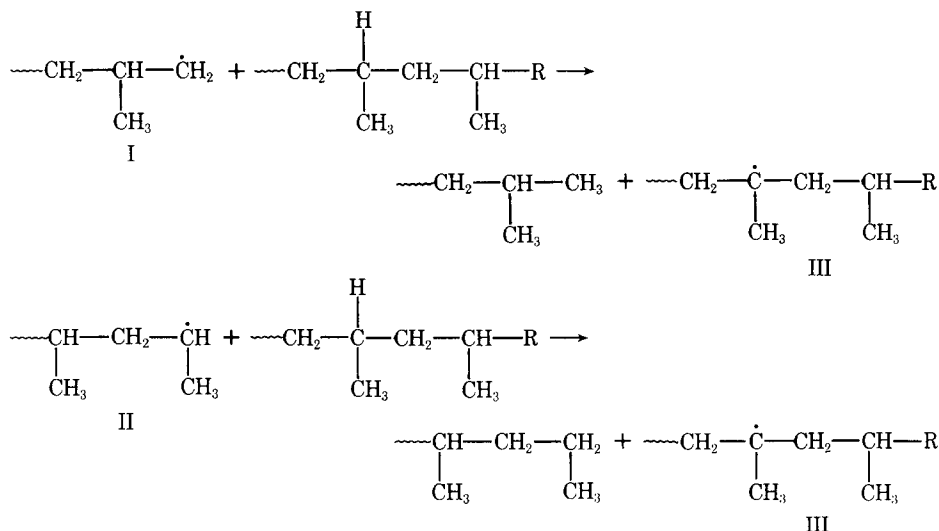
Depolymerization in the primary radical will result in the formation of another primary radical and monomer.



Similarly, depolymerization in the secondary radical will result in the formation of another secondary radical and monomer:

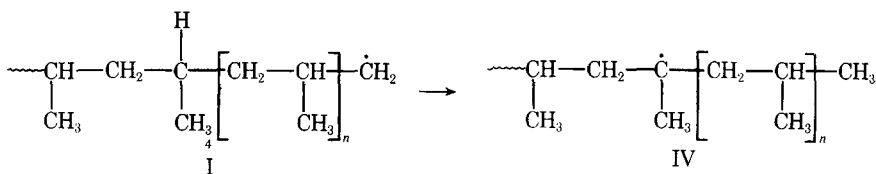


Intermolecular radical transfer reactions, i.e.,

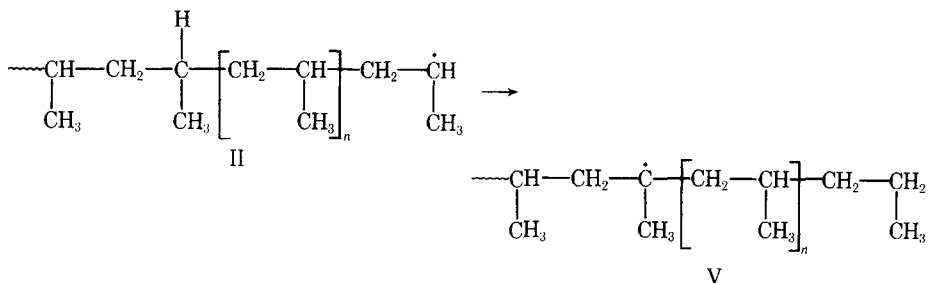


will result in the formation of tertiary radicals (since hydrogen atoms attached to tertiary carbons are more susceptible to abstraction).

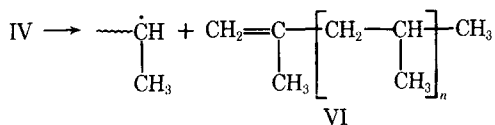
The primary (I) and the secondary radicals (II) can, in principle, also undergo intramolecular radical transfer reactions to form tertiary radicals:



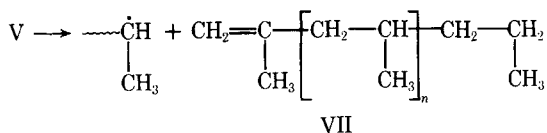
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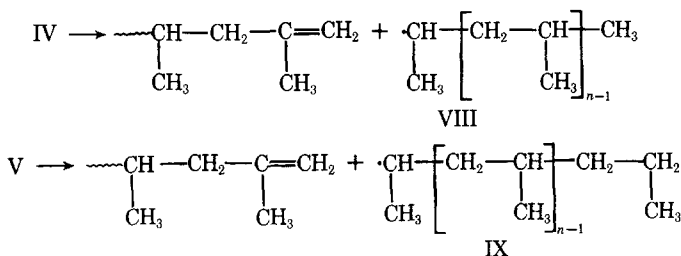
The tertiary radicals IV and V can undergo β -cleavage. If the scission is to the left of the location of the radical, i.e.,



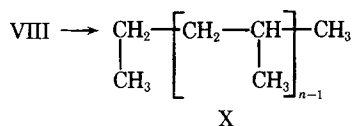
and



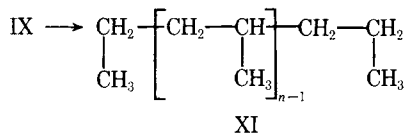
the lower molecular weight products (VI and VII) will be alkenes. On the other hand, if the tertiary radicals IV and V undergo β -scission to the right of the location of the radical, i.e.,



and if the secondary radicals VIII and IX that are formed abstract a hydrogen atom from another molecule, i.e.,



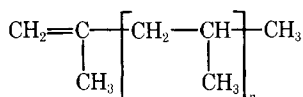
and



the lower molecular weight products (X and XI) will be alkanes.

