Relative Thermophysical Properties of
Some Polyimides

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Synopsis

A comparative thermogravimetric study of ten polyimide films of varying composition revealed that thermal and thermo-oxidative stability of the polymers increases directly with increasing imide content. Films degraded more rapidly in air than in vacuo; the insertion of connecting groups within the polymer repeat unit decreased stability in both environments. The effect of inserting "ladder-like" segments in the polymer structure did not enhance resistance to oxidation; but under vacuum, those segments probably operated beneficially in promoting the retention of the carbon-like residue. Infrared spectral measurements showed little loss of imide bands with progressive weight loss in air, indicating unit-by-unit degradation. Conversely, infrared spectra of films heated under vacuum conditions showed that progressive loss of imide bands occurred simultaneously with an increasing development of bands related to carbon–nitrogen double bonds. Dynamic heating under vacuum developed singularly uniform weight loss curves; however, concurrent mass-spectrographic analyses indicated two distinct reactions. Gaseous carbon monoxide and carbon dioxide species accounted for the major weight change, and their periods of maximum evolution occurred at different temperatures for each film. A subsequent minor weight loss period was associated with the liberation of hydrogen cyanide which maximized at the same temperature for all ten films.

INTRODUCTION

A series of thermogravimetric analyses was conducted on ten structurally different polyimide films in an attempt to relate chemical structure to changes occurring during thermal and thermooxidative degradation. Numerous publications have been concerned with the thermal decomposition of polyimides. Bruck[1] outlined the effect of impurities on weight loss rates and activation energies when a commercial polyimide film was heated isothermally in air and under vacuum. Heacock and Berr[2] analyzed the products evolved in the vacuum pyrolysis of the same polyimide film. Further detailing the pyrolysis of polypyromellitimides, Gay and Berr[3] relied upon changes in infrared spectra to attribute the source of carbon dioxide to be from isoimide decomposition and carbon monoxide to be from normal imide decomposition. Other investigators[4] noted that films derived from wholly aromatic polypyromellitimides retained toughness for months at moderately elevated temperatures in air. Ehlers, Fisch, and Powell[5] reported that no significant differences, either in weight loss or in
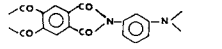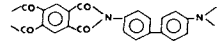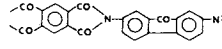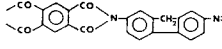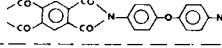
volatile products, resulted when several polyimides of varying composition were degraded isothermally. Jones[6] reviews the principal objectives in thermal stability studies as well as many complications which hinder definitive conclusions with regard to heat-stable polymers.
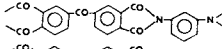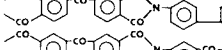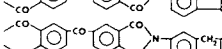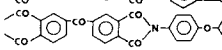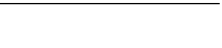
This present study treats the observed differences between the thermal stabilities of ten polyimides, formed from combinations of two dianhydrides and five diamines. All films were synthesized in-house, with close control over film thickness and curing conditions in order to minimize variations in sample geometry and sample history.

EXPERIMENTAL

The theoretical polymer repeat units and their abbreviations are shown in Table I. The polyimides were prepared by standard methods[7] using pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA). Each dianhydride was polymerized with five different diamines: m-phenylenediamine (PDA), benzidine, 2,7-diaminofluorenone (DAFO), 2,7-diaminofluorene (DAF), and 4,4'-diaminodiphenyl ether (ODA).

TABLE I
Polyimide Repeat Units

1.	PMDA-PDA
2.	PMDA-BENZIDINE
3.	PMDA-DAFO
4.	PMDA-DAF
5.	PMDA-ODA
6.	BTDA-PDA
7.	BTDA-BENZIDINE
8.	BTDA-DAFO
9.	BTDA-DAF
10.	BTDA-ODA

Films were formed by casting the polyamic acid solutions onto glass plates and drying them in a forced airflow oven at 125°C for 1 hr. The films were stripped from the plates and postcured in air at 300°C for 2 hr. Weight loss samples consisted of two discs, each 0.635 cm in diameter with nominal thicknesses of 0.0025 cm, to provide initial sample weights of 2.05 ± 0.03 mg. Separate specimens 0.00025–00.00050 cm (0.1–0.2 mil) thick were used for infrared study.

