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### Synthesis of a Photosensitive Poly(Arylene Ether) Containing Pendant Benzoyl Groups

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## **SYNTHESIS OF A PHOTSENSITIVE POLY(ARYLENE ETHER) CONTAINING PENDANT BENZOYL GROUPS**

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**Key Words:** Poly(arylene ether); Pendant benzoyl groups; Photosensitive polymer; Nucleophilic substitution; Positive type resist; Photosensitivity

### **ABSTRACT**

Poly(arylene ether) (**3**) containing 4-isopropylbenzoyl groups was prepared by a nucleophilic substitution reaction of 1,4-bis(4-isopropylbenzoyl)-2,5-difluorobenzene (**1**) with methylhydroquinone (**2**) in the presence of potassium carbonate in *N,N*-dimethylacetamide. The polycondensation proceeded smoothly at 165°C and produced a poly(arylene ether) with an inherent viscosity of 0.93 dL/g. The polymer was quite soluble in common organic solvents and could be processed into uniform films from solution. Thermogravimetry of the polymer showed a 10% weight loss at 430°C in a nitrogen atmosphere. The glass transition

temperature of polymer was 140°C. The polymer functioned as a positive photoresist for UV irradiation. The resist had a sensitivity of 300 mJ/cm<sup>2</sup> and a contrast of 0.67 when it was postbaked at 150°C for 15 minutes followed by development with toluene/2-propanol at room temperature.

## INTRODUCTION

In recent years, thermally stable, photoreactive polymers such as polyimides have been developed for IC (integrated circuit) fabrication processes due to their high thermal stability and direct patterning ability [1–5]. One of the most important photoimageable polyimide systems consists of the benzophenone skeleton containing alkyl pendant groups.

Aromatic poly(ether ether ketone)s are also currently receiving considerable interest as high performance engineering thermoplastics [6]. A group of poly(ether ether ketone)s containing a benzophenone skeleton as well as alkyl groups in the main chain has been shown to be highly sensitive, negative-resist materials as well as photoreactive polyimides. Crosslinks are formed in these materials on exposure to UV irradiation through hydrogen abstraction by triplet benzophenone from the alkyl groups acting as hydrogen donors, and subsequent coupling of the radical formed. Imai and Kakimoto reported that the poly(ether ketone) synthesized from 3,3',5,5'-tetramethyl-substituted biphenol and 4,4'-difluorobenzophenone was found to crosslink by irradiation with UV light due to the presence of the benzophenone moiety [7]. Ueda et al. reported that poly(ether ether ketone)s containing alkyl groups show good negative-type photosensitive polymers with UV irradiation [8, 9].

In a previous paper we reported that synthesis and characterization of poly(arylene ether)s containing pendant benzoyl groups [10]. These polymers are also expected to be candidates for photosensitive polymer. We now report the synthesis of a new poly(arylene ether) containing pendant 4-isopropylbenzoyl groups and its application as a photosensitive material.

## EXPERIMENTAL

### Materials

Methylhydroquinone (**2**) was purified by recrystallization from a mixture of toluene and acetone. *N,N*-Dimethylacetamide (DMAc) was stirred over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over 4A molecular sieves. The other reagents and solvents were obtained commercially and used as received.

### Monomer Synthesis

1,4-Bis(4-isopropylbenzoyl)-2,5-difluorobenzene (**1**) was prepared by reaction of 2,5-difluoroterephthaloyl chloride with cumene in the manner previously described and recrystallized from 2-propanol [10]. Yield = 60%. mp = 110–111°C.

IR: 1178, 1260, 1504, 1604, and 1664  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.30 (d,  $J = 6.92$  Hz, 12H,  $\text{CHCH}_3$ ), 2.96–3.06 (m, 2H,  $\text{CHCH}_3$ ), and 7.26–7.38 ppm (m, 10H, Arom.).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 23.6 ( $\text{CHCH}_3$ ), 34.4 ( $\text{CHCH}_3$ ), 117.6–118.3 (multiplet), 126.9, 130.3, 130.6–131.0 (multiplet), 134.1, 156.0, 157.2 ( $^1J(\text{C},\text{F}) = 247.8$  Hz), 193.8 ppm ( $\text{C}=\text{O}$ ).

Analysis. Calculated for  $\text{C}_{26}\text{H}_{24}\text{F}_2\text{O}_2$ : C, 76.83%; H, 5.95%. Found: C, 76.87%; H, 6.05%.

### Polymer Synthesis

Into a 25-mL, three neck, round-bottom flask equipped with a stirrer, argon inlet, Dean-Stark trap, and a condenser was placed **1** (0.406 g, 1.00 mmol), potassium carbonate (0.463 g, 3.00 mmol), **2** (0.124 g, 1.00 mmol), DMAc (2.0 mL), and toluene (5 mL). The mixture was heated at reflux for 2 hours as water was removed azeotropically with toluene. The mixture was then heated at reflux for an additional 30 minutes as the remaining toluene was distilled. After excess toluene was completely removed, the reaction mixture was heated at 165°C for 3 hours. Upon cooling, the resulting viscous mixture was poured into water, then the isolated Polymer **3** was reprecipitated out of DMAc into methanol. The polymer was collected, washed with methanol, and dried in vacuo at 50°C for 24 hours. The yield was 0.417 g (85%). The inherent viscosity of the polymer in NMP was 0.93 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

IR: 1200, 1250, 1504, 1604, and 1658  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.28 and 1.31 (d and d,  $J = 4.2$  Hz and 4.0 Hz, 12H,  $\text{CHCH}_3$ ), 1.81 and 1.82 (s and s, 3H,  $\text{ArCH}_3$ ), 2.82–2.98 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 6.52–6.72 (m, 3H,  $\text{OArO}(\text{Me})$ ), 6.80, 6.82, 6.97 and 6.98 (4s, 2H,  $\text{Ar}(\text{COAr})_2$ ), 7.18–7.25 and 7.65–7.78 ppm (m, 8H,  $\text{COAr-CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 16.0 ( $\text{ArCH}_3$ ), 23.5 ( $\text{CHCH}_3$ ), 34.2 ( $\text{CHCH}_3$ ), 117.0, 117.8, 118.0, 118.1, 119.2, 119.3, 119.5, 121.3, 126.5, 130.0, 131.0, 133.2, 133.8, 134.3, 134.5, 149.4, 149.5, 149.9, 152.3, 155.2 (aromatic carbons), 193.5, 193.6, 193.9 ppm ( $\text{C}=\text{O}$ ).

