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Pyrolysis–Molecular Weight Chromatography–Vapor-Phase Infrared Spectrophotometry: A New On-Line System for Analysis of Polymers. I. Instrumentation

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Synopsis

An instrumental system consisting of a combination in series of a programmable pyrolyzer, a thermal conductivity detector, a mass chromatograph, and a fast-scan vapor-phase infrared spectrophotometer is described.

INTRODUCTION

Analysis of the products of pyrolysis gives information which is valuable in characterizing polymeric materials.[1] Various pyrolyzers have been designed and coupled with analytical instruments such as the mass spectrometer, the gas chromatograph, and the infrared spectrophotometer.[1–3] The present paper describes a combination in which a programmable pyrolyzer has been coupled in series with a thermal conductivity detector, a mass chromatograph (a gas chromatograph which provides molecular weights as well as separation of constituents of volatile mixtures), and a fast-scan vapor-phase infrared spectrophotometer.

LITERATURE REVIEW

The brief review of this section is instructive in placing the present system in perspective.

In most pyrolytic devices, the temperature of the sample is raised very rapidly (flash heating) by either pulse heating with the sample in place, or by introducing the sample after preheating the oven to the desired temperature.[1,2] In filament pyrolyzers, the sample is placed either on the surface of the filament wire (as a thin film made from a solution of the sample) or inside a small container that is held within the filament coil. Pyrolysis is achieved by passing a current through the filament which, through resistive heating, rais-

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es the temperature of the system to a value which is determined by the applied voltage.

Even when operating under the pulse mode, there is a finite temperature rise time so that the actual temperatures at which pyrolysis takes place are not well defined[4]; pyrolysis of the sample is often completed before the filament reaches its final temperature. In order to eliminate this drawback, methods which shorten the time required to reach the final temperature have been sought. Among these are the Curie-point pyrolyzers.[5] In these, the filament wire is a ferromagnetic material which undergoes induction heating when exposed to a radio-frequency field and rapidly reaches a specific temperature known as the Curie temperature. In such units, however, the temperature of pyrolysis cannot be selected at will since the Curie temperature is fixed by the alloy composition of the filament wire and at present is limited to 356°, 480°, 520°, 600°, 770°, and 980°C.[3]

Laser pyrolyzers, which also operate on the pulse principle, can achieve very high temperatures in extremely short times.[6,7] The rate of cooling of the primary products is also rapid since the laser energy can be directed to heat only a localized region of the pyrolysis chamber. This can be a desirable feature in minimizing secondary reactions. However, pyrolysis by high-energy lasers is not a simple thermal process; it is complicated by plasma formation through ionization.

In furnace-type pyrolyzers, the pyrolysis chamber (such as a quartz tube) is preheated to a selected temperature before the sample is placed in the hot zone. In such units, the pyrolysis temperature is better controlled and the temperature rise time for the pyrolyzer is no longer of concern. However, there is a rise time for the temperature of the sample.

More detailed information on the relative merits of various pyrolyzers can be found elsewhere.[1,2,3,8] The comparative studies that have been reported express concern for the poor interlaboratory reproducibility in pyrolytic experiments.[3,9] In flash pyrolysis, this is an inherent problem since the tendency is to control the upper temperature limit of the pyrolyzer rather than how that temperature is attained. Only recently has attention been paid to this latter aspect. The actual temperature of thermal-pyrolytic events can be better determined (and reproduced) by using controlled heating at slow rates, as in the case of thermogravimetric analysis (TGA) experiments. Some studies on the use of the TGA-type pyrolyzers have been reported.[10–16] Under prescribed conditions, this approach represents perhaps the best candidate to give reproducible results. However, pyrolyzers should not be evaluated as independent units, but rather in conjunction with the subsequent analytical techniques that are intended for separation and identification of the products of pyrolysis. For example, if the unit is to be coupled with a gas chromatograph, consideration must be given to the problems associated with interfacing the two units. This explains, as discussed below, why the slow-heating pyrolysis approach has often been avoided, whereas flash pyrolysis using filament-type units has maintained its popularity.

When a pyrolyzer is directly coupled to the inlet of a gas chromatograph, the pyrolyzer carrier gas acts also as the column carrier gas. This requires that the flow conditions through the pyrolyzer conform with the flow rates and pressures necessary for optimum column performance. In addition,

since for good separation the products of pyrolysis must be introduced to the chromatographic column as a slug, the direct coupling of a pyrolyzer with a gas chromatograph requires rapid pyrolysis conditions, small sample sizes, and small pyrolysis chambers. Such considerations favor filament-type pyrolyzers.

A pyrolyzer can be coupled also to a gas chromatograph by using a valve to permit passage of selected portions of the pyrolyzate. Pyrolysis can then be carried out essentially independently of the fact that it is followed by a gas chromatograph, thus removing the restrictions that are imposed in the direct-coupling configuration. The temperature of the valve assembly must be kept high enough to prevent condensation, and yet low enough not to cause further pyrolysis of the products of pyrolysis. In practice, it may not be possible to transfer all of the pyrolysis products, without further reaction, to the gas chromatograph.

In coupling a TGA-type pyrolyzer unit with a gas chromatograph, a difficulty arises in consequence of the slow program-heating conditions under which decomposition products are formed over a wide temperature range. Even though this would be ideal in investigating the types of products formed versus temperature, instant analysis with a gas chromatograph is not possible, and introduction of samples on the column over a period of time causes loss of resolution. In order to achieve slug introduction, products must be concentrated (which is by no means an easy task).

