

2

AD-A236 255



OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1028

Technical Report No. 7

Ultraviolet Stability of Polymers Containing the Hexafluoroisopropylidene Group

by

C.E. Hoyle¹, R. Nagarajan¹, E.T. Anzures¹, P.E. Cassidy², and K.M. Kane²

Prepared for Publication in

Proceedings of Conference on Polymers in Extreme Environments

¹Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

²Polymer Research Group
Department of Chemistry
Southwest Texas State University
San Marcos, TX 78666-4616



Distribution For DTIC DTIC DTIC DTIC	
by DTIC	
Available to DTIC	
Dist AI	Special

Reproduction in whole or in part is permitted for any purpose of the United States government.

This document has been approved for public release and sale: its distribution is unlimited.

91 6 4 088

91-01204



REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE		1b. RESTRICTIVE MARKINGS NONE		
2a. SECURITY CLASSIFICATION AUTHORITY NONE		3. DISTRIBUTION / AVAILABILITY OF REPORT UNLIMITED		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE NONE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 7		5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N0014-89-J-1028		
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Ultraviolet Stability of Polymers Containing the Hexafluoroisopropylidene Group				
12. PERSONAL AUTHOR(S) C.E. Hoyle, R. Nagarajan, E.T. Anzures, P.E. Cassidy, and K.M. Kane				
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 6-1-90 TO 5-31-91	14. DATE OF REPORT (Year, Month, Day) 91-05-31	15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION Prepared for Publication in Proceedings of Conference on Polymers in Extreme Environments				
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP			SUB-GROUP
19. ABSTRACT (Continue on reverse if necessary and identify by block number) 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. Results for polyamides, polyimides, and polyarylates are also under study.				
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL Ken Wvrine	22b. TELEPHONE (Include Area Code) (601)266-4868	22c. OFFICE SYMBOL		

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.^{1,2} 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

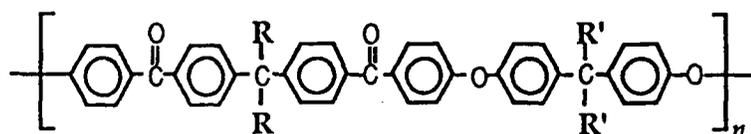
These changes in polymer physical properties are manifestations of the change, among other parameters, in the electronic properties of molecules containing the HFIP moiety. The strong, inductively electron-withdrawing effect of the HFIP group decreases electron density in adjacent functional groups yielding a subsequent change in physical properties. For example, the carbonyl IR absorption in a series of polyarylates³ was observed to increase in wavenumber (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.

*Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi, 39406-0076 U.S.A. †Polymer Research Group, Department of Chemistry, Southwest Texas State University, San Marcos, Texas, 78666-4616 U.S.A.

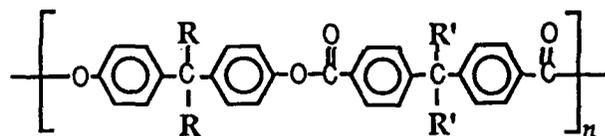


The incorporation of the 6F moiety has been reported to result in the decrease in color in polyimides derived from 6F-containing monomers.⁴ The resultant decrease in the π -conjugation of the aromatic moieties might be expected to increase the resistance of the 6F-polyimides towards photochemical degradation. Indeed, recent results⁵ 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.

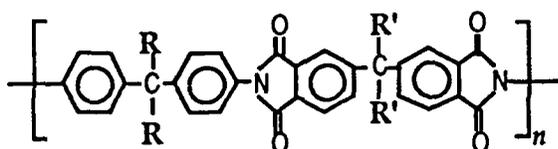
The impetus for this research was to elucidate the effect of incorporation of 6F into polymer backbones on the photostability of four homologous series of polymers containing HFIP and/or isopropylidene (6H) groups. The polymer types are polyarylates (AP), polyamides (PAM), polyimides (PI), and poly-etherketones (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.



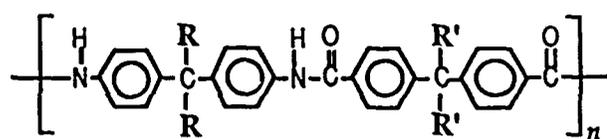
Poly(ether ketone) (PEK)



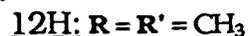
Polyarylate (AP)



Polyimide (PI)



Polyamide (PAM)



EXPERIMENTAL

The polyarylates³ and poly(ether ketones)⁶ 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 CHCl₃ 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 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 cm^{-1} and 1663 cm^{-1} for 12H and 12F-PEK, respectively. This difference is in the same direction as noted for the polyarylates³.

