Polymeric Schiff Bases. VII. Some Parameters in the Evaluation of the Thermal Stability of Poly(*p*-Xylylidene-*p*-phenylenediamine)

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Summary

Thermogravimetric analyses of poly(*p*-xylylidene-*p*-phenylenediamine) in nitrogen, helium, and air yield stability values substantially identical to values obtained from tests in vacuo. The respective thermal stability values in nitrogen and in air are unchanged over a fourfold change in gas flow rates. Slightly lower values are found at heating rates of 5–15°C/min than at 30°C/min. Thermal stabilities are lower in oxygen than in air, but the values are still relatively high. Higher apparent thermal stability values are observed when a powder sample of 10 mg is evaluated as a single mass rather than as a fine powder. Calorimetric measurements indicate that Schiff base polymers which have been heated in nitrogen to 1000–1200°C have not been converted to graphite-type polymers. The Schiff base polymers are resistant to radiation; their stability is shown to be independent of dose rate and of the nature of the ionizing radiation.

In previous studies, (*1–3*) the thermal stability values for a number of Schiff base polymers were reported. The ability of the thermogravimetric and thermodifferential methods of analyses to determine the thermal properties of materials is well known (*4–6*). These two methods are usually employed as complimentary sources of data and together indicate the temperatures at which degradation and phase changes occur (*7*). A number of our studies on the polymeric Schiff bases showed that the inflection points of the thermo-

gravimetric curves, and hence the data derived from them, were dependent to some measure on a number of parameters. Variations in the heating rate, environmental gas flow rate, and particle size were responsible for some shifts in the thermogravimetric curves. A review of the literature (8–10) also showed no general acceptance of standardized conditions or values for these parameters; indeed, in many cases, all parameters are not specified. It was necessary, therefore, in the previous papers (1–4) to specify these parameters, and, to facilitate comparisons among the various polymers, to adopt specific values to be used uniformly for all the samples examined. The conditions used (1–3) were: (1) heating rate of 15°C/min, (2) gas flow rate of 1 standard liter/min, and (3) 10-mg sample ground to approximately 500 particles. There does not appear to be general agreement on how to assign thermal stability values to polymers from the thermogravimetric analysis. Various approaches have been proposed, such as the "differential procedural decomposition temperature" and the "integral procedural decomposition temperature," which give decomposition temperatures based on the areas under the thermogravimetric curves (11–13). Others have based their evaluation of thermal stability on comparisons among the thermogravimetric curves themselves.

In our early studies (1–3), the latter approach (12,13) was taken. Data were abstracted from the curves and placed in tabular form to facilitate analysis and comparison. Tables were assembled which summarized the data in the following categories: per cent weight losses at various temperatures, temperatures of specific per cent weight losses, and temperatures of inflection corresponding to the onset of decomposition or further reaction. The temperatures of inflection were obtained from (1) the intersection of the slope of the curve before a negative change in slope has occurred, and (2) the slope of the curve at maximum decomposition.

In the absence of accepted standardized conditions under which the thermogravimetric determinations are to be performed, it was necessary, therefore, in the previous studies (1–3) to specify the parameters used, and, to facilitate comparisons among the various polymers, to adopt specific values to be used uniformly for all the samples examined. The thermogravimetric temperatures recorded (1) were corrected for the nonlinearity of the chromel-alumel thermocouples. The thermogravimetric determinations were per-

formed in nitrogen and in air to determine both the "true" and the "practical" thermal stabilities.

Since the limits of the parameters were chosen arbitrarily (1–3), it was considered important to reexamine the parameters which were used to establish the thermal stability values assigned to the Schiff base polymers, and to determine what effect, if any, changes in the parameters would have on the thermal stability values assigned.

In previous (1–3) thermogravimetric analyses nitrogen was used as the inert environmental gas. Since the question could be raised as to whether or not nitrogen reacted with the polymers at high temperature, a comparison should be made between nitrogen and other inert gases. Also, air had been used (1) as the reactive gas, and the high thermal resistance of the polymers in air suggested that 100% oxygen should be compared with air. Further, since 1 standard liter/min was used (1) previously as the air flow rate of the gaseous atmosphere, it appeared desirable to evaluate a wider range of flow rates. In addition, since surface area varies greatly with particle size, it was considered necessary to evaluate the thermal stability of the polymers over a range of particle sizes.

Since thermal treatments of polymers can produce changes in their structures, infrared and mass spectral studies were included in previous studies, and these gave evidence of some of these changes. Calorimetric measurements can also give some insight into structural changes. Accordingly, it was deemed important to obtain ΔH values of the polymers and to compare these values with those of pyrolytic graphite to establish a similarity or difference to graphite. The high thermal stability of the polymers led to studies to determine the stability of the polymeric Schiff bases to ionizing radiation; this was to be done by comparing the thermogravimetric curves before and after exposure to the radiation. Dose rate and total dosage were evaluated as parameters.

EXPERIMENTAL

The polymer, I-B-H400, $=\!\!\left[\text{N}\!-\!\!\bigcirc\!\!-\!\text{N}\!=\!\!\text{HC}\!-\!\!\bigcirc\!\!-\!\text{CH}\right]_{\!\!\overline{n}}$, whose synthesis has been reported previously (1), was considered to be typical of the conjugated and pseudoconjugated Schiff base

polymers, and it was selected as representative of these polymers and used in this study of the parameters which could influence the determination of the thermal stability values.

Thermogravimetric Analyses

The thermogravimetric analyses were performed (1) on a du Pont Model 950 thermogravimetric analyzer in conjunction with a Model 900 differential thermal analyzer. To facilitate comparisons among the various samples, sample weights of 10 mg were used in the determinations; the instrument was set to a sensitivity of 2 mg/in. with a time response of 2 sec. A temperature correction has been made in these determinations for the nonlinearity of the chromel-alumel thermocouple.
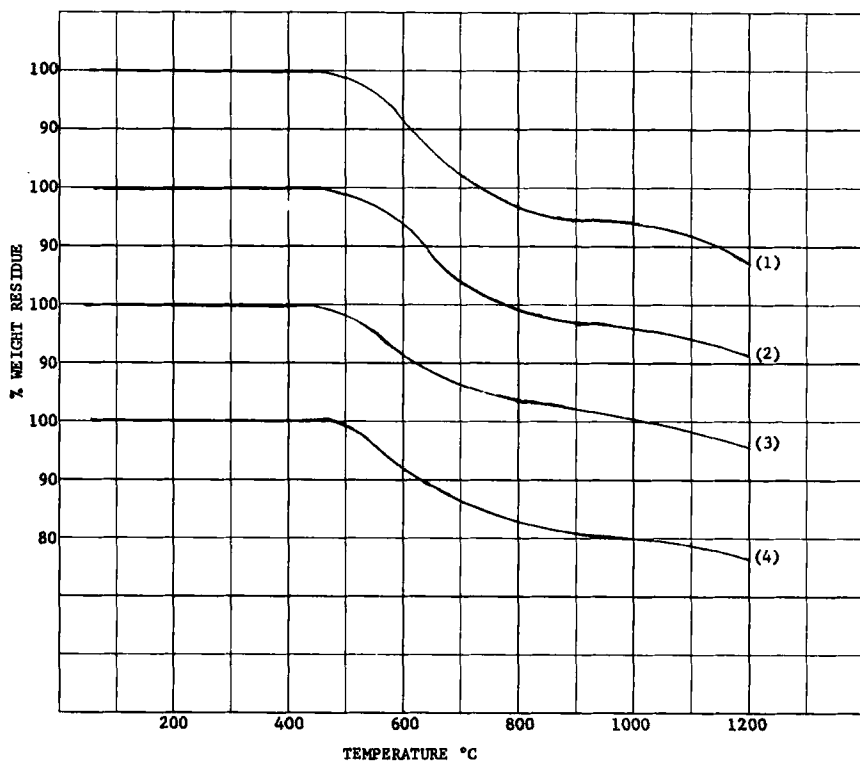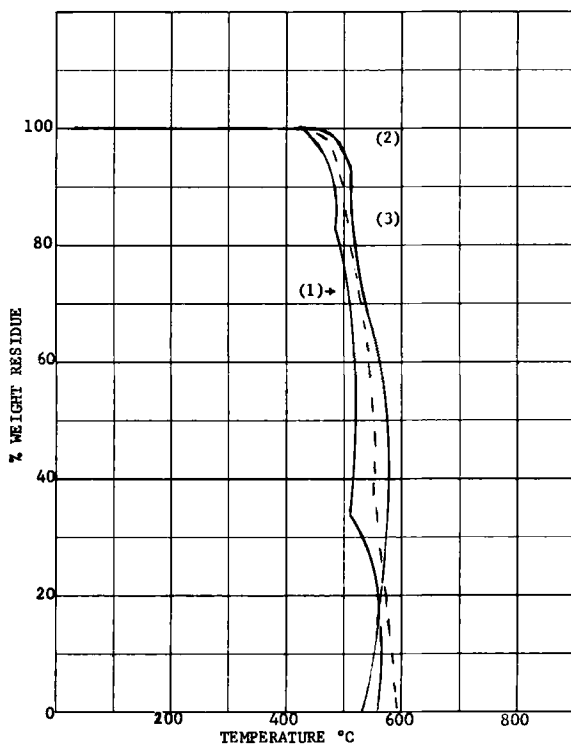

FIG. 1. Thermogram of polymer I-B-H400; in nitrogen, curve (1), in helium, curve (2), in argon, curve (3), and in vacuo, curve (4).

Nature of the Inert Atmosphere. Samples of polymer I-B-H400 were thermoanalyzed at a reduced pressure of 0.5 mm Hg, in nitrogen, helium, and argon, at a heating rate of 15°C/min, and at a gas flow rate of 1 standard liter/min. The helium and argon used were spectrographic-grade gases. The composite thermogram for these tests is shown in Fig. 1.

Nature of the Reactive Atmosphere. Samples of polymer I-B-H400 were thermoanalyzed in air (1) and in oxygen at a heating rate of 15°C/min. The purity of the oxygen used was 99.6%. Table 1 contrasts the relative thermal stabilities of the polymer thermoanalyzed in air with a flow rate of 1 standard liter/min with oxygen at flow rates of 0.5, 1.0, and 2.0 standard liters/min. The composite thermogram for the analyses in oxygen is shown in Fig. 2.

