Determination of the Thermal Stability and Trace Volatiles Content of Polymers. A Hot-Filament Thermal Analysis Technique

F. T. EGGERTSEN and F. H. STROSS, *Shell Development Company, Emeryville, California*

Synopsis

The thermal stability and trace volatiles content of polymers can be determined rapidly and conveniently by using a hot-filament pyrolyzer for heating the sample. The filament unit, of a type employed for pyrolysis-GLC analysis, consists of a platinum coil with an attached platinum/platinum–rhodium thermocouple for measuring the sample temperature. As the sample is heated the volatile products are monitored directly with a flame ionization detector, a dual recorder being used to chart both temperature and volatiles yield. At any stage of heating the products are analyzed, if desired, with a suitable GLC column. Thermal stability measurements of several polymers were generally consistent with results by conventional thermogravimetric analysis. Advantages of the method are high sensitivity for detection of low decomposition rates, speed of the temperature adjustment, simplicity of the apparatus, and small sample requirement.

Methods for determining the rates of pyrolytic decomposition of polymers, as reviewed and classified by Wall,[1] utilize two general techniques: (1) measurement of the weight loss of a sample and (2) measurement of the amount of volatiles produced. In the first method, thermogravimetric analysis (TGA), the weight losses are determined as a function of temperature, with the use of a thermobalance in any of a number of ways as reviewed by Wendlandt.[2] In the second method, sometimes referred to as gas evolution analysis (GEA),[2] the volatile products may be flashed into an evacuated system and evaluated by pressure measurement with a suitable gage,[1] or the volatiles may be observed in a carrier gas stream with a thermal conductivity detector after the manner of Rogers et al.[3] and others.[4,14]

In the method of Rogers et al.,[3] the sample is program-heated in a metal pyrolysis block with the use of helium as the carrier gas. A combustion step converts the volatile carbonaceous material to carbon dioxide prior to thermal conductivity detection. This method can supply thermal stability data analogous to those obtained with a thermobalance. Advantages are that the apparatus is simpler, requires less maintenance, and has greater sensitivity.

This paper describes a method for determining the thermal stabilities of macromolecular materials, particularly organic polymers, which is similar in approach to that of Rogers et al., but has a number of advantages. The pyrolysis is carried out on an electrically heated platinum filament of a type used in pyrolysis-gas-liquid chromatography (GLC) studies.[6,7] This filament has an attached platinum/platinum–rhodium thermocouple which permits precise measurement of the sample temperature. It is a more convenient heater for the sample than the metal block or furnace tube pyrolyzers commonly used. Because of the low thermal mass of the filament, temperature adjustments up or down can be made almost instantaneously. This feature is especially attractive for isothermal studies and for analyses involving stepwise heating.

Flame ionization detection (FID) was used in this study rather than thermal conductivity. Our main interest was in organic polymers, and the FID is much more sensitive to the decomposition products from such materials. The high sensitivity permits one to use small samples and still to observe readily the very beginning of decomposition as well as trace volatiles which give a response with FID.

An attractive feature of the hot-filament thermal analyzer (HFTA) is the simplicity and availability of most of the equipment. It consists basically of a gas chromatograph unit of the FID type and the filament pyrolyzer attachment. A suitable power supply is also required for heating the filament. This apparatus, which is a versatile pyrolysis–GLC unit, is converted to an analog of the thermobalance by program-heating the filament and by substituting a short empty column for the separating column so that total volatiles are monitored by the detector. Of course a GLC column can be used when it is desired to separate and identify products from any stage of the thermal decomposition.

The conventional GLC technique for determining trace volatiles in a polymer is to dissolve the sample and analyze the solution.[5,8] Disadvantages of this approach are the problem of finding a suitable solvent and the diluting effect of the solvent. It seemed that distillation of volatiles directly from the hot wire might be simpler and more effective.

In this report examples are given of application of the apparatus for determining thermal stabilities and trace volatiles, both with and without a GLC separating column.