As indicated in Table II, the molecular weights calculated for the peaks observed in the chromatogram in Figure 4 indeed correspond to the molecular weights of alkenes (structures VI and VII) and alkanes (structures X and XI) that are predicted from the radical transfer processes which start intramolecularly. The compounds predicted by these structures are as follows:

VI (Route: I \rightarrow IV \rightarrow VI)



$n = 0$: isobutylene (MW = 56)

$n = 1$: 2,4-dimethyl-1-pentene (MW = 98)

$n = 2$: 2,4,6-trimethyl-1-heptene (MW = 140)

$n = 3$: 2,4,6,8-tetramethyl-1-nonene (MW = 182)

$n = 4$: 2,4,6,8,10-pentamethyl-1-hendecene (MW = 224)

$n = 5$: 2,4,6,8,10,12-hexamethyl-1-tridecene (MW = 266)

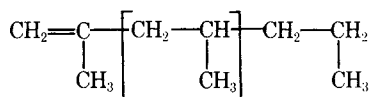
$n = 6$: 2,4,6,8,10,12,14-heptamethyl-1-pentadecene (MW = 308)

$n = 7$: 2,4,6,8,10,12,14,16-octamethyl-1-heptadecene (MW = 350)

$n = 8$: 2,4,6,8,10,12,14,16,18-nonamethyl-1-nonadecene (MW = 392)

etc.

VII (Route: II \rightarrow V \rightarrow VII)



$n = 0$: 2-methyl-1-pentene (MW = 84)

$n = 1$: 2,4-dimethyl-1-heptene (MW = 126)

$n = 2$: 2,4,6-trimethyl-1-nonene (MW = 168)

$n = 3$: 2,4,6,8-tetramethyl-1-hendecene (MW = 210)

$n = 4$: 2,4,6,8,10-pentamethyl-1-tridecene (MW = 252)

$n = 5$: 2,4,6,8,10,12-hexamethyl-1-pentadecene (MW = 294)

$n = 6$: 2,4,6,8,10,12,14-heptamethyl-1-heptadecene (MW = 336)

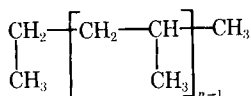
$n = 7$: 2,4,6,8,10,12,14,16-octamethyl-1-nonadecene (MW = 378)

$n = 8$: 2,4,6,8,10,12,14,16,18-nonamethyl-1-uncosene (MW = 420)

$n = 9$: 2,4,6,8,10,12,14,16,18,20-undecamethyl-1-tricosene (MW = 462)

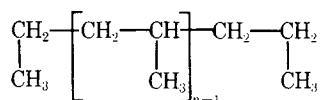
etc.

X (Route: I \rightarrow IV \rightarrow VIII \rightarrow X)



- $n = 1$: propane (MW = 44)
 $n = 2$: 2-methylpentane (MW , 86)
 $n = 3$: 2,4-dimethylheptane (MW = 128)
 $n = 4$: 2,4,6-trimethylnonane (MW = 170)
 $n = 5$: 2,4,6,8-tetramethylhendecane (MW = 212)
 $n = 6$: 2,4,6,8,10-pentamethyltridecane (MW = 254)
 $n = 7$: 2,4,6,8,10,12-hexamethylpentadecane (MW = 296)
 etc.

XI (Route: II \rightarrow V \rightarrow IX \rightarrow XI)



- $n = 1$: pentane (MW = 72)
 $n = 2$: 4-methylheptane (MW = 114)
 $n = 3$: 4,6-dimethylnonane (MW = 156)
 $n = 4$: 4,6,8-trimethylhendecane (MW = 198)
 $n = 5$: 4,6,8,10-tetramethyltridecane (MW = 240)
 $n = 6$: 4,6,8,10,12-pentamethylpentadecane (MW = 282)
 $n = 7$: 4,6,8,10,12,14-hexamethylheptadecane (MW = 324)
 etc.

A comparison of the proposed decomposition products of Table II shows that (with the exception of 2-methyl-1-heptene, peak 7) they can be accounted for by the above intramolecular radical transfer reactions. For example, since the major decomposition products pentane (Fig. 4, Table II, peak 3), 2,4-dimethyl-1-heptene (peak 9), and 2,4,6,8-tetramethyl-1-hendecene (peak 12) are formed from radical V, the degradation of isotactic polypropylene can be considered to proceed to a large extent through intramolecular radical transfer to the 5th and 9th carbon atoms (indexing the initial secondary carbon radical as carbon atom number 1) in the secondary radicals (see structures XI and VII). These observations are interesting in that radical transfers to the 5th and 9th carbons were also major processes in the degradation of polyethylene. The transfer to the 9th carbon probably involves a radical migration process in two steps, i.e., from the 1st carbon to the 5th, and then from the 5th to the 9th.

Other major products 2-methylpentane (Fig. 4, Table II, peak 5), 2,4,6-trimethylnonane (peak 11), and 2,4,6,8-tetramethylhendecane (peak 13) are formed however from radical IV, which arises from intramolecular radical transfer of the primary radical to the 6th, 10th, and 12th carbon atoms, respectively (see structure X).

