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Ultraviolet Stability of Polymers Containing the Hexafluoroisopropylidene Group

by

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# Ultraviolet Stability of Polymers Containing the Hexafluoroisopropylidene Group

C. E. Hoyle\*, R. Nagarajan\*, and E. T. Anzures\* & P. E. Cassidy† and K. M. Kane†

The photodecomposition of four polymer series containing the hexafluoroisopropylidene (6F) moiety was studied. We report herein the photostability of a poly(ether ketone) series when subjected to UV light in air. Replacement of isopropylidene with 6F results in decreased photostability for the PEKs as evidenced by changes in molecular weight and IR and UV-VIS spectra. The results for the polyamides, polyimides, and polyarylates will be discussed at the presentation.

## INTRODUCTION

A sizable research effort has been expended over the past 25 years directed toward incorporation of the hexafluoroisopropylidene (HFIP or 6F) group into polymer backbones.<sup>1,2</sup> This approach has yielded solution- or melt-processable materials from previously intractable polymers. Many of the new polymers developed are good candidates for gas separation membranes, seals, coatings, and in high-temperature applications. The benefits of inclusion of the 6F moiety in polymer backbones can be summarized as:

- Increased  $T_g$
- Improved solubility
- Decreased water absorption
- Increased thermal stability
- Lower dielectric constant
- Decreased color
- Decreased crystallinity

These changes in polymer physical properties are manifestations of the change, among other parameters, in the electronic properties of molecules containing the HFIP moiety. The strong, inductively electron-withdrawing effect of the HFIP group decreases electron density in adjacent functional groups yielding a subsequent change in physical properties. For example, the carbonyl IR absorption in a series of polyarylates<sup>3</sup> was observed to increase in wavenumber ( $\text{cm}^{-1}$ ) as HFIP was incorporated. This observation is consistent with a decrease in electron density on the carbonyl carbon, resulting in a greater partially positive charge on that carbon and a stronger C-O bond. This trend is observed in the IR absorption spectra of acetophenones substituted with methyl or trifluoromethyl groups.

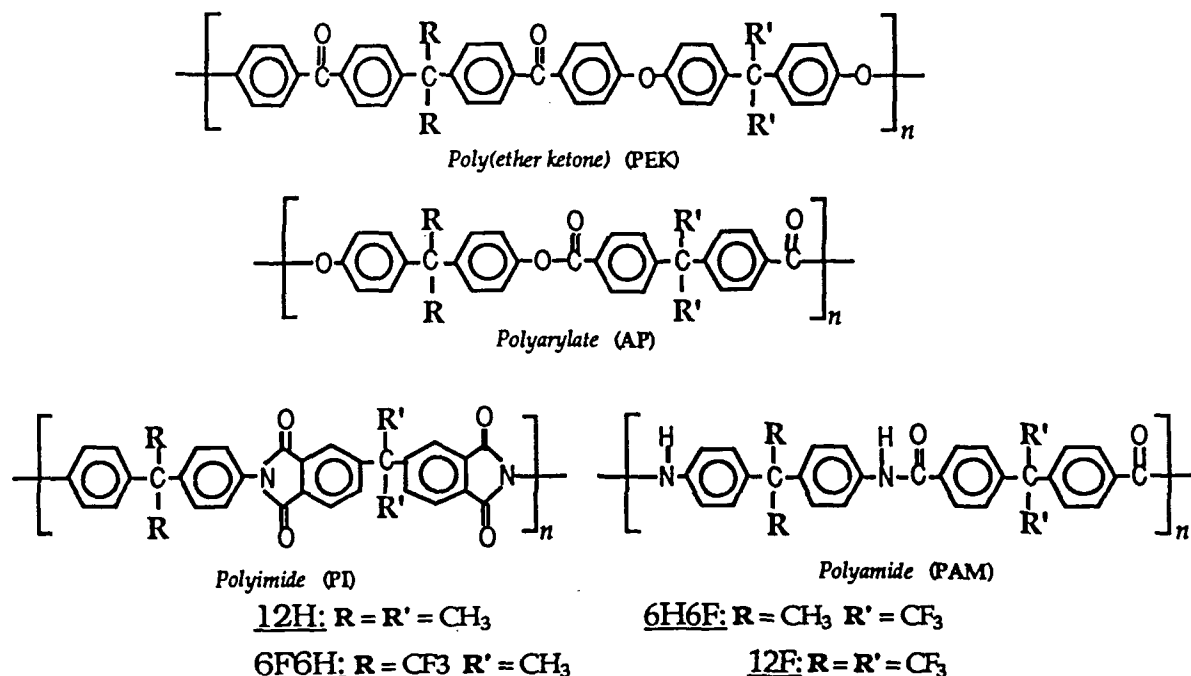
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The incorporation of the 6F moiety has been reported to result in the decrease in color in polyimides derived from 6F-containing monomers.<sup>4</sup> The resultant decrease in the  $\pi$ -conjugation of the aromatic moieties might be expected to increase the resistance of the 6F-polyimides towards photochemical degradation. Indeed, recent results<sup>5</sup> indicate that the incorporation of the HFIP group into polyimide backbones dramatically increases the rate of degradation upon exposure to full-spectrum UV when compared to the degradation rates of non-HFIP polymers.

