Photo-Fries Rearrangement of Fluorene-Based Polyarylates

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Synopsis

The fluorene-based polyarylates, 9,9-bis(4-hydroxyphenyl)fluorene isophthalate (BPF-I), 9,9-biscresol fluorene isophthalate (BCF-I), and 9,9-bis(3,5-dimethyl-4-hydroxyphenyl) fluorene isophthalate (BDMPF-I), are synthesized. The formation of the o-hydroxybenzophenone moiety upon UV irradiation of BPF-I and BCF-I is observed in the UV and IR spectra. The degradation of the polymer structure of BDMPF-I is due to its inability to rearrange into the hydroxybenzophenone structure which functions as an internal UV stabilizer. A mechanism for this degradation is postulated based on the evidence from the IR spectra.

INTRODUCTION

The Fries rearrangement has been shown to occur in aromatic polyesters in the presence of Friedel–Crafts catalysts,[1,2] and also upon UV irradiation.[3-7] For instance, the photo yellowing of poly(4,4'-diphenylol propane isophthalate) is attributed to the Fries rearrangement resulting in o-hydroxybenzophenone as part of the chain structure. The rate of photolysis falls off at higher exposure times because of the self-screening effect of the rearranged products.[8] Cohen and coworkers[9] have also found that thin coatings of a number of phenyl polyesters completely protect the substrates ordinarily sensitive to UV light. Such a "skin" of o-hydroxybenzophenone containing polymer formed *in situ* during the irradiation functions to protect both the original polyester coating and the coated substrate from degradation by UV irradiation.

The Fries rearrangement in a polymeric system involves a shift of an acyl group to the ortho position.[8] Therefore, free ortho positions become the requirement for the photo-Fries rearrangement.

In an aromatic polyester this requirement is demonstrated in the poly[9,9-bis(4-hydroxyphenyl) fluorene isophthalate] system. Two polymer analogs with either or both the ortho positions of the phenol rings occupied by the methyl groups show a decrease in or inability to undergo the photo-Fries rearrangement.

EXPERIMENTAL

Materials

9,9-Bis(4-hydroxyphenyl) fluorene (BPF), 9,9-biscresol fluorene, and 9,9-bis(3,5-dimethyl-4-hydroxyphenyl) fluorene (BDMPF) are prepared by the

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TABLE I
Characteristics of Polyisophthalates

Polymer	η_{inh}, 0.45 g/dL in methylene chloride	T_g (°C)	T_d (°C)	Char yield at 800°C (%)	Oxygen index
BPF-I	0.91	265	500	59	37
BCF-I	0.25	287	520	40	36
BDMPF-I	0.85	315	510	34	35

method of Morgan.[10] Excess phenol, cresol, and 2,6-dimethyl phenol are used in the condensation reaction with fluorenone. A small amount of mercaptoacetic acid is used as cocatalyst. Dry hydrogen chloride is bubbled through the reaction mixture for 20 min while the reaction is kept at 140–150°C. At the end of the reaction, the viscous mass is washed with hot water several times and dissolved in sodium hydroxide solution. The product is obtained by titrating with concentrate hydrochloric acid. One recrystallization from toluene gives white crystals. BPF is obtained in 56% yield, mp 224–225°C. The NMR spectrum exhibits the absorptions at δ 6.78 (phenolic protons), δ 7.10–7.80 (fluorenyl protons), and δ 8.10 (hydroxyl protons).

9,9-Bis(4-Hydroxyphenyl) Fluorene (BPF).

ANAL. Calcd for $C_{25}H_{18}O_2$: C, 85.71%; H, 5.1%. Found: C, 85.62%; H, 5.21%.
BCF is obtained in 70% yield, mp 110–111°C.

9,9-Biscresol Fluorene (BCF).

