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Pyrolysis-Molecular Weight Chromatography of Polymers: A New Technique

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ABSTRACT

A pyrolyzer with programming capability has been coupled in series with a thermal conductivity cell and a mass chromatograph. The thermal conductivity cell gives the flexibility for selective trapping of decomposition products, and also provides data that are complementary to thermogravimetric and differential thermal analyses. The mass chromatograph is composed of two gas chromatographs that are run parallel from a common injection port. Each chromatograph uses a different carrier gas and is equipped with a gas density balance detector. The instrument simplifies identification of mixtures of unknowns in directly providing molecular weights, absolute quantities, and gas chromatographic retention times of the constituents. In this respect, the present system is analogous to pyrolysis-gas chromatography-mass spectrometry.
Discussion of the technique and its application to the investigation of the thermal degradation of low-density polyethylene are presented.

INTRODUCTION

Identification of decomposition products is a necessary precursor to the study of the mechanism of thermal degradation of polymers. Among the separation techniques, gas chromatography has received much attention in the past decade; in particular, pyrolysis-gas chromatography has gained wide acceptance as a technique of polymer analysis [1-4]. However, positive identification by gas chromatography is not unambiguous without the use of additional analytical techniques [5-7] such as IR, mass spectrometry, and NMR.

Molecular weight chromatography (which is not to be confused with mass spectrometry) is a relatively new technique [8-10]. The commercially available instrument is called a mass chromatograph [11]. The single instrument directly provides molecular weights, absolute quantities and gas chromatographic retention times of the constituents of a mixture by using gas density balances as the detectors for the effluents from gas chromatographic columns. It thus upgrades gas chromatography and facilitates the process of identification of unknowns.

The present paper discusses a series combination of a pyrolyzer, a thermal conductivity cell, and a mass chromatograph as applied to polymer degradation. The pyrolyzer is designed to carry out decomposition by either program- or flash-heating. The thermal conductivity cell is included to monitor the formation of volatile decomposition products and to permit their selective trapping and subsequent selective desorption from a trap. The mass chromatograph achieves separation of the decomposition products in the manner of a gas chromatograph, but also provides information on their molecular weights with ease (compared with mass spectrometry).

EXPERIMENTAL

Apparatus

A schematic drawing of the present system is shown in Fig. 1. The pyrolyzer-thermal conductivity probe assembly consists of a tubular reactor and heater (pyrolyzer), a detector oven (dotted enclosure) which houses the thermal conductivity cell and the two six-port valves (X and Y), and an external trap (pyrolyzer trap). This assembly was custom-designed for this laboratory and in a modified form is now commercially available [11]. The pyrolysis chamber is a quartz tube (3/16 in. i.d.) which can be program- or flash-heated to 800°C. The sample to be pyrolyzed is placed in the (heat-cleaned) quartz

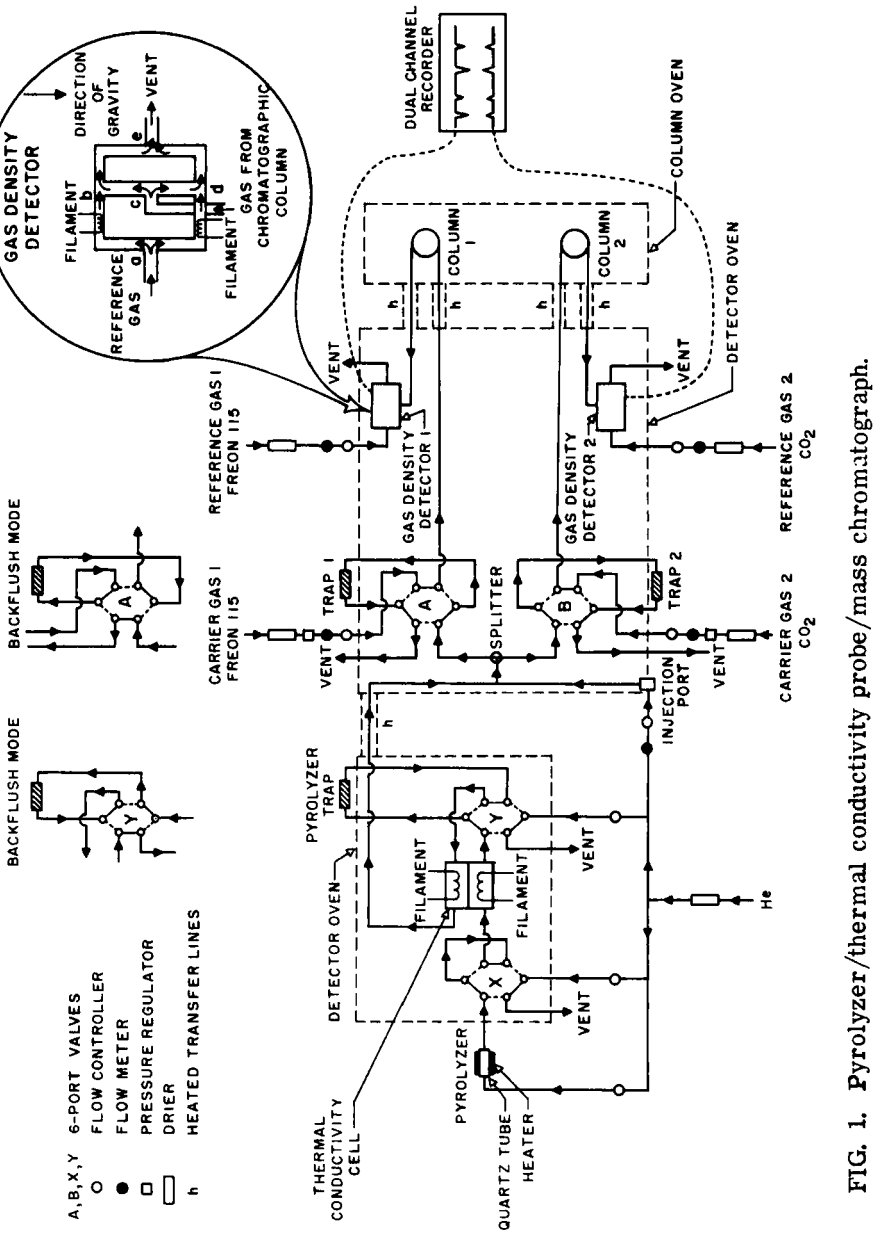

FIG. 1. Pyrolyzer/thermal conductivity probe/mass chromatograph.