FIG. 2. Thermogram of polymer I-B-H400 in oxygen; curve (1) at 0.5, curve (2) at 1.0, and curve (3) at 2.0 standard liters/min.

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TABLE 1

Data from Thermoanalyses of Polymer I-B-H400 in Air and in Oxygen

</div>

Atmosphere	Flow rate 1 standard liter/min	Point of inflection, °C	Figure no. (curve no.)
Oxygen	0.5	447	2 (1)
	1.0	467	2 (2)
	2.0	488	2 (3)
Air	1.0	579	4

Variations in Flow Rates of Gas. Nitrogen. Samples of polymer I-B-H400 were thermoanalyzed in nitrogen at gas flow rates of 0.5, 1.0, and 2.0 standard liters/min, respectively, at a heating rate of 15°C/min. The composite thermogram is shown in Fig. 3.
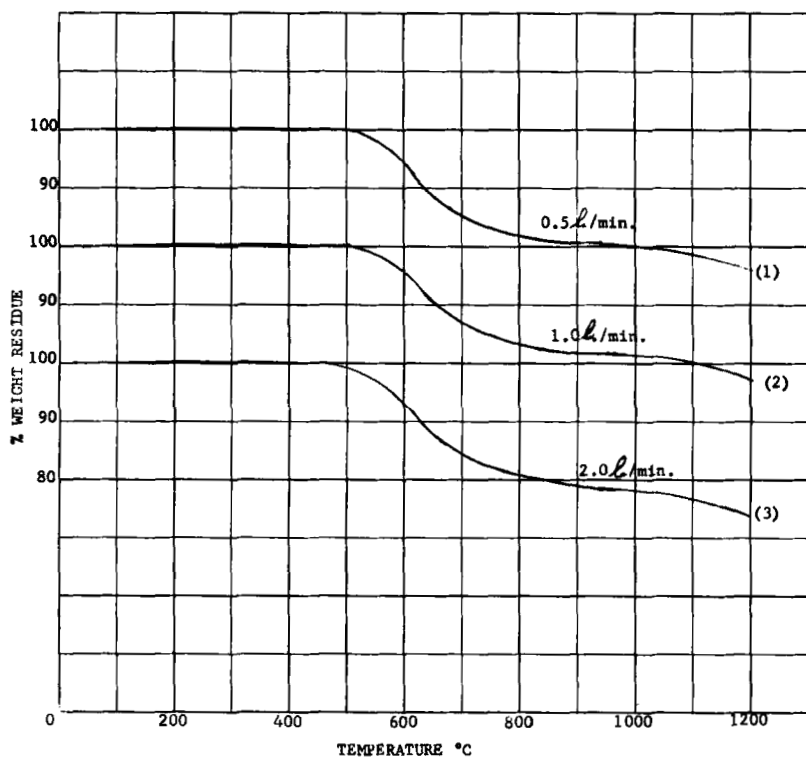

FIG. 3. Thermogram of polymer I-B-H400 in nitrogen; curve (1) at 0.5, curve (2) at 1.0, and curve (3) at 2.0 standard liters/min.
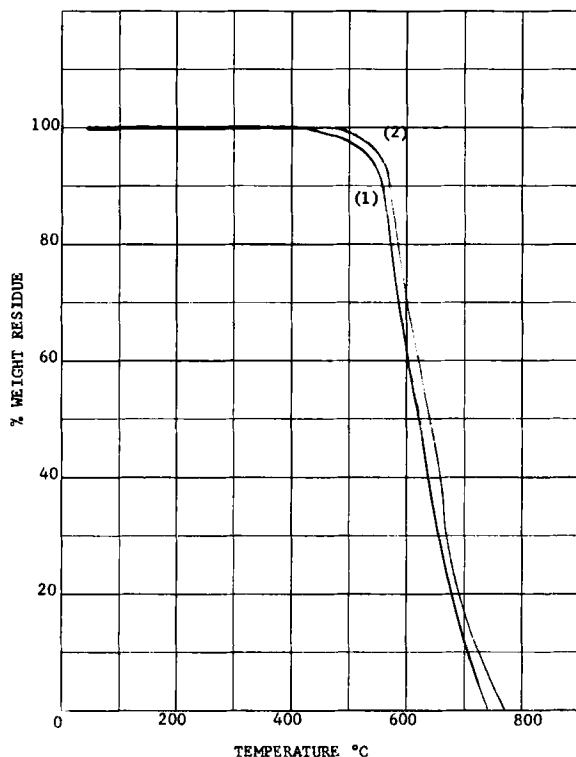
FIG. 4. Thermogram of polymer I-B-H400 in air; curve (1) at 0.5 and curve (2) at 2.0 standard liters/min.

Air. Samples of polymer I-B-H400 were thermoanalyzed in air at gas flow rates of 0.5, 1.0, and 2.0 standard liters/min, respectively, at a heating rate of 15°C/min. The composite thermograms showing the tracings at 0.5 and 2.0 flow rates are shown in Fig. 4. The curve for the 1.0 flow rate lies between those of the 0.5 and 2.0 tracings.

Variations in Heating Rate. Samples of polymer I-B-H400 were thermoanalyzed in nitrogen at a flow rate of 1 standard liter/min and at heating rates, respectively, of 5, 15, and 30°C/min. The thermogravimetric data are given in Table 2, and the consolidated thermogram is given in Fig. 5, in which the tracing at heating rates of 5, 15, and 30°C/min is recorded.

The polymer I-B-H1176 obtained by heating the I-B-H400 polymer to 1176°C was thermoanalyzed in nitrogen and in air, at a flow rate of 1 standard liter of gas/min and at heating rates, respectively,

TABLE 2

Per Cent Weight Loss in Polymer I-B-H400 While Heated in
Nitrogen at Various Heating Rates

Heating rate, °C	Per cent weight loss at °C									
	300	400	500	600	700	800	900	1000	1100	1176
5	0.4	1.2	2.8	9.0	17.6	21.0	22.0	23.8	28.2	29.2
15	0.0	1.2	2.4	10.0	18.4	22.0	23.4	24.4	26.6	29.4
30	0.0	0.4	1.7	5.4	15.0	18.4	20.4	20.8	22.6	25.0

of 5, 15, and 30°C/min. The thermogravimetric data in nitrogen for
polymer I-B-H1176 are given in Table 3. The consolidated thermo-
gram for the heating rates at 5, 15, and 30°C in nitrogen is shown in
Fig. 6.
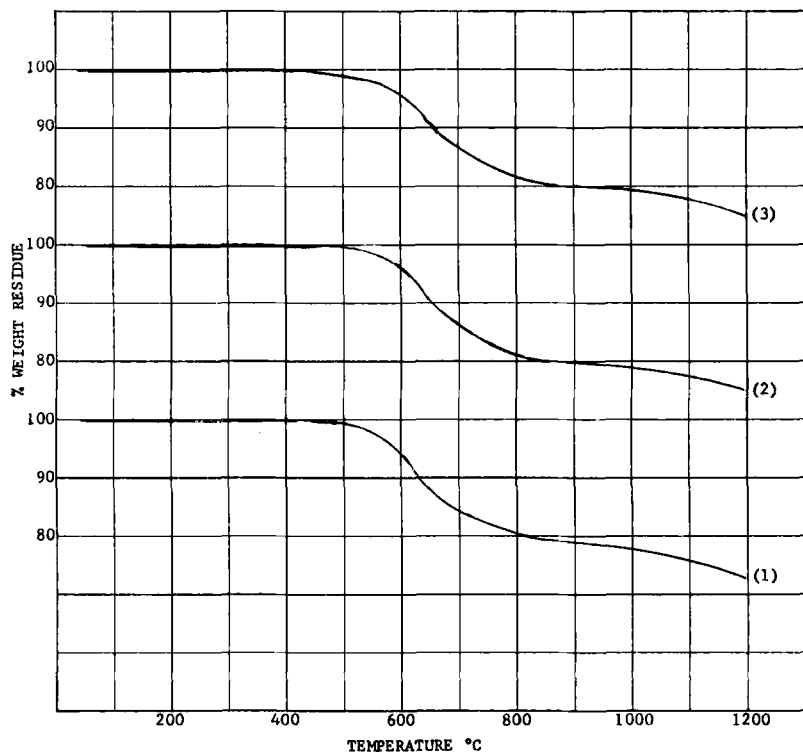
FIG. 5. Thermogram in nitrogen of polymer I-B-H400 at heating rates of
5°C/min, curve (1); at 15°C/min, curve (2); and at 30°C/min, curve (3).

FIG. 6. Thermogram of polymer I-B-H1176 in nitrogen at heating rates of 5°C/min, curve (1); 15°C/min, curve (2); and 30°C/min, curve (3); and in air at 5°C/min, curve (1′); 15°C/min, curve (2′); and 30°C/min, curve (3′).

The thermogravimetric data for polymer I-B-H1176 in air are given in Table 4, and the corresponding thermograms are shown in Fig. 6.