ANAL. Calcd for $C_{27}H_{22}O_2$: C, 85.7%; H, 5.8%. Found: C, 85.2%; H, 5.43%.
BCF is obtained in 35% yield, mp 271–272°C. The NMR spectrum shows the absorptions at δ 2.13 (methyl protons), δ 6.73 (phenolic protons), and δ 7.10–7.72 (fluorenyl protons).

9,9-Bis(3,5-Dimethyl-4-Hydroxy Phenyl) Fluorene (BMDF).

ANAL. Calcd for $C_2H_{26}O_2$: C, 85.71%; H, 6.40%. Found: C, 85.52%; H, 6.26%.

Polymerization

The polyarylates are synthesized by interfacial polymerization. For a typical run, 3.5 g (0.01 mol) of BPF, 1.6 g (0.04 mol) of sodium hydroxide, and 2.1 g (0.1 mol) of tetraethyl ammonium bromide are dispersed in 120 mL of water in a blender. To this mixture is added quickly with vigorous stirring 2.03 g (0.01 mol) of isophthaloyl chloride in 30 mL of 1,2-dichloroethane. After stirring for 3 min, the addition of 200 mL of n-hexane is made. The separated polymer is collected, washed with water, and dried. The product is redissolved in methylene chloride and precipitated in 500 mL methanol to yield 4.0 g (95%) of polymer.

Polymer Characterization

All polymers are characterized for structure by use of a Digilab FTS-20B Fourier Transform Spectrometer (FT-IR), for thermal properties with a DuPont 990 Thermal Analyzer and 951 Thermogravimetric Analyzer, for flammability with a General Electric CR 280 FM 11B Oxygen Index Flammability Gauge. The characteristics of the polymers are shown in Table I. The viscosities are measured with a Ubbelohde viscometer.
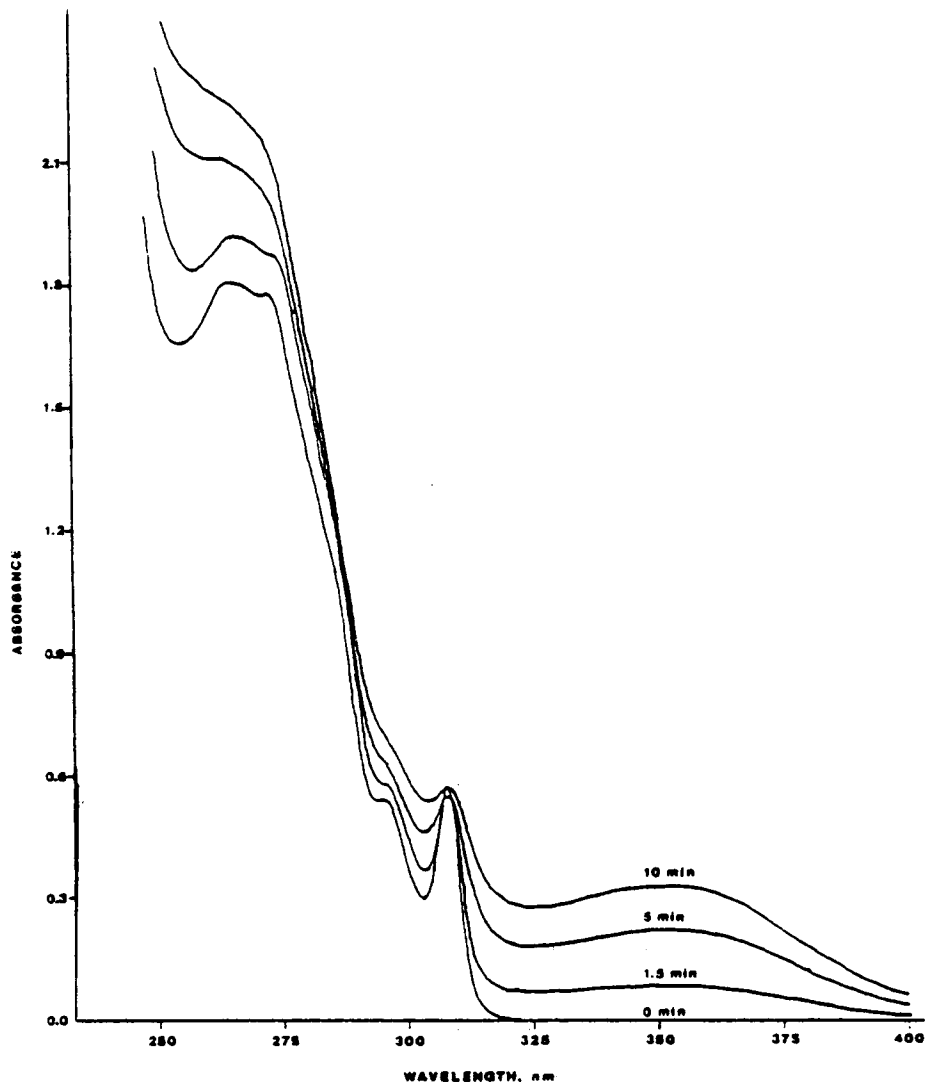
Fig. 1. UV spectra of BPF-I in methylene chloride solution before and after irradiation for different periods of time.