The thermogravimetric apparatus used has been described previously.[8] Infrared spectra were obtained with a Perkin-Elmer 421 spectrophotometer.

The initial weight was taken as the weight of the sample after it had been preconditioned at 100°C for 30 min to eliminate absorbed moisture. The temperature was then increased 1°C/min until sample pyrolysis was complete or until 800°C was reached.

Residual gas measurements were obtained at 10°C intervals over the 2–110 mass range, with emphasis placed upon peaks from mass 2 to 50. Spectra were recorded from 1×10^{-8} torr, the background pressure, to 3×10^{-6} torr. For each spectrum individual partial pressures additively accounted for no less than 90% and no more than 100% of the observed total pressure.

RESULTS AND DISCUSSION

Figure 1 compares the behavior in air of one of the polymers, PMDA–PDA, with its behavior in vacuo. It can be seen that thermo-oxidation begins to deviate from an initial "straight line" decomposition at about 480°C, and similarly that thermal degradation in vacuo begins at about 580°C. The difference in behavior in the two environments shown by PMDA–PDA is typical of the ten polymers. In the following discussion, the temperature of onset of increasing rate of weight loss, as marked by a triangle in Figure 1, was considered the criterion for loss of stability. Garn[9] noted that initial changes in the slopes of thermogravimetric curves are probably more characteristic of the apparatus than of the reaction proper, and any temperatures associated with this region of weight change have no validity in quantitative evaluations of the reaction. However, under a given set of conditions, temperatures denoting "onset of decomposition" are fairly reproducible, so that differences in the initial thermal behavior of closely related polymers can be qualitatively discussed.
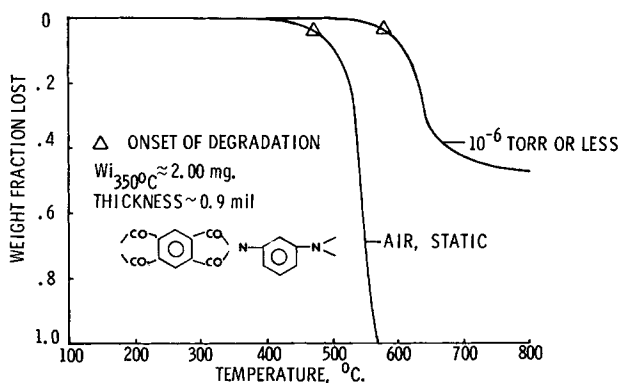

Fig. 1. Thermograms of PMDA–PDA heated in air and in vacuo at 1°C/min.

Stability in Air

Figure 2 compares polymers prepared by the reaction of a common dianhydride (PMDA) with five different diamines.   Figure 3 presents similar results for a series in which the common dianhydride was BTDA.   The relative order of thermo-oxidative stability was the same for both series of polymers.   The decreasing order of stability was benzidine, PDA, DAFO, DAF, and ODA.   Onsets of rapid change occurred over the temperature region of 445°C to 495°C.