Among the higher molecular weight fragments, peaks 16 and 17 are formed in larger amounts. The compounds 2,4,6,8,10,12-hexamethyl-1-tridecene (formed from a primary radical by radical transfer to the 12th carbon atom, see structure VI, $n = 5$) and 2,4,6,8,10,12-hexamethyl-1-pentadecene (formed from a secondary radical by radical transfer to the 13th carbon atom, see structure VII, $n = 5$) have molecular weights 266 and 294, respectively, which are comparable to those calculated for peaks 16 and 17. The reason for their preferential formation compared to other high molecular weight fragments is

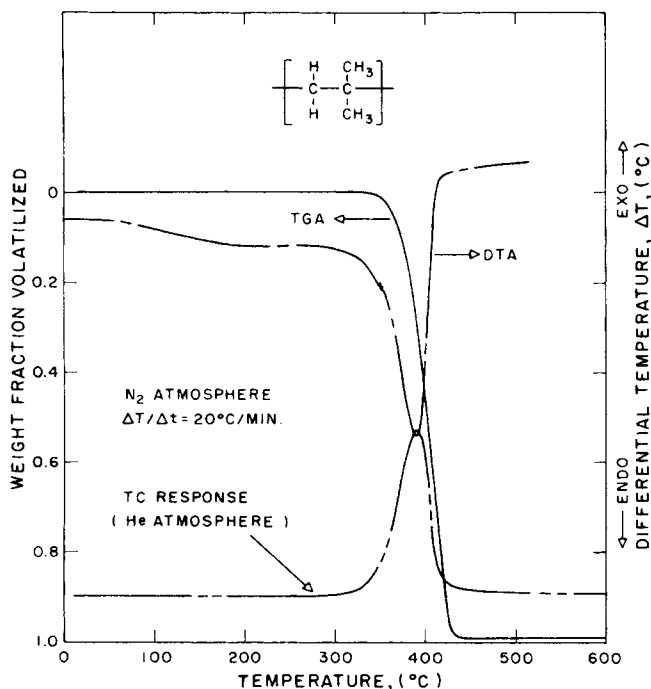


Fig. 5. Thermal history before and during pyrolysis of polyisobutylene.

understandable since radical transfer to the 12th carbon already accounts for one of the major decomposition products, namely, 2,4,6,8-tetramethylhendecane, and since transfer to the 13th carbon atom is probable through sequential radical transfers from the 5th to the 9th and then to the 13th carbon atom as was discussed in connection with polyethylene in the previous section. Thus, the formation of peaks 16 and 17 may be regarded as a continuation of the processes which lead to peaks 12 and 13 (see Fig. 4).

A comparison of the present results with the literature^{1,2,4,6,10,11,14,15,22,24,25,32-39} is not easy since previous publications have not reported on the pyrolysis of polypropylene under programmed heating conditions. However, similarities exist as to the major products of pyrolysis^{4,25,36} and the formation of homologous series^{4,10,24,33,36,38} which are also apparently characteristic of flash pyrolysis conditions.

Polyisobutylene.

The third member of the polyolefins studied in this investigation was polyisobutylene.

A 5.5-mg sample of polyisobutylene ($\bar{M}_v = 120,000$) was pyrolyzed in a helium atmosphere by program heating at 20°C/min, and the volatile fraction formed between 300° and 600°C was collected and analyzed by the mass chromatograph. Here again, the response from the thermal conductivity cell during pyrolysis was complementary to the results of thermogravimetric and differential thermal analyses (Fig. 5). The results from the mass chromatograph are shown in Figure 6.