Studies of Photo-Fries Rearrangement

Irradiation Chamber. The equipment for photo-Fries rearrangement consists of a power source (Hanovia 27801), an ultraviolet light source (Mercury-Xenon Compact Arc Lamp, Hanovia 509 B 0080) with 1000 W of power and a lamp housing system (Schoeffel Instrument Co., LH 152 N Lamp Housing).

UV Spectroscopic Studies. The polymer samples are dissolved in methylene chloride to make $6.0 \times 10^{-4}M$ solutions. After the initial UV-visible spectra are taken on a Beckman ACTA C III Spectrophotometer, the quartz cells containing the sample solutions are then placed in the irradiation chamber for irradiation. The spectra are taken after certain periods of irradiation time.
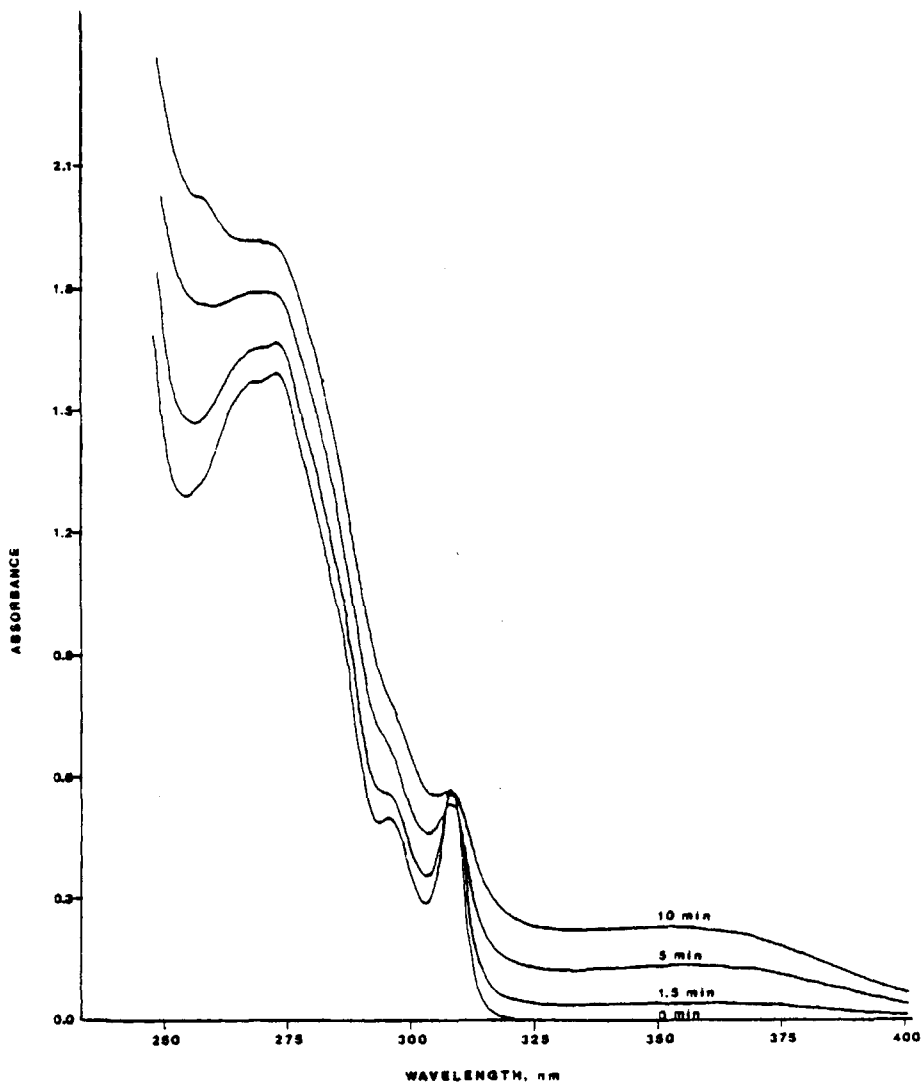
Fig. 2. UV spectra of BCF-I in methylene chloride solution before and after irradiation for different periods of time.