The function of the gas chromatograph is to separate the various constituents in the pyrolysis mixture. For a complete analysis, however, specific methods of identification are needed. These are in general chromatographic, chemical, or spectrometric in nature.[17,18] The common gas-chromatographic method involves measurement of retention (or elution) times of the unknown compounds and comparison with those of known compounds. Utilization of chemical reactions such as hydrogenation and comparison of the chromatograms before and after treatment can give information on the functionality of some of the constituents. If a sufficient quantity of the sample can be collected, then conventional methods such as elemental analysis, chemical tests for functional groups, nuclear magnetic resonance, mass spectrometry, and infrared and ultraviolet spectrophotometry can be used for unambiguous identification.

Samples can, in principle, be trapped from the gas chromatograph exit in a cold trap. The process is rather difficult, however, when the individual components of interest are highly volatile and are present in small quantities. An additional concern is the possibility of components which have been separated in the chromatographic column being remixed in the process of trapping. Furthermore, when columns are operated at high temperatures, there may be contamination from the column bleed. The ideal solution is to combine the gas chromatograph with analytical instruments for "on the fly" analysis, thereby eliminating the need for trapping. In this respect, considerable effort has gone into gas chromatograph–mass spectrometer combinations. Gas chromatograph–infrared spectrophotometer combinations are now receiving attention. As in the coupling of a pyrolyzer to a gas chromatograph, there are difficulties associated with interfacing a gas chromatograph with a mass spectrometer or infrared spectrophotometer.

The fact that gas chromatography achieves separation of components of a mixture by a process in which the constituents are diluted by the eluent carrier gas is a major concern in coupling a gas chromatograph with a mass spectrometer. In order to maintain a workable (low) pressure in the ion source of the mass spectrometer, the sample in the gas chromatograph effluent must be concentrated by selectively removing the carrier gas. Interface systems referred to as molecular separators have been described in the literature.[18,19] They enrich the sample with respect to the chromatographic carrier gas and achieve the necessary pressure drop (from about atmospheric at the gas chromatograph exit to 10^{-4} to 10^{-5} mm Hg at the entrance of the ion chamber of the mass spectrometer). There are limitations, however, in that a given interface is suitable only for certain flow rates, carrier gases, and column types. The interfacial systems involved in pyrolyzer–gas chromatograph–mass spectrometer combinations are all eliminated if pyrolysis is performed in the vacuum chamber of the mean spectrometer.[20] This approach, although convenient, is limited to vacuum conditions.

The infrared spectra of gas-chromatographic effluents are taken either from liquid (trapping technique) or gaseous ("on the fly" technique) samples.[18,21] The spectra of samples in the gaseous phase differ from their liquid phase counterparts in that gas phase spectra contain rotational structure. The spectra of liquids are more familiar than those of gases. However, analysis in the gas phase is often desirable since this approach eliminates the difficult process of condensing the sample from a vapor stream. In contrast to conventional infrared spectrophotometers which cannot provide a spectrum as fast as the gas chromatograph provides a peak, fast scan infrared spectrophotometers are now available and permit "on the fly" analysis of gas-chromatographic effluents. One system is capable of providing spectra in 6 sec[22] another system that uses a liquid crystal film combines the features of trapping and "on the fly" techniques.[23] At present, the difficulty with "on the fly" techniques is that, operating on the effluents as they exit from the gas chromatograph, the technique must record spectra of dilute solutions of samples in a carrier gas. No efforts appear to have been directed to designing separators as in the gas chromatograph–mass spectrometer interface systems. One approach involves trapping the gaseous sample in the infrared cell and taking a large number of spectra; the spectra are added and averaged with a computer which also subtracts background spectra due to carrier gas and column bleed.[24–26]

PRESENT SYSTEM AND DISCUSSION

Figure 1 is a diagram of the pyrolytic system that is being used in this laboratory for analysis of polymers. The part of the system consisting of the thermal conductivity detector, the trap, the mass chromatograph and the infrared spectrophotometer (which are depicted in detail in Figs. 2 and 3) represent the subject matter of the present paper. Coupling of the system with the computer has been accomplished.[25,26] (See Fig. 1.)

The assembly of the pyrolyzer and the thermal conductivity probe consists of a tubular reactor and a concentric heater (pyrolyzer), a detector oven (dotted enclosure) which houses the thermal conductivity cell and the two six-

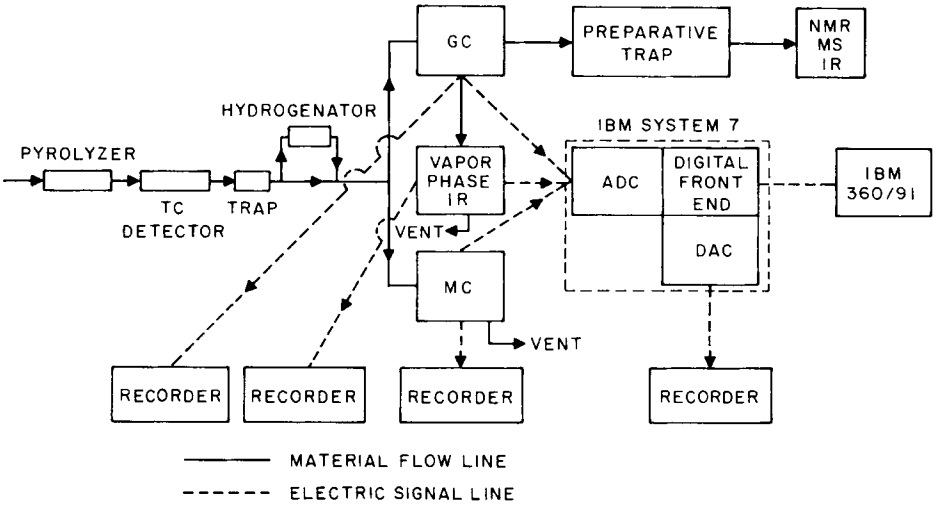

Fig. 1. Schematic of the laboratory for pyrolytic studies.

port valves (X and Y), and a trap external to the detector oven (pyrolyzer trap) (Fig. 2). The assembly was custom designed for this laboratory[27] and in a modified form is now commercially available.[28]

The pyrolyzer consists of a quartz tube (3/16 in. I.D.) and an external heater which provides the flexibility for either program heating or flash heating to 800°C. The program heating capability has been incorporated for better control of the temperature of pyrolysis. Use of controlled heating at slow rates, in addition to defining better the temperature at which pyrolysis starts to take place, can minimize secondary reactions because, in contrast to flash pyrolysis, the products of pyrolysis are formed over a temperature range and can be carried away from the hot zone as they are formed.