EXPERIMENTAL AND RESULTS

Apparatus

A schematic diagram of the equipment is shown in Figure 1. The basic GLC unit, built locally and of conventional design, has a special hot-filament pyrolyzer attachment at the inlet.[6] For measuring thermal stabilities a GLC separating column is not normally employed. In its stead is used a 10-in. length of $^3/_{16}$-in. diameter stainless steel tubing packed with glass wool to retain condensibles and reduce fouling of the FID detector. Thus the
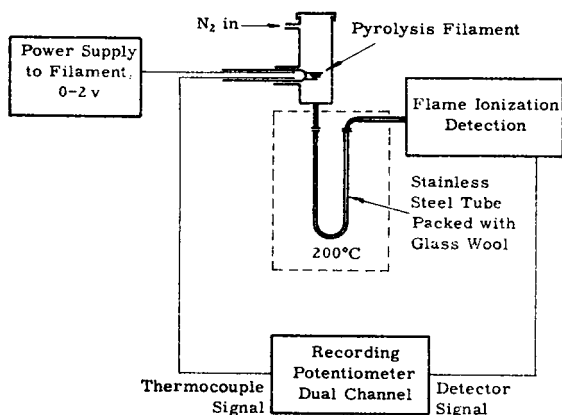
Fig. 1. Hot filament thermal analysis unit.

detector monitors total volatiles which are vaporizable at the temperature of the tube and which are responsive to the FID. The tube and the base of the flame detector were maintained at 200°C.

The pyrolyzer coil, described in detail previously,[6] is a 2-in. length of platinum wire wound in the shape of a cone about 3 mm. deep and 3 mm. in diameter at the opening. The capacity of the pyrolyzer is 1–2 mg. of polymer. At the center winding of the coil is spotted a platinum/platinum–10% rhodium thermocouple. The coil and thermocouple are attached to Pt (or Pt–Rh) wire posts sealed in the end of a soft glass tube. The filament is coated with glass (soft glass microbeads) to form a cup and thus allow use of powder samples. In addition, the glass coating improves the temperature uniformity throughout the coil.

The filament is heated by applying a steadily increasing voltage, 0–2 v., by means of a Labac solid-state ac power supply (Model 10–1, Research, Inc., Minneapolis, Minnesota) together with a filament-type transformer (2.5 v. ac, 6 amp.). The input (control) signal is supplied from a battery (3, 6, 9, etc., v.) through a motor-driven (¼ rpm) Beckman 10-turn Helipot potentiometer. A wide range of heating rates is obtained merely by changing batteries and/or the power control dial on the instrument.

A simpler and less expensive power source, employed in much of the work, consisted of a motor-driven variable transformer operated on line voltage (115 v. ac), together with a 5-v., 6-amp. filament transformer. The motor employed operated at 0.5 revolution/hr. through gears selected to give a range of heating rates of about 3–30°C./min. This method of heating the filament gives occasional sudden temperature steps (about 3–5°C.) and flat portions in the heating curve, probably because of discontinuities produced as the contact point on the variable transformer moves from one winding to the next.

The Labac–Helipot arrangement gives smoother heating curves and allows rates to be changed more simply since it does not require gear

changes.   With this power supply unit, the temperatures can be read from the chart to within about ±3°C.

Thermal Stability Measurements

The filament is cleaned by heating in air at a bright red heat.   Then up to 1 mg. of sample is placed in the helix, and the unit is attached to the heated pyrolysis tee.   The sample may be bulk polymer or a polymer solution.   Solutions are preferably injected from a syringe into the heated helix, which is maintained at just below the boiling point of the solvent in order to evaporate the solvent continuously.   This prevents the solution from creeping out of the filament helix which, if allowed to occur, often results in double or trailing decomposition peaks.   The conditions for the test are adjusted as follows: carrier gas (nitrogen) flow, 30 ml./min.; flame detector, hydrogen, 25 ml./min., air, 700 ml./min.; chart speed, 12 in./hr.; pyrolysis tee temperature, 170–180°C.; stainless steel tubing to detector, 200°C.; filament heating rate, usually 6°C./min.