FT-IR Spectroscopic Studies. The aluminum plates coated with the polymer films are subjected to UV irradiation. The infrared spectra are taken before and after the irradiation, using a reflectance attachment.

RESULTS AND DISCUSSION

UV Spectroscopic Studies

The UV spectra of the polymers in methylene chloride are recorded periodically during the irradiation (Figs. 1, 2, and 3). An increase in absorption in the region from 325 to 375 nm, with a maximum at 355 nm for BPF-I and BCF-I, are related to the hydroxybenzophenone structure if one takes into consideration the fact that low-molecular substituted benzophenone derivatives absorb in the
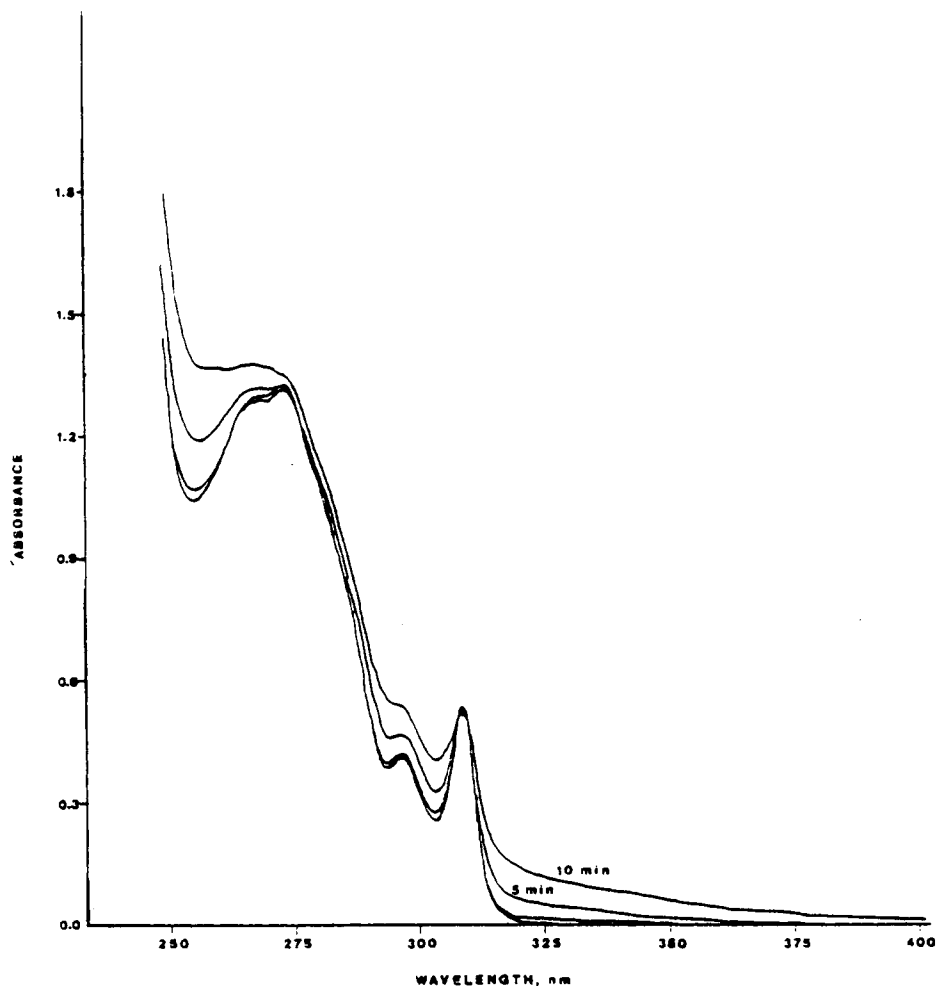
Fig. 3. UV spectra of BCF-I in methylene chloride solution before and after irradiation for different periods of time.