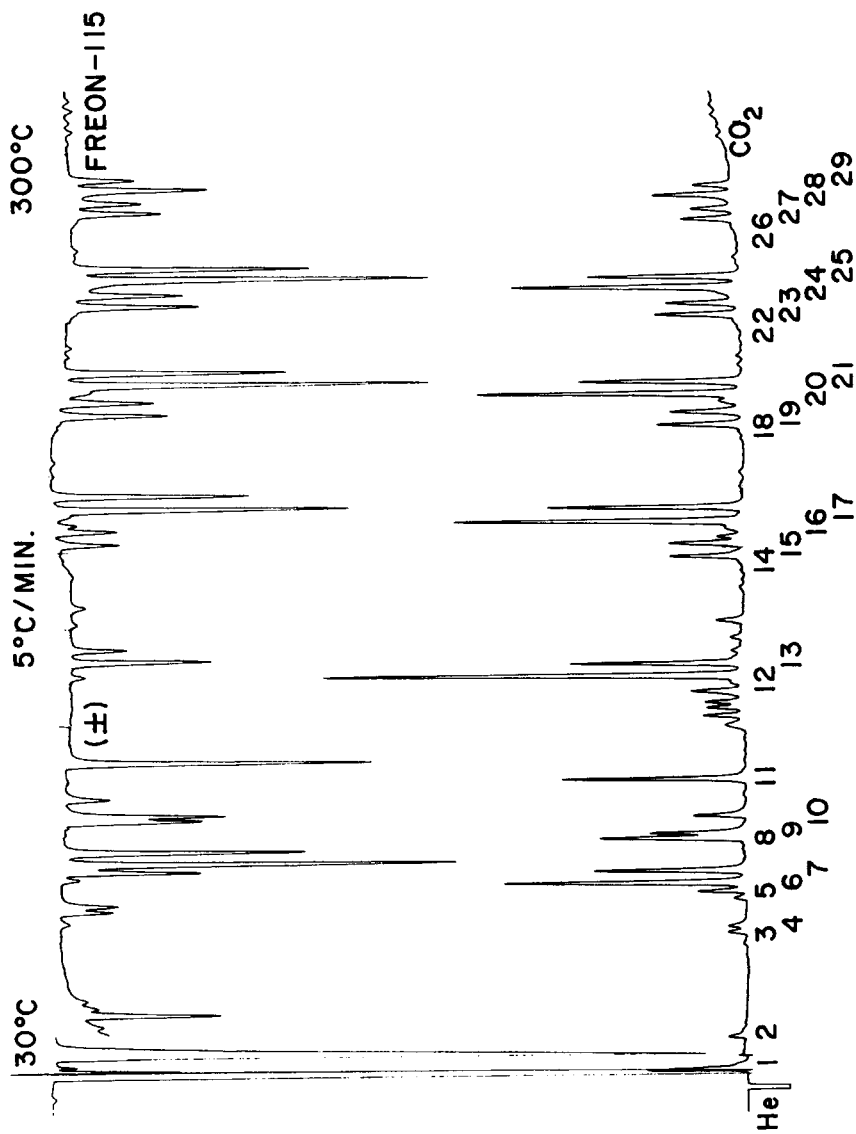


Fig. 6. Mass chromatogram of the pyrolysis products of polyisobutylene. Columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C and held isothermally at 300°C. Peak attenuations were $\times 8$ in both channels, except for peaks 1 and 2 for which the settings were $\times 128$. The symbol \pm indicates the location of which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table III. Detector response for peak 1 (the major product) was beyond the dynamic range of the detector. In this experiment, the Freon-115 and CO_2 detector currents were 100 and 130 mAmp, respectively. Under these conditions, the instrument constant was 0.385.

TABLE III
Decomposition Products of Polyisobutylene

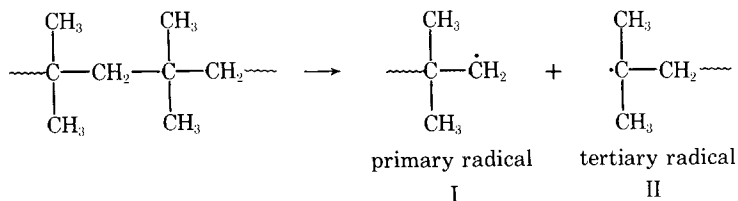
Peak no.	$\left(\frac{A_1}{A_2}\right)^a$	MW calculated	Compound with comparable MW Structure (MW)
1	- ^b	-	isobutylene (56)
2	-7.42	72.6	neopentane (72)
3	-2.83	96.9	2,4-dimethylpentane (100)
4	-3.21	93.4	2,4-dimethyl-1-pentene (98)
5	-2.81	96.2	2,4-dimethyl-2-pentene (98)
6	-1.61	112.2	2,2,4-trimethyl pentane (114)
7	-1.59	112.5	2,4,4-trimethyl-1-pentene (112)
8	-0.89	126.0	2,2,4,4-tetramethylpentane (128)
9	-1.67	111.2	2,4,4-trimethyl-2-pentene (112)
10	-0.87	126.6	-
11	-1.60	112.3	-
12	0.33	170.5	2,4,4,6,6-pentamethyl-1-heptene (168)
13	0.32	169.9	2,4,4,6,6-pentamethyl-2-heptene (168)
14	0.84	207.2	2,4,4,6,6,8-hexamethyl-1-nonene (210)
15	0.84	207.2	2,4,4,6,6,8-hexamethyl-2-nonene (210)
16	1.03	227.0	2,4,4,6,6,8,8-heptamethyl-1-nonene (224)
17	1.01	225.0	2,4,4,6,6,8,8-heptamethyl-2-nonene (224)
18	1.27	260.2	2,4,4,6,6,8,8,10-octamethyl-1-hendecene (266)
19	1.26	258.5	2,4,4,6,6,8,8,10-octamethyl-2-hendecene (266)
20	1.36	277.2	2,4,4,6,6,8,8,10,10-nonamethyl-1-hendecene (280)
21	1.35	273.9	2,4,4,6,6,8,8,10,10-nonamethyl-2-hendecene (280)
22	1.54	315	2,4,4,6,6,8,8,10,10,12-decamethyl-1-tridecene (322)
23	1.54	315	2,4,4,6,6,8,8,10,10,12-decamethyl-2-tridecene (322)
24	1.57	325	2,4,4,6,6,8,8,10,10,12,12-undecamethyl-1-tridecene (336)
25	1.58	326	2,4,4,6,6,8,8,10,10,12,12-undecamethyl-2-tridecene (336)
26	1.64	344	2,4,4,6,6,8,8,10,10,12,12,14-dodecamethyl-1-pentadecene (378)
27	1.69	360	2,4,4,6,6,8,8,10,10,12,12,14-dodecamethyl-2-pentadecene (378)
28	1.71	367	2,4,4,6,6,8,8,10,10,12,12,14,14-tridecamethyl-1-pentadecene (392)
29	1.67	358	2,4,4,6,6,8,8,10,10,12,12,14,14-tridecamethyl-2-pentadecene (392)

^a Response ratio, Freon-115/CO₂.

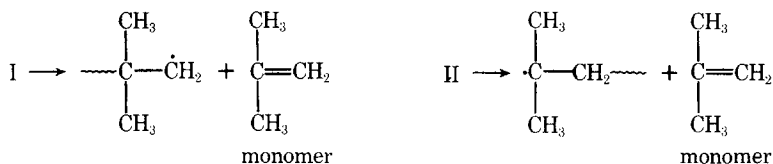
^b Responses beyond the dynamic range of the detectors.

The presence of a series of regularly spaced groups of peaks in the chromatogram is characteristic of a homologous series of products. The molecular weights calculated from the response ratios (Table III) show that monomer, dimers, trimers, and higher oligomers constitute the volatile degradation products of polyisobutylene.