The detector sensitivity is adjusted at a suitable level for the size of sample employed.   When the baseline is steady, the power supply and the input signal to it (potentiometer) are adjusted to give the desired starting temperature (usually about 200°C.) and heating rate.   The heating cycle is started by turning on the motor operating the potentiometer.   The temperature (thermocouple output) and decomposition products (flame detector output) are charted simultaneously with a two-channel recorder Servoriter, Texas Instrument Co. a 10-mv. channel being used for the
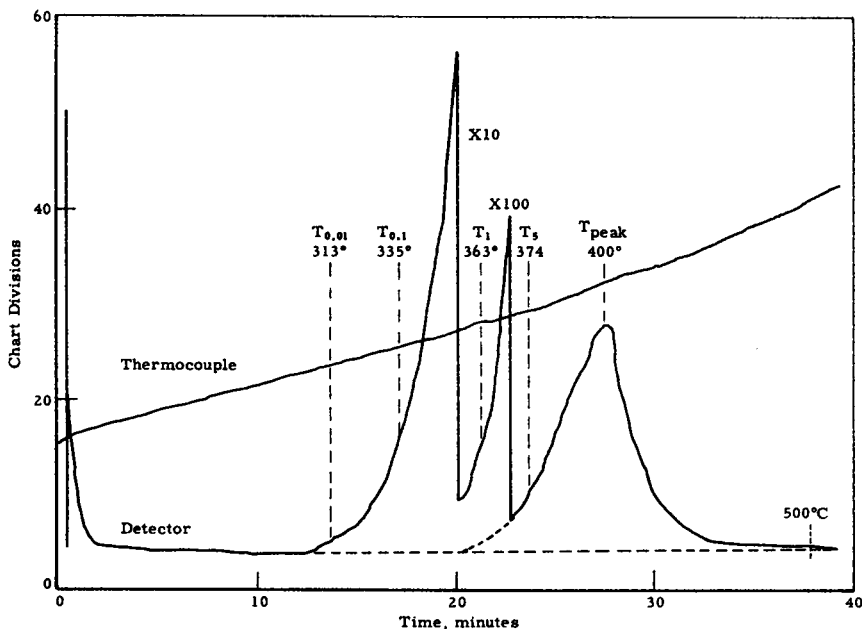

Fig. 2. Thermal decomposition of polystyrene (0.2 mg.; 6°C./min.).

TABLE I
Thermal Decomposition of Polystyrene[a]

Decomposition rate A, %/min.	Chart area B, in.^{2}/min. (total area $\times$ A)	Height above baseline, in. (B/chart speed)	Temp., °C.
0.01	0.022	0.11	313 ($T_{0.01}$)
0.1	0.22	1.1	335 ($T_{0.1}$)
1	2.18	10.9	363 (T_1)
5	10.9	54.5	374 (T_5)

[a] Data from Figure 2. Total peak area at full sensitivity = 218 in.^{2}; chart speed = 0.2 in./min.

temperature and a 1-mv. channel for the pyrolysis products. The test is continued until a temperature of about 600°C. is reached or when the evolution of volatile products has virtually ceased.

A blank test is occasionally made by heating the empty filament in the pyrolysis tee up to 800°C. This serves to check on buildup of residues on the filament and in the filament cavity and at the same time cleans the system for subsequent analyses.

Polymer stabilities were generally compared by determining from the charts the temperatures required to attain decomposition rates corresponding to 0.1, 1, and 5% of the total measured peak area per minute. The temperatures at these rates of volatiles evolution are designated $T_{0.1}$, T_1, and T_5, respectively. In a few tests a sufficiently high detector sensitivity was used to show decomposition at 0.01%/min. and thus permit a determination of $T_{0.01}$. One of these examples is shown in Figure 2 for a 0.2 mg. sample of powdered polystyrene. Data obtained from this thermogram are given in Table I to illustrate how the decomposition rates and the corresponding temperatures were computed.

Thermal stabilities were compared also on the basis of temperatures at which certain percentages of the total peak area have appeared. The temperatures at certain area percentages were checked directly against the temperatures at the same weight percentages lost by TGA.