The sample which is to be pyrolyzed is placed in the (heat-cleaned) quartz 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 high-temperature (silicone) 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 Fig. 2), 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. For flash pyrolysis, the furnace is heated in advance to the desired temperature and then moved over the sample.

The volatile products are transported by helium through valve X and then through one arm of the thermal conductivity cell. The thermal conductivity detector has been included to monitor the formation of the products of pyrolysis as a function of temperature and time. It provides immediate information about the onset and the progress of thermal events that result in the formation of volatile products (see Figs. 4 and 5, for example). The tempera-

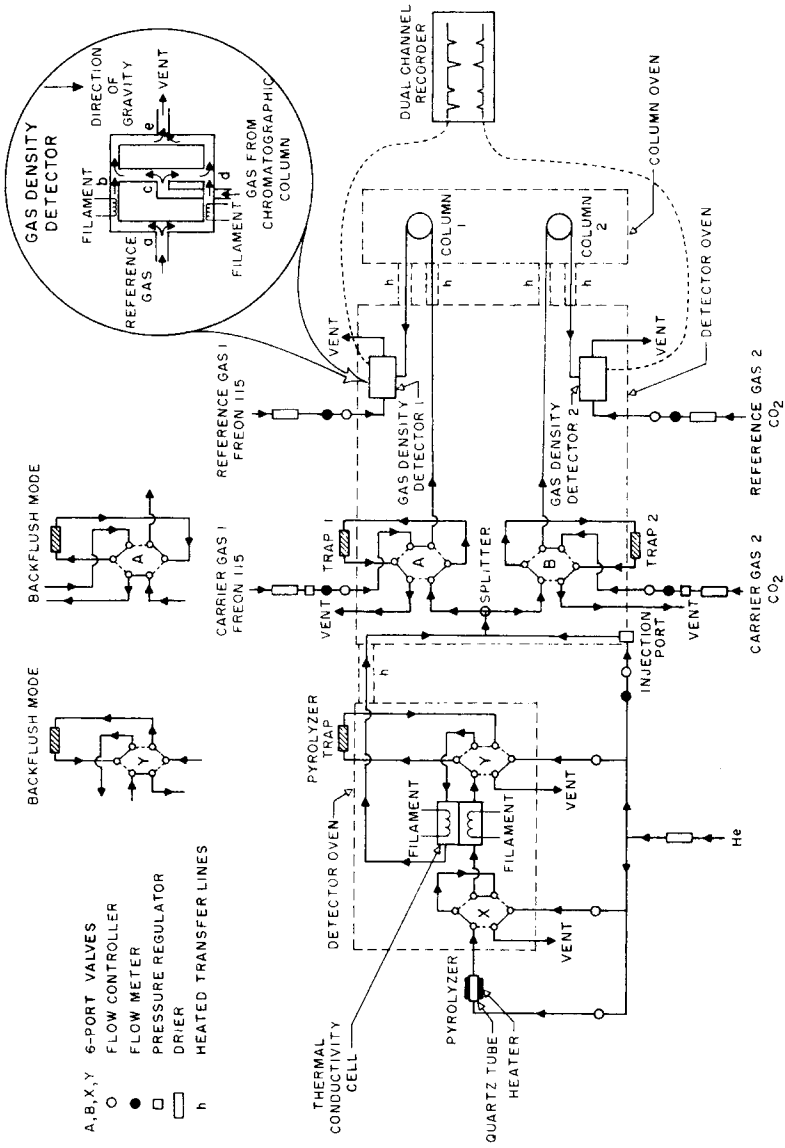

Fig. 2. Schematic of the coupling of the pyrolyzer with the thermal conductivity detector, the trap, and the mass chromatograph.

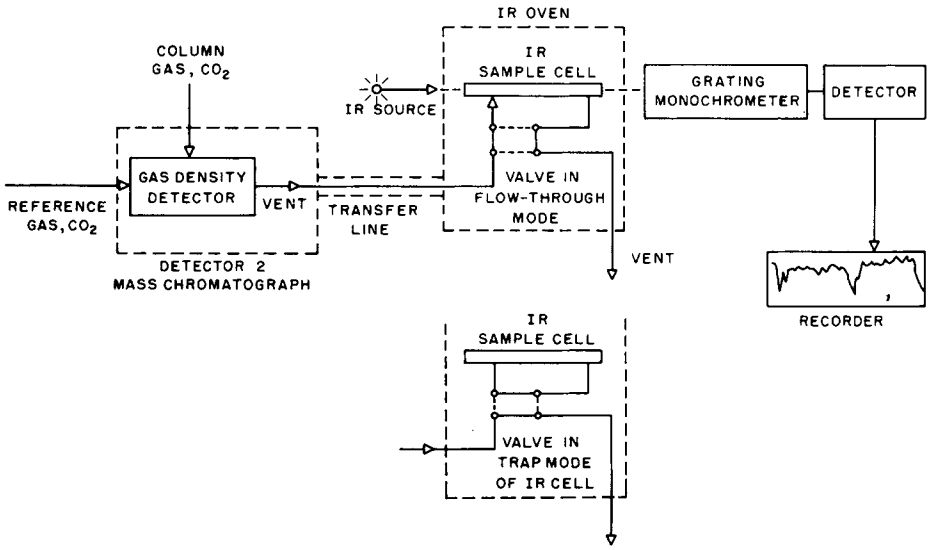

Fig. 3. Schematic of the coupling of the mass chromatograph with the fast-scan vapor-phase infrared spectrophotometer.