A comparison of polymers prepared from a common diamine but with different dianhydrides indicates that the PMDA imparts slightly more re-
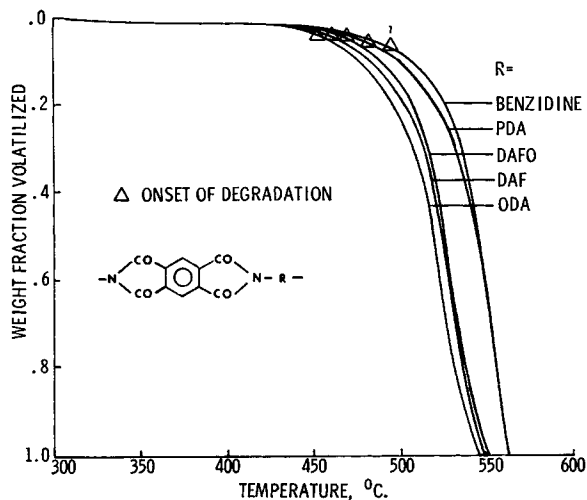

Fig. 2. Thermograms of polyimide films prepared from pyromellitic dianhydride and heated in air at 1°C/min.
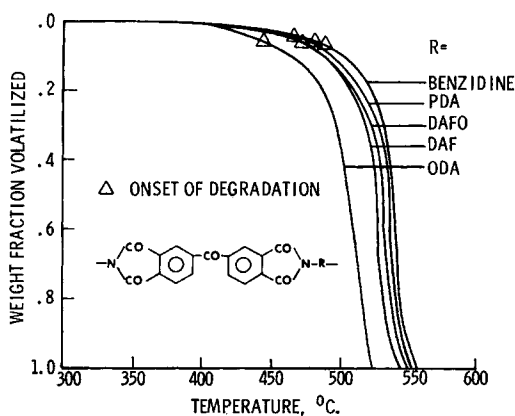

Fig. 3. Thermograms of polyimide films prepared from 3,3′,4,4′-benzophenone tetra-carboxylic dianhydride and heated in air at 1°C/min.
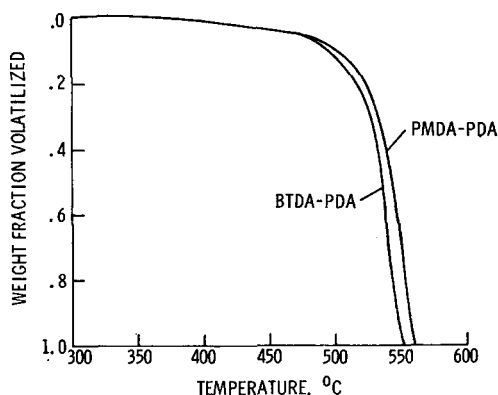
Fig. 4. Effect of dianhydride structure on weight loss of PDA polyimide films heated in air at 1 °C/min.
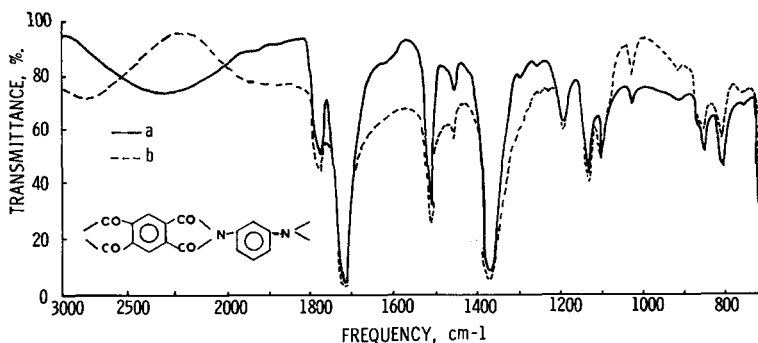

Fig. 5. Change in IR spectra for PMDA–PDA thin film: (a) cured in air at 400°C for 1 hr; (b) subsequently heated in air at 1°C/min to 520°C, reflecting a 20% weight loss.