tube between two loosely packed (heat-cleaned) glass-wool plugs. The glass wool plugs help position the sample and prevent mechanical loss. The quartz tube, with sample in place, is assembled using O-rings and Swagelok fittings. After assembly, the tube is purged with helium while Valve X is at the vent position (in which mode the dotted lines in the valve are connected and the solid lines are broken). The Valve X is then turned to the sampling mode (as in the figure) and the reactor heater (which surrounds the tube and is movable along it) is properly positioned and activated to perform the decomposition at a selected heating rate. Flexibility for flash pyrolysis has been provided, in which case the furnace, which is movable along the quartz tube, is heated in advance to the desired temperature, and then moved over the sample. The volatile products are transported by helium carrier gas through Valve X and then through one arm of the thermal conductivity cell where they are detected and then either trapped or vented from Valve Y. Trapping of the decomposition products is achieved by having Valve Y in its sampling mode (as shown in the figure) in which position the fragments are carried to a trap situated outside the detector oven. The trap is a stainless-steel column (1/8 in. o.d. by ~16 in.) packed with cross-linked polystyrene beads (Porapak Q, 80-100 mesh, Waters Associates). The trap has the proper configuration so that a fraction of it (~4 in. section) can be placed in a Dewar for subambient cooling. When the decomposition products enter the trap, the high molecular weight constituents are retained by the packing at the entrance of the trap, which is at room temperature. The more volatile constituents are retained by the packing downstream which is in the section cooled by liquid nitrogen. After trapping, Valve Y is turned to the backflush mode which reverses the direction of helium flow (Fig. 1, top left), the Dewar is removed, and the trap is flash-heated to a desired temperature below 250°C (the limit of thermal stability of Porapak Q), upon which the trapped constituents are released and carried by helium through Valve Y and then through the other arm of the thermal conductivity cell where they are again detected, this time as a sharp front, and then are delivered through a heated transfer line into the mass chromatograph. If desired, the trap heater can be program-heated. This will result in the fractional release of the trapped constituents. Subsequent detection by the thermal conductivity cell will therefore provide a gas chromatographic output in its own right.

The mass chromatograph was introduced about 3 years ago [8, 11]. It consists of two independent gas chromatographic systems using two different carrier gases which are run parallel from a common injection port. Each system is composed of a six-port valve (A, B), an external trap (Trap 1, Trap 2), a gas density balance detector (Detector 1, Detector 2), and a chromatographic column (Column 1, Column 2). The detectors and the valves are housed in the detector oven. When a sample

is introduced to the mass chromatograph, whether directly from the pyrolyzer or through the one injection port, it is carried by helium and split into two approximately equal fractions (splitter). Each fraction is carried by helium through the respective valves into the respective external traps. The traps are similar to the pyrolyzer trap. After trapping, Valves A and B are simultaneously turned to the back-flush positions (shown for Valve A at top center of Fig. 1). Then, carrier gases 1 and 2 flow through the respective traps and, after flash heating of the traps, carry the released fractions into the respective columns where separation is achieved. The constituents are detected as they elute from the matched columns by the respective gas density balance detectors Gow-Mac type, equipped with tungsten wire filaments). The recorder output displays two sets of peaks corresponding to the responses from the two gas chromatographic systems for the same constituents of the mixture. The ratio of responses are then related to the molecular weights of the constituents, as explained in the next section.

Gas Density Balance and Molecular Weight Determination

The introduction of the first gas density balance was motivated by a desire to develop a detector where response would be independent of the chemical structure of the substance being analyzed [12]. It was, however, immediately realized that the detector had an additional unique feature in that it could be used for determination of molecular weights [13, 14]. Later, a simplified gas density detector was developed [15] which formed the basis of the Gow-Mac gas density balance [16].

A schematic of the Gow-Mac type gas density balance detector is shown in Fig. 1 (top right). The reference gas, which is the same as the chromatographic carrier gas, is split at "a" and flows in parallel over the lower and upper filaments which are part of a Wheatstone bridge. If no solute is carried by the carrier gas from the column, the flow of the reference gas over the filaments is not disturbed. However, when a solute with a greater density than the carrier gas enters the cell at c, the density of the gas in the vertical conduit bd becomes greater than that of the pure carrier gas, and consequently the pressure at d increases. This causes the flow of the reference gas to decrease over the lower filament but to increase over the upper filament. The converse phenomenon applies for a solute which has a lower density than that of the carrier gas. The change in the flow rate of the reference gas over the filaments leads to a change in temperature and in turn to a change in the resistance between the upper and the lower filaments. This unbalance is recorded as a gas chromatographic peak.

It should be noted that the flow rate at the exit (vent) remains

constant and that the variation of pressure (at d) leads to a variation only in the interior flow rates of the gases. The change in density $\Delta\rho$ can be related [15] to the change in flow rate ΔQ by

$$\Delta\rho = \frac{8\mu L\Delta Q}{\pi g r^4 h} \tag{1}$$

where μ, L, g, r, and h represent the viscosity of the gas, the total length of the conduit abcde, the gravitational constant, the radius of the conduit, and the height of the gas stream in the conduit bd where the change in density occurs respectively. It should be noted that the presence of a solute will affect the viscosity of the carrier gas mostly in the conduit bd. However, the change in viscosity induced by the introduction of small amounts of solute can be considered to be negligible, since at a given temperature the viscosities of gases are of the same magnitude. Even though the validity of the assumptions (i.e., that incompressible steady-laminar flow conditions prevail, and that the pressure variation at d leads to identical variation in flow rate in all conduits of the loop abcda) that are invoked [15] in deriving Eq. (1) may be questionable, the proportional relationship between $\Delta\rho$ and ΔQ has been experimentally verified [15]. Furthermore it has been experimentally shown [15] that the electrical response of the detector is also linearly related to the change in flow rate, which therefore is proportional to the change in density. (The assumptions that lead to Eq. 1 are more suitable for liquids and, in fact, it has been reported [17] that the gas density balance can be used as a detector in liquid-solid chromatography.)

To a first approximation, the density of a gas is given by the ideal gas law expression, and at a given pressure and temperature it is proportional to its molecular weight:

$$\rho = (P/RT)M \tag{2}$$

[Under standard conditions $\rho = (1/22.4)M$, where ρ is expressed as grams/liter and M as grams/mole.] The instantaneous average molecular weight of the carrier gas (M) eluting from the chromatographic column can be expressed as

$$M = (1 - Y)M_c + YM_x \tag{3}$$

where Y is the instantaneous mole fraction of a solute X, and M_x and M_c are the molecular weights of the solute X and the carrier gas, respectively. Therefore, since the instantaneous density change is

$$\Delta\rho = \rho - \rho_c$$

where ρ and ρ_c are the densities of the carrier gas with and without the solute, respectively,

$$\Delta\rho = \frac{P}{RT}[M - M_c]$$

$$= \frac{P}{RT}[(1 - Y)M_c + YM_x - M_c]$$

$$= \frac{P}{RT} Y[M_x - M_c] \tag{4}$$

The instantaneous electrical response (E) is given by $E = k\Delta\rho$, and therefore

$$E = k(\frac{P}{RT})Y[M_x - M_c] \tag{5}$$

where k is a proportionality constant.

The instantaneous mole fraction of solute is related to the instantaneous number of moles of solute (n_x) and carrier gas (n_c) by

$$Y = \frac{n_x}{n_x + n_c} \tag{6}$$

The total electrical response is evaluated by substitution of this expression into Eq. (5) and integration with respect to time. It is directly proportional to the chromatographic peak area A_x. (In the following derivation, however, this constant of proportionality has not been explicitly introduced since its effect would have been nothing more than a redefinition of k in Eq. 7.)

$$A_x = \int_0^\infty E\, dt$$

$$= \int_0^\infty k(\frac{P}{RT})[M_x - M_c][\frac{n_x}{n_x + n_c}]dt$$

$$= k(\frac{P}{RT})[M_x - M_c] \int_0^\infty [\frac{n_x}{n_x + n_c}]\, dt \tag{7}$$

Here it has been assumed that, in the time interval for the elution of solute X, the pressure and temperature of the carrier and solute remain unchanged so that the (P/T) term can be taken outside the integral. For small n_x, one can make the approximation

$$\int_0^\infty \left[\frac{n_x}{n_x + n_c}\right] dt \approx \int_0^\infty \left(\frac{n_x}{n_c}\right) dt \approx \frac{1}{n_c} \int_0^\infty n_x \, dt \tag{8}$$

The integral $\int_0^\infty n_x \, dt$ is equal to the total number of moles of solute X that has eluted, i.e., N_x. Equation (7) now becomes

$$A_x = k\left(\frac{P}{RT}\right)\frac{N_x}{n_c}(M_x - M_c)$$

or

$$= k'\left(\frac{P}{RT}\right)N_x(M_x - M_c) \tag{9}$$

or

$$= k'\left(\frac{P}{RT}\right)W_x\left(1 - \frac{M_c}{M_x}\right) \tag{10}$$

where k' $(=k/n_c)$ is a new constant, and $W_x (=N_x M_x)$ is the total mass of solute that has eluted.