The impetus for this research was to elucidate the effect of incorporation of 6F into polymer backbones on the photostability of four homologous series of polymers containing HFIP and/or isopropylidene (6H) groups. The polymer types are polyarylates (AP), polyamides (PAM), polyimides (PI), and poly-etherketones (PEK), general structures of which are given below (Figure 1). Preliminary results from the exposure data of only the PEKs will be presented in this manuscript. Results from the other series will be presented orally.



### EXPERIMENTAL

The polyarylates<sup>3</sup> and poly(ether ketones)<sup>6</sup> were synthesized according to published procedures. The polyamide series was prepared by low-temperature condensation of the appropriate diamine with a diacid chloride in *N,N*-dimethylacetamide (DMAc), precipitation into water, and purification. The polyimide series was prepared by reacting the diamine and dianhydride in DMAc at room temperature for eight hours under nitrogen. The polyamic acid solution was cast onto glass plates, dried, and then cyclized to the polyimide *via* thermal conversion.

The arylates, ether-ketones, and amides were cast onto quartz or NaCl plates to yield thin films from 1% (w/v) solutions of polymer in either CHCl<sub>3</sub> or DMAc. UV-visible spectra were recorded using a Perkin-Elmer Lambda 6 UV-VIS

spectrophotometer with 1 nm resolution. Infrared spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrophotometer with 4  $\text{cm}^{-1}$  resolution. Ultraviolet exposures were conducted in air using a Rayonet Model RPR-100 photochemical reactor equipped with 300 nm lamps or the full arc of a 450 watt Canrad-Hanovia lamp (medium pressure) in air. Size-exclusion chromatography of the polymers was conducted using Waters Ultrastyrigel columns with THF solutions of the polymers. Polystyrene standards were used to calculate the molecular weight from the peak maxima of the elution curves.

## RESULTS AND DISCUSSION

Figures 1 and 2 show UV absorption spectra of unphotolyzed 12H- and 12F-PEK films. The spectral differences below 300 nm suggest an effect due to the presence of the 6F moiety. Figures 3 and 4 show FTIR spectra of unphotolyzed 12H- and 12F-PEK films. The carbonyl peak absorptions are at 1659  $\text{cm}^{-1}$  and 1663  $\text{cm}^{-1}$  for 12H and 12F-PEK, respectively. This difference is in the same direction as noted for the polyarylates<sup>3</sup>.

Photolysis of all four PEK samples using either the 300 nm or 254 nm lamps of a Rayonet reactor resulted in the loss of absorbance around 290 nm accompanied by a new absorption band above 300 nm. A representative example is shown in Figure 5 for 12F-PEK. The change in the absorption spectra of 12F-PEK is accompanied by a decrease in the polymer molecular weight. Figure 6 shows GPC for the 12F-PEK polymer film before and after exposure in air to the unfiltered output of the mercury lamp for 25 hours. The peak maxima molecular weights (compared to polystyrene standards) before and after photolysis are 158,000 and 84,000, indicating substantial chain cleavage. The molecular weight decreases for the other PEK films were not so dramatic as for the 12F-PEK, at least under the constraints of the experimental procedure. It should be noted that the initial molecular weight of the 12F-PEK sample was substantially larger than for the 12H-PEK.