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 cm^{-1} to 3000 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 cm^{-1} for 12F- and 12H-PEK; again the absorbance appears to be greater for 12-PEK. The 6H6F- and 6F6H-PEK samples show likewise generation of new absorption bands at 1720 cm^{-1} and the broad band at 3500 cm^{-1} to 3000 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 polyimides⁵ 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

The authors at USM acknowledge the financial support of the Office of Naval Research. The authors at SWTSU acknowledge the financial support of the Robert A. Welch Foundation (Grant No. AI-5024) and the NASA Langley Research Center (Grant No. NAG-1-631).

REFERENCES

1. P. E. Cassidy, T. M. Aminabhavi, and J. M. Farley, J. Macromol. Sci., Rev. Macromol. Chem. Phys., C29 (2 & 3), 365-429 (1989).
2. Fluorine-containing Polymers Symposium, Meeting of the American Chemical Society, April 18-23, 1990, Boston, Massachusetts.
3. K. M. Kane, D. L. Meurer, L. A. Hoelscher, P. E. Cassidy, and L. A. Wells, ACS Polymer Preprints, 30 (1), 346 (1990).
4. F. L. Hedberg and F. E. Arnold, U. S. Air Force Tech. Rep., AFML-TR-78-198, March 1977.
5. C. E. Hoyle, etc, 33rd IUPAC International Symposium on Macromolecules, Montreal, Quebec, Canada, July 7-12, 1990.
6. G. L. Tullos, P. E. Cassidy, and A. K. St. Clair, ACS PMSE Preprints, 60, 310 (1988) and Macromolecules, accepted for publication.

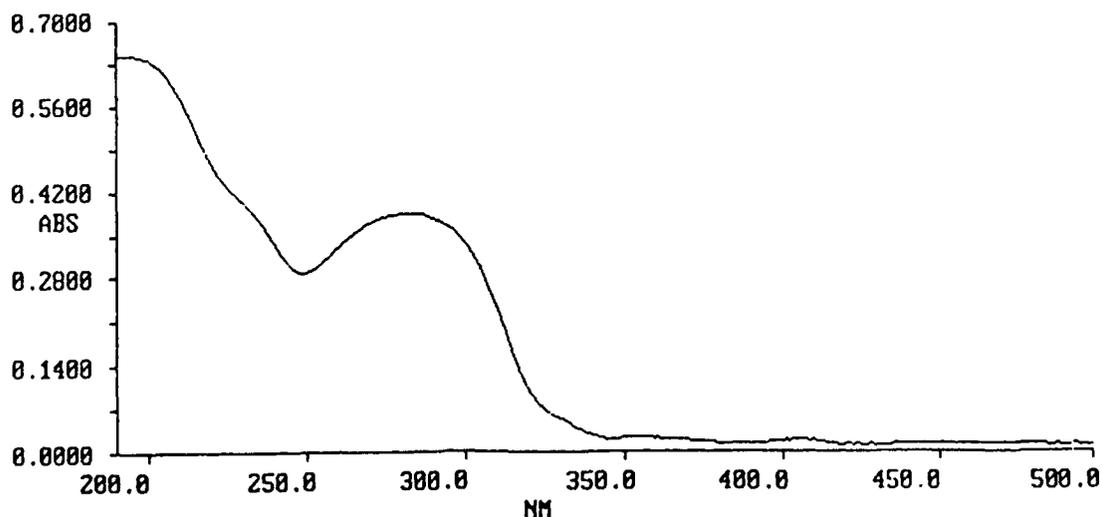


Figure 1. UV-vis spectrum of 10% DMSO solution of poly(arylate).

