Photodegradation of Polyimides. II. Thermal Property Changes of Polyimides Based on a Hexafluorinated Dianhydride

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SYNOPSIS

Polyimides based on a hexafluorinated dianhydride decrease in thermal and thermal-oxidative stability upon photolysis with an unfiltered medium pressure mercury lamp source in air. Additionally, the glass transition of photolyzed polyimides containing the hexafluorinated moiety is lowered with increasing photolysis time. By contrast, pyromellitic-dianhydride-based polymers are relatively thermally stable even after prolonged photolysis under similar conditions.

INTRODUCTION

The degradation of polymeric materials which are exposed to ultraviolet radiation continues to be the subject of a large number of investigations. Despite extensive studies on most engineering plastics and surface coatings comprised of almost every conceivable type of basic polymer structure, there are surprisingly few reports in the literature on the photostability of polyimides.[1-4] Perhaps the scarcity of data on the photodegradation of polyimides is due to the well-known relative stability of polyimides based on pyromellitic dianhydride and aromatic diamines such as 4,4'-oxydianiline. Because such polymers are only degraded upon prolonged exposure to a broad band UV source,[1] the tendency is to assume that all aromatic-based polyimides regardless of structure are equally photostable.

As shown in the literature,[5] polyimides derived

from bisaromatic dianhydrides with a bridging hexafluoroisopropylidene (6F) group have thermal decomposition properties which are comparable to those of polyimides based on bisaromatic dianhydrides containing other bridging groups such as oxygen or carbonyl moieties. The so-called 6F polyimides[3,5-8] are also readily soluble in a number of solvents and due to their structure do not display a significant red shifted absorbance above 350 nm as is characteristic of so many aromatic based polyimides. In a recent paper,[9] we reported on the spectroscopic (UV, Fluorescence, FT-IR), chromatographic (GPC), and viscometric (inherent viscosity) changes resulting from photolysis of two 6F-based polyimides (shown below—designated 6F-ODA and 6F-MDA) and analogous polyimides based on pyromellitic dianhydride (PMDA) and the same two diamines (designated PMDA-ODA and PMDA-MDA). In addition, weight loss measurements were conducted for films photolyzed with a broad band (unfiltered) 450 W medium pressure mercury lamp. All of our results indicate the photolability of the 6F-based polyimides. In this second

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paper in a series of reports on the photochemistry of polyimides, we concentrate on the thermal changes resulting from the photolysis of the two 6F-based polyimides 6F-MDA and 6F-ODA in air:
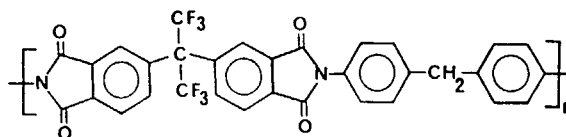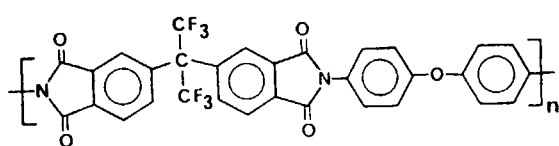
EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA, Aldrich) was recrystallized from methyl ethyl ketone (MEK) and vacuum sublimed prior to use. Polymer grade 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride (6F, Hoechst Celanese) was used without further purification. 4,4'-Oxydianiline (ODA, American Tokyo Kasei) was recrystallized from ethanol and sublimed under vacuum. 4,4'-Methylenedianiline (MDA, Aldrich) was vacuum distilled. Dimethylacetamide (DMAc, Aldrich) used as the solvent in the polymerizations and the viscometric analyses was dried over molecular sieve 4A and fractionally distilled under vacuum from calcium hydride.

Synthesis

The preparation of the polyimide thin films has been described in the first paper of this study.[9]

Photolysis

The photolyses were conducted using the full unfiltered arc of a 450 W Canrad-Hanovia medium pressure mercury lamp in air. Films were placed approximately 9 cm from the lamp.