Figures 7 and 8 show the changes in the infrared absorption spectra of 12F-PEK and 12H-PEK films upon exposure to the medium pressure mercury lamp for 25 hours. In both cases a new broad absorbance from 3500  $\text{cm}^{-1}$  to 3000  $\text{cm}^{-1}$ , perhaps indicative of acid group formation, is seen. This broad band absorption seems to be more pronounced for the 12F-PEK film. There are also bands generated in the carbonyl region around 1720  $\text{cm}^{-1}$  for 12F- and 12H-PEK; again the absorbance appears to be greater for 12F-PEK. The 6H6F- and 6F6H-PEK samples show likewise generation of new absorption bands at 1720  $\text{cm}^{-1}$  and the broad band at 3500  $\text{cm}^{-1}$  to 3000  $\text{cm}^{-1}$ .

In summary, it seems apparent that the incorporation of 6F moieties into PEK polymers does not yield enhanced photostability in air, at least under the constraints of our photolysis conditions. These results are in accordance with those reported elsewhere for polyimides<sup>5</sup> where the incorporation of HFIP in the dianhydride component actually results in enhanced photodecomposition. Interestingly, we have found recently that incorporation of 6F moieties in both the dianhydride and diamine leads to even greater photodecomposition rates. Data for the polyimides

polyarylates, and polyamides, as well as for the poly(ether ketones) reported herein, will be presented and contrasted in the presentation. Mechanistic implications will be discussed.

### ACKNOWLEDGEMENTS

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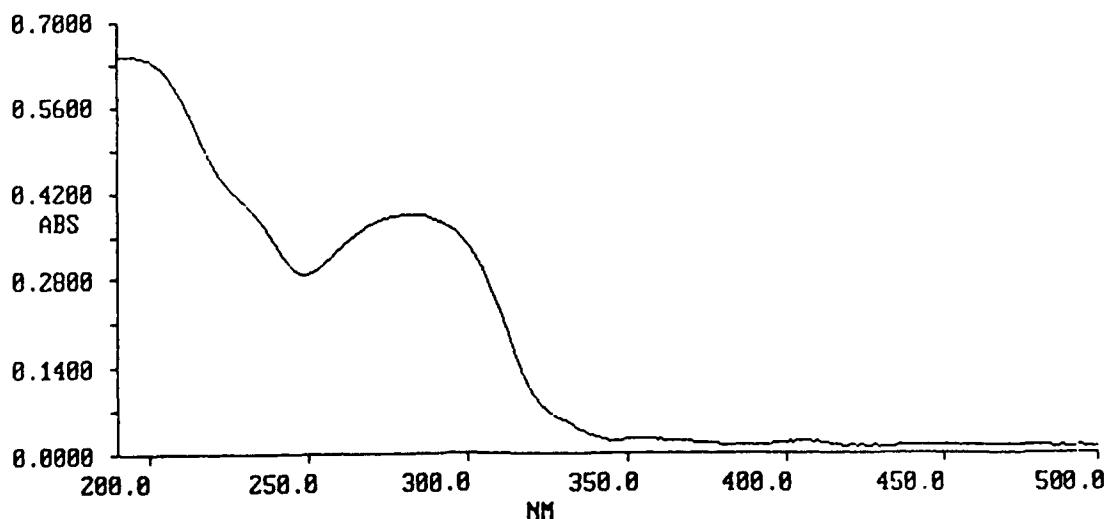


Figure 1. UV-vis spectrum of poly(ether ketone).