In polyisobutylene, initiation by chain scission results in primary and tertiary radicals:



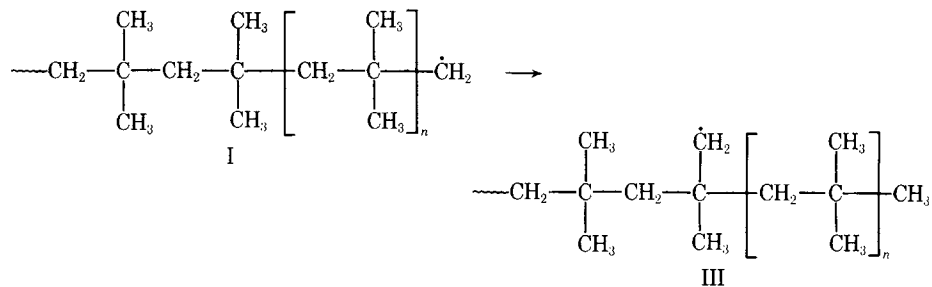
Either one of these radicals can undergo depolymerization and produce the monomer, isobutylene:



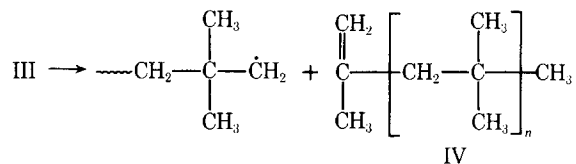
In polyisobutylene, these depropagation reactions are expected to take place to a greater extent than in polyethylene and polypropylene in part for the reason that the methyl groups on the alternate quaternary carbon atoms sterically hinder intramolecular hydrogen transfer processes. The chain lacks the flexibility of polyethylene for local coiling. In addition, the easily abstractable tertiary hydrogens of polypropylene are absent. As can be deduced from Figure 6, isobutylene (peak 1) is indeed by far the principal product of pyrolysis.

In principle, secondary hydrogens are more easily abstractable than primary hydrogens. However, in polyisobutylene, the secondary hydrogens (of methylene groups) are sterically shielded by the two methyl groups attached to the neighboring carbon atoms. This renders hydrogen abstraction more difficult than usual. In view of the fact that 75% of the hydrogens are primary, the possibility of abstraction from primary as well as from secondary hydrogens will be considered.

Consider the intramolecular radical transfer process in a primary macroradical to a methyl group:



This radical (III) can dissociate in two ways. If it undergoes β -scission to the left of the radical center, i.e.,



the lower molecular weight products depicted by structure IV will be the following alkenes:

IV (Route: I \rightarrow III \rightarrow IV)

$n = 0$: isobutylene (MW = 56)

$n = 1$: 2,4,4-trimethyl-1-pentene (MW = 112)

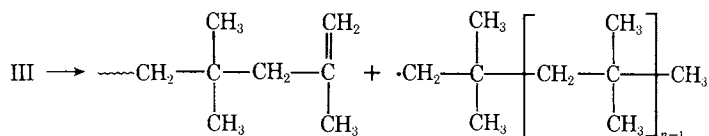
$n = 2$: 2,4,4,6,6-pentamethyl-1-heptene (MW = 168) = 2

$n = 5$: 2,4,4,6,6,8,8,10,10,12,12-undecamethyl-1-tridecene (MW = 336)

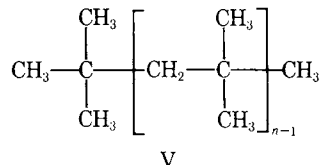
$n = 6$: 2,4,4,6,6,8,8,10,10,12,12,14,14-tridecamethyl-1-pentadecene (MW = 392)

etc.

If, on the other hand, radical III undergoes β -scission to the right of the radical center, i.e.,



and if the primary radical thus formed abstracts a hydrogen atom from another molecule, the lower molecular weight products formed will be alkanes of the following structure:



V (Route: I \rightarrow III \rightarrow V)

$n = 1$: neopentane (MW = 72)

$n = 2$: 2,2,4,4-tetramethylpentane (MW = 128)

$n = 3$: 2,2,4,4,6,6-hexamethylheptane (MW = 184)

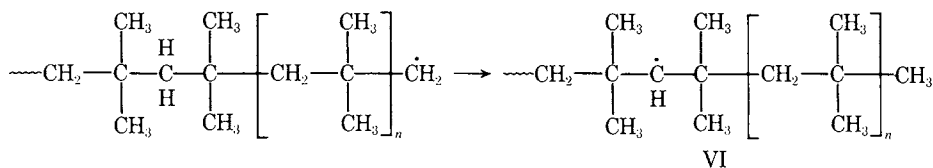
$n = 4$: 2,2,4,4,6,6,8,8-octamethylnonane (MW = 240)

$n = 5$: 2,2,4,4,6,6,8,8,10,10-decamethylhendecane (MW = 296)

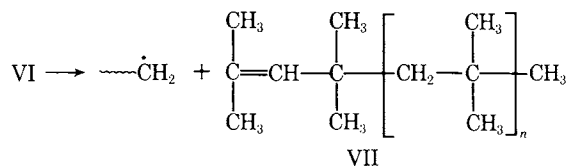
$n = 6$: 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyltridecane (MW = 352)

etc.