Effect of Pyrolysis Variables

Different filament pyrolyzers give the same results provided the thermocouple beads are spotted carefully on the coils. In tests with six of them with samples of polystyrene the decomposition temperatures were duplicated within ±5°C. With two of these filaments the thermocouple was spotted to the coil at the inside of the conical winding and this made no significant difference in the results.

As with thermogravimetric analysis, the measured decomposition temperatures increase with heating rate. This effect is illustrated in Table II for polystyrene. A similar trend with increasing heating rate was observed with other polymers. It is worthy of note that the higher heating rates employed here are not as practicable with conventional TGA with large samples because of thermal lag.

TABLE II
Effect of Heating Rate[a]

Heating rate, °C./min.	Decomposition temperature, °C.			
	$T_{0.1}$	T_1	T_5	T_{peak}
1.6	326	345	369	366
3.6	345	359	375	384
5.6	340	366	372	390
7.1	355	369	378	393
13.4	—	372	382	393
19.8	—	379	386	426

[a] Sample: 0.09 mg. polystyrene added to the filament as 5 μl. of 2 wt.-% solution in benzene.

The effects of sample variables were studied with polystyrene, polyisobutylene, and polybutadiene. The results are shown in Table III. Within the precision of the measurements (about ±5°C.) the decomposition temperatures were the same with solid and solution samples and were not affected by up to 20-fold variations in sample size. In general, the pyrolysis curves were smoother with solutions. Large samples are of course preferable for observing the onset of decomposition.

TABLE III
Effect of Amount and Form of Sample[a]

Polymer[b]	Wt. sample, mg.	Decomposition temperature, °C.			
		$T_{0.1}$	T_1	T_5	T_{peak}
Polystyrene					
Solution	0.02	—	357	370	387
	0.04	336	357	374	398
	0.06	—	357	366	387
	0.09	340	366	372	390
	0.12	340	358	369	387
Solid (powder)	0.14	—	365	374	395
	0.22	335	360	372	399
	0.33	—	365	370	397
	0.44	336	354	368	393
Polyisobutylene					
Solution	0.02	295	329	346	373
	0.09	—	318	339	368
	0.09	—	324	342	368
Solid (2 or 3 granules)	0.21–0.25[c]	—	323–329[c]	338–347[c]	369–376[c]
	0.34	—	319	336	371
Polybutadiene					
Solid (2 or 3 granules)	0.10	—	377	416	443
	0.22	—	373	420	438
	0.33	—	383	430	451
	0.44	—	379	431	445
	0.63	—	369	430	446

[a] Heating rate: 6°C./min.
[b] The solution samples were 2 wt.-% polymer in benzene.
[c] Six tests.

Comparison with Thermogravimetric Analysis

The thermal stabilities of several polymers were determined both by the HFTA and by the TGA methods with results shown in Table IV.   In all cases the temperatures listed represent averages of data from at least two tests.   The TGA analyses were made by a conventional method in which 50 mg. of sample, in a platinum crucible, was heated in a stream of nitrogen (50 ml./min.) at 2.5°C./min.   The heating rate chosen for the new method was 6°C./min. because in our initial tests (with polystyrene) the decomposition temperatures were close to those obtained by TGA.   With this heating rate it is apparent from the data in Table IV that also with other polymers the agreement is fairly good.   A few rather large differences are apparent, generally in the direction of lower decomposition temperatures with the hot-filament method.   With regard to the relative thermal stabilities of the five polymers the ranking is the same by the two methods.

Because of the higher heating rate and higher starting temperature the new method was faster, requiring about 1 hr. per sample, compared with 3–4 hr. by the TGA method.