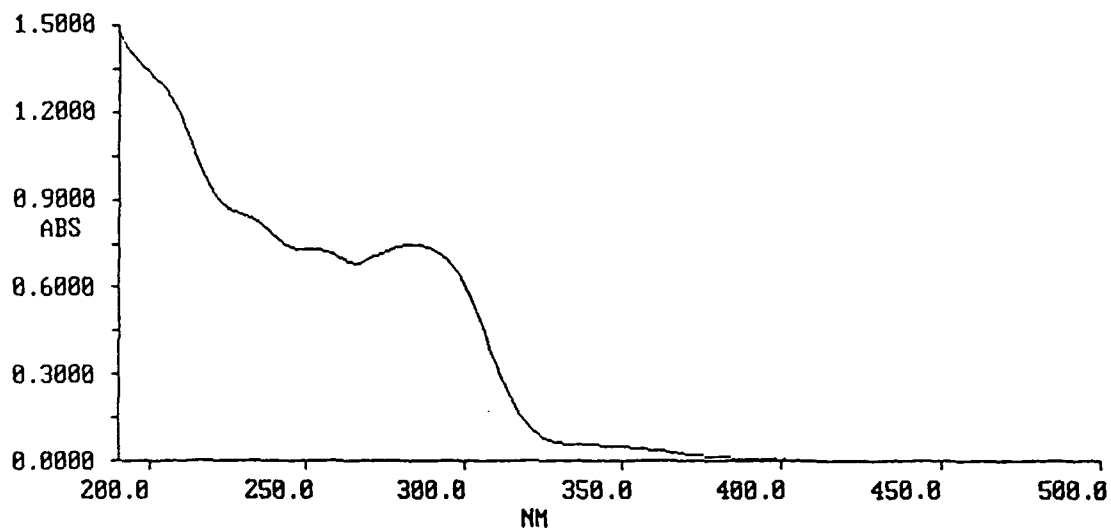


Figure 2- UV-vis spectrum of 12F-PEK before exposure.

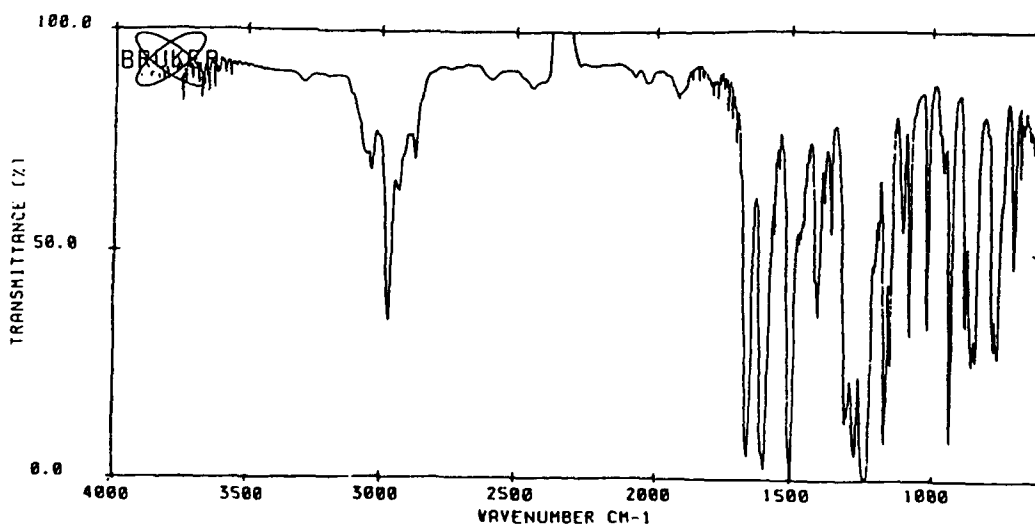


Figure 3- FTIR spectrum of 12H-PEK before exposure.