Thermal Analysis

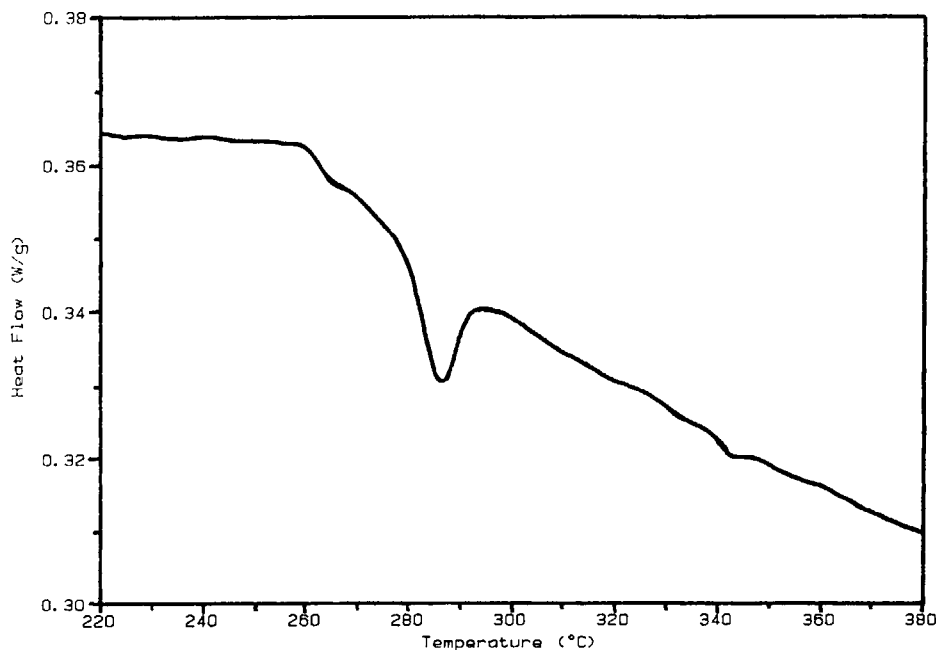A DuPont 9900 thermal analyzer was used for the thermogravimetric analysis (TGA) and DSC scans.

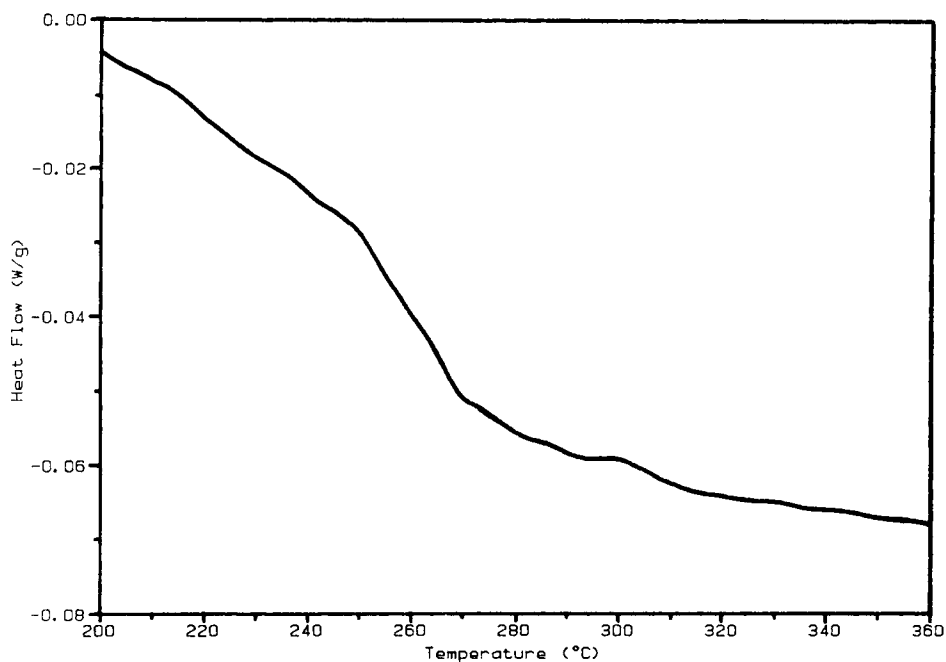**Figure 1**   DSC thermogram of unphotolyzed 6F-ODA film.

Figure 2   DSC thermogram of 6F-ODA film photolyzed for 20 h in air using a medium pressure mercury lamp (unfiltered).