TABLE IV
Thermal Stabilities of Several Polymers[a]

Polymer	Temperature, °C.[b]					
	10% volatilized		50% volatilized		1%/min.	
	TGA	HFTA	TGA	HFTA	TGA	HFTA
Ethylene, commercial, (Hi-Fax 1400-J)	437	428	458	444	429	408
Butadiene, experimental preparation	423	405	448	444	422	373
Propylene, experimental preparation	405	395	436	405	395	376
Styrene, experimental preparation	380	378	397	393	378	360
Isobutylene, commercial (Vistanex L-100)	341	346	376	366	330	324

[a] TGA: sample weight, 50 mg.;   heating rate, 2.5°C./min., N_2 flow, 50 ml./min. HFTA: sample weight, 0.2 mg.;   heating rate, 6°C./min.; N_2 flow, 30 ml./min.
[b] The temperatures listed are averages for 2 or 3 tests.

Isothermal Tests

Thermal stabilities are often compared by the constant temperature, rather than rising temperature, technique.   An elegant isothermal gravimetric method has been described by Madorsky and Straus.[9,10]   In this method, the sample is heated rapidly to a preselected temperature.   The observed weight loss in a specified time provides a measurement of thermal stability.

Use of the isothermal technique together with hot-filament pyrolysis was tried briefly in this study;   results are illustrated in Figure 3.   In this experiment 0.02 mg. of polystyrene, deposited on the filament from 1
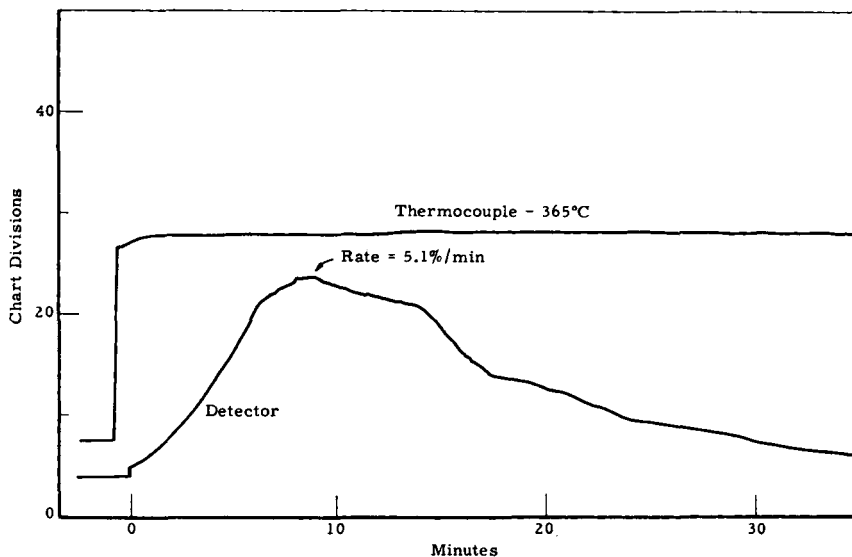
Fig. 3. Isothermal decomposition of polystyrene (0.2 mg.).

μl. of a 2% benzene solution, was heated to 365°C. in 2–3 sec. by adjusting the power to the filament quickly to give the proper thermocouple reading. The volatiles were monitored over a period of 40 min. while holding the filament at temperature.

The decomposition rate increased slowly, reaching a peak in about 8 min. The peak decomposition rate at this temperature was 5% of the total area per minute. This is in fair agreement with results by the rising temperature technique in which the temperature corresponding to 5% decomposition per minute was 370°C. (Table III). Of course, exact agreement is not necessarily expected, in view of the effect of the heating schedule on the decomposition rate at a given temperature (see Table II).

It should be noted that the HFTA technique is especially well suited for isothermal tests because the temperature adjustment can be made almost instantaneously.

Yield of Volatile Pyrolysis Products

Not all of the pyrolysis products are monitored by the detector. Material of very low volatility may be partially condensed in the pyrolysis tee (170°C.) or in the stainless steel tube (200°C.) en route to the detector. Also more or less of the sample may be degraded to coke and remain on the filament.

In some of the tests, calculations were made of the yields of volatile material represented by the peak area observed. To do this, the absolute response of the detector to n-heptane was determined, and the pyrolysis peak area was converted to milligrams assuming that the pyrolysis products respond in the flame as would n-heptane. The yields of observed volatiles,

TABLE V
Yield of Volatile Products[a]

Polymer	Volatiles observed, % (basis sample weight)[b]
Styrene	85
Isobutylene	40
Butadiene	35
Propylene	20
Ethylene	15

[a] Sample size: 0.2–0.3 mg.; heating rate: 6°C./min. (to about 550°C.).