Equations (9) and (10) show that at a given temperature and pressure $k'(P/RT)$ becomes a cell constant for a given carrier gas and can be evaluated from a measurement of the peak area due to a known number of moles, N_x (or known mass, W_x), of a solute of known molecular weight, M_x. The molecular weight of an unknown is then evaluated from a measurement of the peak area due to a known mass or number of moles of the unknown [13, 14]. If, however, a mixture of an unknown and a standard is chromatographed using two different carrier gases, the measurement of the masses (or number of moles) of the unknown and of the calibration compound is no longer required [13, 18] (see below).

If a sample of a mixture containing the unknown of molecular weight M_x and a standard of molecular weight M_s is chromatographed using a carrier gas of molecular weight M_{c_1}, the following equations can be written for the detector response for the standard (A_s) and the unknown (A_x):

$$A_s = k'\left(\frac{P}{RT}\right)(mW)\left(1 - \frac{M_{c_1}}{M_s}\right) \tag{11}$$

$$A_x = k' \left(\frac{P}{RT}\right)(nW)\left(1 - \frac{M_{c_1}}{M_x}\right) \tag{12}$$

where m and n are the weight fractions of standard and unknown, respectively, in the total amount of sample (W) injected.

Division of Eq. (11) by Eq. (12) leads to

$$\left[\frac{A_s}{A_x}\right]_1 = \left(\frac{m}{n}\right)\left[\frac{M_s - M_{c_1}}{M_x - M_{c_1}}\right]\left[\frac{M_x}{M_s}\right] \tag{13}$$

Therefore, if the ratio of the weight fractions of the unknown and standard is known, which in practice usually necessitates knowing the weight fraction of each, then M_x can be calculated from the known molecular weights and the ratio of the areas of the chromatographic peaks.

If, however, another sample of the same mixture is chromatographed using a different carrier gas of molecular weight M_{c_2}, one can similarly derive a new expression:

$$\left[\frac{A_s}{A_x}\right]_2 = \left(\frac{m}{n}\right)\left[\frac{M_s - M_{c_2}}{M_x - M_{c_2}}\right]\left[\frac{M_x}{M_s}\right] \tag{14}$$

Therefore, from division of Eq. (13) by Eq. (14),

$$\frac{\left[\frac{A_s}{A_x}\right]_1}{\left[\frac{A_s}{A_x}\right]_2} = \left[\frac{M_s - M_{c_1}}{M_s - M_{c_2}}\right]\left[\frac{M_x - M_{c_2}}{M_x - M_{c_1}}\right] \tag{15}$$

Equation (15) does not involve terms related to the masses of the standard or the unknown. Since molecular weights of standard and carrier gases are known, and since the response ratios can be measured from the chromatographic outputs, M_x can be readily calculated.

It has also been shown that by using several carrier gases with molecular weights greater and less than the molecular weight of the unknown, the molecular weight of the unknown is accurately bracketed and interpolated [18].

This concept of using more than one carrier gas forms the basis of molecular weight chromatography. However, in the mass chromatograph, instead of chromatographing two samples of an unknown mixture containing a standard, the first with one carrier gas and the second with another, a sample (which does not require inclusion of a standard once the instrument has been calibrated) is injected directly and split automatically into two fractions (αW and βW, where $\alpha + \beta = 1.0$, and W = amount injected), and each fraction is simulataneously analyzed by the respective chromatographic system. Therefore, for a given solute X, two simultaneous responses, describable by two equations of the form of Eq. (10), are obtained:

$$A_1 = k_1' \left(\frac{P}{RT}\right)_1 (\alpha W)\left[1 - \frac{M_{c_1}}{M_X}\right] \tag{16}$$

and

$$A_2 = k_2' \left(\frac{P}{RT}\right)_2 (\beta W)\left[1 - \frac{M_{c_2}}{M_X}\right] \tag{17}$$

where A_1 and A_2 are the chromatographic peak areas for unknown X, k_1' and k_2' are detector constants, and M_{c_1} and M_{c_2} are the molecular weights of the carrier gases 1 and 2.

Division of Eq. (16) by Eq. (17) leads to

$$K\left[\frac{A_1}{A_2}\right] = \left[\frac{M_X - M_{c_1}}{M_X - M_{c_2}}\right] \tag{18}$$

where

$$K = \frac{\beta k_2'}{\alpha k_1'}$$

(Since both columns and detectors are operated under identical temperature and pressure conditions, P/RT terms cancel.) The knowledge of the actual value of the split ratio (β/α) is not required, provided that it does not vary from one experiment to the next. If this condition is satisfied, K becomes an instrument constant which can be determined by using a compound of known molecular weight and measuring the response ratio A_1/A_2 from the chromatographic output. Once K is established,

the molecular weight of an unknown can be determined from Eq. (19) which is obtained by rearranging Eq. (18):

$$M_X = \frac{[(A_1/A_2)K M_{C_2} - M_{C_1}]}{[(A_1/A_2)K - 1]} \tag{19}$$

It is clear from Eq. (10) that the detector response is positive if $M_X > M_C$, negative if $M_X < M_C$, and zero if $M_X = M_C$. Some limiting conditions are observed if $M_X \gg M_C$ or $M_X \ll M_C$. When $M_X \gg M_C$, then $M_C/M_X \ll 1$, and $A_X \sim W_X$; that is, the detector response becomes proportional to the mass of the sample and insensitive to its molecular weight. When, however, $M_X \ll M_C$, then $M_C/M_X \gg 1$, and $A_X \sim W_X(M_C/M_X) \sim N_X$; that is, the response becomes proportional to and more sensitive to the number of moles of the sample. Therefore any given carrier gas is expected to display optimal functionality only in a certain molecular weight range. In the mass chromatograph, whereas the use of two carrier gases makes it possible to write Eqs. (16) and (17), and consequently obtain Eqs. (18) and (19), the selection of a high and a low molecular weight carrier gas provides a wide range of operation for calculations of molecular weight. However, selection of the low molecular weight carrier gas requires special considerations. Light gases such as helium or hydrogen should not normally be chosen. This is because, as can be seen from Eq. (10), the detector response is proportional to $(M_X - M_C)/M_X$ and will tend to a constant very rapidly as M_X increases, thus resulting in a narrow molecular weight range of functionality for the detector. Furthermore, with light gases back-diffusion in the detector conduits may become appreciable.