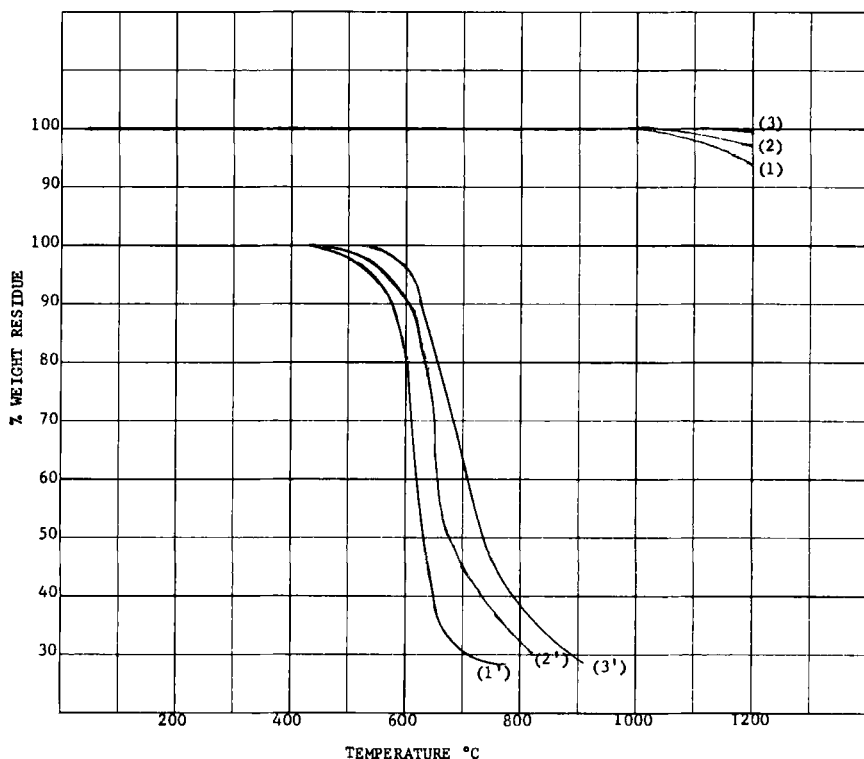**Variations on Particle Size of Samples.** Samples of I-B-H400 poly-

TABLE 3

Per Cent Weight Loss in Polymer I-B-H1176 While Recycling in Nitrogen at Various Heating Rates

Heating rate, °C	Per cent weight loss at °C				
	800	900	1000	1100	1176
5	1.0	1.1	1.2	3.2	6.0
15	0.2	0.6	1.0	1.8	2.6
30	0.6	0.6	0.6	0.8	1.2

TABLE 4

Temperature of Inflection of Polymer I-B-H1176 in Air After
Recycling in Nitrogen at Various Heating Rates

Heating rate, °C/min	Temp. of inflection, °C	Figure no. (curve no.)
5	570	6 (1)
15	580	6 (2)
30	588	6 (3)

mer were reduced to widely varying particle sizes, and a series of
thermograms was performed in nitrogen and in air at a flow rate of
1 standard liter/min and at heating rates of 15°C/min for samples
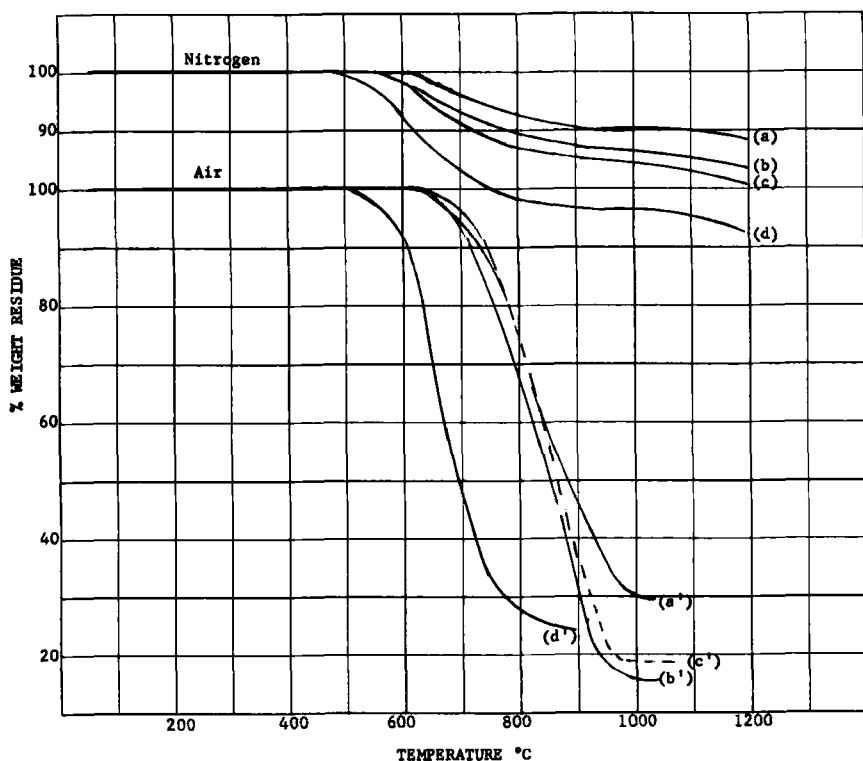having the following number of particles per 10 mg of sample:

FIG. 7. Thermogram of polymer I-B-H400 at various particle sizes in nitro-
gen, curves (a, b, c, d) and in air, curves (a', b', c', d').

sample a, 1 piece; b, 4 pieces; c, 22 pieces; and d, 500 pieces (approximately). The composite thermograms are shown in Fig. 7.

Calorimetry

Cell Constant. The calorimetric studies were performed in a du Pont calorimetric cell in conjunction with a du Pont Model 900 differential thermal analyzer. The cell was calibrated from the known heats of fusion for indium, tin, zinc, and aluminum. Platinum liners were used, and the procedure outlined in the du Pont "Manual for the Calorimetry Cell" was followed. The calibration coefficients were calculated from the following equation:

$$E = \frac{(\Delta H)\,(m)\,(a)}{(A)\,(\Delta T_s)\,(T_s)}$$

where E = calibration coefficient, mcal/°C-min
ΔH = heat of fusion of the metal, mcal/mg
m = sample, mg
a = heating rate, °C/min
A = peak area, in.²
ΔT_s = Y-axis sensitivity, °C/in.
T_s = X-axis sensitivity, °C/in.

The peak areas were obtained by using a polar planimeter. The calculated values for E were plotted against the transition temperature to give the calibration curve. Platinum liners with silver caps were used in the cell for temperatures above 350°C to reduce heat loss by radiation.

Polymers. Pyrolytic graphite was used as the reference polymer in the calorimetric study. The pyrolytic graphite, obtained through the courtesy of the National Aeronautics and Space Administration, had been produced at temperatures in the range of 1800°C. The behavior of the pyrolytic graphite was compared to the behavior of I-B-H1176 polymer, which had been prepared by heating the I-B-H400 polymer to 1176°C. Included in this comparison was the I-B-H400 polymer and the corresponding low molecular weight yellow, brick-dust polymer 1-Y, prepared by solution methods previously reported (1). The tests were run in nitrogen and in air with flow rates of 1 standard liter/min; heating rates of 5 and 15°C/ min were used.

The calorimetry measurements cover the temperature range of

TABLE 5

Calorimetric Data on Poly-Schiff Bases and Graphite

Polymer	Atmosphere	Heating rate, °C/min	Calorimetry peak temp., °C	Initial sample weight, mg	Calcd. heat of reaction, cal/g
Pyrolytic	Nitrogen	15	—	4.7	—
graphite	Air	15	680	4.7	520–550
I-B-H1176	Nitrogen	15	—	1.7	400–450
I-B-H1176	Air	15	· 575	1.7	4900–5500
I-B-H400	Nitrogen	15	420	4.5	170–180
I-B-H400	Nitrogen	15	500	4.5	75–85
I-B-H400	Air	15	550	4.5	2700–3000
I-B-H400	Air	5	535	3.2	3000–3500
I-Y	Air	5	400	2.7	1700–2000
	Air	5	525	1.4[a]	4900–5500

[a] Weight of sample after first peak.

ambient to 700°C, and the Y-axis sensitivity was 1.0°C/in. The calorimetric data are shown in Table 5.

The calorimetric thermogram for pyrolytic graphite in nitrogen and in air is shown in Fig. 8, that for polymer 1-B-H1176 in Fig. 9, that for polymer I-B-H400 in Figs. 10 and 11, and that for polymer 1-Y in Fig. 12.

Ionizing Radiation

The polymers I-B-H400 and I-B-H600, obtained by heating I-B-H400 to 600°C in nitrogen, were selected as candidates for exposure to ionizing radiation. Environmental conditions under which the polymers were to be irradiated were divided into three parts: (1) polymers irradiated while sealed in vacuo, (2) polymers irradiated while sealed in an air atmosphere, and (3) polymers irradiated while exposed to air during irradiation.

The general procedure consisted of irradiating polymer samples to the desired dosage, subjecting them to thermogravimetric analyses in nitrogen and in air, and comparing the resulting thermograms with those of nonirradiated samples already reported in previous reports (1–3). The experimental parameters for these analyses were those used in the earlier studies (1): (1) gas flow rate of 1 standard liter/min, (2) heating rate of 15°C/min, and (3) 10-mg sample con-