DSC and dynamic TGA scans were obtained with 10°C/min temperature ramps. During the TGA experiments a continuous flow of the desired gas (nitrogen or air) was maintained through the sample compartment.

RESULTS AND DISCUSSION

Data will be presented for thermal property changes resulting from photolysis with the unfiltered output of a medium pressure mercury lamp. Actual iden-
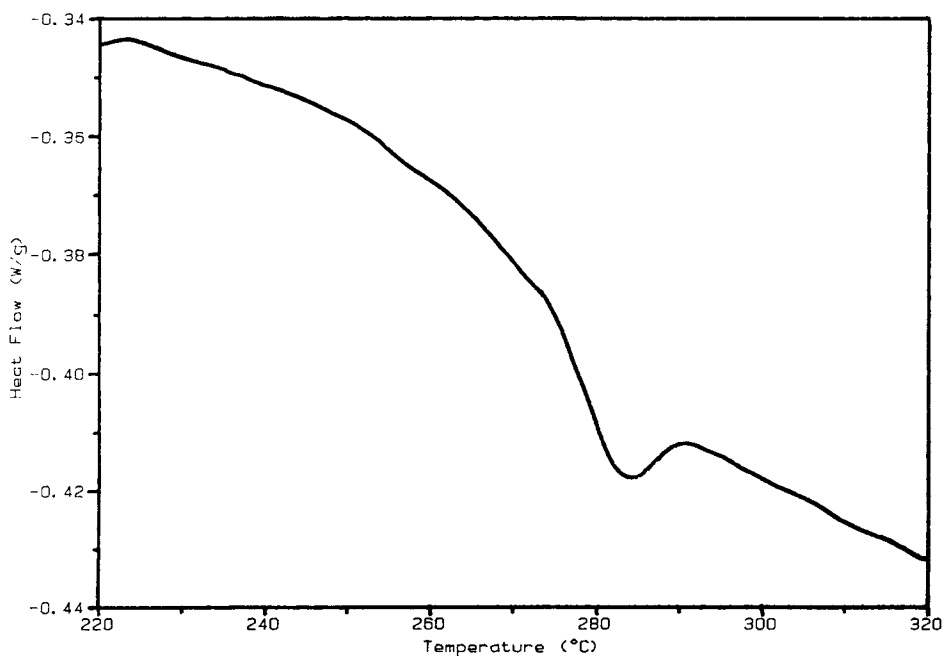

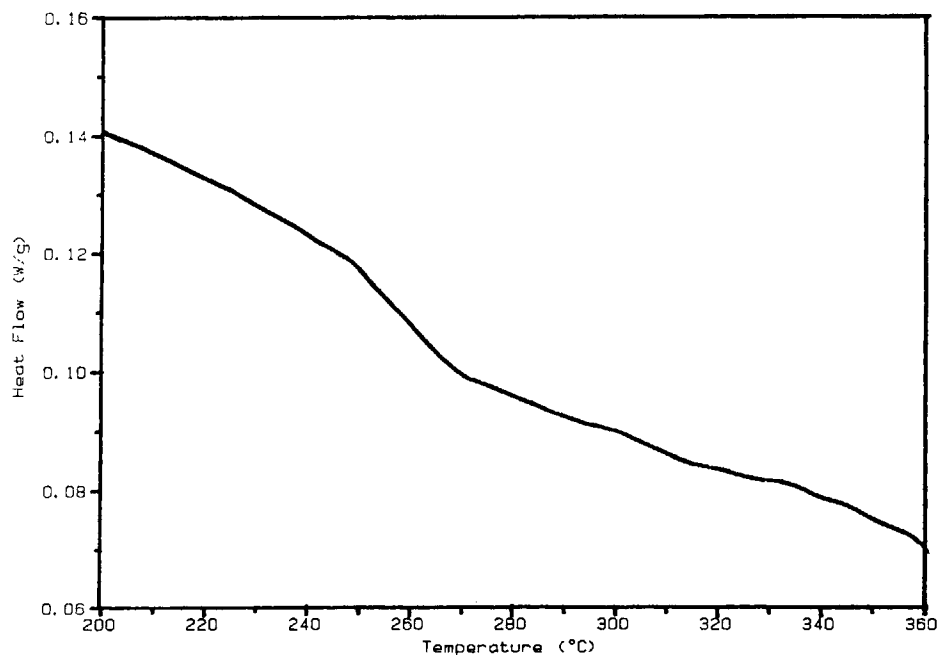**Figure 3**   DSC thermogram of unphotolyzed 6F-MDA film.