region from 300 to 400 nm depending on the type and position of the substituent in the structure. The absorption maxima of polymeric benzophenone also differ markedly from one another.[8,12] By comparing Figures 1 and 2, the increase is found to be less in the case of BCF-I. In the spectra of BDMPF-I (Fig. 3) only slight changes in the region of 325–375 nm are observed. A more direct comparison of the changing rates is shown in Figure 4. The curves result from plotting the absorption at 350 nm for each sample as a function of the irradiation time.

With the polyarylates examined in this work, the structural requirement to produce the photo-Fries rearrangement under UV irradiation is the presence of at least one unsubstituted position on the phenol rings ortho to the ester groups. Thus, BDMPF-I does not rearrange under the irradiation conditions. The substitution on one-half of the ortho positions of the phenol rings with the methyl groups (e.g., BCF-I) apparently reduces the formation of o-hydroxy-benzophenone.
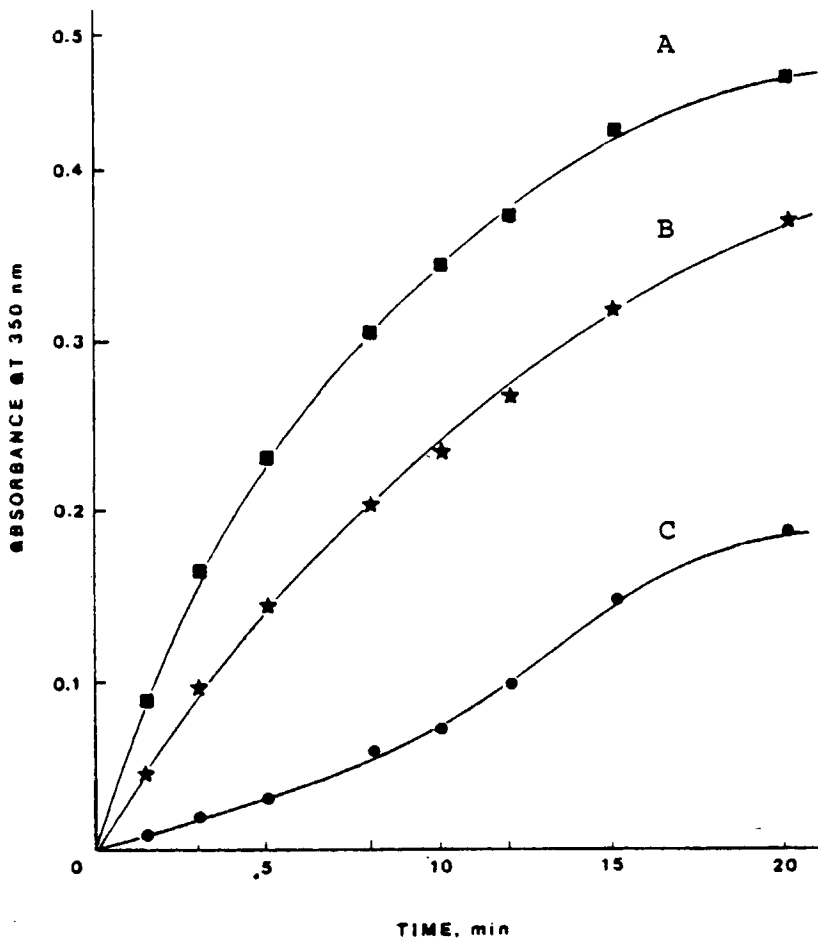
Fig. 4. Changes in absorbance at 350 nm with irradiation time: (A) BPF-I; (B) BCF-I; (C) BDMPF-I.