Now consider the intramolecular radical transfer in a primary radical to a methylene group:



The secondary radical formed (VI) can also dissociate in two ways. If it undergoes β -cleavage to the left of the radical center, i.e.,



the lower molecular weight products that are formed (VII) are the following alkenes:

VII (Route: I \rightarrow VI \rightarrow VII)

$n = 0$: 2,4,4-trimethyl-2-pentene (MW = 112)

$n = 1$: 2,4,4,6,6-pentamethyl-2-heptene (MW = 168)

$n = 2$: 2,4,4,6,6,8,8-heptamethyl-2-nonene (MW = 224)

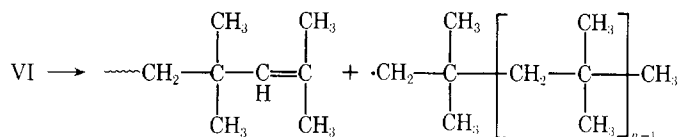
$n = 3$: 2,4,4,6,6,8,8,10,10-nonamethyl-2-hendecene (MW = 280)

$n = 4$: 2,4,4,6,6,8,8,10,10,12,12-undecamethyl-2-tridecene (MW = 336)

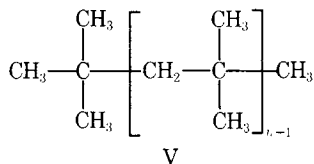
$n = 5$: 2,4,4,6,6,8,8,10,10,12,12,14,14-tridecamethyl-2-pentadecene (MW = 392)

etc.

If, however, the radical VI undergoes β -cleavage to the right of the radical center, i.e.,



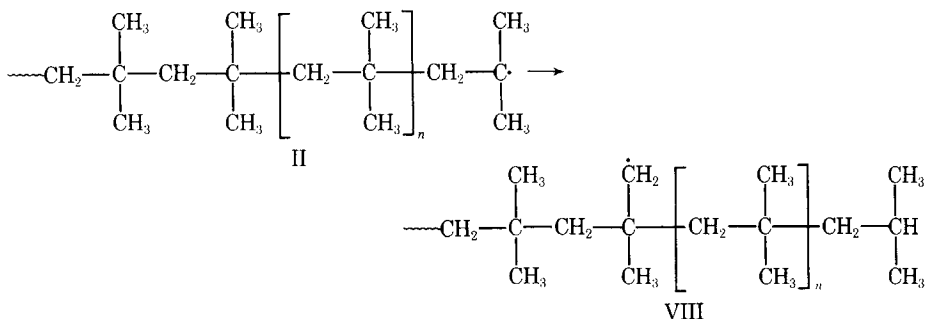
and if the primary radical thus formed abstracts a hydrogen atom from another molecule, lower molecular weight alkanes of the following structure are formed:



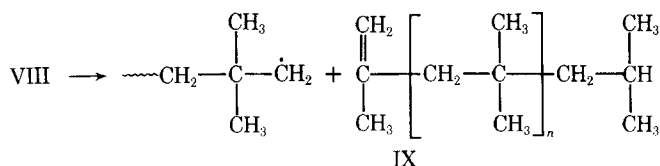
These alkanes are identical to those that are formed from radical transfer to a methyl group described above.

Radical transfer processes which start intramolecularly in primary macroradicals have been considered. Consideration will now be given to radical transfer reactions which start intramolecularly in a tertiary macroradical.

If the transfer is to a methyl group, a primary radical is formed, i.e.,



This radical can undergo dissociation in two ways. If it undergoes β -cleavage to the left of the radical center, i.e.,



the products formed (IX) are the following alkenes:

IX (Route: II \rightarrow VIII \rightarrow IX)

$n = 0$: 2,4-dimethyl-1-pentene (MW = 98)

$n = 1$: 2,4,4,6-tetramethyl-1-heptene (MW = 154)

$n = 2$: 2,4,4,6,6,8-hexamethyl-1-nonene (MW = 210)

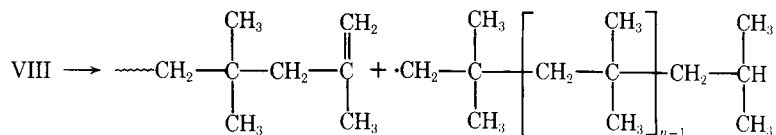
$n = 3$: 2,4,4,6,6,8,8,10-octamethyl-1-hendecene (MW = 266)

$n = 4$: 2,4,4,6,6,8,8,10,10,12-decamethyl-1-tridecene (MW = 322)

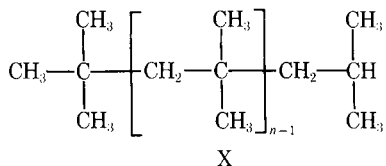
$n = 5$: 2,4,4,6,6,8,8,10,10,12,12,14-dodecamethyl-1-pentadecene (MW = 378)

etc.

If the radical VIII undergoes β -scission to the right of the radical center, a primary radical is formed, i.e.,



which can abstract a hydrogen atom from another molecule and form alkanes with the structure



More explicitly, the following alkanes will form:

X (Route: II \rightarrow VIII \rightarrow X)

$n = 1$: 2,2,4-trimethylpentane (MW = 114)

$n = 2$: 2,2,4,4,6-pentamethylheptane (MW = 170)

$n = 3$: 2,2,4,4,6,6,8-heptamethylnonane (MW = 226)

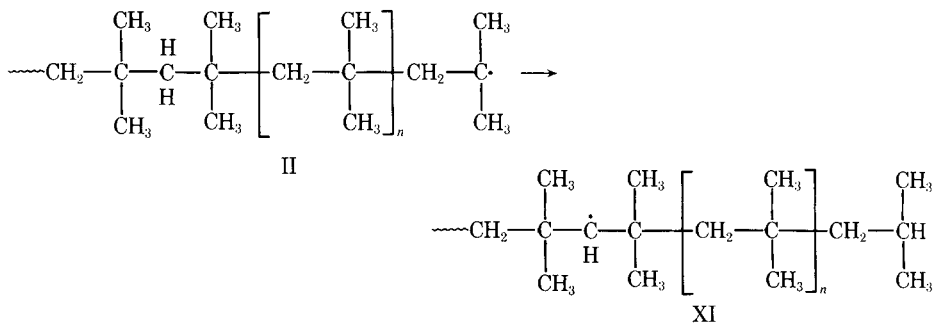
$n = 4$: 2,2,4,4,6,6,8,8,10-nonamethylundecane (MW = 282)