FIG. 8. Calorimetric thermogram of pyrolytic graphite, in nitrogen, curve (1), and in air, curve (2).
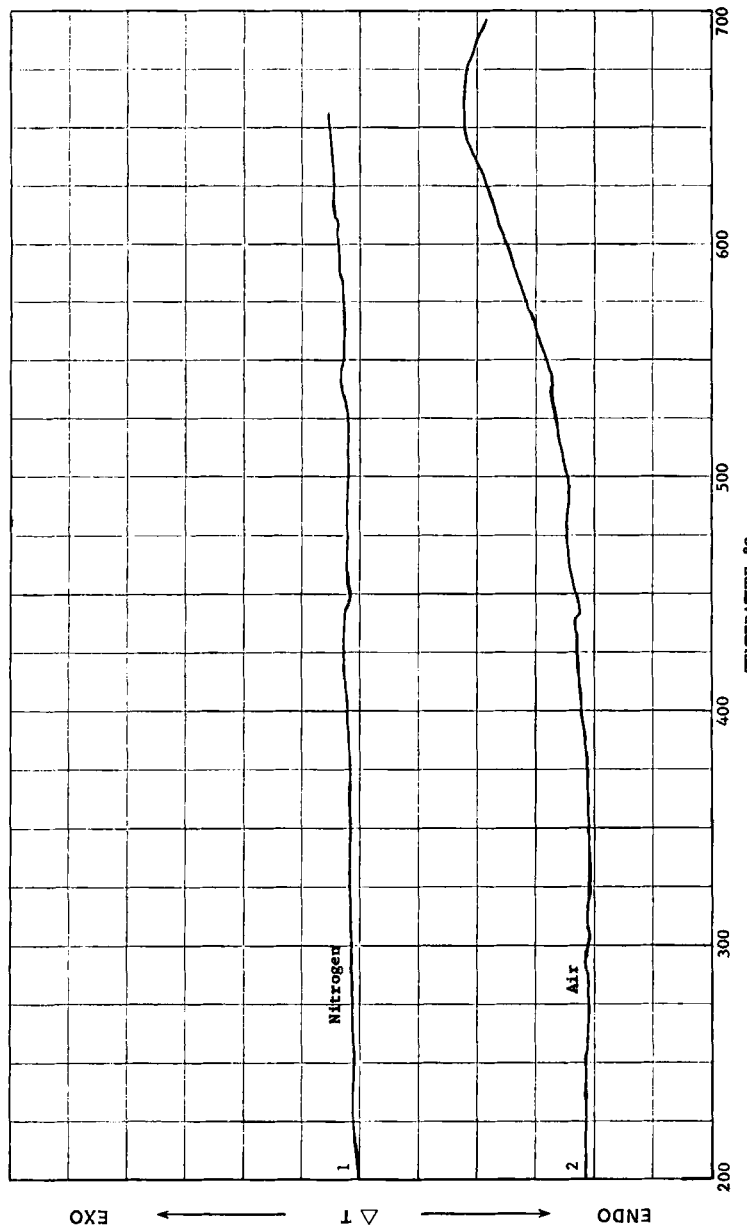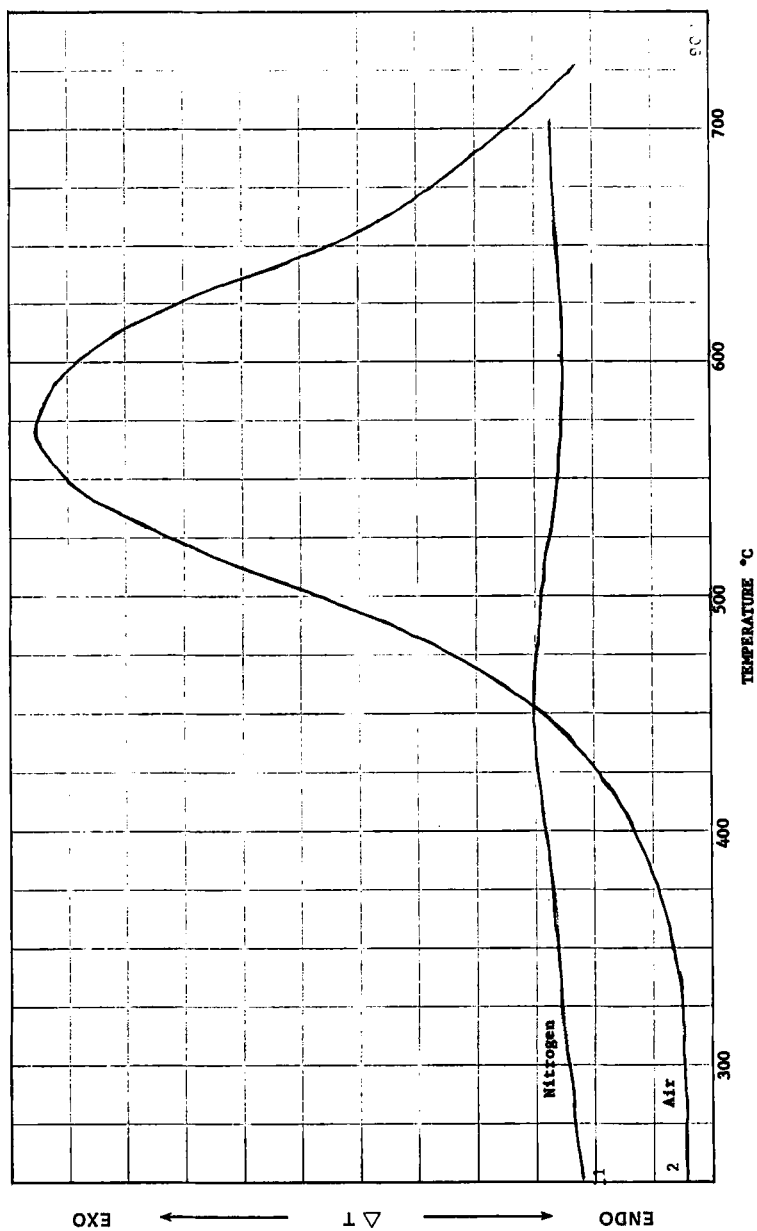
FIG. 9. Calorimetric thermogram of polymer 1-B-H1176 in nitrogen, curve (1), and in air, curve (2).
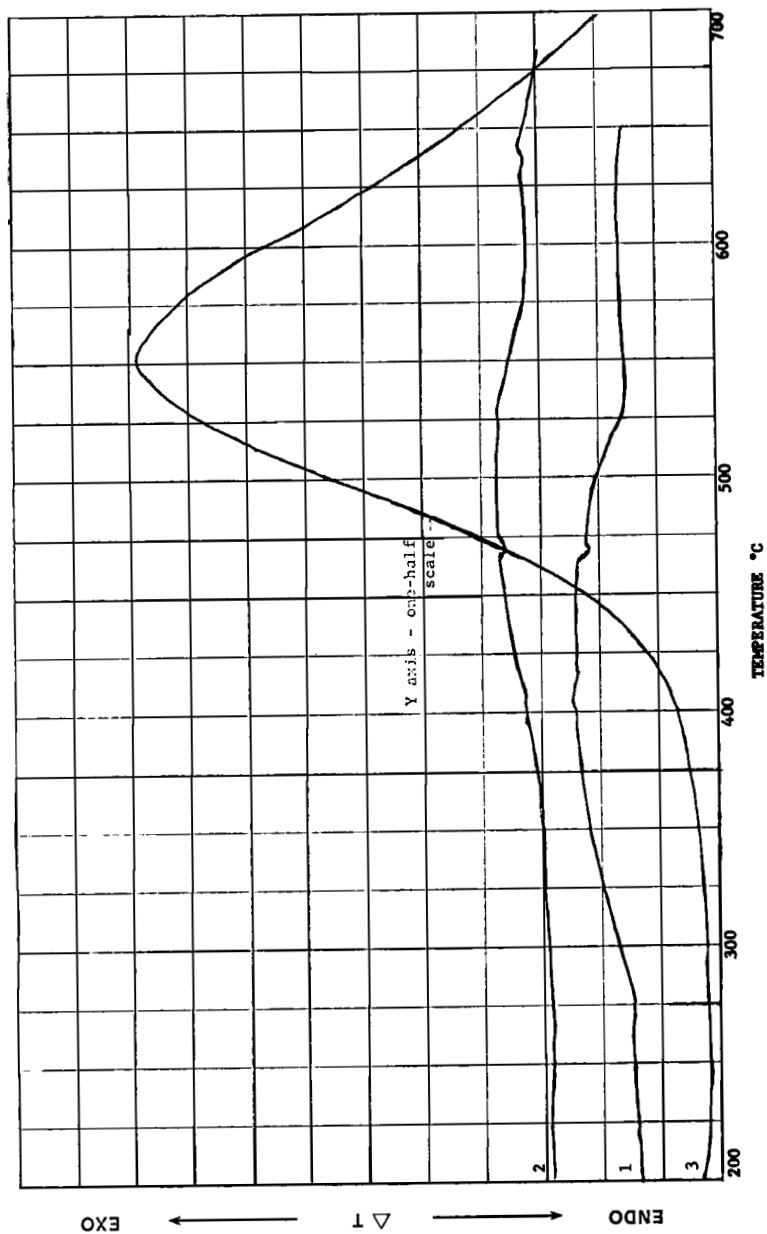
FIG. 10. Calorimetric thermogram of polymer I-B-H400 (4.5 mg) in nitrogen, curves (1) and (2), and in air, curve (3).
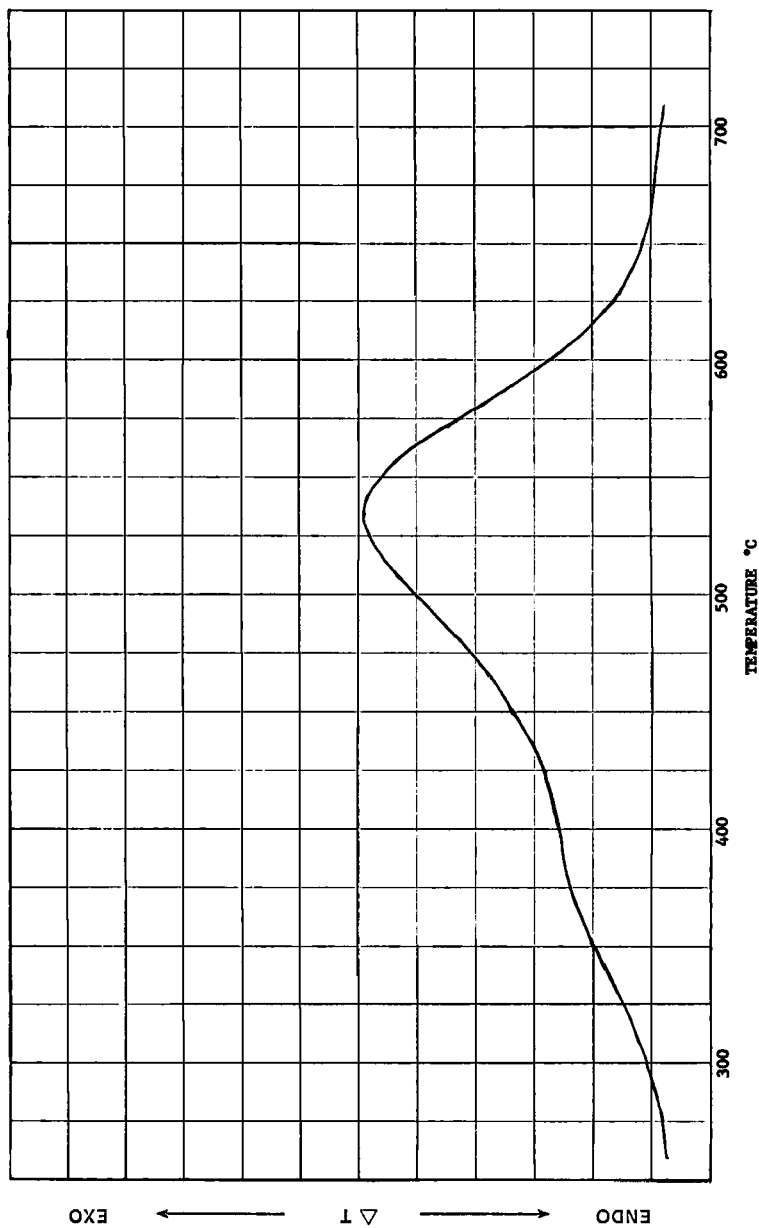
FIG. 11. Calorimetric thermogram of polymer I-B-H400 (3.2 mg) in air.
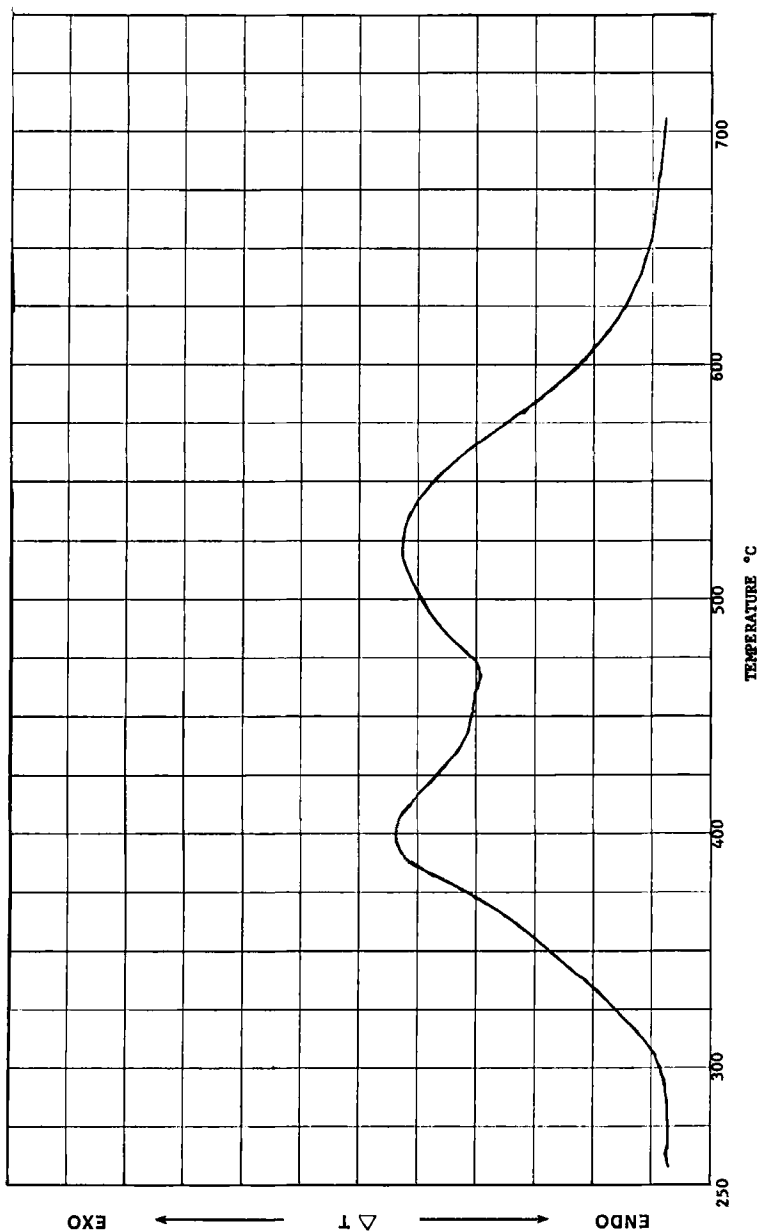
FIG. 12. Calorimetric thermogram of polymer 1-Y in air.