FT-IR Spectroscopic Studies

The infrared spectra shown in Figures 5, 6, and 7 for the samples before and after 60-min irradiation provide further information on the structural changes resulting from the rearrangement. The difference spectra are generated by digitally subtracting two spectra on a 1:1 basis assuming no change in thickness of the samples after irradiation. The absolute changes are obtained with the scale expanded five times.

In Figure 5 the OH stretching vibration is observed as a weak band in the region near 3300 cm^{-1}. Broadening and weakening of the band are due to the intra-molecular hydrogen bonding between the hydroxyl group and the carbonyl group at the ortho position.[13] The intermolecular hydrogen bonding causes a slight shift of the ester carbonyl absorption towards a lower frequency at 1745 cm^{-1}.[14] The positive peak at 1630 cm^{-1} in the difference spectrum is attributed to the highly polarized hydroxybenzophenone carboxyl groups.[8,14] The ester C—O breaking involved in the photo-Fries rearrangement is observed as a decrease in intensity of a band at 1290 cm^{-1}. The most notable change in the difference
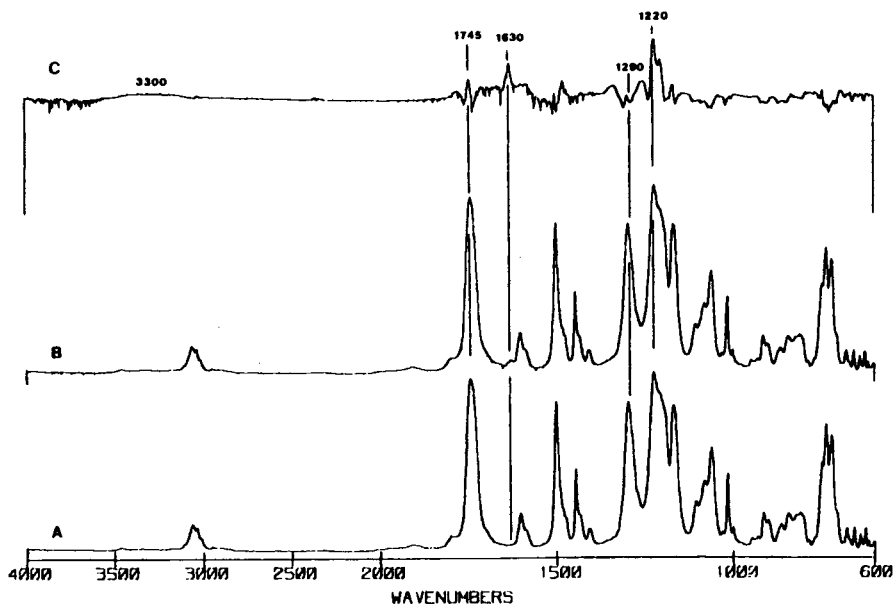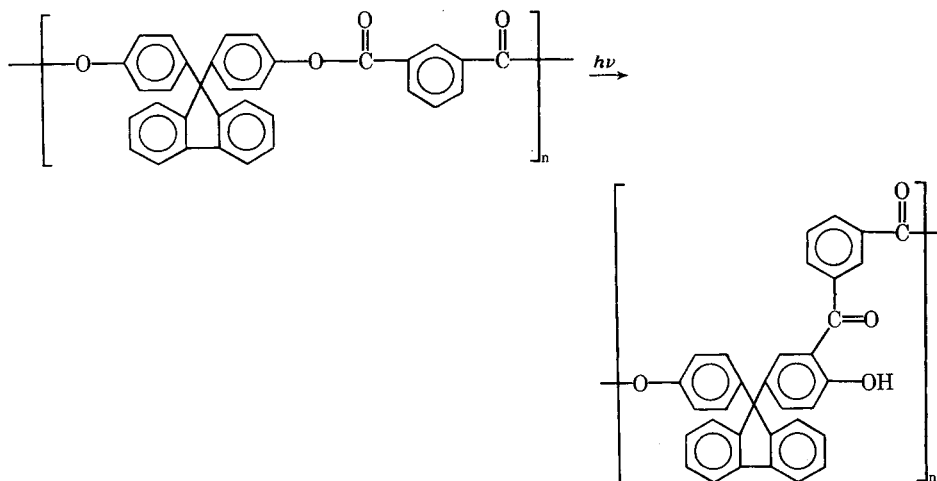
Fig. 5. Infrared spectra of (A) BPF-I, (B) BPF-I after 60 min irradiation, and (C) difference spectrum B-A. Reflectance attachment.