Figure 4   DSC thermogram of 6F-MDA film photolyzed for 20 h in air using a medium pressure mercury lamp (unfiltered).

tification of the photoproducts generated and the mechanism of primary photolysis is relegated to a separate paper which will deal with the photochemistry of small molecule aromatic imides as well as the imide chromophores in the polyimides. Due to

the complexity of the photochemistry, it is necessary to treat this subject in a separate paper.

Figures 1-4 show the DSC scans of the 6F-ODA and 6F-MDA polymer films in air before and after exposure of films for 20 h to the broad unfiltered
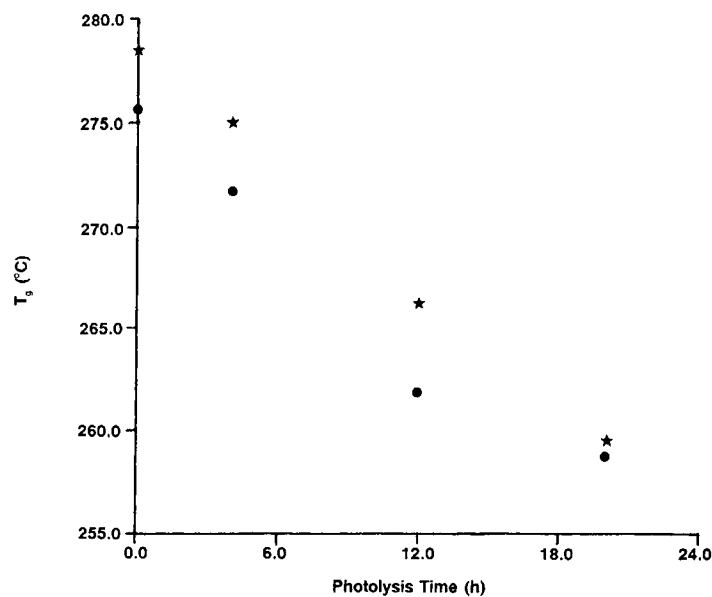

Figure 5 T_g change on photolysis of polyimide films in air using a medium pressure mercury lamp (unfiltered): (a) 6F-ODA (★); (b) 6F-MDA (●).
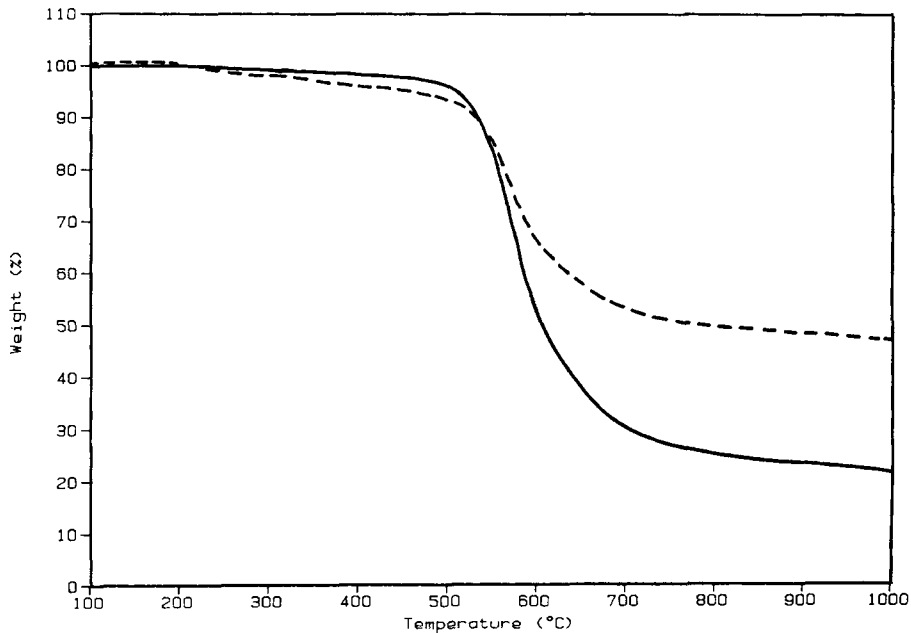
Figure 6   Change in TGA thermograms (nitrogen) on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (——); (b) 12 h (– – –).