The accuracy of molecular weight determinations depends upon invariance of the instrument constant K, and the accuracy with which the response ratios are measured (see Eq. 19). The relative errors in K and A_1/A_2 are not linearly related to the error they cause in the molecular weight, as is illustrated in Table 1. In the preparation of Table 1, the theoretical value of the factor $K(A_1/A_2)$ was evaluated from Eq. (18) for carrier gases carbon dioxide and monochloropentafluoroethane. Then a defined error was purposefully introduced to the $K(A_1/A_2)$ value, and the molecular weight corresponding to this new value was back-calculated and compared with the initial molecular weight. The errors that are reflected in the molecular weight due to 1 and 5% errors in the ratio $K(A_1/A_2)$ are shown (Table 1). Error in terms of mass units becomes magnified in the high molecular weight region. There is an optimum range of molecular weights for operation.

TABLE 1. Influence of Error Made in Evaluation of $K(\frac{A_1}{A_2})$ on the Calculation of Molecular Weights

M_x	$K\frac{A_1}{A_2}$ $\left[=\frac{M_x - M_{c_1}}{M_x - M_{c_2}}\right]$	M'_x $\left[=\frac{\xi M_{c_2} - M_{c_1}}{\xi - 1.0}\right]^b$	% error $\left[\frac{M_x - M_x}{M_x} \times 100\right]$	M''_x $\left[=\frac{\xi M_{c_2} - M_{c_1}}{\xi - 1.0}\right]^c$	% error $\left[\frac{M''_x - M_x}{M_x} \times 100\right]$
4	3.76	4.53	13.25	6.54	63.50
10	4.25	10.42	4.20	12.11	21.10
20	5.60	20.28	1.40	21.37	6.85
30	8.88	30.15	0.50	30.74	2.47
40	28.54	40.04	0.10	40.19	0.47
50	17.44	49.94	0.12	49.73	0.54
60	5.91	59.85	0.25	59.33	1.11
70	3.25	69.80	0.28	69.04	1.37
80	2.07	79.76	0.30	78.81	1.48
90	1.40	89.84	0.18	88.73	1.41
100	0.97	99.70	0.30	98.67	1.01
110	0.67	109.70	0.27	108.68	1.20
120	0.45	119.79	0.17	118.85	0.95
130	0.28	129.83	0.13	129.02	0.75
140	0.15	139.85	0.11	139.34	0.47
150	0.04	149.96	0.02	149.79	0.14

160	0.04	160.04	0.02	160.27	0.17
170	0.12	170.09	0.05	170.81	0.47
180	0.19	180.36	0.20	181.62	0.90
190	0.24	190.30	0.15	192.25	1.18
200	0.29	200.67	0.33	204.00	2.00
210	0.33	210.60	0.28	214.12	1.96
220	0.37	220.73	0.33	225.36	2.43
230	0.40	231.21	0.53	236.53	2.84
240	0.43	241.38	0.57	247.71	3.21
250	0.46	251.85	0.74	259.39	3.75
260	0.49	261.86	0.72	270.52	4.04
270	0.51	272.20	0.81	282.30	4.39
280	0.53	282.56	0.91	294.23	5.08
290	0.55	292.77	0.95	306.04	5.53
300	0.57	303.09	1.03	317.67	5.89
320	0.59	323.63	1.13	341.63	6.76
340	0.62	344.96	1.46	367.34	8.04
360	0.65	365.08	1.41	391.88	8.85
380	0.67	386.70	1.76	417.91	9.97
400	0.69	407.33	1.83	443.31	10.82
450	0.73	460.80	2.40	512.81	13.95
500	0.75	512.01	2.40	582.39	16.47

[a] M_{c_1} = 154.46 (molecular weight of Freon-115). M_{c_2} = 44.01 (molecular weight of carbon dioxide).

[b] $b_\xi = K\frac{A_1}{A_2} + 0.01K\frac{A_1}{A_2}$.

[c] $c_\zeta = K\frac{A_1}{A_2} + 0.05K\frac{A_1}{A_2}$.

Carrier and Reference Gases

Experimental studies on the response of the gas density balance as a function of the nature of the carrier gas, flow rates, and density changes have been reported [18-22]. In particular, hydrogen [12, 14, 21], helium [21, 22], nitrogen [12-14, 18, 19, 21, 22], argon [18, 19, 22], carbon dioxide [18, 19, 21], chloromethane [21], difluoroethane [18], dichlorodifluoromethane [18, 21], sulfur hexafluoride [20-22], bromotrifluoromethane [21], and octafluorocyclobutane [18] have been investigated. The manufacturers of the mass chromatograph have recommended carbon dioxide and sulfur hexafluoride as the low and high molecular weight carrier gases [8, 9, 11].

In this laboratory, carbon dioxide (Matheson, Coleman instrument grade, with a minimum purity of 99.99%) is used as the low molecular weight carrier (and reference) gas, but monochloropentafluoroethane ClC_2F_5 (Freon-115, Du Pont food grade) is used as the high molecular weight carrier (and reference) gas. The fluorocarbon (bp -38.72°C) is shipped in cylinders from which it can be drawn in liquid form at a higher purity level than the designated 99.98 volume-based percent. Its molecular weight is 8.46 mass units higher than sulfur hexafluoride and extends the upper molecular weight limit of sensitivity of the mass chromatograph.

Helium (Matheson, ultra high purity grade, with minimum purity of 99.999% on a neon-free basis) is used as the carrier gas for the pyrolyzer and the mass chromatograph injection port (Fig. 1). [The commercial mass chromatograph has been slightly modified to accommodate helium (instead of carbon dioxide) as the injection port carrier gas.] Use of the same gas at identical flow rates insures that calibration and in-use conditions are the same. Furthermore, the use of helium as the injection port carrier gas gives the flexibility of using liquid nitrogen-cooling with the mass chromatograph traps when in the sampling mode.

An independent cylinder is used for each carrier and reference gas. Freon-115 is vaporized before entry into the instrument. Room temperature fluctuations are kept at a minimum to prevent condensation and reevaporation which upset the detector response. Since the response mechanism of the gas density balance involves pressure variation in the cell, any sudden external variations in pressure are immediately detected; this becomes especially important with the Freon-115 reference gas for which flow rates are low.

Helium (carrier) and Freon-115 (carrier and reference) are dried by passing through a column of P_2O_5/firebrick, and then through a column of molecular sieves (Linde, type 5A). Carbon dioxide (carrier and reference) is dried by passing through a column of silica gel, and then through a column of P_2O_5/firebrick. The reason for high purity requirements and extensive drying of gases is to

prevent large baseline drifts that become a special problem with the detector using the high molecular weight carrier gas, due to its high sensitivity to low molecular weight constituents (see Eq. 10). In this connection, elimination of leaks in the system becomes a strict requirement. It was observed that the 6-port valves can suffer from leaks, and meticulous care must be taken to eliminate these if proper operation is to be achieved.

Operational Conditions

The gas flow rates were set as follows: 20 ml/min at 50 psig for helium flow; 10 ml/min at 100 psig for carbon dioxide and Freon-115 carrier gases; 41 ml/min at 56 psig for Freon-115 reference gas, and 122 ml/min at 100 psig for carbon dioxide reference gas.

The thermal conductivity and gas density detector currents were set at 100 mA. The temperatures of the thermal conductivity and gas density detector ovens were maintained at 230 and 242°C, respectively. The pyrolyzer and the mass chromatograph trap temperature limits were set at 230 and 235°C, respectively. (Thus the constituents that are released from the pyrolyzer trap are not later retained in the mass chromatograph traps.) The transfer line temperature from the pyrolyzer to the mass chromatograph was maintained at 300°C.