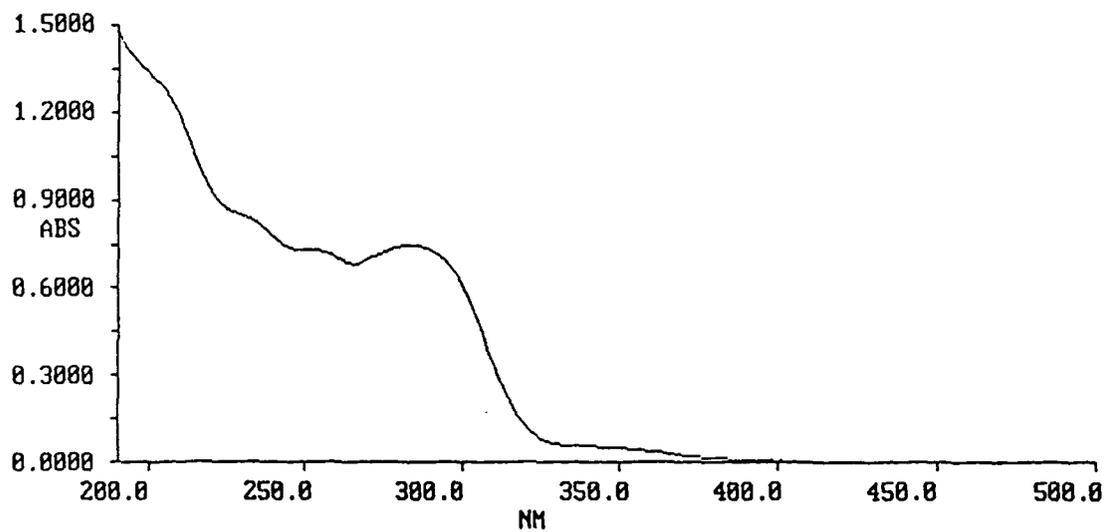


Figure 2- UV-vis spectrum of 12F-PEK before exposure.

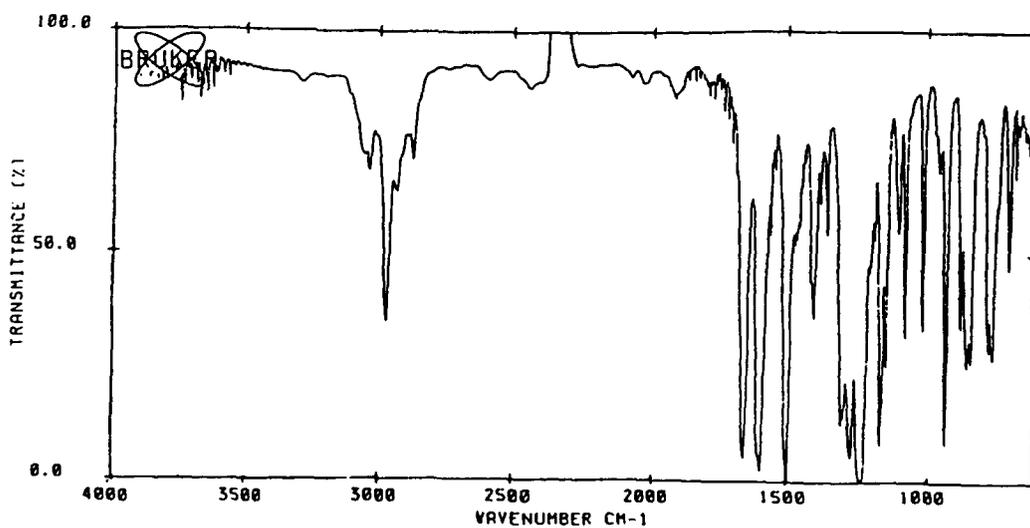


Figure 3- FTIR spectrum of 12H-PEK before exposure.