sisting of approximately 500 particles. Two sources of irradiation were used, a cobalt source and an electron source.

Polymers Irradiated in Cobalt Source. One set of samples was irradiated by exposure to a cobalt source at NASA Langley Research Center, Hampton, Virginia, at a dose rate of 1.2 Mrad/hr at an ambient temperature of 47°C. The polymer samples were contained in Pyrex tubes. The samples were exposed to the ^{60}Co source for 176 hr to a total dosage of 200 Mrad.

In Vacuo. The powdered polymer samples were degassed in Pyrex containers at 10^{-6} torr for 1 hr and sealed in the container. The thermograms in nitrogen and in air for the irradiated I-B-H400 and I-B-H600 polymers following irradiation in vacuo are given in Figs. 13 and 14.

Sealed in Air. The powdery polymer samples in Pyrex containers
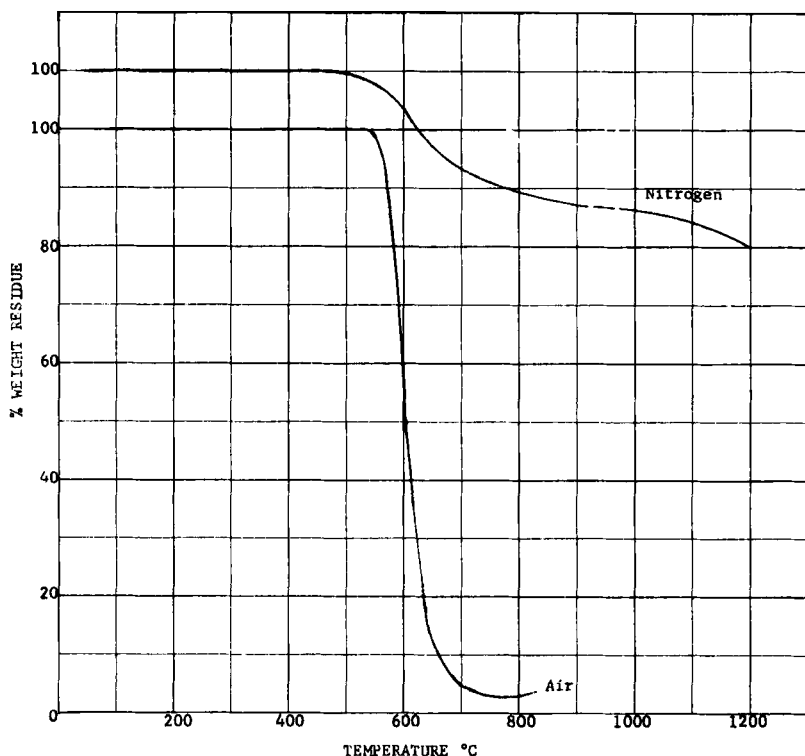
FIG. 13. Thermogram of polymer I-B-H400 in nitrogen and in air, after being irradiated in vacuo. Total dosage 200 Mrad from ^{60}Co source.
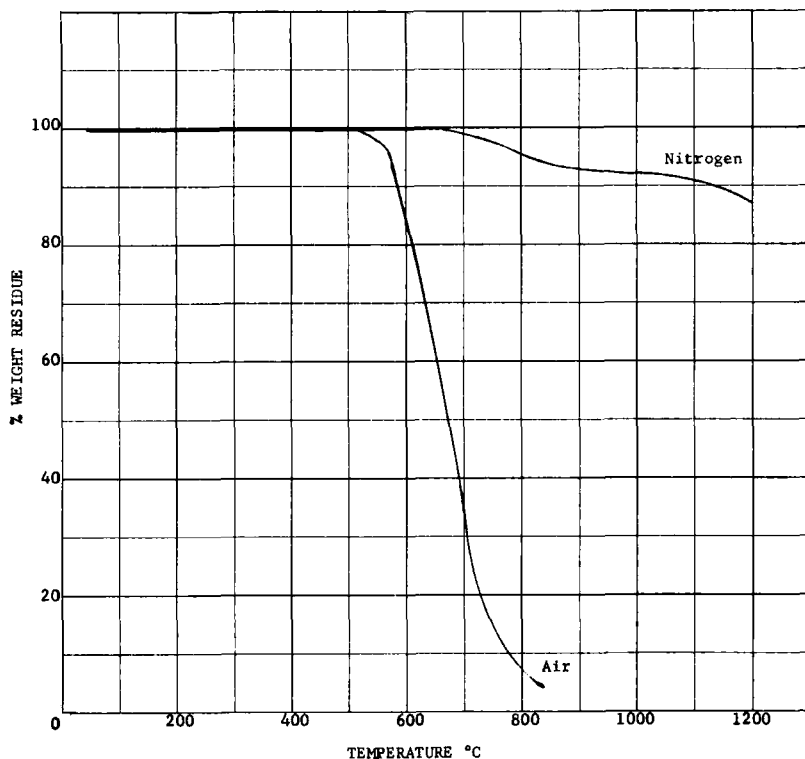
FIG. 14. Thermogram of polymer I-B-H600 in nitrogen and in air after being irradiated in vacuo. Total dosage 200 Mrad from ^{60}Co source.

were degassed at 10^{-6} torr for 1 hr and the container, of 5 cc volume, was refilled with air at atmospheric pressure. The thermograms in nitrogen and in air of these polymers following irradiation while sealed in an air atmosphere are shown in Figs. 15 and 16.

While Exposed to Air. Powdered samples of polymers I-B-H400 and I-B-H600 were placed in opened 5-ml vials and left uncovered during irradiation. The thermograms in nitrogen and in air following irradiation while exposed to air are given in Figs. 17 and 18.