Chromatographic Columns

Two stainless steel (1/8 in. × 12 ft) matched columns packed with 10% silicone gum SE-30 on 60/80 mesh Chromosorb W-AW were used for analysis of the degradation products of hydrocarbon polymers.

Instrument Calibration

The process of instrument calibration involves the determination of the constant K in Eq. (18). In principle, K can be evaluated by chromatographing just one solute of known molecular weight and measuring the response ratio A_1/A_2 from the chromatographic output. However the accuracy of measuring the response ratio varies with molecular weight and therefore, in practice, K should be evaluated using a mixture of known compounds.

Furthermore, in practice, more accurate values of molecular weights of unknowns can be obtained by using more than one value for K, according to the molecular weight range of interest. Accurate measurements of response ratios are difficult to determine in the vicinity of molecular weights of the carrier gases since, as $M_x \to M_c$, $A_x \to 0$, and change in response with molecular weight becomes small.

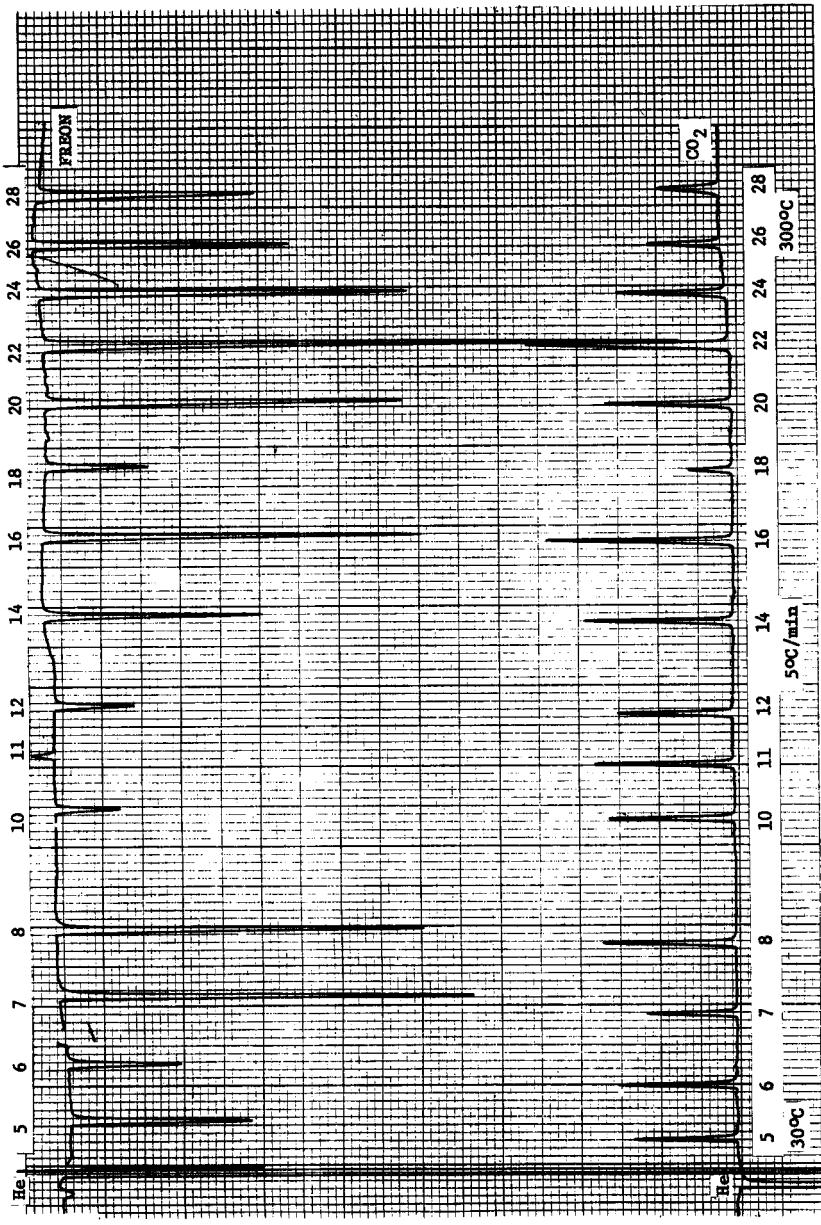

FIG. 2. Mass chromatogram of a mixture of known saturated normal hydrocarbons (C_5 to C_{28}). The chromatogram was obtained by operating isothermally at 30°C until helium peaks eluted, and then by temperature-programming the columns from 30 to 300°C at 5°C/min. The columns were then held isothermally at 300°C. The peak attenuations were ×8 except for the C_5 to C_6 peaks in the Freon-115 channel for which the settings were ×64. After elution of the C_{11} peak, the polarity of the Freon-115 detector response was reversed to result in downward peaks for constituents with molecular weights greater than the molecular weight of Freon-115.

The chromatogram of a mixture of known saturated normal hydrocarbons (C_5 to C_{28}) is shown in Fig. 2 where peaks have been identified with respect to their carbon numbers. The top and bottom series of peaks correspond to the detector responses using Freon-115 and CO_2 carrier gases, respectively.

The instrument constant K was evaluated to be, using the ratios of peak heights, 0.189 in the molecular weight range above the molecular weight of Freon-115 (154.46) and 0.206 in the molecular weight range below the molecular weight of Freon-115. (Due to the intrinsic inaccuracies in measurement as $M \rightarrow M_C$, the molecular weight region $154.46 \pm \sim 30$ was not used in the evaluation of the instrument constant.) Back-calculation of the respective molecular weights of the constituents using the respective K values estimated their molecular weights with, on the average, less than 1.5% and less than 0.5% errors in the respective regions. Calculation of the molecular weights in the region $154.46 \pm \sim 30$ is not affected appreciably by which K value is used since in this region A_1/A_2 is very small and KA_1/A_2 is not sensitive to changes in K. This fact and the difficulty of measurement of A_1 (and thus A_1/A_2) with accuracy in this region justify not considering the compounds with molecular weights in this region as standards in evaluating the instrument constant. Furthermore, this approach eliminates the need to use "effective" [10] rather than actual molecular weight values for the carrier gases.

It should be evident from Eq. (18) and Table 1 that, in the range of molecular weights greater than the molecular weights of the carrier gases, the change in KA_1/A_2 with molecular weight becomes small as molecular weight increases. Thus small errors in K or A_1/A_2 can lead to significant errors in molecular weight calculations. Analysis of the factor KA_1/A_2 shows that at low molecular weight regions A_1/A_2 varies significantly as molecular weight changes and small errors in K are not magnified; however at high molecular weight regions A_1/A_2 tends to a constant and KA_1/A_2 becomes very sensitive to errors in K. Therefore, a K value evaluated using low molecular weight standards may, in practice, lead to large errors in estimating molecular weights of unknowns in the high molecular weight range. In contrast, a K value determined using high molecular weight standards will in general be good in estimating molecular weights of low molecular weight unknowns due to the fact that in the low molecular weight range, A_1/A_2 rather than K is the governing factor. However, as pointed out earlier, more accurate values of molecular weights of unknowns can be obtained using more than one K value applicable to the molecular weight ranges of interest.

In principle, in calibration and later in molecular weight calculations, peak areas rather than peak heights should be used. The use of peak heights can be permissible only if the peaks are not skewed and the peak base widths are identical on both channels (which imposes a strict

requirement for identical columns). However, area measurements are not without ambiguities with respect to limits of integration, especially in the case of partially overlapping peaks.