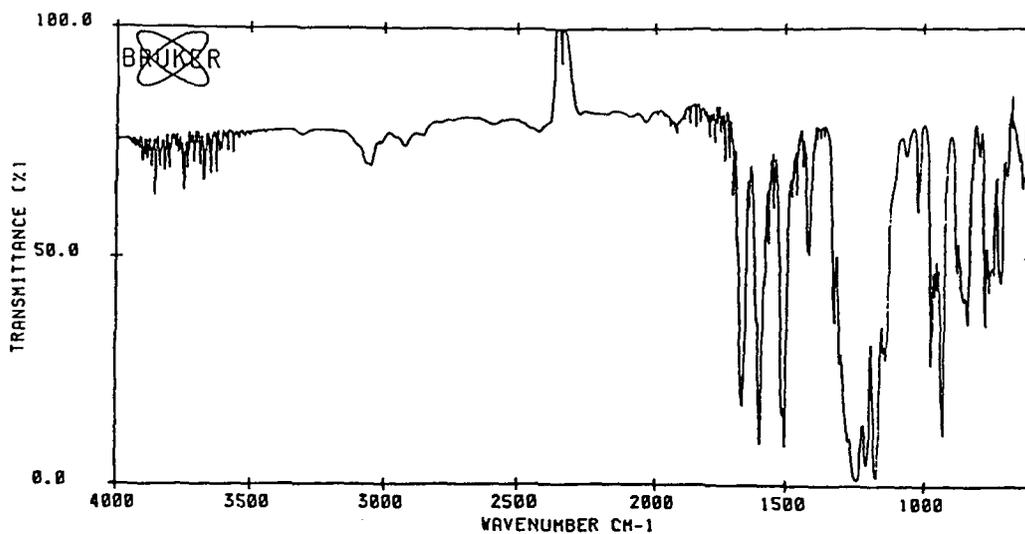


Figure 4- FTIR spectrum of 12F-PEK before exposure.

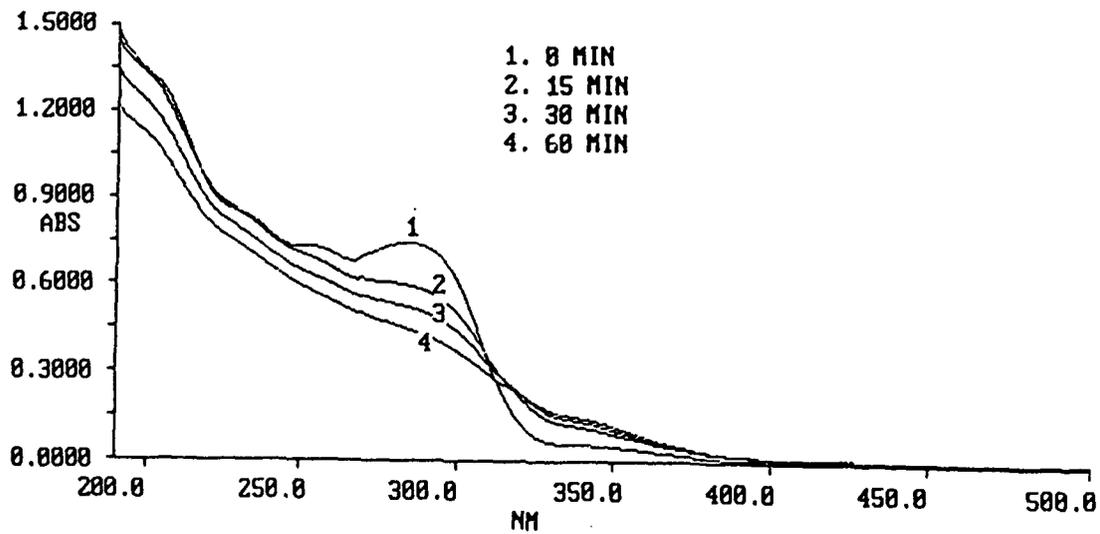


Figure 5- UV-vis spectra of photolyzed 12F-PEK

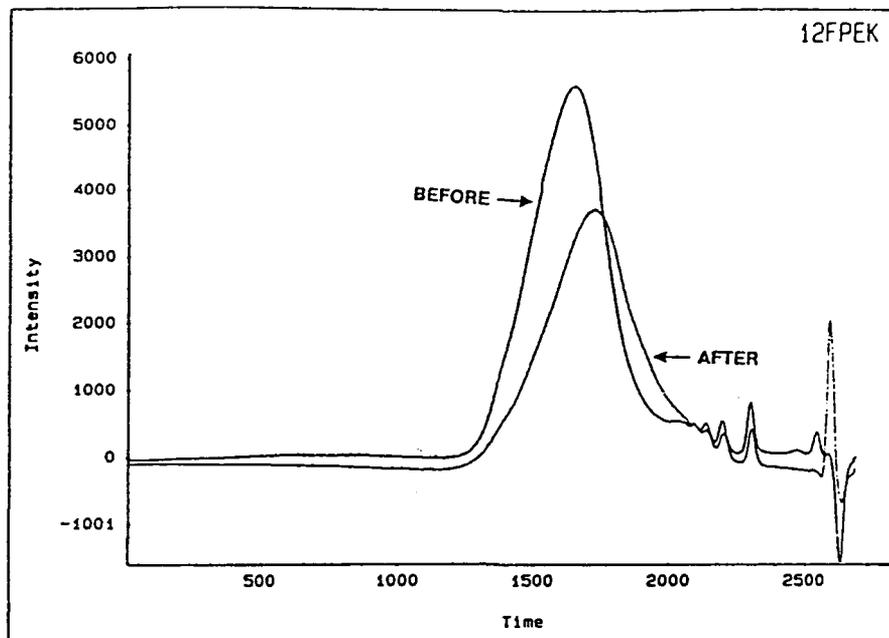


Figure 6- Gel-permeation chromatogram of 12F-PEK before and after photolysis.