sistance to degradation in air than does BTDA, regardless of the diamine used. This effect of changing the dianhydride structure is illustrated in Figure 4 for polymers based on PDA. The most significant difference between the two dianhydrides, PMDA and BTDA, is the carbonyl group separating the two aromatic rings in the benzophenone structure. This seems to signal a more general effect: The insertion of connecting groups between phenyl and benzimide rings in the polymer structure, whether in the dianhydride portion or the diamine portion, decreases the thermo-oxidative stability of the polymer. Figures 2, 3, and 4 are consistent with this interpretation, which is further confirmed by Figure 5, in which it is shown that little loss of imide infrared absorption bands results upon heating a well-cured thin film of PMDA–PDA to a 20% weight loss. This particular infrared spectrum, which is typical of those for the other polymer compositions, probably more properly demonstrates simple changes in optical density resulting from a decrease in film thickness by a unit-by-unit surface degradation.
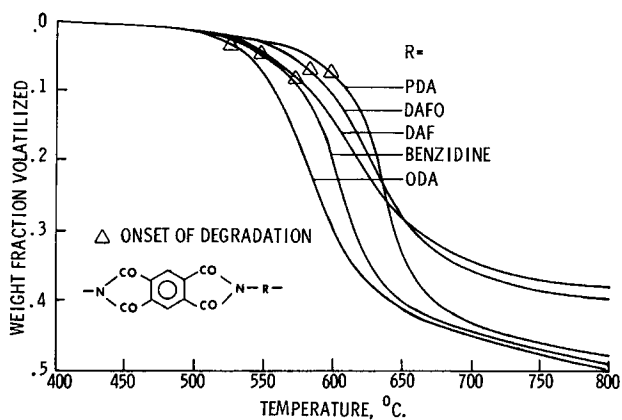
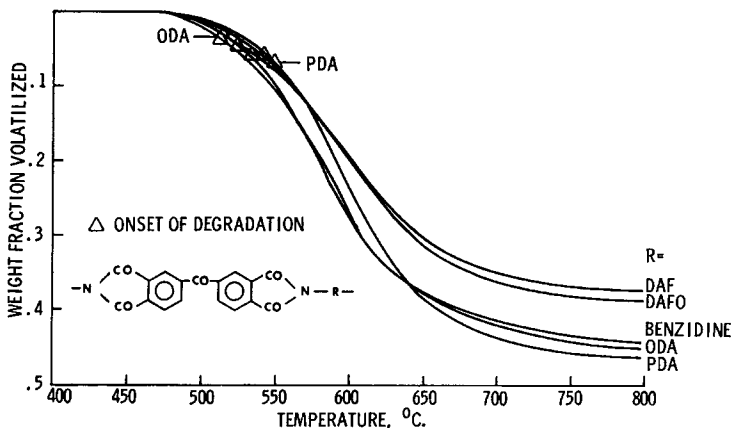Fig. 6. Thermograms of polyimide films prepared from pyromellitic dianhydride and heated in vacuo at 1°C/min.

Fig. 7. Thermograms of polyimide films prepared from 3,3',4,4'-benzophenone tetra-carboxylic dianhydride and heated in vacuo at 1°C/min.