POLYETHYLENE

The degradation of polyethylene by pyrolysis has an extensive literature and thus serves to demonstrate the capabilities of the present system on a comparative basis.

Literature Review

Prior to the introduction of pyrolysis-gas chromatography in 1954 [23], analyses of the products of pyrolysis were dependent upon fraction collecting and subsequent analysis of the fractions by IR and/or mass spectrometry, or by chemical methods. In one of the earlier studies, pyrolysis of a sample of polyethylene of average molecular weight 20,000, for 30 min at 475°C in vacuum, resulted in a solid residue, a waxlike fraction (which was not volatile at room temperature), and a fraction which was volatile at room temperature [24]. Only this volatile fraction was analyzed in a mass spectrometer and was reported to be composed of hydrocarbons up to heptanes. The waxlike fraction, which accounted for 95.5% of the decomposition products, was not analyzed, except for testing for its average molecular weight by a microfreezing point lowering method in camphor. The average molecular weight was reported to be 692, which corresponds to an average fragment of about 50 carbon atoms.

These initial studies were thus limited to the analysis of only the low molecular weight volatile decomposition products. A detailed review has been published [25].

The technique of gas chromatography combined with pyrolysis initiated two types of studies. Earlier applications were in the establishment of the so-called "fingerprint" pyrograms for purposes of identification of unknown polymer samples, and did not require identification of the individual peaks appearing in the pyrograms. A large number of fingerprint pyrograms of polyethylene has been published (e.g., Refs. 26-30). The pyrograms are difficult to compare due to the differences in pyrolysis and chromatographic conditions and the types of pyrolyzers utilized in various laboratories. The question of interlaboratory reproducibility in pyrolysis-gas chromatography is indeed a major concern [4, 31].

The pyrolysis-gas chromatographic techniques have been gradually directed more toward investigation of degradation mechanisms and molecular structures of polymers. These require, in particular, identification of the decomposition products.

The first detailed work which was directed to the analysis of the

decomposition products of polyethylene by pyrolysis-gas chromatography was reported in 1964 [32]. A sample of polyethylene (presumably of low density) was pyrolyzed for 10 sec at 1000°C using a filament pyrolyzer. The chromatogram displayed a homologous series of triplet peaks which upon hydrogenation reduced to a homologous series of single peaks corresponding to normal hydrocarbons from C_7 to C_{17}, thus indicating that the other two peaks in the triplets corresponded to unsaturated hydrocarbons. In the same year it was reported [33] that pyrolysis of low- or high-density polyethylene samples at 690°C, using this time a reaction chamber technique, also led to a chromatogram composed of repeated triplet peaks, the resolution of which improved when capillary columns were used for separation. The peaks were indicated to correspond to C_7 to C_{27} hydrocarbons; however, verification was provided only for C_7, C_{12}, and C_{16}.

In a later study, in order to simplify identification, products of pyrolysis (for about 1 sec at 500°C) of a linear polyethylene (i.e., polymethylene) sample were hydrogenated before entry into the gas chromatographic column [34]. The peaks were identified by comparison of retention times of model compounds and found to correspond to normal hydrocarbons up to C_{13}. The pyrolysis products above C_{13} were not detected due to condensation of higher molecular weight fragments in the pyrolyzer and hydrogenation sections. A further investigation [35] addressed itself to the analysis of the nature of the triplets that were formed upon pyrolysis of polyethylene samples of different densities. Pyrolysis was carried out for 10 sec at 1000°C. By mixing the original sample with a number of normal hydrocarbons and α-olefins, the identity of two peaks of the triplets were determined to be a normal paraffin and an α-olefin. In the case of the triplet corresponding to C_{12}, the third peak was identified indirectly from chemical reaction analyses to be the α,ω-diolefin. It was then assumed that the third peak in each triplet corresponded to the α,ω-diolefin. The triplet formation was observed also in pyrolysis by electric discharge [36]; however, the peaks observed in this study were not identified. Later, in a study [37] of the pyrolysis products of polyethylene, where C_1 to C_6 hydrocarbons were identified by comparison of retention time data of model compounds, it was observed that the amount of butadiene and butene generated at a given pyrolysis temperature (in the range 450 to 900°C) depended upon the degree of branching, and an index was derived which was based on the relative peak heights of butene to determine the composition of linear and branched polyethylene samples. In the same year there appeared another report [38] on a combination of hydrogenation with pyrolysis-gas chromatography to identify decomposition products of (low- and high-density) polyethylene up to 1-hexene. In 1968 a technique was described [39] which combined thermogravimetry and gas chromatography. The philosophy of this approach differed from earlier experiments in that pyrolysis was

carried out by program heating. The chromatogram of the decomposition products of a sample of low-density polyethylene pyrolyzed at a program heating rate of 5°C/min up to 500°C displayed a series of evenly spaced doublet peaks which were assumed to correspond to unsaturated and saturated straight chain hydrocarbons. This doublet formation differs from the often reported homologous series of triplets which appears to be representative of flash pyrolysis. For example, in the same year it was again reported [40] that flash pyrolysis (at 680°C for 20 sec) of polyethylene leads to the formation of triplets which reduce to singlets upon hydrogenation. The range of detectable fragments was claimed to be up to C_{36} even though, in the published pyrogram, the assignment is only up to C_{24} (from C_5). By modification of the chromatographic conditions, it was reported in the same paper that hydrocarbons up to C_{50} could be detected. However, the pyrogram shows assignments only from C_{10} to C_{40}. Two additional studies appeared in the same year [41, 42]. In a detailed study of the volatile decomposition products up to C_9, 30 peaks were detected for hydrocarbons from C_1 to C_6 and were identified by comparing retention times [41]. Samples were pyrolyzed in vacuum isothermally at various temperatures in the range of 375 to 425°C. The same authors also investigated the thermal decomposition products of polymethylene and reported that in the chromatogram in which the products from C_1 to C_{16} hydrocarbons were analyzed, the low molecular weight fragments below C_8 were doublets consisting of α-olefin and n-alkane; however, above n-C_8 hydrocarbons, a small peak appeared before the α-olefin peak, resulting in a series of triplet peaks In a later study reported in 1970 [43], hydrocarbons up to C_{12} were analyzed. More recent studies [44, 45] have concerned themselves with the structure of ethylene-propylene copolymers with respect to the determination of sequence length distribution in these copolymers by pyrolysis-gas chromatography.

The formation of the saturated and unsaturated hydrocarbons reported in these studies has been interpreted in terms of a random chain scission process involving a free radical mechanism [25, 34, 35, 41, 42, 46]. Considerable intramolecular radical transfer, especially,to the 5th carbon by a coiling mechanism, is operative [34, 41, 42] under mild conditions.

Present Results

A 20-mg sample of low-density polyethylene (ρ = 0.925, $\overline{M}_w$ = 140,000, $\overline{M}_n$ = 16,000, 13 methyl groups/1000 C-atoms) was pyrolyzed in the present system by program heating (at 20°C/min) from room temperature to 600°C, and the fraction volatilizing between 300 and 600°C was analyzed in the mass chromatograph.

The thermal conductivity cell response during pyrolysis and also the complementary results of thermogravimetric and differential thermal analyses (obtained at same heating rate but in a nitrogen atmosphere, using a Du Pont 950 TGA and a 900 DTA unit) are shown in Fig. 3. This documents the important thermal history before and during pyrolysis.