Polymers Irradiated in Electron Source. An insulating core transformer electron accelerator was used as the electron source. The particular electron accelerator was operated at a beam energy of 500 keV; the beam can penetrate 0.40 cm of unit density material. The accelerator is equipped with a 1-in. by 48-in. scanner, and the beam is scanned at 200 cycles/sec over the 48-in.^{2} effective radia-
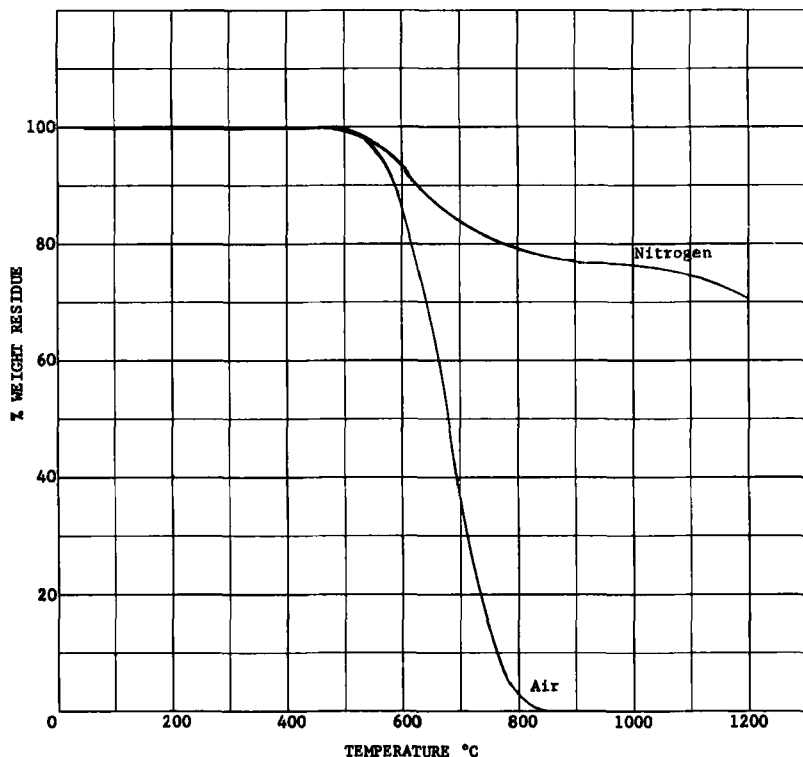
FIG. 15. Thermogram of polymer I-B-H400 in nitrogen and in air after being irradiated while sealed in air.

tion area. The effective beam power is 10 kW and the beam current is 20 mA. The dosage rate was 5 Mrad/sec.

Powdered samples of polymers I-B-H400 and I-B-H600 were placed in open Petri dishes and exposed uncovered to the electron beam for approximately 3.33 min, to a total dose of 1000 Mrad. The thermograms in nitrogen and in air following irradiation while exposed to air are substantially identical to those given in Figs. 17 and 18.

DISCUSSION

The thermogravimetric analyses of the Schiff base polymers described in previous publications (1–3) were performed in dry deoxygenated nitrogen, which was presumed to be inert. The thermal

stabilities determined in this gas were presumed to reflect the "true" thermal stability of the polymers, that is, the thermal stability based on the strengths of the bonds between the atoms. However, the question arose as to the actual nonreactivity of nitrogen at high temperatures, especially in the region above 1000°C. It is possible that at these temperatures nitrogen may be sufficiently reactive to attack the polymer structure and thus to contribute either to a loss in weight by degradation or to an increase in weight by addition.

To adequately evaluate the possible effect of nitrogen at high temperatures in these polymer systems, it was necessary to determine their thermal stability in an atmosphere known to be inert. Helium and argon, being inert gases, would be expected to be nonreactive even at the high temperatures employed in these studies.
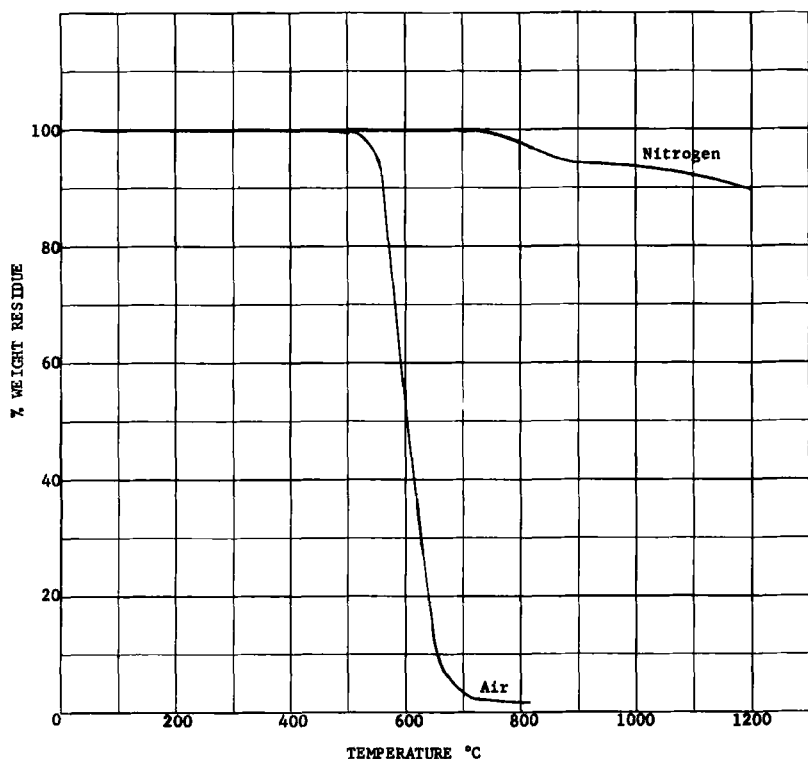
FIG. 16. Thermogram of polymer I-B-H600 in nitrogen and in air after being irradiated while sealed in air.
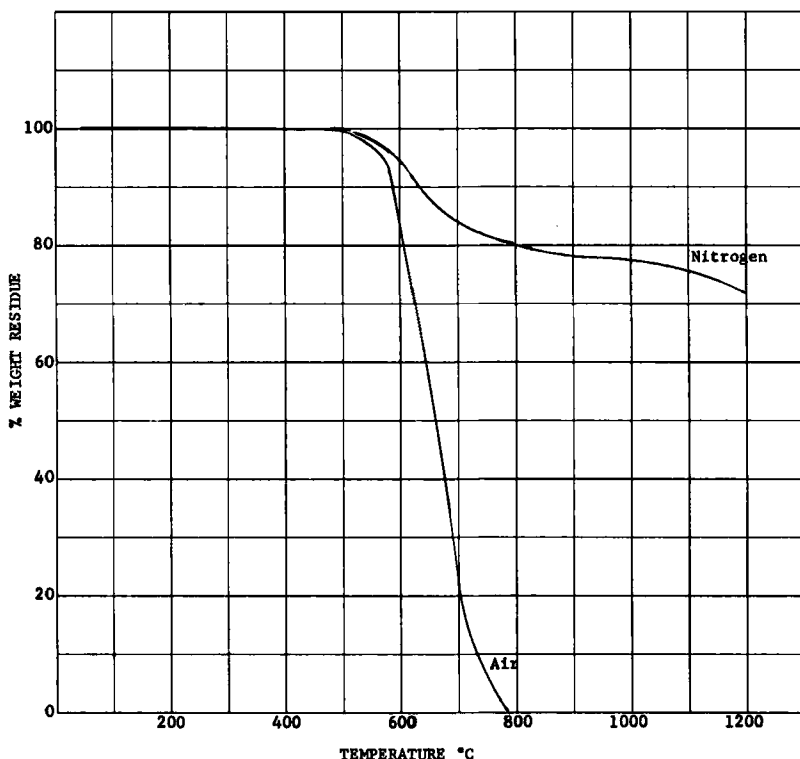
FIG. 17. Thermogram of polymer I-B-H400 in nitrogen and in air after irradiation while exposed to air.

Thus samples of polymer I-B-H400 were thermoanalyzed in helium and in argon to 1176°C and the thermogram compared with the thermograms of the same polymer thermoanalyzed in dry nitrogen and in vacuo.

A comparison of the thermogravimetric plots in Fig. 1 shows little difference either in the shape of the thermogravimetric curves or in the resulting weight losses. It follows thus that nitrogen is non-reactive toward Schiff base polymers even at high temperatures in excess of 1000°C. Nitrogen, therefore, may be considered an inert sample gas, and the thermal stabilities determined in this atmosphere may be considered "true" thermal stabilities. The thermogravimetric plots were substantially identical with those obtained when the test was run in vacuo.

In previous reports (*1–3*) studies were conducted to determine the thermal behavior of the Schiff base polymers in air as the active gas environment. In this case, an active environment is defined as a medium which, because of its chemical reactivity, aids the thermal degradation of the polymer. The thermal stabilities of the conjugated and pseudoconjugated polymers in this environment were shown to be very high (*1*), of the order of 500–600°C. Because of this high stability, it was of interest to determine the thermal stability of Schiff base polymers in a more active environment, particularly in pure oxygen. Accordingly, a thermogravimetric analysis was made using 100% oxygen; thermograms were recorded in the gas at flow rates of 0.5, 1.0, and 2.0 standard liters/min.

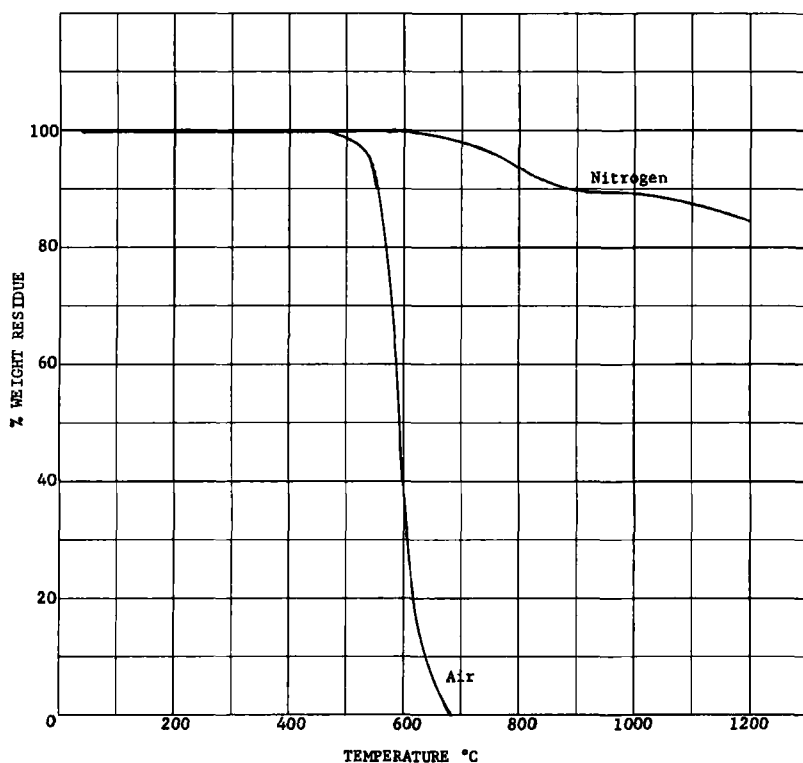An analysis of Fig. 2 shows that polymer I-B-H400 shows a high

FIG. 18. Thermogram of polymer I-B-H600 in nitrogen and in air after irradiation while exposed to air.

degree of thermal stability in oxygen when compared to the values in air. Table 1 contrasts the relative thermal stabilities of the polymer thermoanalyzed in air with a flow rate of 1 standard liter/min with oxygen at 0.5, 1.0, and 2.0 standard liters/min.