spectrum is the increased absorption in the phenolic OH deformation and C—O stretching regions around 1220 cm^{-1} which also represents the ϕ-C—O vibration.[15]

It is proposed that the irradiation of BPF-I occurs with molecular rearrangement to form a new polymer, in part, of linear o-hydroxybenzophenone moieties as the product:

The spectral changes of BCF-I upon irradiation (Fig. 6) are almost identical to that of BPF-I except for the less intense peak at 1630 cm^{-1}, indicating that the formation of o-hydroxybenzophenone is inhibited by the substitution of one of the ortho positions in the phenol rings with the methyl groups. This is in agreement with the result from the UV spectroscopic observations.
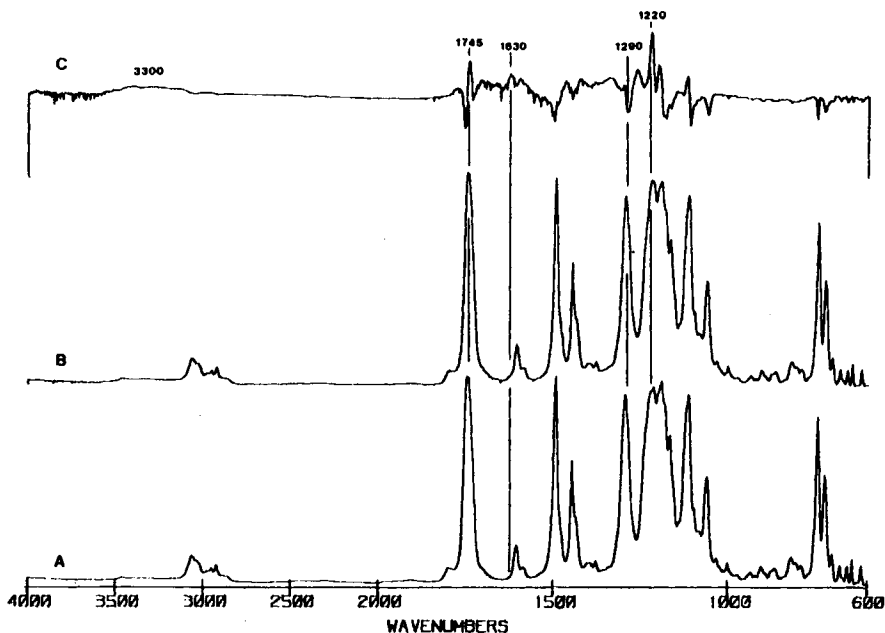
Fig. 6. Infrared spectra of (A) BCF-I, (B) BCF-I after 60 min irradiation, and (C) difference spectrum B-A. Reflectance attachment.