output of a 450 W medium pressure mercury lamp. The unphotolyzed samples exhibit a hysteresis after passing through glass transition at 278°C (Fig. 1, 6F-ODA) and 276°C (Fig. 3, 6F-MDA). The hys-

teresis is present on both the first and second heating runs. The photolyzed samples (Figs. 2 and 4) show loss of the hysteresis accompanied by a shift in the glass transition by approximately 20°C in each case.
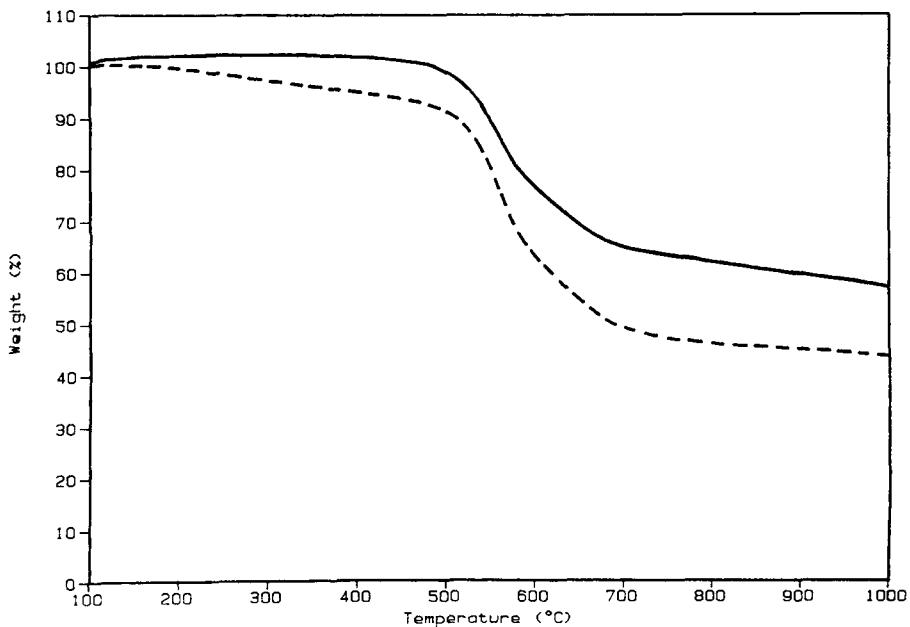

Figure 7   Change in TGA thermograms (nitrogen) on photolysis of 6F-MDA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (——); (b) 12 h (– – –).
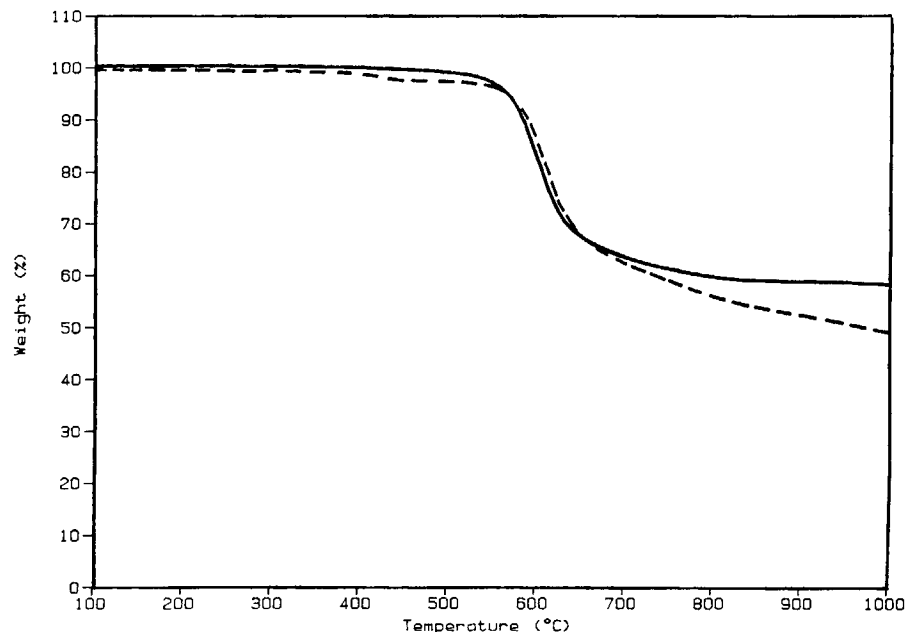
Figure 8   Change in TGA thermograms (nitrogen) on photolysis of PMDA-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (———); (b) 12 h (- - -).