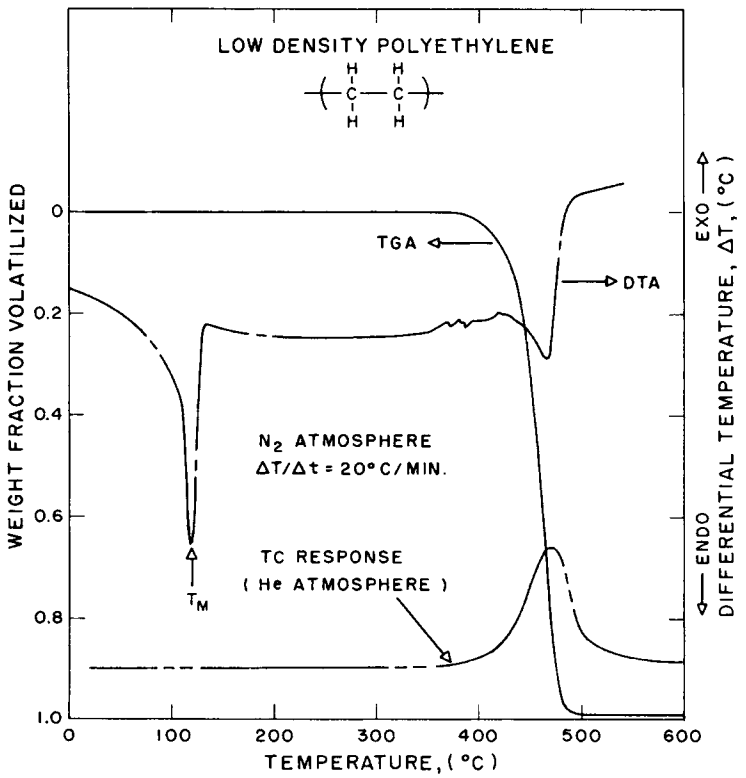

Fig. 4. Thermal history before and during pyrolysis of low-density polyethylene. Comparison of results obtained from thermogravimetric analysis (TGA), differential thermal analysis (DTA), and the response from the thermal conductivity (TC) detector of the pyrolyzer.

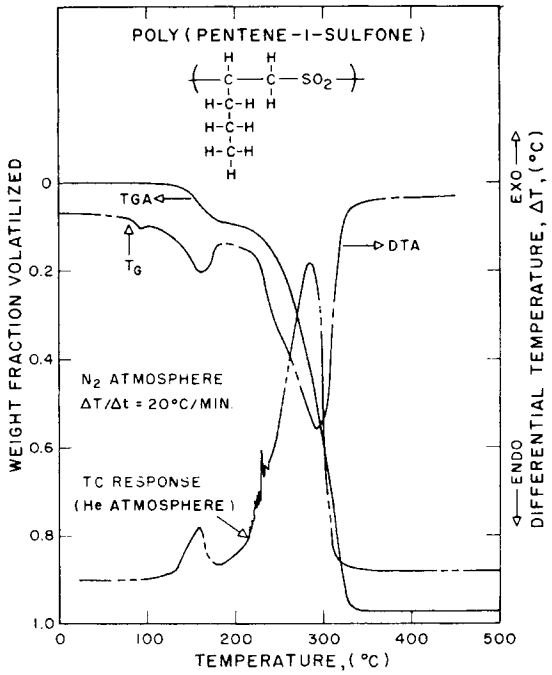

Fig. 5. Thermal history before and during pyrolysis of poly(pentene-1-sulfone). Comparison of results obtained from TGA, DTA, and the response from the thermal conductivity (TC) detector of the pyrolyzer.

ture at which an event is taking place is thus conveniently recorded. The response curves contain features that are characteristic of the material under investigation. In these respects, tne combination of the pyrolyzer and the thermal conductivity detector is complementary to a thermogravimetric analyzer (TGA) and/or a differential thermal analyzer (DTA). The data (see Figs. 4 and 5) can be used, for example, to distinguish between endotherms in a differential thermal analysis (DTA) experiment which represent physical transitions and those which correspond to processes which produce volatile material. Furthermore, since a thermal conductivity detector responds to differences in the thermal conductivity of the carrier gas (helium) and the volatiles, it can be more sensitive (in detection of decomposition) than weight loss measurements utilized in TGA.

After having passed through the thermal conductivity detector, the volatile products are 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 Fig. 2) in which position the fragments are carried to a trap situated outside the detector oven.

The trap is the crucial part of the interface between the pyrolysis assembly and the chromatographic unit. It is a short stainless steel column (⅛ in. O.D. by ~16 in.) packed with crosslinked polystyrene beads (Porapak Q, 80–100 mesh, Waters Associates) and has a geometry which permits a fraction of it (~4 in. section) to be placed in a Dewar flask for subambient cooling.