The mass chromatograph output which is shown in Fig. 4 displays a series of regularly spaced (doublet) peaks. Calculations of the molecular weights of each prominant peak indicate that the molecular weights of the compounds corresponding to these peaks are comparable to those of C_2 to C_{26} hydrocarbons (Table 2) and have been so-designated in the figure. The constituents more volatile than C_3 are not discussed herein. The molecular weight calculations further indicate that the first peak in each doublet has a molecular weight comparable to that of an unsaturated hydrocarbon (with one double bond) and the second peak to that of a saturated hydrocarbon. The doublets merge beyond C_{16} and below C_5; they are not resolved under the present chromatographic conditions. Each peak is probably a mixture of a saturated hydrocarbon of the indicated carbon number.

Discussion

A direct comparison of the present results with those reported in the literature is not easy due to differences both in the pyrolysis and the chromatographic conditions. However, certain similarities exist.

As mentioned earlier, there has been only one published study in which pyrolysis of polyethylene was carried out by program heating rather than by flash heating and the decomposition products were analyzed by gas chromatography [39]. In that study, also, the pyrogram displayed a homologous series of doublet peaks similar to the present observations. In contrast, flash-pyrolysis experiments have been reported to lead to triplet formation [32, 33, 35, 36, 40, 44]. A close examination of Fig. 4 indicates that starting with the doublet corresponding to the C_9 hydrocarbons, a small peak starts to appear as a shoulder before the alkene peak, which is similar to a phenomenon reported in an isothermal-pyrolysis experiment with polymethylene [42].

The relative amounts of alkadiene produced are dependent upon the mechanism of degration. Homolytic chain scission followed by simultaneous saturation and unsaturation at the site of scission predicts a yield of n-alkane, 1-alkene, and alkadiene in the mole ratio 1:2:1

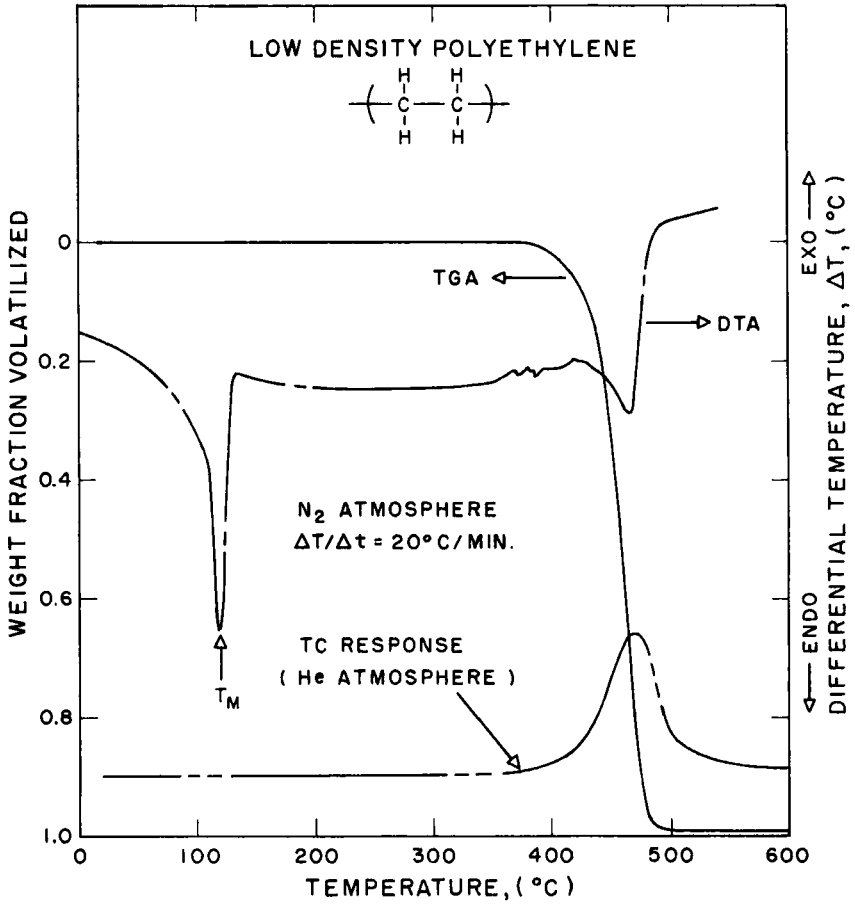

FIG. 3. Thermal history before and during pyrolysis of low-density polyethylene (ρ = 0.925, $\overline{M}_w$ = 140,000, $\overline{M}_n$ = 16,000, 13 methyl groups/1000 C-atoms).

[35, 42], indicating that the quantity of alkadiene produced should be as much as n-alkane. A predominantly intermolecular radical transfer process, however, predicts [42] that the amount of alkadiene produced should be greater than that of n-alkane. In contrast, a predominantly intramolecular radical transfer process by back-biting predicts that the amount of alkadiene should be very small, being zero if it is the only process that is operative [42].

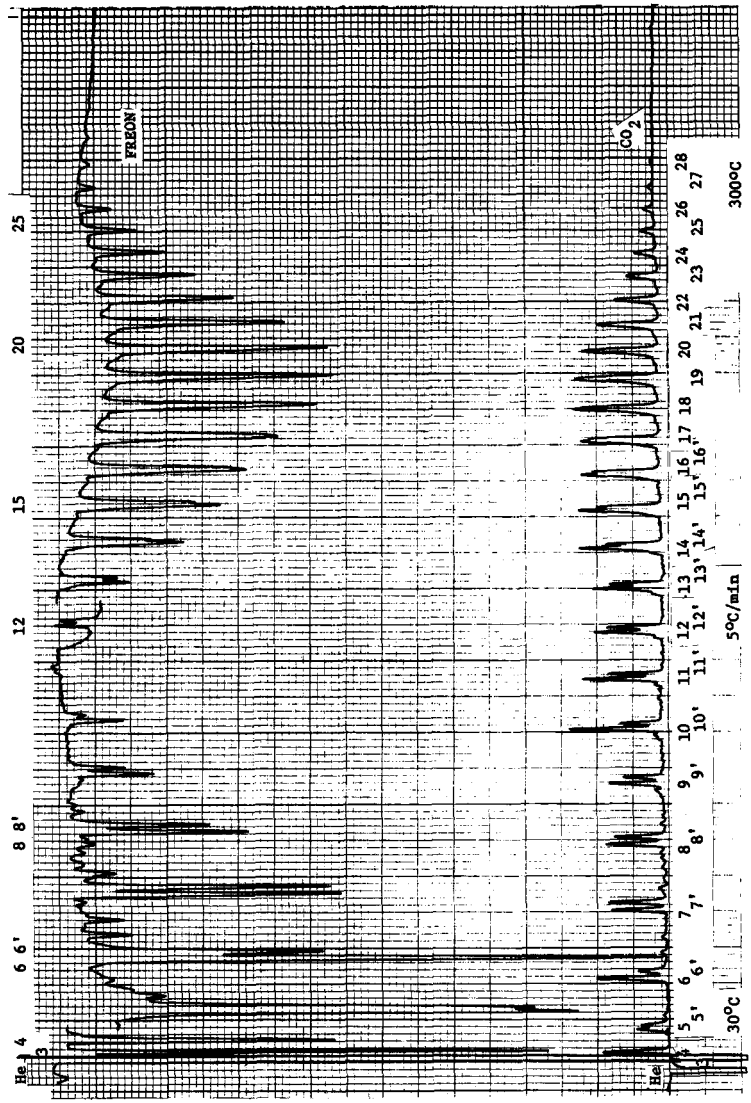

FIG. 4. Mass chromatogram of the pyrolysis products of low-density polyethylene ($\rho = 0.925$, $\bar{M}_w = 140{,}000$, $\bar{M}_n = 16{,}000$, 13 methyl groups/1000 C-atoms). A 20-mg sample was pyrolyzed by program-heating (at 20°C/min) in helium atmosphere, and the fraction from 300 to 600°C was analyzed. The columns were operated isothermally at 30°C until C_4 peaks eluted and then program-heated (at 5°C/min) to 300°C and held isothermally at 300°C. The peak attentuations were ×8 except for the C_3 and C_4 peaks in the Freon-115 channel for which the settings were ×64. After elution of C_{12} peaks, the polarity of the Freon-115 detector response was reversed to result in downward peaks for constituents of higher molecular weight. For a comparison of the retention times, see Fig. 2.