$n = 5$: 2,2,4,4,6,6,8,8,10,10,12-undecamethyltridecane (MW = 338)

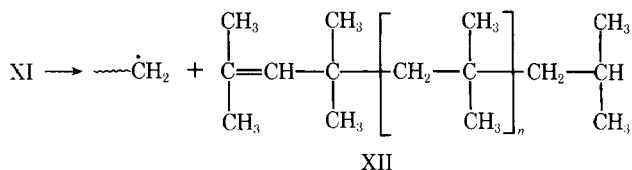
$n = 6$: 2,2,4,4,6,6,8,8,10,10,12,12,14-tridecamethylpentadecane (MW = 394)

etc.

Finally, intramolecular radical transfer in a tertiary macroradical to a methylene group will be considered:



If this secondary radical undergoes β -cleavage to the left of the radical center, i.e.,



the products are the following alkenes:

XII (Route: II \rightarrow XI \rightarrow XII)

$n = 0$: 2,4,4,6-tetramethyl-2-heptene (MW = 154)

$n = 1$: 2,4,4,6,6,8-hexamethyl-2-nonene (MW = 210)

$n = 2$: 2,4,4,6,6,8,8,10-octamethyl-2-hendecene (MW = 266)

$n = 3$: 2,4,4,6,6,8,8,10,10,12-decamethyl-2-tridecene (MW = 322)

$n = 4$: 2,4,4,6,6,8,8,10,10,12,12,14-dodecamethyl-2-pentadecene (MW = 378)

etc.

If, however, the radical XI undergoes β -cleavage to the right of the radical center and then a hydrogen abstraction step, the products are alkanes which are identical to the alkanes (structure X) which were predicted also by radical transfer to a methyl group.

The products predicted by structures IV, V, VII, IX, X, and XII are observed in the chromatogram (Fig. 6) to varying extents. The major product, the trimer 2,4,4,6,6-pentamethyl-1-heptene (peak 12) is formed from a primary radical by abstraction of hydrogen from the methyl group attached to the 7th carbon (see structure IV, $n = 2$). In each quartet (peaks 14 through 29), the first two peaks correspond to alkenes formed from tertiary radicals and the last two (which are formed in larger amounts) to alkenes formed from primary radicals. Degradation of polyisobutylene apparently involves more intramolecular transfer in the primary radicals for energetic reasons. Constituents formed via this route represent the major products of pyrolysis.

It may be argued that the alkanes depicted by structure X having molecular weights 170, 226, 282, 338, 394 (for $n = 2$ to 6) compare in molecular weight to the last two chromatographic peaks in each quartet from peak 14 to 29. However, it is unlikely that these peaks are alkanes. If they were, then, contrary to the observations, alkenes IX and XII (the first two chromatographic peaks in each quartet) should have formed in larger amounts since they are more direct products of tertiary radicals in not involving the intermolecular hydrogen abstraction step.

Compared to polyethylene and polypropylene, literature on the pyrolysis products of polyisobutylene is not extensive. Nonetheless, there have been some studies under flash and isothermal pyrolysis conditions.^{3,4,34,39,40,41} It is interesting to note, however, that there are striking similarities between the present results obtained under program heating conditions and the results obtained in a previous study⁴¹ where the sample was pyrolyzed under vacuum at 365°C (isothermally). In that study, however, only the constituents up to trimers were identified and the other chromatographic peaks were speculated to correspond to higher oligomers. The chromatogram in Figure 6 confirms this and represents the widest range of assigned molecular weights thus far published for a single pyrogram of polyisobutylene.

FURTHER DISCUSSION

Chain scission in polyethylene results initially only in primary macroradicals; in polypropylene, in a primary and a secondary macroradical; and in polyisobutylene, in a primary and a tertiary macroradical. These factors together with differences in the flexibility of the backbone chains and the avail-

ability of abstractable hydrogen atoms are the major factors which affect the thermal degradation of the polymers. The extent of monomer formation increases in going from polyethylene to polypropylene and polyisobutylene, monomer formation being most extensive in polyisobutylene. In polyethylene, decomposition proceeds primarily through an intramolecular radical transfer process to the 5th and 9th and also the 13th and 17th carbon atoms of the chain. In polypropylene, intramolecular radical transfers to the 5th and 9th and also the 13th carbon atoms in the secondary macroradicals and to the 6th, 10th, and 12th carbon atoms in the primary macroradicals account for the major products of decomposition. In polyisobutylene, in addition to the primary depolymerization process which leads to large amounts of monomer, decomposition involves intramolecular transfer in the primary as well as tertiary macroradicals; however, transfer in the primary radicals is more dominant.

It is interesting to note that for the three polymers the volatile products of their decompositions appear to have been accounted for on the basis of the initial steps of intramolecular sequences of reactions without having to consider the subsequent intermolecular reaction steps.