[b] Response of volatiles per unit weight in the flame detector was assumed to be the same as that for n-heptane.

calculated as weight percentages of sample which had been carefully weighed on a microbalance, are shown in Table V.   These values are only approximate, partly because of our assumption that all products respond as would heptane.   An additional inaccuracy may be caused by tailing of the pyrolysis peak, which persists even beyond 550°C., the temperature arbitrarily selected as the cutoff point for the area measurements.   The amount of tailing is sometimes difficult to estimate because it may be indistinguishable from a slow baseline drift.

Monomers and Other Trace Volatiles

Application of the apparatus for determining trace volatiles was explored with several acrylonitrile–butadiene–styrene polymers.   The general procedure was to heat quickly about 1 mg. of sample, contained in the filament to a temperature just below the decomposition point of the polymer.   After once having established conditions at which the volatiles can be expelled quickly and completely without decomposing the sample, analyses were made of the trace volatiles by using a suitable GLC column.

The approximate decomposition temperature of this type of polymer was determined for one of the samples by the thermal stability method already described; the thermogram is shown in Figure 4.   To make this analysis, 1 mg. of polymer was placed in the inlet pyrolysis tee at 40°C.   The filament temperature was raised suddenly to 130°C. and then programmed at 15°C./min. to a final temperature of about 500°C.   When the heating cycle was started the heater on the inlet tee was turned on so that it reached the usual temperature of 170°C. in about 10 minutes.

A peak for the volatiles is observed, beginning immediately upon heating the filament and ending at about 250°C.   The initial decomposition point of the polymer appears to be about 280°C., because at this point the tracing begins to curve sharply upward.   The baseline drift in this test makes it difficult to establish the decomposition point precisely, but this was done in other experiments to be described below.   The amount of total volatiles, estimated by applying the absolute calibration factor for styrene to the peak area, was found to be 0.36% of the sample.
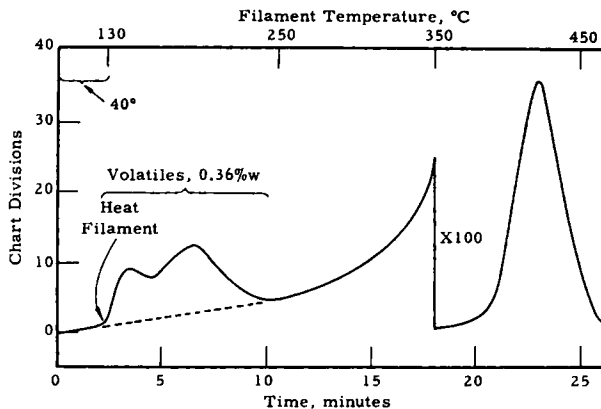
Fig. 4. Volatiles in an acrylonitrile–butadiene–styrene copolymer (polymer A, Table VI).

Two heating techniques were used for removing the volatiles in conjunction with their analysis by a suitable GLC column: (1) heating for short periods or "pulses," so that the vapors are driven off sharply into the GLC column to obtain good resolution of the components; and (2) continuous heating, which insures complete recovery of the volatiles but gives poor resolution. For these analyses the GLC conditions were as follows: Columns, 10% Ucon (DLB-130BX, Carbide and Carbon Chemicals Company) or 10% SE-30 silicone oil (General Electric Company) on Chromosorb W, 80–100 mesh, 15 ft. of ³/₁₆-in. coiled copper, operated at 100°C. (both columns satisfactory); temperature of inlet tee, 40–50°C.; carrier gas, nitrogen at 30 ml./min., saturated with water vapor at room temperature in the case of the SE-30 column (to minimize adsorption of acrylonitrile); hydrogen flow rate to the detector, 25 ml./min.; sample size, ca. 1 mg., weighed on a semimicrobalance.