Figure 6 compares thermograms, developed in vacuo, of polymers pre-pared from the common dianhydride PMDA with five different diamines and Figure 7 presents similar results for the BTDA series. Onsets of rapid weight loss occurred between 520°C and 600°C. The relative orders of thermal stability were the same for polymers from both dianhydrides; and, with the exception of the thermograms for the benzidine films, the order of stability was quite similar to that found upon heating in air. Figure 8 shows the effect of changing dianhydride for the two benzidine films and typifies the decrease in resistance to thermal degradation where BTDA is used. As in air, the insertion of connecting groups into the polymer structure lowers the temperature at which weight loss com-mences; that is, a reduction of imide content by adding nonaromatic con-nectors decreases stability. The fact that the PMDA–benzidine and
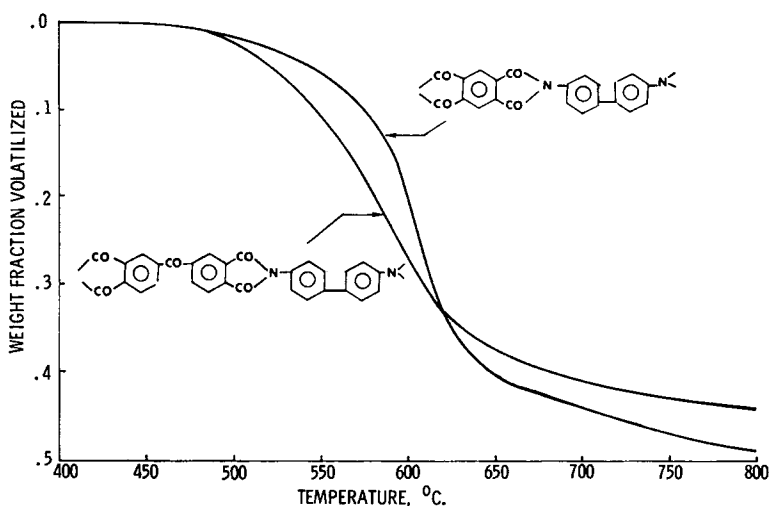
Fig. 8. Effect of dianhydride structure on thermal stability of benzidine type polyimide films heated in vacuo at 1°C/min.
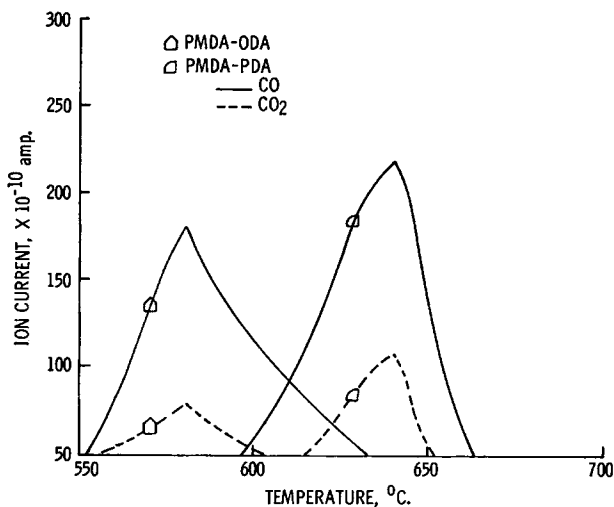

Fig. 9. Rates of evolution of masses 28 and 44 for two polyimide films heated in vacuo at 1°C/min. (Data uncorrected except for background contributions.)

BTDA–benzidine films rank so high in thermo-oxidative stability, yet display only moderate thermal stability under vacuum environment, deserves special mention. Although others[4] reported the thermal stability of PMDA–benzidine film to be slightly superior to several other PMDA-derived polyimides in air and in dry helium, it is well known that the behavior of a polymer in a vacuum may be quite different from that in an inert atmosphere. These particular contrasting results serve as a reminder that one must draw conclusions from thermogravimetric analysis (TGA) studies with caution.

Mass-spectrographic analysis of gases evolved during thermal degradation showed that CO and CO_2 were the major species liberated for each of the ten polymers. Their rates of evolution for two films, PMDA–PDA and PMDA–ODA, are presented in Figure 9, in which the temperatures at which maximum evolution of CO occurs coincides with the temperatures at which maximum rates of weight loss occurs. In Figure 10, the CO maxima for all ten of the polyimides range widely between 580°C and 640°C, representing a difference of 1 hour in total heating time. This suggests that in the polyimides studied, the stability of the imide group is sensitive to external structural features, such as the connectors between the benzene rings. In the same graph, the CO evolution for eight polyimidazopyrrolone
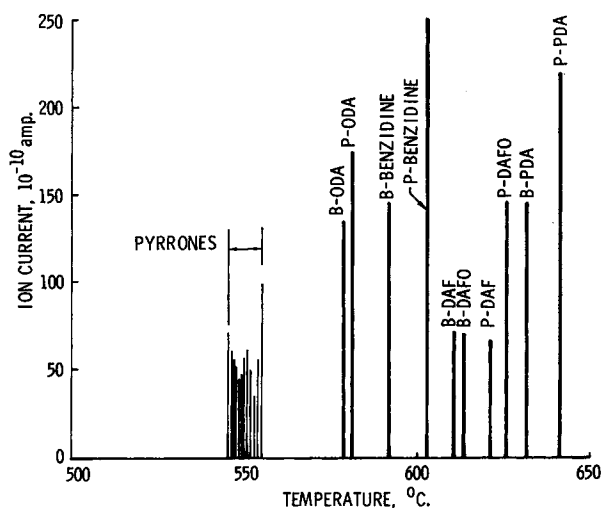