Figure 5 shows a plot of T_g versus photolysis time for the 6F-ODA and 6F-MDA polymers films in air. In view of the reported loss in molecular weight reported in our previous paper,[9] for 6F-ODA and 6F-MDA upon photolysis, the drop in T_g and subsequent loss of heteresis seems fairly reasonable since one might expect considerable reorientation to result from chain cleavage. This is consistent with the reported relative photolytic stability of the PMDA-based polyimides.[9]

One of the prime considerations for any polyimide is its thermal stability in the absence of oxygen. Figures 6 and 7 show TGA scans for unphotolyzed and photolyzed 6F-ODA and 6F-MDA polymers films in air. For comparison a TGA scan of PMDA-ODA is also shown in Figure 8 before and after photolysis. The temperatures for weight loss (nitrogen atmosphere) at 5% ($T_{5\%}$) as well as the temperature (T_{max}) at the derivative maximum $(dw/dT)_{max}$ are listed in Table I for PMDA-ODA, 6F-ODA, and 6F-MDA. From the rather straightforward results in Table I, the loss in simple thermal stability in nitrogen atmosphere of the 6F-ODA and 6F-MDA polyimides is quite evident as judged by the reduction in temperature required for weight loss of 5% for the photolyzed samples. Interestingly, however, the temperature at the derivative maximum (T_{max})

did not change to any appreciable extent after photolysis.

To assess the thermal oxidative stability of the 6F polymers after photolysis, dynamic and static (isothermal) TGA scans were conducted for the 6F-ODA polyimide for photolyzed and unphotolyzed samples. The dynamic scan (Fig. 9) shows a temperature for 5% weight loss of 351°C for the photolyzed sample compared to 524°C for the unphotolyzed sample. The isothermal results (continuous air purge, 460°C) in Figure 10 show an immediate drop in weight of about 20% for the photolyzed sample (curve b) as the system is establishing thermal

Table I   TGA Results for Photolyzed Samples

Polymer	Photolysis Time (h)[a]	$T_{5\%}$ (°C)	T_{max} (°C)
6F-ODA	0	513	575
6F-ODA	12	446	568
6F-MDA	0	532	561
6F-MDA	12	384	561
PMDA–ODA	0	564	600
PMDA–ODA	12	568	609

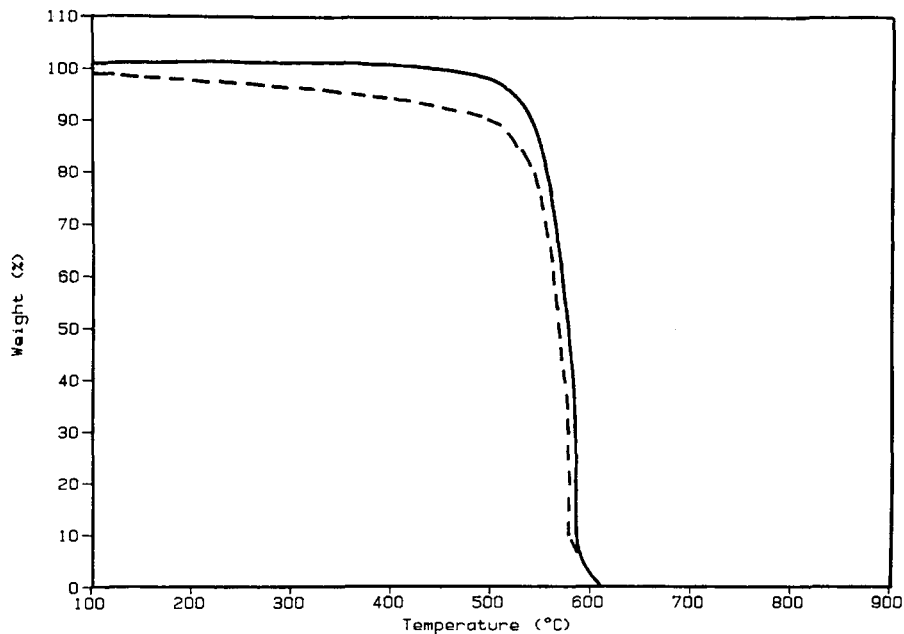[a] Photolysis with a medium pressure mercury lamp in air.