The function of the trap is to collect the fragments of pyrolysis that are formed in any given temperature range (i.e., selective trapping). The use of

such a trap external to the gas chromatograph is a more effective way of collecting samples than collection on the actual column of the gas chromatograph by maintaining the column oven at subambient temperatures during collection (as was done in a study[16] involving the combination of a TGA unit with a gas chromatograph). Clearly, a chromatographic column designed to achieve separation is not necessarily an efficient trapping medium; and due to the continual flow of the carrier gas, the fraction that is trapped cannot be maintained within short boundaries in the column which results in peak broadening. The present trapping system is free of these difficulties. The trap is packed with crosslinked polystyrene beads which are efficient in stopping vapors. The fraction that is collected is conveniently released (by heating) and introduced into the chromatographic columns as a sharp plug for efficient separation.

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, and the more volatile constituents are retained downstream in the section of the trap cooled by liquid nitrogen. After trapping, valve Y is turned to the backflush mode which reverses the direction of helium flow (Fig. 2, top left), the Dewar flask is removed, and the trap is flash heated to a selected 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. They are then delivered through a heated transfer line into the mass chromatograph. (If desired, the trap heater can be program heated so as to permit the fractional release of the trapped constituents. In this mode, subsequent detection by the thermal conductivity cell can provide a gas-chromatographic output in its own right.)

The limit of thermal stability of Porapak Q and also of the Teflon sliders of the valves restricts operation of the whole pyrolyzer assembly, except for the reactor part, to temperatures below 250°C.

The mass chromatograph[28,29] provides the molecular weights as well as gas-chromatographic retention times and, in so doing, even though operating on a different principle, combines the functions of a gas chromatograph and a mass spectrometer in one instrument. The instrument 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 and B), an external trap (trap 1 and trap 2), a gas density detector (detector 1 and detector 2), and a chromatographic column (column 1 and column 2) (Fig. 2). The detectors and 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 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 backflush positions (shown for valve A at top center of Fig. 2). Then carrier gases 1 (monochlorotrifluoroethane, du Pont Freon-115) and 2 (carbon dioxide) flow through the respective traps at constant rate and pressure and carry the pyrolysis products released by

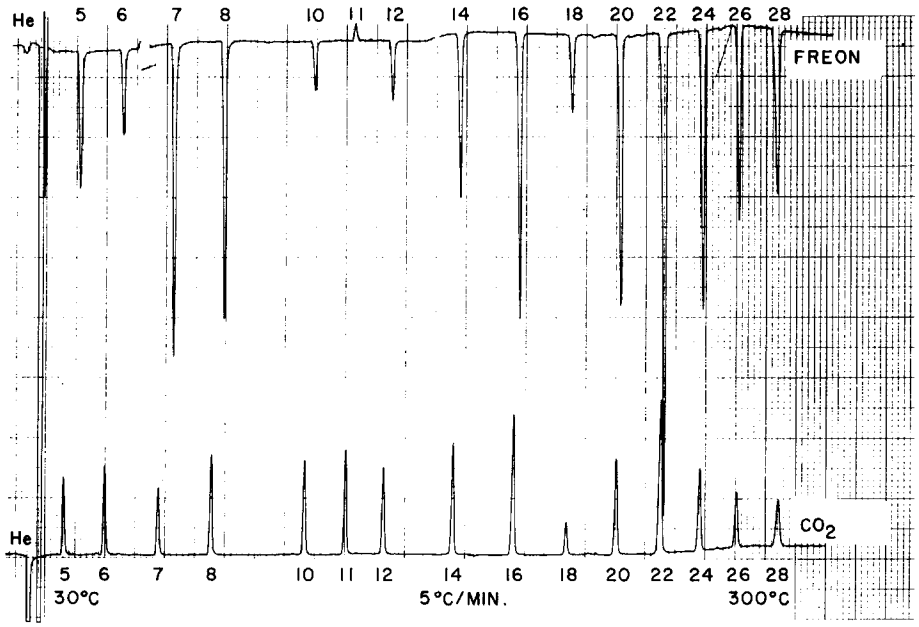

Fig. 6. Mass chromatogram of a mixture of known saturated normal hydrocarbons (C_5 to C_{28}). Columns (10% SE-30 on 60–80 mesh Chromosorb W-AW) were program heated (at 5°C/min) from 30°C to 300°C. The peak attenuations were X8 except for C_5 and C_6 peaks in the Freon-115 channel for which the setting was X64. After elution of the C_{11} peak, the polarity of the Freon-115 detector response was reversed to produce downward peaks for constituents with molecular weights greater than the molecular weight of Freon-115. By measuring the response ratio for each hydrocarbon in the chromatogram, the instrument constant K can be calculated and shown to have an average value of 0.206 in the molecular weight range below the molecular weight of Freon-115 (154.46) (which is below C_{11}) and an average value of 0.189 in the higher molecular weight regions. (These constants have been used to back calculate the molecular weights of the constituents, see Table I.)

flash heating the traps to the matched chromatographic columns where separation is achieved. As they elute from the columns, the constituents are detected by two gas density balance detectors.

In the detector (a schematic diagram of which is included in Fig. 2, 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. As long as no solute is carried by the carrier gas from the column, the flow of the reference gas over the filament is not disturbed. However, when a solute with a density greater than that of 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 the resistance between the upper and lower filaments. This imbalance is recorded as a chromatographic peak. The peak area A is related to the molecular weight M_x of solute through an equation of the form

$$A = kW_x \left[1 - \frac{M_c}{M_x} \right] \tag{1}$$

where k is a proportionality constant, W_x represents the total mass of the solute eluting from the detector, and M_c is the molecular weight of the carrier gas. (This relationship is a restricted form; more general expressions can be derived from references 30 and 31.)