Fig. 10. Maximum rate of evolution of mass 28 for 10 polyimide films heated in vacuo at 1°C/min.

films maximized over a very narrow range at 550 ± 5°C, denoting not only the slight variation in energy, irrespective of structure, required to split out the carbonyl moiety, but also a relatively early loss of imide character in the imidazopyrrolone grouping.[10]

Figure 11 presents plots of the temperatures at maximum evolution of carbon monoxide versus the temperatures at onset of decomposition in vacuo for the ten polyimides. The straight-line function developed for each dianhydride set indicates not only a correlation between residual gas measurements and thermogravimetric data but perhaps more importantly demonstrates the homologous polymeric structure of each set. The slopes of the straight lines, 1.03 for the PMDA films and 0.65 for the BTDA films, delineates the increase in thermal stability exhibited by use of PMDA.

Infrared spectra of thin films heated in vacuo at 1°C/min showed progressive loss of imide bands at 1780, 1720, and 720 cm^{-1}, as well as the emergence of absorption bands at 1620 and 740 cm^{-1} assigned to C=N
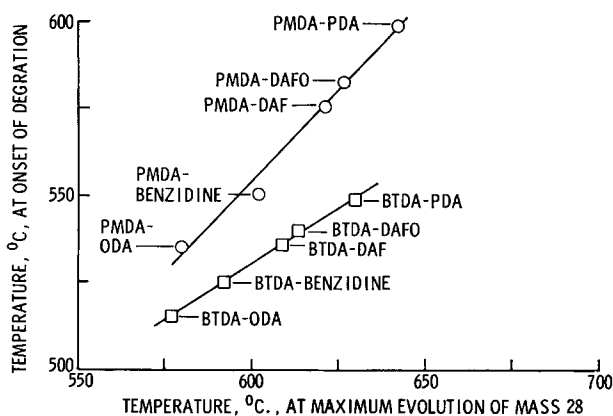
Fig. 11. A plot of the temperature at maximum evolution of mass 28 vs. the temperature at onset of decomposition for ten polyimide films heated in vacuo at 1°C/min.
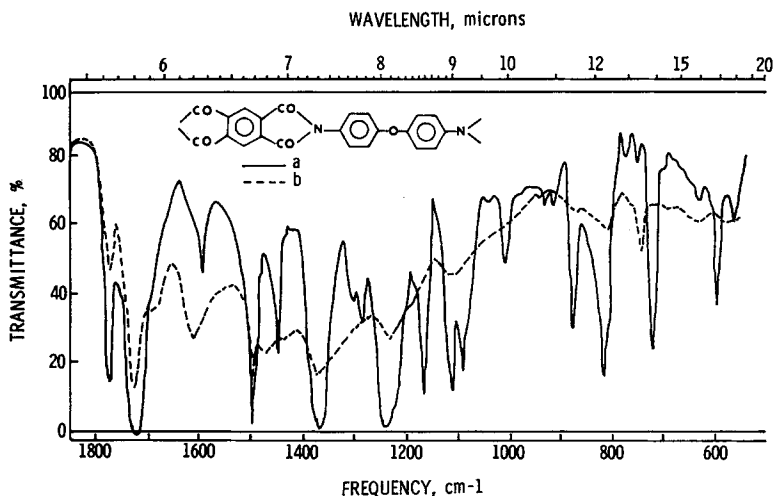