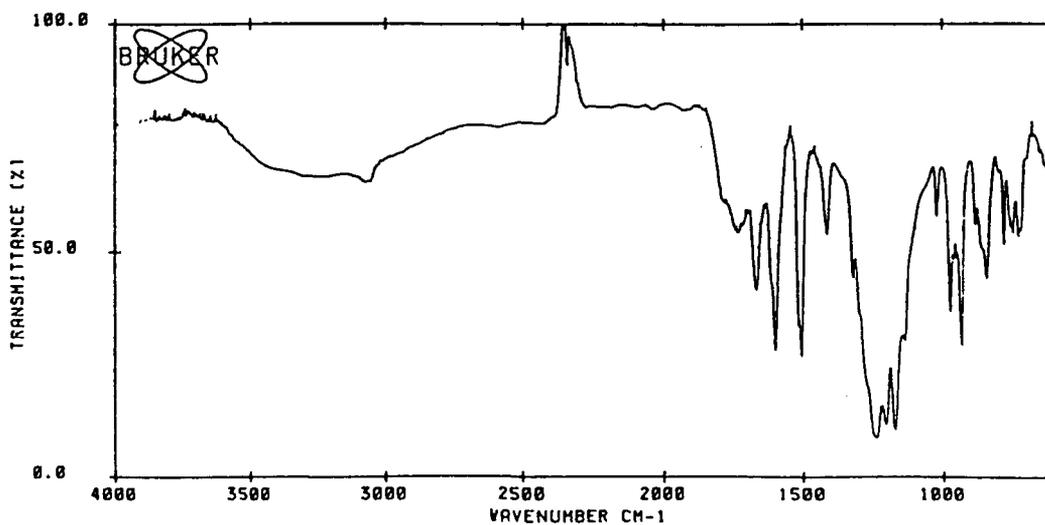


Figure 7- FTIR spectrum of 12F-PEK after photolysis

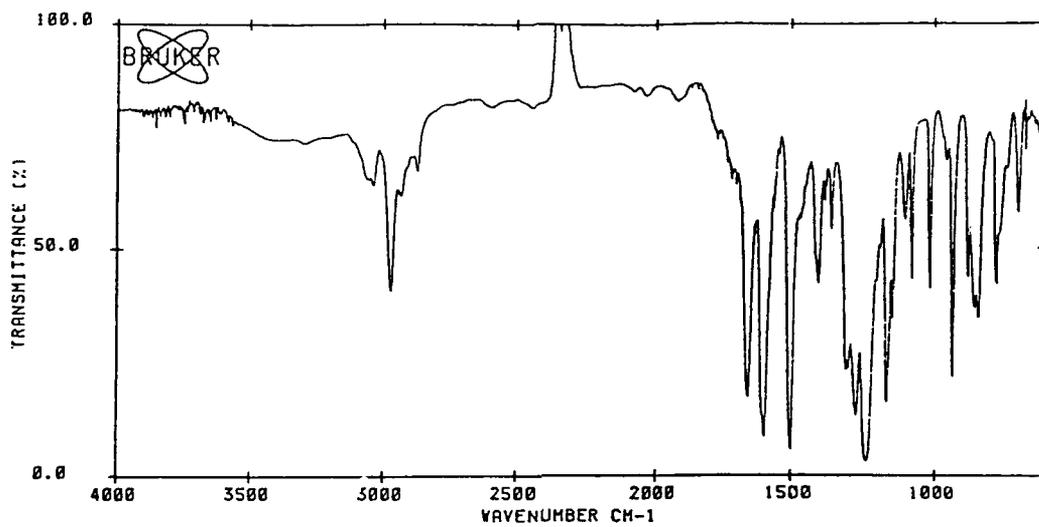


Figure 8- FTIR spectrum of 12H-PEK after photolysis.