The recorder output from the mass chromatograph displays two sets of peaks corresponding to the responses from the two gas-chromatographic systems for the same constituents of the mixture (see Figs. 6 and 7). The ratios of the responses are related to the molecular weights of the constituents through

$$K \left(\frac{A_1}{A_2} \right) = \left(\frac{M_x - M_{c_1}}{M_x - M_{c_2}} \right) \tag{2}$$

which can be rearranged to give an explicit expression for M_x, i.e.,

$$M_x = \frac{\left(\frac{A_1}{A_2} \right) KM_{c_2} - M_{c_1}}{\left(\frac{A_1}{A_2} \right) K - 1} \tag{3}$$

TABLE I
Molecular Weights of Normal Saturated
Hydrocarbons Analyzed by Mass Chromatograph (see Fig. 6)

Carbon number	Mol. wt[a]	Response ratio (A_1/A_2)[b]	Mol. wt (Calculated)[c]
C_5	72.15	−14.25	72.08
C_6	86.18	−7.81	86.37
C_7	100.21	−4.68	100.24
C_8	114.23	−2.76	114.46
C_{10}	142.29	−0.52	143.77
C_{11}	156.32	+0.16	157.90
C_{12}	170.34	+0.70	171.30
C_{14}	198.40	+1.46	196.55
C_{16}	226.45	+2.04	223.76
C_{18}	254.51	+2.43	248.28
C_{20}	282.56	+2.83	280.47
C_{22}	310.61	+3.12	312.43
C_{24}	338.67	+3.35	344.08
C_{26}	366.72	+3.55	378.67
C_{28}	394.78	+3.63	394.84

[a] *CRC Handbook of Physics and Chemistry.*

[b] Freon-115/CO_2 response ratio as measured from the chromatogram in Fig. 6.

[c] Calculated from eq. (3), i.e.,

$$M_x = \frac{K\left(\frac{A_1}{A_2} \right)(44.01) - 154.46}{K\left(\frac{A_1}{A_2} \right) - 1.0}$$

using $K = 0.206$ for $M_x < 154.46$ and $K = 0.189$ for $M_x > 154.46$.

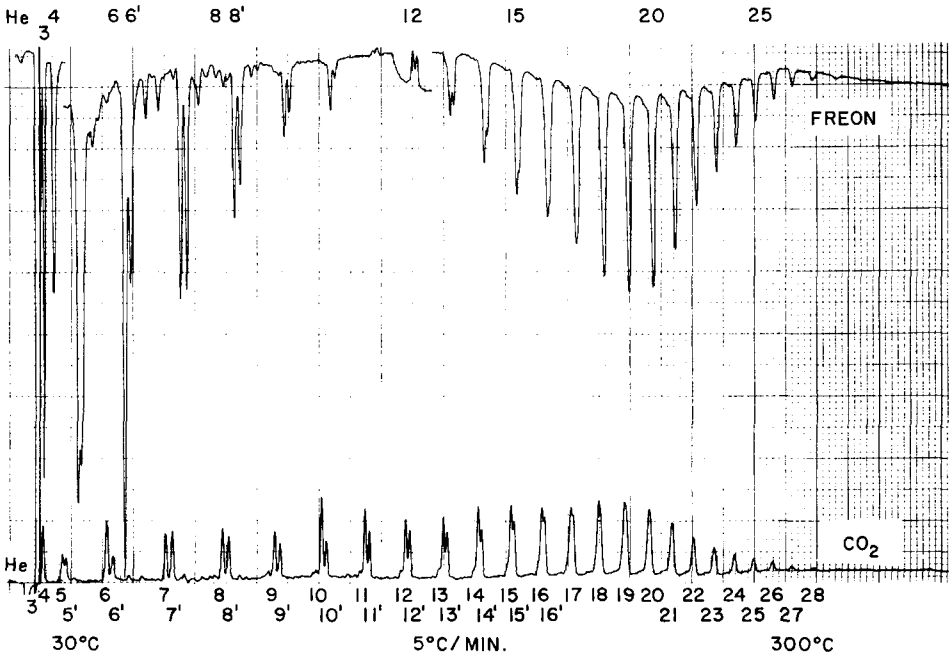

Fig. 7. Mass chromatogram of the pyrolysis products of low-density polyethylene. Columns (SE-30) were program heated (at 5°C/min) from 30°C to 300°C. The peak attenuations were X8 except for C_3 and C_4 peaks in the Freon-115 channel for which the settings were X64. After elution of the C_{12} peak, the polarity of the Freon-115 detector was reversed to produce downward peaks for constituents of higher molecular weight. Using the instrument constants $K = 0.206$ (mol. wt < 154.46) and $K = 0.189$ (mol. wt > 154.46), the molecular weights of the peaks can be calculated from measurement of peak height ratios. The molecular weights of the peaks correspond to the molecular weights of a homologous series of saturated and unsaturated hydrocarbons.[27,30]

where M_x, M_{c_1}, M_{c_2} = molecular weights of the unknowns, carrier gas 1, and carrier gas 2, respectively; A_1, A_2 = chromatographic peak areas for the unknown constituents; and K = instrument constant (determined from analysis of samples of known molecular weights; see, for example, Fig. 6). (For assumptions involved in deriving eq. (3), see references 30 and 31.)

Since the response of the gas density detector is proportional to $[(M_x - M_c)/M_x]$, see eq. (1), for a given carrier gas of molecular weight M_c the response tends to a constant as M_x increases; the lower the molecular weight of the carrier gas, the faster is this tendency. Thus, for a given carrier gas, there is an optimum range of molecular weights in which the detector response can differentiate two species of different molecular weights. In the mass chromatograph, in order to cover a wide range of molecular weights, the two carrier gases are chosen to be of sufficiently different molecular weights. The carrier gases that are used in this laboratory are carbon dioxide and ClC_2F_5 (du Pont, Freon-115).