The thermogravimetric plots show two interesting features which result from the use of oxygen as a sample atmosphere. First, the negative slope indicating thermal degradation is very steep, suggesting that very rapid oxidative decomposition is taking place. Second, the curves show that during the thermoanalysis the sample temperature rises higher than the cell temperature, and thus the samples are burning. Samples thermoanalyzed in air show a smooth oxidative decomposition and not a catastrophic and fast decomposition.

From these studies it follows that the thermal stability of black conjugated Schiff base polymers is influenced by the use of a very reactive atmosphere of pure oxygen; however, the thermal stability of these polymers in this environment remains about the same order of magnitude as in air.

Another parameter which must be considered in the evaluation of thermal stabilities is the gas flow rate of the sample atmosphere. When low gas flow rates are used, hot gaseous products arising from the thermal degradation of the sample remain in the immediate vicinity of the polymer. Combustion of these products may raise the temperature of the sample and aid in its decomposition. If faster flow rates are used, these degradation products are removed as they are formed and thus do not contribute to thermal degradation.

A sample gas flow rate of 1 standard liter/min was used in the previous studies (1–3) and was regarded as adequate to sweep most of the degradation products away from the main polymer sample. This gas flow rate was the value recommended by du Pont for general use in thermoanalysis with the Model 950 thermogravimetric analyzer. In these new studies, gas flow rates of 0.5, 1.0, and 2.0 standard liters/min were employed to assess the effect of higher and lower gas flow rates on thermoanalyses of Schiff base polymers. The variation in flow rates was used for studies in two sample atmospheres, air and nitrogen.

Samples of polymer I-B-H400 were thermoanalyzed in nitrogen, at gas flow rates of 0.5, 1.0, and 2.0 standard liters/min. The thermograms in Fig. 3 show little variation due to changes in gas flow rate and are almost identical in all details. It may be concluded, there-

fore, that within the limits of this experiment, the thermal stability
in nitrogen is not appreciably changed over a fourfold change in
gas flow rate.

Samples of polymer I-B-H400 were thermoanalyzed in air, at a
gas flow rate of 0.5, 1.0, and 2.0 standard liters/min. Examination
of the thermograms in Fig. 4 indicates that there is only a small
effect which results from a fourfold variation in the gas flow rates
in air. Hence in these studies of Schiff base polymers, the gas flow
rate, within the limits studied, appears to play a very minor role in
the total assessment of their thermal stability.

The thermal stability of polymers is based not only on the ex-
tremes of environmental conditions which they can withstand, but
also upon the duration of exposure to such conditions. Various re-
searchers have adopted a wide variety of heating rates in the
evaluation of their polymers. Heating rates from 30 to 150°C/min
have been used to determine thermal stabilities. In our previous
reports (*1–3*) a heating rate of 15°C/min was adopted as a standard
and used throughout the determinations. It is recognized that
thermal stabilities of different polymers determined at different
heating rates cannot be easily compared. Thus it was desirable to
perform several thermoanalyses at different heating rates to deter-
mine the magnitude of effect of this parameter on the thermal
stability of Schiff base polymers.

In this study the polymer I-B-H400 was thermoanalyzed in nitro-
gen, recycled again in nitrogen, and then recycled in air. The heat-
ing rates chosen were 5 and 30°C/min for comparison with the
15°C/min rate. The thermogram for I-B-H400 in nitrogen at 5, 15,
and 30°C/min is given in Fig. 5. The thermogram for I-B-H1176 in
nitrogen and in air is given in Fig. 6. The thermograms clearly show
the expected results. When the heating rate is slow, as in the case
where 5°C/min was used, the overall thermal stability of the poly-
mer is lower than when the heating rate is six times faster, that is,
when the heating rate is 30°C/min. Table 2 contrasts the data ob-
tained from the thermoanalysis of the polymer in nitrogen at heat-
ing rates of 5, 15, and 30°C/min. The data contained in this table
show that there is very little difference in the weight losses ob-
tained at the two lower heating rates, 5 and 15°C/min. However,
when the heating rate is increased to 30°C/min, the polymer shows
lower weight losses and hence a slightly higher thermal stability.
For example, the resulting weight loss at 1176°C with a heating rate

of 30°C/min is approximately 4% less than at heating rates of 5 and 15°C/min.

Table 3 summarizes the data obtained by recycling the polymer in nitrogen at heating rates of 5, 15, and 30°C/min; the thermograms are shown in Fig. 6. It is apparent that the greatest weight losses occur on recycling in nitrogen when the slowest heating rate is used. The weight loss in this case (5°C/min) is five times greater (6%) than when the fastest heating rate (30°C/min) (1.2%) is used. It is also interesting to note that the major portion of this weight loss at the slowest heating rate occurs within the last 200°C and that up to 1000°C the curves for both heating rates are essentially identical.

The greatest effect of a variation in the heating rate on the thermal stability would be expected to take place in an active atmosphere. In this case the polymer would be subjected to chemical attack for longer periods of time at the lower heating rates, and thus should show higher weight losses for the same temperature than at higher heating rates. Such a result is observed in polymer I-B-H1176 in air, the thermograms for which are given in Figs. 6 and 7; the data are summarized in Table 4. The thermograms and the data show that oxidative degradation occurs earlier in those samples using slower heating rates. Also the curves obtained at slower heating rates show steeper slopes during the degradation, indicating that the rate of decomposition may be higher in these cases.

Variations in heating rate have thus been shown to produce some shifts in the thermal stability of Schiff base polymers. The magnitude of the differences in thermal stabilities, however, is not large; thus the values set forth in previous reports (1–3) represent a realistic evaluation of the thermal stabilities of these polymers.

Thermal stabilities are often reported in the literature without reference to the particle size of the samples examined by thermal analysis. That particle size is a parameter in the consideration of thermal stabilities appears reasonable, since many degradative processes are partially dependent on the amount of surface area. For example, diffusion of degradative products generated within a powdered sample is very much more rapid than in a bulk sample. Accordingly, powdered samples would be expected to show greater weight losses in inert atmospheres than bulk samples. In active atmospheres the chemical attack of the active agent is greatly dependent on surface area. Since powdered samples possess very

large surface areas when compared to bulk samples, they would be
expected to exhibit lower thermal stabilities.

To evaluate particle size as a parameter, a study using 10-mg
samples of polymer I-B-H400, which had been reduced to widely
differing particle sizes, was performed in air and in nitrogen. These
thermograms are shown in Fig. 7. The thermograms show a pro-
gressive increase in weight loss as the particle size becomes
smaller. In nitrogen the bulk sample shows little or no weight loss
up to 600°C; this is contrasted with about 500°C for the same weight
of a sample consisting of 500 pieces. A similar 100°C difference oc-
curs when the samples are thermoanalyzed in air. In air, in the bulk
sample, thermodegradation begins at about 600°C, while the sam-
ple consisting of 500 pieces starts to decompose at about 500°C.
These data indicate that there is a marked dependency between
particle size and thermostability. Accordingly, particle size should
be specified in any determination of thermal stability for compari-
sons to be made among various polymers with respect to their
thermal stability.

Calorimetric measurement can yield values which would indi-
cate similarity between two materials which are presumed to be
identical or closely related. The calorimetric studies were directed
to obtaining ΔH values of the I-B-H1176 polymer in air and in
nitrogen to determine whether or not the polymer has been graphi-
tized. This determination would be made by comparing the be-
havior of the I-B-H1176 polymer with the 1-Y, I-B-H400, and I-B-
H600 polymers.

The calorimetric thermogram for pyrolytic graphite up to 700°C
in nitrogen and in air is shown in Fig. 8. There is no evidence of an
exotherm or an endotherm in the tests under nitrogen. The test in
air shows a broad and relatively weak exotherm beginning at about
400°C and reaching a maximum at 680°C. The area of the curve was
obtained by doubling the area of the first half of the thermogram.

It should be noted that the heat of reaction obtained for the graph-
ite in air, 520–550 cal/g, is much less than the 2700–3000 cal/g ob-
tained for the polymer I-B-H400, and that the maximum in the
graphite curve is over 100°C higher than that in the I-B-H400
polymer curve.

The thermogram for the I-B-H1176 polymer is given in Fig. 9. A
very broad and relatively small exotherm is evident in the test in
nitrogen, and a broad and very large exotherm is evident in the

test in air, reaching a peak temperature of 575°C. The heat of reaction is 4900–5500 cal/g, compared to 520–550 cal/g for pyrolytic graphite. The thermogravimetric curve in air is similar to that of the I-B-H400 polymer in air rather than to that of pyrolytic graphite in air.

The thermograms for I-B-H400 obtained by heating in nitrogen and in air at 15°C/min are shown in Fig. 10.

The first test with I-B-H400 in nitrogen (Fig. 10, curve 1) showed a relatively small and very broad exotherm between 150 and 520°C. This appears to be a composite of two peaks, the first beginning at 150°C and the second at about 250°C. The second test (Fig. 10, curve 2) showed an even smaller exotherm between 370 and 560°C. The third test, in air (Fig. 10, curve 3) shows a very large and broad exotherm from 330 to 700°C. These results compare favorably with the thermogravimetric data (TGA) obtained on the same polymer under the same conditions. Four features, in particular, should be noted:

1. The exotherm in the nitrogen atmosphere is much smaller than that in the air atmosphere.

2. The exotherms are all very broad, suggesting a relatively slow degradative process rather than a phase change.

3. The peak of the exotherms in the calorimetry curves correspond quite well to the initial weight losses under the same conditions in the thermogravimetric curves.

4. The exotherms in the calorimetry curves begin at temperatures somewhat lower than the temperatures which show significant weight loss for the same polymer in the thermogravimetric curves.