Figure 9   Change in TGA thermograms (air) on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (———); (b) 12 h (– – –).

equilibrium. Subsequent heating for 2 h shows a marked decrease in weight to about 30% of the original value. By contrast, the unphotolyzed sample shows a rather modest decrease to about 70% of the

original weight in two hours. The combined results in Figures 9 and 10 demonstrate the destructive nature of the photolysis of the 6F-ODA polyimide film with respect to thermal oxidative stability. Similar
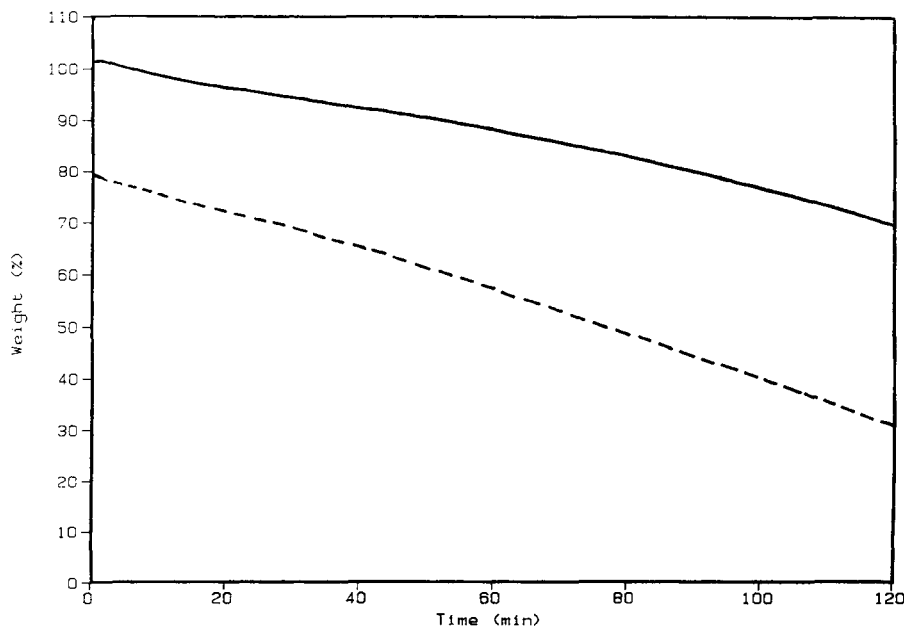

Figure 10   Change in isothermal TGA thermograms (air) at 460°C on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (———); (b) 12 h (– – –).

results were obtained for the 6F-MDA polyimide. The PMDA–ODA polyimide, however, shows essentially no loss in thermal oxidative stability upon photolysis under similar conditions.

CONCLUSIONS

We have demonstrated the results of exposure of 6F-based polyimide films in air to a medium pressure mercury lamp on their thermal stability. In oxygen and nitrogen atmospheres the thermal stability of the 6F-ODA and 6F-MDA polymers are measurably impaired. In addition, DSC scans show a significant drop in the glass transitions of photolyzed films with accompanying loss of the hysteresis present in the unphotolyzed films. We are currently in the process of conducting similar studies on a wide variety of polyimides with different structural features. We also plan to extend our investigations to higher molecular weight polyimides. Also photolysis with lamp sources which have been filtered to remove radiation below 300 nm will no doubt yield somewhat different results from those reported in this manuscript. However, the present study is valuable since it serves to illustrate the deleterious effect of a moderate intensity broad band mercury lamp source on the thermal stability of a certain class of 6F polyimides generated under a specific set of reaction conditions. Finally, it should be noted that photolysis of both the 6F-ODA and 6F-MDA films in the absence of oxygen results in a substantial decrease in the rate of degradation.

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