The retention times with the silicone column (from the injection point) ranged from 3 min. for acrylonitrile to 13 min. for styrene, with the Ucon column the corresponding times were 4 and 27 min.

Results obtained for several polymers are given in Table VI. The first three samples, (A, B, and C), were analyzed by heating for about 30 sec. at 280–300°C. Complete recovery of the volatiles was indicated by a constancy of the yields obtained in this temperature range with varying heating times. None of these samples contained sufficient free acrylonitrile to be detected; the lower limit of detection in these tests was estimated at about 10 ppm, which corresponds to 0.01 μg. in the 1-mg. sample. At 335°C. these samples gave off acrylonitrile, but this is due to thermal decomposition because it was accompanied by lower boiling components and other decomposition products which did not appear at the lower temperatures.

Sample D was more difficult to analyze because it was less stable thermally. With pulse heating decomposition occurred at 260°C., and with continuous heating some decomposition at 240°C. was indicated. This sample differed from the others also in that it contained considerable free acrylonitrile. Results are given in Table VI for several modes of heating.

TABLE VI

Trace Volatiles in Acrylonitrile–Butadiene–Styrene Polymers[a]

| Polymer | Heating | | Acrylonitrile, ppm | | Toluene, wt.-% | Ethyl-benzene, wt.-% | Styrene, wt.-% |
	Temp., °C.	Time, sec.	Known[b]	Found			
A	300	30	<0.5	<10	0.06	0.003	0.28
B	300	30	1.0	<10	0.06	0.003	0.34
C	300	30	4	<10	<0.001	0.01	0.22
D	210	40	224	127	<0.001	0.004	0.16
	260	40		320[c]	<0.001	0.008	0.48
	190 ⎱	Continuous Heating		166	<0.001	—	—
	210 ⎰			172	<0.001	—	0.41
	240			298[c]	<0.001	—	0.42

[a] Sample size, 1 mg.

[b] Obtained by D. B. Bruss[11] using a polarographic method.

[c] Probably includes some acrylonitrile formed by thermal decomposition which occurred at the temperatures for these tests.

The values in italics are considered the most reliable, since they were made under conditions as severe as possible without causing decomposition.   The result for acrylonitrile was somewhat lower than the value obtained polarographically, which is given in the third column of Table VI.   The other polarographic data shown in the table confirm that the acrylonitrile contents of samples A, B, and C were indeed less than 10 ppm, as indicated in our tests.

The results for styrene and toluene given for sample B in Table VI are in agreement with those obtained by Knight[12] using a GLC method in which a solution of the sample is analyzed.   He reported 0.4% styrene and 0.08% toluene, to be compared with our values of 0.34 and 0.06%, respectively; he also reported less than 10 ppm of acrylonitrile.   This agreement gives additional assurance that the hot-wire method can be expected to yield reliable results.

DISCUSSION AND CONCLUSIONS

The sensitivity of the method makes it attractive for studying pyrolytic decomposition at low rates.   Madorsky[10] has developed a sensitive TGA method for measuring rates down to 0.01%/min., but the equipment is relatively elaborate and the analysis requires many hours.   With the HFTA-flame detection method the first traces of decomposition products are registered immediately, in contrast to TGA methods which require a long time before significant weight changes are observed.   In the present study decomposition rates of 0.01%/min. could be readily observed with less than a milligram of polymer sample.

As in reduced-scale TGA with a recording microbalance, the new method has several advantages associated with the use of small samples.   Faster heating rates can be employed because the temperature lag in the sample

is greatly reduced. In addition, the volatiles escape more rapidly, and therefore better resolution of peaks in the thermogram can be expected.

The data presented show that only part of the decomposition products was sufficiently volatile to reach the detector, and that the fraction of the total products observed varied with the type of polymer. In this respect the results are not as straightforward as those by TGA, which measures all of the material lost from the sample. In the present method the amount of observed volatiles might be increased somewhat by using a higher temperature and a shorter connecting line between the pyrolyzer and the detector. The yield of decomposition products would then approach more closely that determined by TGA. In order for any volatiles detection method to produce TGA type data it is necessary that the amount of volatiles observed at various temperatures be proportional to the corresponding weight losses. This was approximately true in the tests reported here, as indicated by the generally good correlation with the results obtained by TGA.