The third and fourth features are especially evident in the third test (Fig. 10, curve 3) performed in an air atmosphere. The third feature may possibly be due to an ablative effect. If the decomposition products are gases, it is expected that they would carry away a substantial amount of heat when they escape from the system. This possible ablative effect and the loss of material make the calculation of an accurate ΔH very difficult. The calculation is complicated further in the air-atmosphere run by the fact that the curve does not return to the base line by 700°C, which is the maximum temperature for the calorimeter cell. However, heats of reaction were calculated from the curves for comparative purposes and are reported in Table 5. The area of the curve for the air atmosphere

test was obtained by doubling the area of the first half of the curve. The limitations and problems involved should be kept in mind when evaluating the relative heats of reaction. No corrections were made for weight losses. The calculated values probably represent the correct order of magnitude for the lower limit of the heats of reaction in each case. Even with these limitations, it is apparent that the heat of reaction in air of 4900–5500 cal/g for I-B-H1176 is more closely related to the value at 2700–3000 for I-B-H400 than the value of 520–550 cal/g for pyrolytic graphite. The very large value of ΔH for the air-atmosphere test should especially be noted.

To determine the effect of heating rate on the curve, a sample of I-B-H400 was tested at 5°C/min in air. The resulting curve in Fig. 11 appears to be a composite of two exotherms, the first with a maximum around 400°C and the second with a maximum at 535°C. The calculated heat of reaction of 3000–3500 cal/g is for the complete curve. In this case the curve returns to a base line by 700°C. The value of 3000–3500 cal/g is more closely related to the value of 4900–5500 cal/g for I-B-H1176 than to the value of 520–550 cal/g for pyrolytic graphite.

Another observation should be mentioned in connection with this test. The initial weight of sample was 3.2 mg. The amount of sample remaining after the test to 700°C was 2.1 mg. Under the same conditions of heating rate and air flow, the thermogravimetric curve (Fig. 2) shows that the polymer is completely decomposed by 700°C. This discrepancy shows that care must be used in comparing the thermogravimetric results with the calorimetric results. The difference is probably due to the fact that, in the calorimeter cell, the sample is placed in a platinum liner inside a small cup which is then covered by a cap. In addition, a cover is placed over the cell compartment. As a result, the air flow over the sample is undoubtedly much less in the calorimeter cell than in the thermogravimetric boat, where the air flows directly over the sample.

The presence in the tests in air of two exotherms, a minor one at 400°C and a major one at 535°C, in the I-B-H400 polymer and the absence of the exotherm at 400°C in the I-B-H1176 polymer was considered as being due to molecular weight differences in the two polymers. It had been previously shown (1) that the polymers obtained by condensation to 400°C were not fully condensed. Accordingly, a calorimetric test was made on a sample of the low molecular weight yellow polymer, 1-Y (Fig. 12), for comparison with

the black polymer. The test was made in an air atmosphere at a heating rate of 5°C/min. The curve shows two exotherms, the first with a maximum at 400°C and the second with a maximum at 525°C. It should be noted that the black polymer sample, I-B-H400, under the same conditions of test, gave a very similar calorimetric curve, except that the 400°C peak was much weaker. Calculated heats of reaction for the two distinct exotherms are 1700–2000 for the first and 4900–5500 cal/g for the second exotherm. The areas of the curves were obtained by doubling the area of the first half of the first peak and the last half of the second peak, respectively. The thermogravimetric curve for the same polymer under the same conditions of air flow and heating rate showed a large weight loss between 410 and 425°C, which probably corresponds to the first exotherm of the calorimetry curve. Approximately 50% of the initial weight of sample had been lost after the first exotherm; therefore 1.4 mg was used as the mass of the polymer in the calculation of ΔH from the second exotherm.

Even though the calculated heats of reaction in this study can be considered to reflect only the relative order of magnitude of the true heats of reaction, it seems evident that much more information can be obtained from calorimetric studies than from simple differential thermal analysis. The evidence, however, indicates that when the Schiff base polymers are heated to 1000°C, they have not been converted to graphitic polymers.

When a polymer is subjected to ionizing radiation, either a cross-linked or degraded polymer is obtained (14–19). The amount of cross-linking and degradation which occurs in a polymer has been shown to be dependent on a number of factors: (1) the monomer and polymer structures, (2) the effect of oxygen, (3) the protection of aryl groups, (4) the linkages present in the polymer, and (5) the molecular weight. Hence the requirements for radiation stability parallel those for thermal stability, and polymers which have been shown to possess thermal stability are also generally radiation-resistant. For example, the thermally stable polyimidazopyrrolones possess good rediation stability as well as thermal stability (20). Polymers possessing aromatic structures in the backbone appear to be especially resistant to radiation. Thus it has been shown that aliphatic saturated polyesters possess poorer radiation resistance than polyesters containing aromatic moieties such as polyethyleneterephthalate (21). The effect of these aromatic moieties is to act

as energy sinks which are able to delocalize either thermal or radio-lytic energies and hence to protect the polymer structure from gross degradation.

From these considerations, the high molecular weight, conjugated Schiff base polymers prepared in this research are also expected to possess very high radiation resistance. A Schiff base polymer which would be expected to possess high radiation resistance is the completely conjugated polymer, poly(p-xylylidene-phenylenediamine),

$$\text{=}N\text{--}\langle\bigcirc\rangle\text{--}N\text{=}HC\text{--}\langle\bigcirc\rangle\text{--}CH\text{=}_n$$
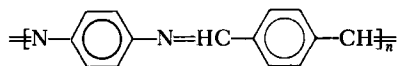
This polymer has been shown (1–3) to possess high thermal stability in nitrogen and in air. Owing to the nature of its conjugation, this polymer would be expected similarly to dissipate and delocalize radiolytic energies.

Thus it was decided to evaluate the radiation resistance of the Schiff base polymers by comparing the thermal stability of the polymers before and after irradiation. The polymers I-B-H400, poly(p-xylylidene-p-phenylenediamine), as prepared at 400°C, and I-B-H600, which was condensed to 600°C, were taken to be representative of Schiff base polymers in general, and were investigated in this study. This study was undertaken with polymers which had been irradiated (1) in vacuo, (2) sealed in an atmosphere of air, and (3) exposed to air during irradiation.

The thermograms in nitrogen and in air for polymers I-B-H400 and I-B-H600 irradiated in vacuo are shown in Figs. 13 and 14, respectively. Comparisons of these thermograms with the corresponding thermograms of nonirradiated samples show no detectable difference in thermal stabilities of polymers before and after irradiation. The pressure in the sample vials, after irradiation, was still very low, indicating that no appreciable amounts of gas was generated during the irradiation process.

That oxygen contributes to the overall effect of radiation damage is well known. It was, therefore, decided to determine the effect of this parameter on the radiation stability of polymers irradiated in this atmosphere. The thermograms in nitrogen and in air for I-B-H400 and I-B-H600 after irradiation while sealed in an atmosphere of air are given in Figs. 15 and 16, respectively.

Comparison of these thermograms with those obtained from pre-

vious nonirradiated samples shows no detectable diminution of the thermal stability due to irradiation.

Since there could be a difference in the thermal stabilities of samples sealed in air and samples left exposed to air during irradiation, it was decided to investigate this parameter. The thermograms in nitrogen and in air of these polymers, I-B-H400 and I-B-H600, after irradiation while exposed to air are shown in Figs. 17 and 18, respectively. In these cases, as in the others, little or no difference can be distinguished in the thermograms before and after irradiation.

The thermograms in air of polymer I-B-H600 before and after irradiation in air under an electron beam to a dose of 1000 Mrad were substantially identical to each other and to the thermogram in air of I-B-H600 in Fig. 18.

These irradiation studies confirm the prior assumption that Schiff base polymers possessing a high degree of thermal stability would also possess high radiation stabilities. The radiation stability was shown to be independent of dose rate, varying from 1.2 to 18,000 Mrad/hr; and the nature of two sources, electron and cobalt, at dosages varying from 200 to 1000 Mrad.

Acknowledgments

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Zassumenfassung

Thermogravimetrische Analysen von Poly(*p*-Xylyliden-*p*-phenylendiamin) in Helium und Luft ergeben Stabilitätswerte, die im wesentlichen mit im Vacuum erhaltenen Daten übereinstimmen. Die entsprechenden thermischen Stabilitätswerte in Stickstoff und Luft ändern sich nicht bei vierfacher Änderung der Gasflussgeschwindigkeit. Etwas geringere Werte wurden bei Erhitzungsgeschwindigkeiten von 5°C bis 15°C pro Minute erhalten als bei 30° pro Minute. Die thermischen Stabilitäten sind geringer in Sauerstoff als in Luft, sind aber immer noch relativ hoch. Höhere scheinbare thermische Stabilitäten werden beobachtet, wenn die pulverförmige Probe von 10 mg als einheitliche Masse und nicht als feines Pulver betrachtet wird. Kalorimetrische Messungen zeigen, dass Polymere auf der Basis von Schiff'schen Basen, wenn sie in Stickstoff auf 1000 bis 1200°C erhitzt worden waren, nicht in graphitartige Polymere umgewandelt werden. Die Polymeren auf der Basis von Schiff'schen Basen sind strahlungsbeständig; ihre Stabilität ist unabhänig von der Strahlungsmenge und der Art der ionisierenden Strahlung.

Résumé

Les analyses thermogravimétriques de la poly(*p*-xylylidène-*p*-phenylenediamine) en atmosphère d'azote, d'hélium et dans l'air donnent des valeurs de stabilité identiques aux valeurs obtenues avec des éssais dans le vide. Les valeurs respèctives de stabilité thermique dans l'azote et dans l'air restent unchangées dans un intervale quadruplé du debit. Avec des vitesses de chauffage de 5°C à 15°C per minute on a trouvé des valeurs légèrement

plus petites qu'avec des vitesses de 30°C per minute. Les stabilités thermiques sont plus basses dans l'oxygène que dans l'air, mais ces valeurs sont encore relativement hautes. Des valeurs apparentes de stabilité thermique plus elevées sont observées lorsq'un échantillon de 10 milligrams en poudre est traité comme une masse simple plutôt qu'une poudre fine. Les mésures calorimétriques indiquent que les polymères de bases de Schiff chauffés à 1000–1200°C en atmosphère d'azote ne se transforment pas en polymères du type graphitique. Les polymères de bases de Schiff sont résistants à la radiation; leurs stabilité est indépendent du debit de dose et de la nature de la radiation ionisante.

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