Fig. 12. Changes in infrared spectra of PMDA–ODA; (a) cured at 400°C for 1 hr in vacuo; (b) subsequently heated in vacuo at 1°C/min to 35% weight loss.

stretching vibrations. Figure 12 depicts the changes in IR spectra for a PMDA–ODA specimen which experienced a 35% weight loss. The growth of the 1620-cm^{-1} band could suggest significant decomposition of previously formed isomide structure, as proposed by Gay and Berr,[3] and/or formation of carbodiimide linkages, as proposed by Ehlers, Fisch, and Powell.[5]

Although each thermogram was singularly smooth such that even a first derivative (rate of weight loss curve) developed one maximum, mass spectral data indicated a secondary period of weight loss, associated with nitrogenous gaseous species and particularly with mass 27, which was assumed to be HCN. Unlike the evolution of CO, CO_2, H_2O, and other minor
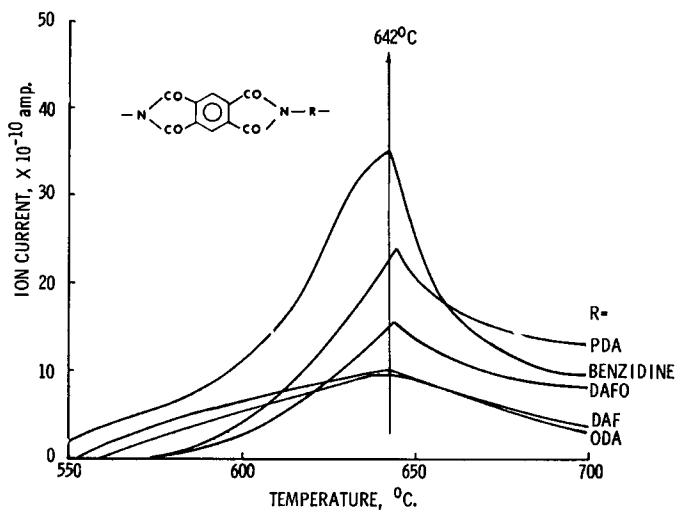
Fig. 13. Rate of evolution of mass 27 for 5 polyimide films prepared from pyromellitic dianhydride and heated in vacuo at 1°C/min.

gases which maximized at different temperatures for each polymer, the release of HCN was mainly centered at the same temperature, 640°C, for all ten films. Figure 13 shows the rate of evolution of mass 27 for the five films prepared from PMDA. In conjunction with the IR spectral changes previously noted, the source of HCN evolution might arise from remnant C=N linkages in isoimide or carbodiimide groupings, which prompts the suggestion that polyimide thermal degradation is a two-step process. While studying the thermal conversion of a polyimide into a semiconductor, Bruck[11] noted such two-step results, but attributed the second step to molecular reorganization rather than to weight change.

At 800°C in vacuo, thermograms (Figs. 6 and 7) developed plateaus where weight losses ranged between 37% and 49%. The DAF and DAFO films, with the doubled bridging along the benzenoid backbone, retained considerably more carbonaceous polymeric residue. The slopes of their curves are more gentle by comparison. These results suggest that such bridges probably exert a beneficial effect on the stability of the carbonaceous residue.

CONCLUSIONS

Thermal and thermo-oxidative stability of polyimides appears to increase directly with increasing imide content, to such an extent that insertion of connecting groups into the polymer repeat unit decreases resistance to degradation because of dilution of the percentage of imide content.

The effect of inserting ladder-like segments in polyimides probably does not enhance their thermo-oxidative stability. However, when polyimides are subjected to dynamic heating in vacuo, this added bridging probably

operates in some manner to reduce the rate of weight loss, as well as the total weight loss, of the carbonaceous residue upon heating to 800°C.

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