A complete inhibition of the Fries rearrangement may occur in BDMPF-I. Figure 7 indicates no formation of hydroxybenzophenone (1630 cm^{-1}). The free hydroxyl groups are observed as a strong band at 3300 cm^{-1}. The hydroxyl groups are most likely to be the phenolic type which also gives rise to a sharp peak at 1220 cm^{-1} due to ϕ-OH stretching vibration. The slightly decreased band at 2920 cm^{-1} indicates a loss of aliphatic hydrogens presumably from the methyl groups. A decreased absorption peak at 1745 cm^{-1} and an increased absorption peak at 1710 cm^{-1} are observed, suggesting the formation of an aromatic aldehyde at the expense of the ester groups. The cleavage of the ester C—O band is also evident, indicated by the negative difference band at 1290 cm^{-1}.

CONCLUSIONS

An investigation of the photo-Fries rearrangement in fluorene based polyarylates has been made. It is shown that the structural changes of the polymers having free *ortho* positions on the phenol rings are connected with the formation of *o*-hydroxybenzophenone structures in the polymer as a result of the photo-Fries rearrangement. UV spectroscopy provides a direct detection of *o*-hydroxybenzophenone. Digital subtraction of infrared data obtained by Fourier transform infrared spectroscopy has been applied in observing the chemical changes occurring in the photo-Fries rearrangement process. Substitution in the *ortho* positions of the phenol rings results in a different route for degradation. The degradation products include the aldehyde moieties, phenols, and the possible quinone structures.

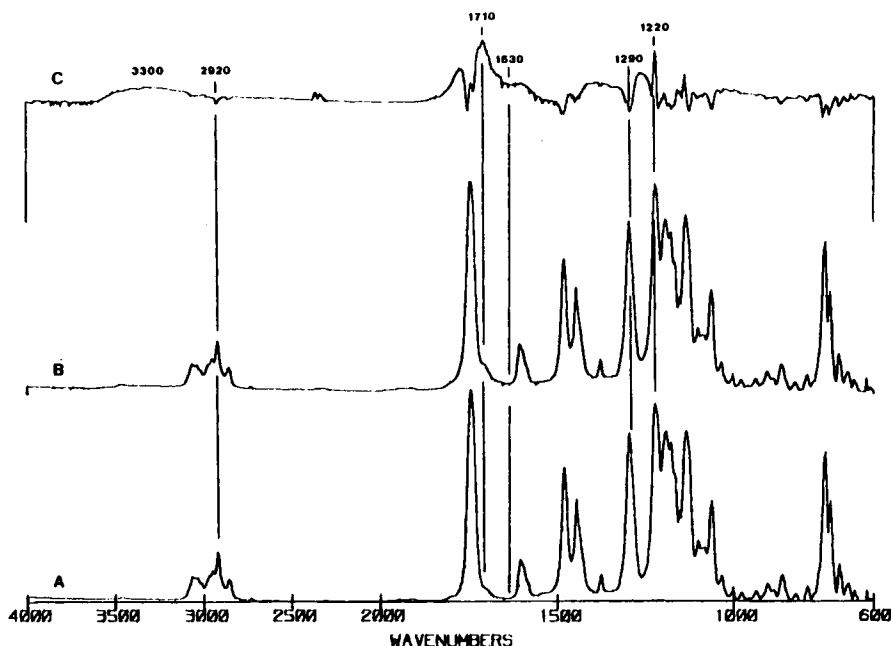The authors gratefully acknowledge the National Aeronautic and Space Ad-

Fig. 7. Infrared spectra of (A) BDMPF-I, (B) BDMPF-I after 60 min irradiation, and (C) difference spectrum B-A. Reflectance attachment.

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