Since the molecular weights of the carrier gases are known and since the response ratios (A_1/A_2) can be measured from the chromatographic output, after the instrument constant is evaluated, calculation of the molecular weights of constituents is a simple process (see Fig. 6 and Table I).

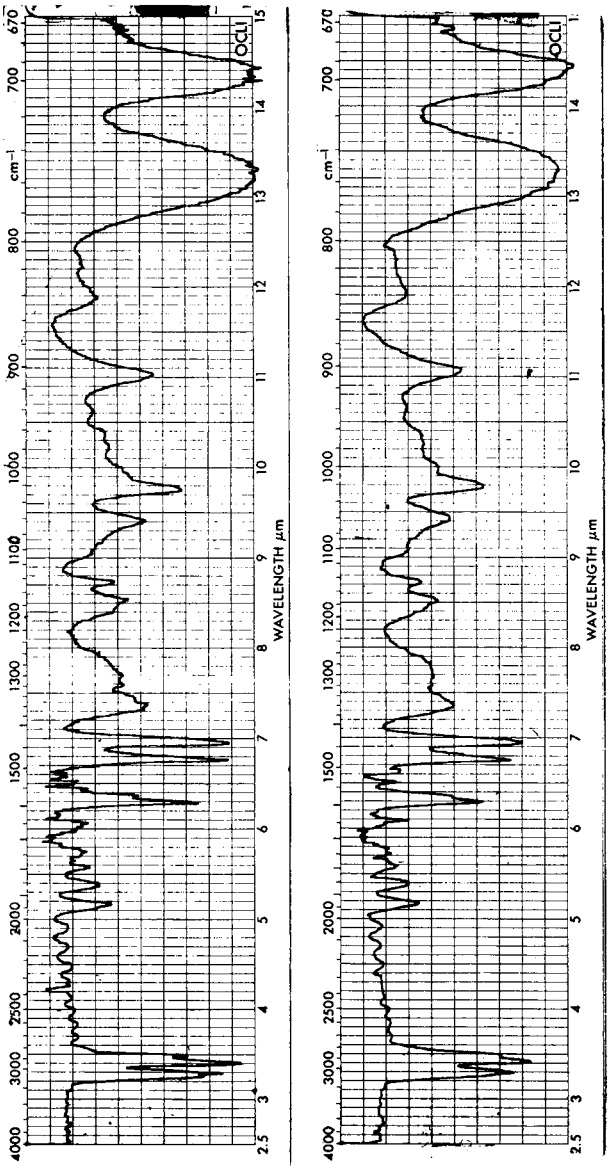

Fig. 8. Fast-scan infrared spectra of a polystyrene film. Top spectrum: 30-sec scan; lower spectrum: 6-sec scan.

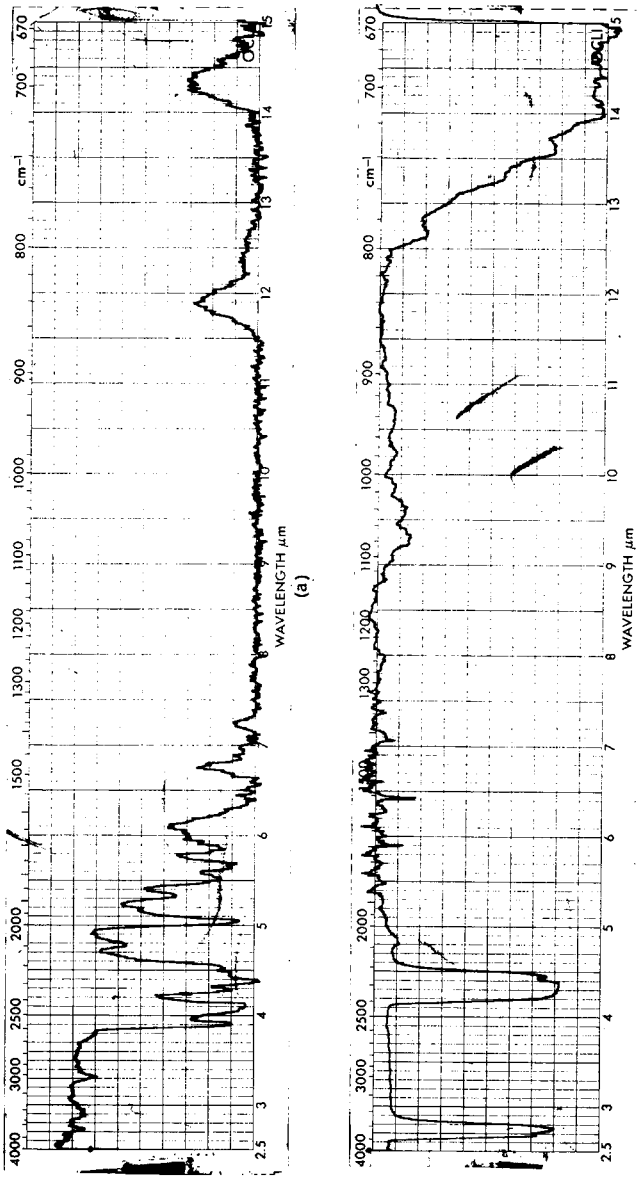

Fig. 9 (*continued*)