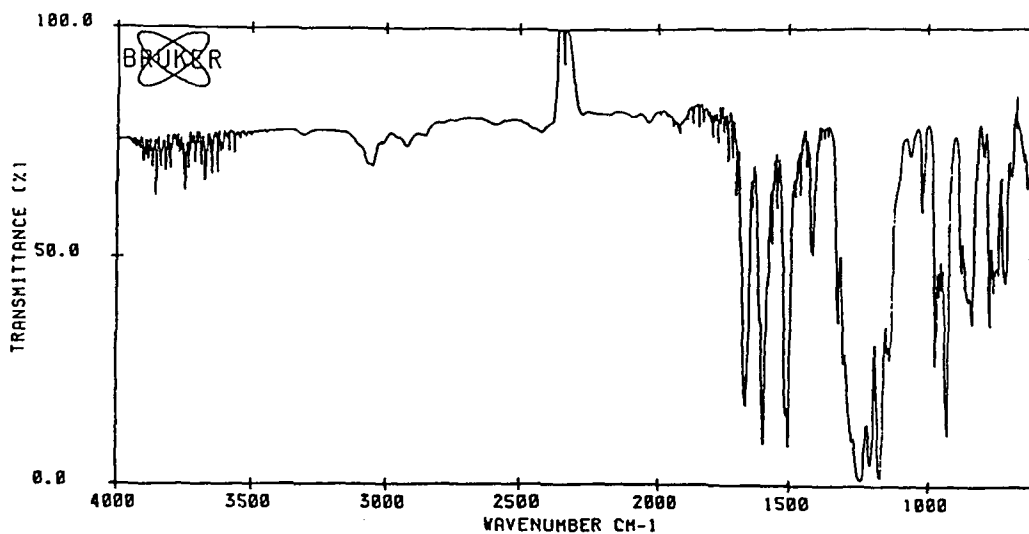


Figure 4- FTIR spectrum of 12F-PEK before exposure.

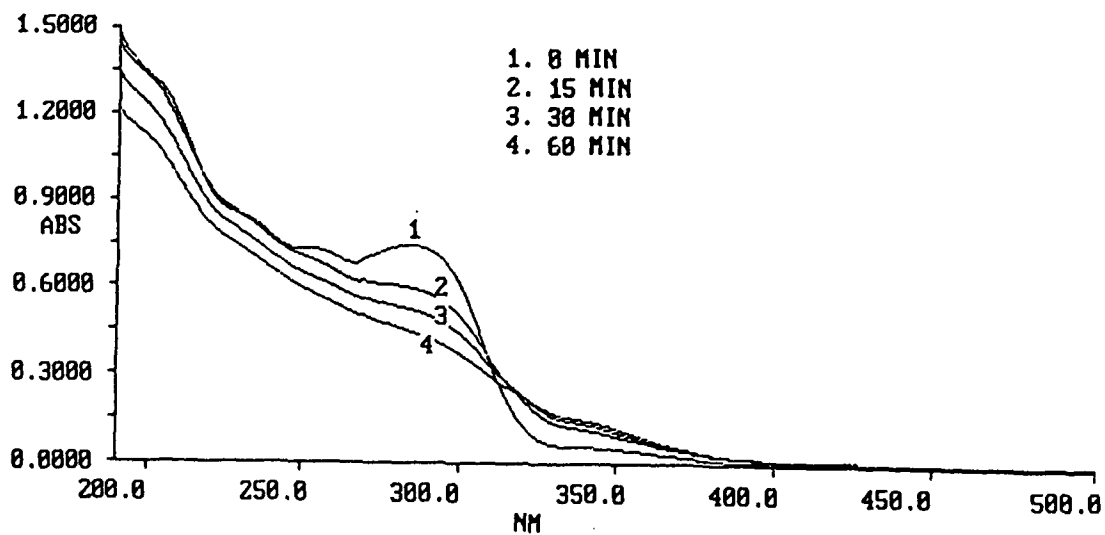


Figure 5- UV-vis spectra of photolyzed 12F-PEK

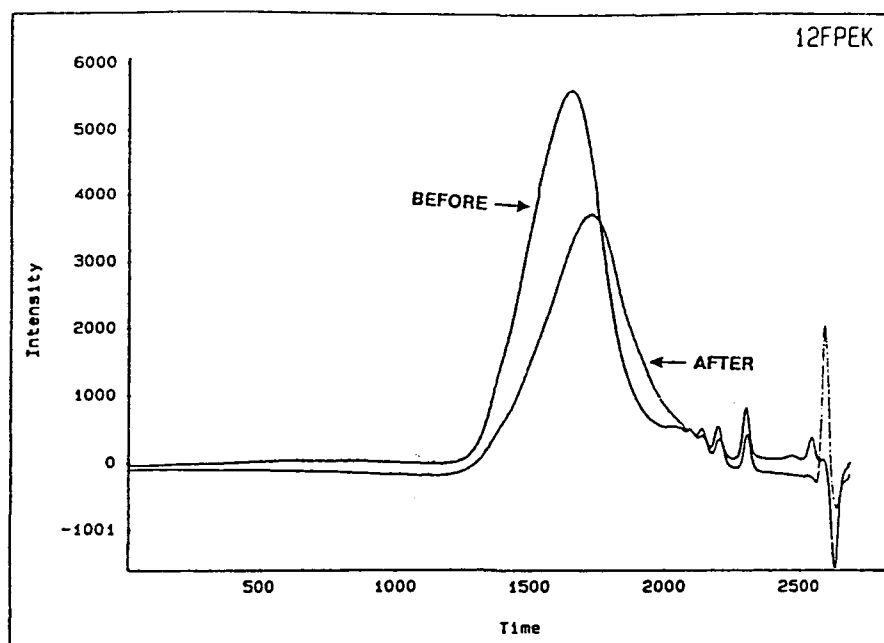


Figure 6- Gel-permeation chromatogram of 12F-PEK before and after photolysis.