TABLE 2. Molecular Weights of Degradation Products of Polyethylene

Peak number (x)	Response ratio A_1/A_2 (Freon/CO_2)	Molecular weight (calcd)	Molecular weight of saturated x-hydrocarbon[a]	Tentative assignments C number (n, saturated; $n^=$, olefin)
3	406	42.67	44.09	$3^=$,3
4	-39.13	56.20	58.12	$4^=$,4
5	-14.32	71.97		5
5'	-15.19	70.74	72.15	$5^=$
6	- 8.20	85.08		$6^=$
6'	- 8.08	85.46	86.18	6
7	- 4.87	99.16		$7^=$
7'	- 4.41	101.91	100.21	7
8	- 3.08	111.58		$8^=$
8'	- 2.78	114.21	114.23	8
9	- 1.61	126.95		$9^=$
9'	- 1.44	129.19	128.26	9
10	- 0.64	141.60		$10^=$
10'	- 0.57	142.86	142.29	10
11	0.074	156.03		$11^=$
11'	0.174	158.22	156.31	11

12	0.60	168.59		$12^{=}$
12'	0.66	170.21	170.34	12
13	1.00	180.20		$13^{=}$
13'	1.11	183.78	184.27	13
14	1.43	195.36		$14^{=}$
14'	1.51	198.57	198.40	14
15	1.74	208.58		$15^{=}$
15'	1.86	214.34	212.31	15
16	2.02	222.67		$16^{=}$
16'	2.14	229.47	226.45	16
17	2.33	241.37	240.35	$17^{=}$, 17
18	2.49	252.64	254.50	$18^{=}$, 18
19	2.72	267.12	268.39	$19^{=}$, 19
20	2.89	287.40	282.56	$20^{=}$, 20
21	2.96	294.71	296.43	$21^{=}$, 21
22	3.08	308.32	310.59	$22^{=}$, 22
23	3.17	319.53	324.47	$23^{=}$, 23
24	3.29	336.06	338.66	$24^{=}$, 24
25	3.38	349.81	352.51	$25^{=}$, 25
26	3.50	370.30	366.72	$26^{=}$, 26

[a]CRC Handbook of Chemistry and Physics, 48th ed.

Evidence for predominant intramolecular radical transfer by backbiting in the degradation of polyethylene can thus be found [42] in the experimental observations of relative amounts of alkadiene formation In Fig. 4 the 1-alkene peak is larger than the n-alkane peak in each doublet but only small amounts of alkadienes are detectable (beyond C_8). This suggests that in the program-heating mode the radicals that are formed apparently have enough time to coil and abstract a hydrogen intramolecularly. In flash-pyrolysis experiments, however, radicals are subject to a large number of secondary reactions and do not have time for intramolecular transfer reactions.

It is interesting to note that the shape of the chromatogram (Fig. 4) in the C_{12} to C_{28} region is pyramidal and peaks at about C_{19}. A similar phenomenon was reported in pyrograms of both high- and low-density polyethylene [40], even though the experiments were carried out by flash pyrolysis. It was observed that low-density polyethylene showed a maximum in the vicinity of C_{18} to C_{19}, in agreement with the present observations, whereas high-density polyethylene showed two maxima occurring around C_{22} to C_{23} and C_{30} to C_{32}. (This difference was indicated to be useful in differentiation between different polyethylene samples.) The small peaks that are observed between the doublets (in Fig. 4) presumably result from branching in low-density polyethylene and thus may correspond to branched hydrocarbons. The formation of such branched hydrocarbons is reported to take place to a lesser extent in high-density polyethylene, and this observation also has been suggested for differentiation between polyethylene samples [40].

It is evident from this example with polyethylene and studies conducted with polyisobutylene, polypropylene, polystyrene, and a series of polysulfones [47] that the present technique of pyrolyzer/thermal conductivity probe/mass chromatograph gives the molecular weights of constituents of pyrolysis with useful accuracy and probably with greater ease than conventional methods. The accuracy of the results can no doubt be improved with improved resolution of the peaks. The present system offers certain other advantages. The program-heating capability of the pyrolyzer is most suitable for studying mechanisms of the onset of thermal decomposition and for following its progress. Furthermore, pyrolysis is conducted with minimum thermal energy which is essential to minimize secondary reactions. Use of program-heating pyrolysis has been previously reported only in a few studies where a thermogravimetric analyzer was combined with a gas chromatograph [39, 48] or a mass spectrometer [49]. The importance of this approach is more evident if it is realized that in most cases in flash pyrolysis, pyrolysis is completed well below the temperature of the heat source [50]. The uncertainties with respect to the temperature of pyrolysis can thus be resolved by utilizing program heating, and interlaboratory reproducibility can be achieved. Perhaps one of the reasons for not using program heating in earlier studies was because complete pyrolysis is not achieved rapidly, which would mean introduction of pyrolysis products onto the column over an extended period of time, and the question of broadening

of peaks in the chromatogram would arise. The utilization of traps in the present system eliminates this problem. The decomposition products can be collected for any period of time and later can be released and introduced directly to the gas chromatographic column as a sharp plug by flash heating.

The thermal conductivity cell detector provides the flexibility for selective trapping and is most useful in monitoring the progress of decomposition under experimental pyrolysis conditions. However, the detector oven cannot be maintained above 250°C, and thus introduces a limitation for analysis of high molecular weight decomposition fragments. Only those constituents that are volatile at the detector oven temperature are carried to the pyrolyzer trap (Fig. 1), and later released and analyzed with the mass chromatograph.

The utilization of gas density balance detectors provides another unique feature to the present system in that oxidative studies can be conducted since constituents analyzed in the mass chromatograph never come in contact with the filaments of the detectors (Fig. 1).

The effect of temperature programming in pyrolysis and the nature of the decomposition products generated in different temperature ranges in the course of decomposition of polyethylene and other polyolefins are being investigated [51]. Finally, it is interesting to note that the present pyrogram shown in Fig. 4 covers the widest range of compounds (from C_3 to C_{26}) with determined molecular weights that has been published in a single pyrogram of polyethylene.

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Note added in proof. A detailed analysis of the hydrodynamics of operation of the gas density balance is now available [51]. A more extensive discussion of the technique of pyrolysis-molecular weight chromatography and its applications to the study of the thermal degradation of polyolefins, polyalkylmethacrylates, and olefin/sulfone copolymers are also presented in Ref. 51.