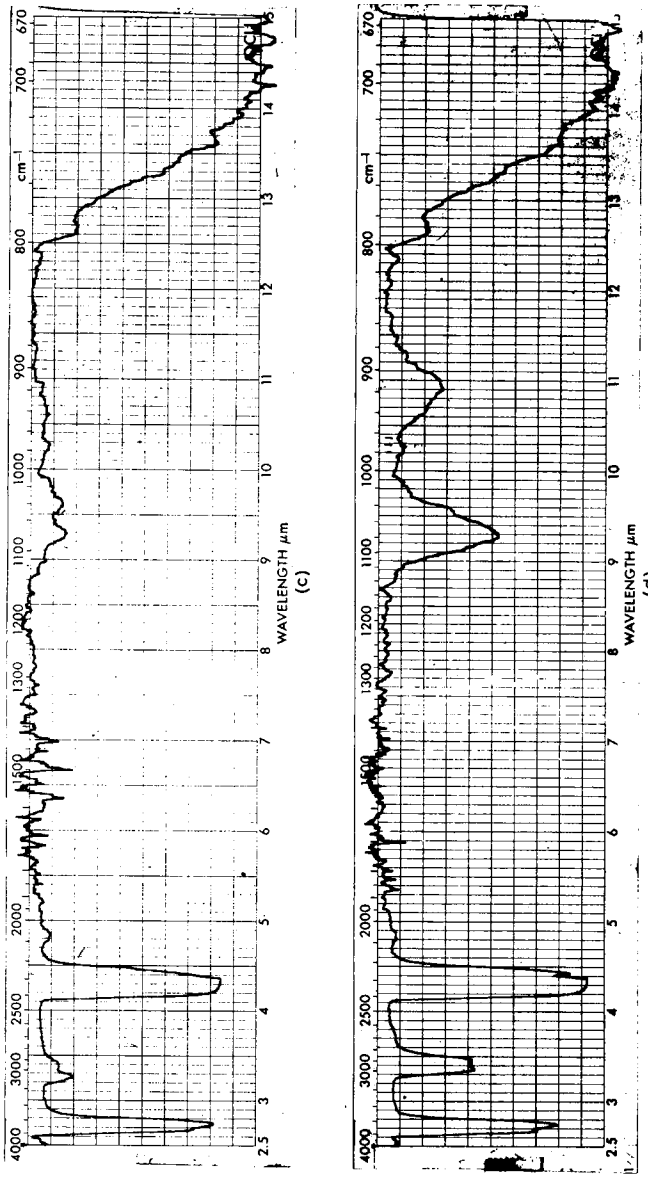

Fig. 9. Vapor-phase infrared spectra (6-sec scans) of: (a) Freon-115 carrier gas; (b) CO_2 carrier gas; (c) toluene in CO_2; (d) tetrahydrofuran in CO_2; 1 μl of toluene and THF were injected into the mass chromatograph.

The accuracy of the mass chromatograph is much less than that of a mass spectrometer; however, in providing gas-chromatographic retention times and molecular weights in one unit, it offers a convenience that is lacking in the usual gas chromatograph–mass spectrometer combinations requiring elaborate interfacial systems and sophisticated data-reduction procedures.

The effluents from one of the detectors (detector 2) of the mass chromatograph are introduced through a heated transfer line into the sample cell (which is housed in a heated oven) of the infrared spectrophotometer (Fig. 3).

The infrared spectrophotometer is of the type reported in the literature.[22] It is a new instrument which is capable of scanning from 2.5 to 15 μm (4000 to 670 cm^{-1}) in either 6 sec or 30 sec. In Figure 8, the spectrum at the top is a scan of polystyrene film taken in 30 sec. The lower spectrum is a 6-sec scan of the same sample which shows some loss in resolution.

The instrument is suitable for taking "on the fly" spectra of constituents eluting from a gas chromatograph. By setting the monochrometer to a particular wavelength, the instrument can be used to monitor the change in transmittance at that particular wavelength. By varying the grating angle of the monochrometer, the wavelength region from 2.5 to 15 μm can be scanned in 6 or 30 sec. The infrared scans are easily synchronized with the elution times of chromatographic peaks. The valve in the inlet line to the sample cell (Fig. 3) permits the trapping of fractions inside the cell for either taking multiple scans[24,25,26] or for holding the sample in the cell during a single 30-sec scan, by converting the sample cell from a flow-through cell to a closed-cell system. (In this trap mode, subsequent chromatographic effluents bypass the sample cell.)

The mass chromatograph has two columns and detectors. Therefore, in coupling the instrument with the infrared unit, a choice must be made as to which exit of the mass chromatograph should be connected to the infrared spectrophotometer. Since column effluents are necessarily diluted by the reference gas in the gas density detectors, from the point of view of sensitivity, the channel involving a smaller rate of flow for the reference gas is preferable. Consequently, in the present system, involving Freon-115 and CO_2 gases, the Freon-115 channel would be more attractive since the Freon-115 reference flow rate (41 ml/min) is lower than the CO_2 reference flow rate (122 ml/min). However, the background spectrum due to Freon-115 (Fig. 9A) is complex compared with that due to carbon dioxide (Fig. 9B) and can mask absorptions due to an unknown constituent which is being analyzed. Therefore, the infrared unit was coupled with the carbon dioxide exit of the mass chromatograph. The spectra shown in Figures 9C and 9D represent a 6-sec scan of toluene in CO_2 and a 6-sec scan of tetrahydrofuran also in CO_2 carrier gas stream obtained by injecting 1-μl samples into the mass chromatograph. These spectra must be compared with the spectrum due to CO_2 (Fig. 9B) in order to subtract the background spectra. Due to the large CO_2 flow rate, the spectra are weak. In view of this, the pyrolyzer was connected through a conventional gas chromatograph to the infrared unit (Fig. 1).

CONCLUDING REMARKS

The pyrolytic system described above has been found to be versatile in investigations of thermal decomposition of polymeric materials.[30] The utility

of the present system will be further illustrated in a series of articles[32] which will be devoted to thermal degradation of polyolefins, aliphatic polysulfones, tactic methacrylate polymers, and also polystyrene.[33]

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