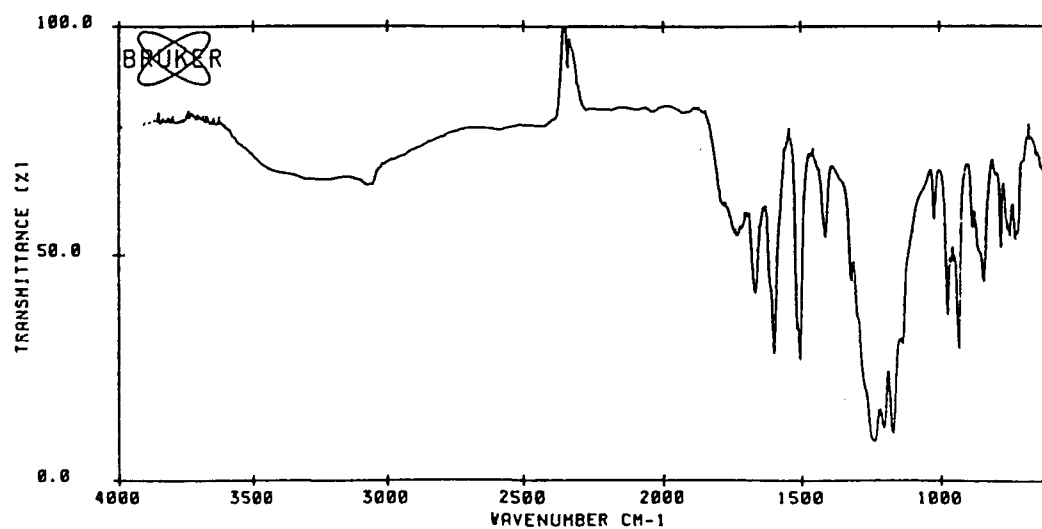


Figure 7- FTIR spectrum of 12F-PEK after photolysis

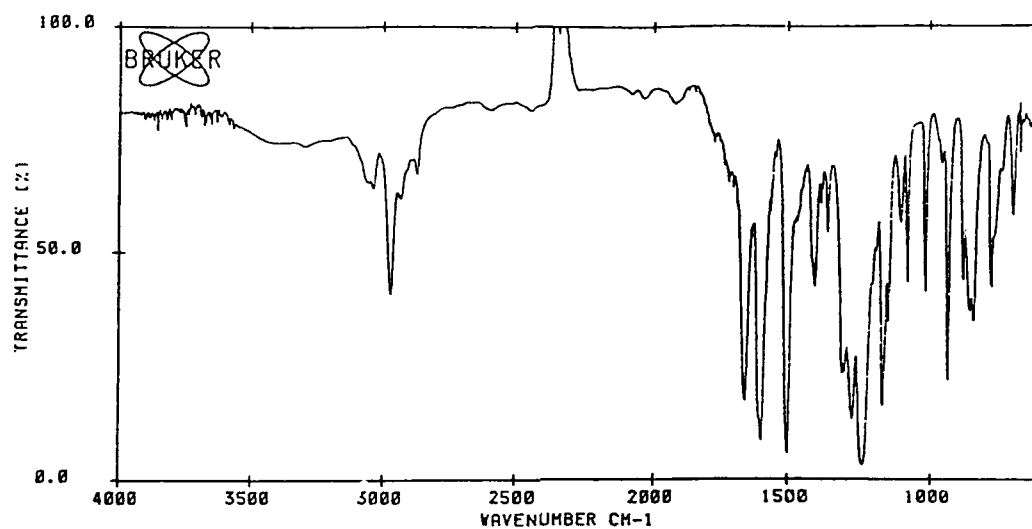


Figure 8- FTIR spectrum of 12H-PEK after photolysis.