The accuracy of the mass chromatograph is not sufficient to differentiate, unambiguously, between saturated and unsaturated constituents which differ by 2 mass units, especially if the molecular weights of the constituents⁴² are greater than 200. However, the results presented in the foregoing sections have shown the utility of this system. In providing gas-chromatographic retention times and acceptable values for molecular weights in one unit, it offers a convenience and simplicity that are not found in the usual gas chromatograph-mass spectrometer combinations requiring elaborate interfacial systems and tedious or sophisticated data reduction procedures. The capabilities of the system will be further illustrated in future articles.⁴³⁻⁴⁵

Financial support for this project was provided by the Chemistry Branch of the Office of Naval Research.

References

1. B. C. Cox and B. Ellis, *Anal. Chem.*, **36**(1), 90 (1964).
2. B. Groten, *Anal. Chem.*, **36**(7), 1206 (1964).
3. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley, New York, 1964.
4. J. van Schooten and J. K. Evenhuis, *Polymer*, **6**, 343 (1965).
5. Y. Tsuchia and K. Sumi, *J. Polym. Sci. A1*, **6**, 415 (1968).
6. M. Dimbat, in *Gas Chromatography 1970*, R. Stock and S. C. Perry, Eds., Elsevier, New York, 1971, p. 237.
7. T. Shono and K. Shinra, *Anal. Chim. Acta*, **56**, 303 (1971).
8. M. Galin, *J. Macromol. Sci.-Chem.*, **A7**(4), 873 (1973).
9. S. Tsuge, T. Okumoto, and T. Takeuchi, *Makromol. Chem.*, **123**, 123 (1969).
10. L. Michajlov, H.-J. Cantow, and P. Zugenmaier, *Polymer*, **12**, 70 (1971).
11. H. Seno, S. Tsuge, and T. Takeuchi, *Makromol. Chem.*, **161**, 195 (1972).
12. O. Kysel, *Collect. Czech. Chem. Commun.*, **31**, 943 (1966).
13. F. Armitage, *J. Chromatogr. Sci.*, **9**(4), 245 (1971).
14. M. P. Stevens, *Characterization and Analysis of Polymers by Gas Chromatography*, Marcel Dekker, New York, 1969.
15. G. M. Brauer, in *Techniques and Methods of Polymer Evaluation*, Vol. 2, Marcel Dekker, New York, 1970, p. 41.
16. L. Reich and S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971.

17. E. Kiran, Ph.D. Thesis, Princeton University, Department of Chemical Engineering, Princeton, N. J., 1974.
18. E. Kiran and J. K. Gillham, *J. Macromol. Sci.-Chem.*, **A8**(1), 211 (1974).
19. E. Kiran and J. K. Gillham, *J. Appl. Polym. Sci.*, **20**, 931 (1976).
20. J. Chiu, *Anal. Chem.*, **40**(10), 1516 (1968).
21. B. Kolb and K. H. Kaiser, *J. Gas Chromatogr.*, **2**, 233 (1964).
22. E. W. Cieplinski, L. S. Ettre, B. Kolb, and G. Kemmner, *Z. Anal. Chem.*, **205**, 357 (1964).
23. B. Kolb, G. Kemmner, K. H. Kaiser, E. W. Cieplinski, and L. S. Ettre, *Z. Anal. Chem.*, **209**, 302 (1965).
24. J. C. Sternberg and R. L. Little, *Anal. Chem.*, **38**(2), 321 (1966).
25. L. Michajlov, P. Zugenmaier, and H.-J. Cantow, *Polymer*, **9**, 325 (1968).
26. Y. Tsuchia and K. Sumi, *Polym. Lett.*, **6**, 357 (1968).
27. W. J. Bailey and L. J. Baccei, *ACS Polym. Prepr.*, **12**(2), 313 (1971).
28. W. H. Pariss and P. D. Holland, *Brit. Plast.*, **33**, 372 (1960).
29. J. G. Cobler and E. P. Samsel, *Soc. Plast. Eng. SPE Trans.*, **2**, 145 (1962).
30. D. Deur-Siftar, *J. Gas Chromatogr.*, **5**, 72 (1967).
31. S. K. Yasuda, *J. Chromatogr.*, **27**, 72 (1967).
32. A. A. Buniyat-Zade et al., *Polym. Sci. USSR*, **A12**, 2825 (1970).
33. M. Seeger, Dissertation, Freiburg, 1972.
34. A. Zeman, *Angew. Makromol. Chem.*, **31**, 1 (1973).
35. D. Noffz, W. Benz, and W. Pfab, *Z. Anal. Chem.*, **239**, 121 (1968).
36. Y. Tsuchia and K. Sumi, *J. Polym. Sci.*, **A1**(7), 1599 (1969).
37. M. A. Magrupov and I. Gafurov, *Polym. Sci. USSR*, **11**(12), 3180 (1969).
38. D. Deur-Siftar and V. Svab, *J. Chromatogr.*, **51**, 59 (1970).
39. D. O. Hümmel, H. J. Dussel, and K. Rubenacker, *Makromol. Chem.*, **145**, 267 (1971).
40. E. M. Barrall, R. S. Porter, and J. F. Johnson, *J. Chromatogr.*, **11**, 177 (1963).
41. Y. Tsuchia and K. Sumi, *J. Polym. Sci.*, **A1**(7), 813 (1969).
42. E. Kiran and J. K. Gillham, *Anal. Chem.*, **47**(7), 983 (1975).
43. E. Kiran and J. K. Gillham, *J. Appl. Polym. Sci.*, in press.
44. H. H. Kuo, H. A. Pfeffer and J. K. Gillham, *ACS Coat. Plast. Prep.*, **35**(1), 434 (1975).
45. S. Tamura and J. K. Gillham, *J. Appl. Polym. Sci.*, in press.

Received September 18, 1975