The filament can be heated to very high temperatures if desired (up to about 900°C.), and therefore the method could be used advantageously to test polymers of very high thermal stability. For such applications the simplicity of the heater, the rapid adjustment of temperature and the sensitivity of detection would be especially attractive features.

In order to observe volatiles which do not respond with the FID (for example, water, nitrogen, oxygen, and the oxides of carbon and nitrogen) another detector, such as thermal conductivity, is necessary. In the case of water, the highly sensitive FID still can be usefully applied if the water is passed through a calcium carbide column to produce acetylene in the manner described by Knight and Weiss.[13] We confirmed the feasibility of this detection scheme in a few tests with polyacrolein, a polymer that yields water as a major pyrolysis product.

It is expected that the HFTA technique will be useful for pyrolysis mechanism studies, especially when it is combined with GLC analysis of the products in the manner employed by Hunter and Forbes.[7] Temperatures can be adjusted rapidly and precisely so that the decomposition rate and the product distribution can be determined readily at any stage of the pyrolysis.

The HFTA technique provides a simple and effective means for vaporization and direct analysis of trace volatiles. They may be observed as total volatiles or as separated components after passage through a GLC column. Since the solution step employed in other methods is eliminated, the method should be especially useful for analysis of difficultly soluble samples. The sensitivity achieved in this study (10 ppm) is about equal to that for GLC methods using polymer solutions.[5,12] However, it may be possible to lower the detectable limit by scaling up the hot-filament unit to handle larger samples.

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Résumé

La stabilité thermique et la teneur de traces de produits volatiles au sein traces de polymères peuvent étre déterminées rapidement et de façon convenable en utilisant un appareil à pyrolyse à filaments chauffés permettant le chauffage de l'échantillon. Le filament semblable à celui analysés pour la pyrolyse GLC consiste dans un spirale en platine munie d'un thermocouple platine/platine–rhodium pour mesurer la température de l'échantillon. Quand l'échantil on est chauffé les produits volatiles sont détectés directement par ionisation de flamme utilisant un enrégistreur qui note à la fois la température et le rendement en produits volatiles. À chaque moment de chauffage, les produits sont analysés si on le désire avec une colonne GLC. Les mesures de stabilité thermique de nombreux polymères sont généralement consistantes avec les résultats obtenus par analyse thermogravimétrique habituelle. Les avantages de cette méthode sont la grande possibilité de détection à des vitesses de décomposition faibles, la vitesse d'adjustement de la température, la simplicité de l'appareil et les faibles exigences de poids des échantillons.

Zusammenfassung

Die thermische Stabilität und der Gehalt an Spuren flüchtiger Stoffe von Polymeren kann bei verwendung eines Hitzedraht-Pyrolysators zur Erhitzung der Probe rasch und bequem bestimmt werden. Der Drahtkörper, vom Typ, wie er für die Pyrolyse-GLC-Analyse verwendet wird, besteht aus einer mit einem Platin/Platin–rhodium-thermoelement zur Messung der Probentemperatur versehenen Platinspirale. Bei Erhitzung der Probe werden die flüchtigen Produkte direkt mit einem Flammenionisationsdetektor ermittelt und mit einem Dualrekorder werden Temperatur und Ausbeute an flüchtigen Stoffen aufgezeichnet. In jedem Erhitzungsstadium können die Produkte nach Belieben mit einer geeigneten GLC-Säule analysiert werden. Thermostabilitätsmessungen an einigen Polymeren lieferten im allgemeinen mit der konventionellen thermogravimetrischen Analyse übereinstimmende Ergebnisse. Die Vorteile der Methode sind die hohe Empfindlichkeit zur Bestimmung kleiner Zersetzungsgeschwindigkeiten, die Raschheit des Temperaturausgleichs, die Einfachheit des Apparats und der kleine Probenbedarf.