Analysis. Calculated for  $(\text{C}_{33}\text{H}_{20}\text{O}_4)_n$ : C, 80.79%; H, 6.16%. Found: C, 80.84%; H, 6.18%.

### Photosensitivity

A film (3  $\mu\text{m}$ ) on a silicon wafer was exposed to 365 nm UV irradiation using a filtered (U 330) super high-pressure mercury lamp. An exposed film was post-baked at 150°C for 10 minutes, developed with toluene/2-propanol (1:1, vol%) for 40 seconds at room temperature, and rinsed with 2-propanol. The characteristic sensitivity curve was obtained by plotting a normalized film thickness against the logarithmic exposure energy.

### Characterization

Infrared spectra were obtained on a Horiba FT-210 infrared spectrometer, and all nuclear magnetic resonance spectra were obtained using a Jeol EX 270 spectrometer. Viscosity measurements were carried out using a Cannon-Fenske viscometer at 30°C. Thermal analyses were performed on a Seiko SSC/5200 (TG/

DTA 220) thermal analyzer at a heating rate of 10°C/min for thermogravimetric analysis (TGA). The glass transition temperature was measured on a Seiko SSC/5200 (DSC 200) instrument; the heating rate was 20°C/min in nitrogen. The molecular weight was determined by size exclusion chromatography (SEC) with polystyrene calibration using a Jasco HPLC equipped with a Shodex KD-80M column at 40°C in THF. The film thickness was measured by the Dektak 3030 system (Veeco Instrument Inc.).

## RESULTS AND DISCUSSION

### Monomer Synthesis

In order to synthesize poly(arylene ether) with a high sensitivity for UV irradiation, the isopropyl group was introduced into the monomer. Because the stability order of free radicals is tertiary > secondary > primary, dissociation of C–H bonds in the isopropyl group is easier than that of methyl and ethyl groups [11].

A new polymer-forming monomer, 1,4-bis(4-isopropylbenzoyl)-2,5-difluorobenzene (**1**), was prepared by the Friedel-Crafts reaction of 2,5-difluoroterephthaloyl chloride with cumene in excellent yield (Scheme 1).

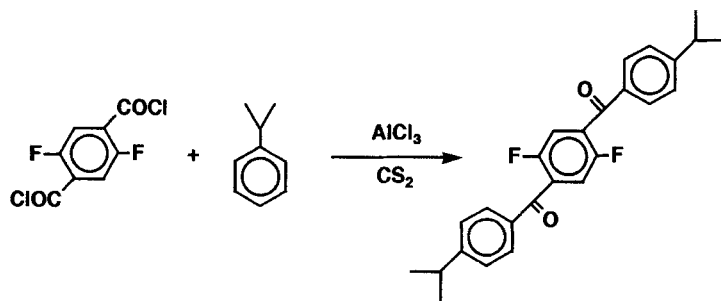
### Polymer Synthesis

The synthesis of the poly(arylene ether) containing pendant isopropylbenzoyl groups (**3**) was achieved by nucleophilic substitution of 1,4-bis(4-isopropylbenzoyl)-2,5-difluorobenzene (**1**) with methylhydroquinone (**2**) by aromatic nucleophilic substitution polycondensation (Scheme 2).

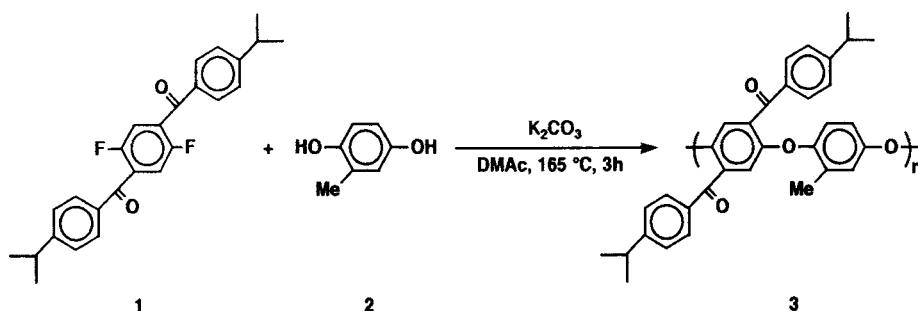
The polycondensation of **1** with **2** was carried out in DMAc in the presence of excess potassium carbonate. First, the water formed during the reaction was most effectively removed as an azeotrope with toluene at 135°C. Then the mixture was heated at 165°C for 3 hours. Polymer **3** was easily produced in excellent yield with an inherent viscosity of 0.93 dL/g.

### Polymer Characterization

Polymer **3** was confirmed to be the corresponding poly(arylene ether) by IR and NMR spectroscopy and elemental analysis. The IR spectrum exhibited characteristic adsorptions at 1658 and 1200 cm<sup>-1</sup> due to C=O and C–O–C stretching,

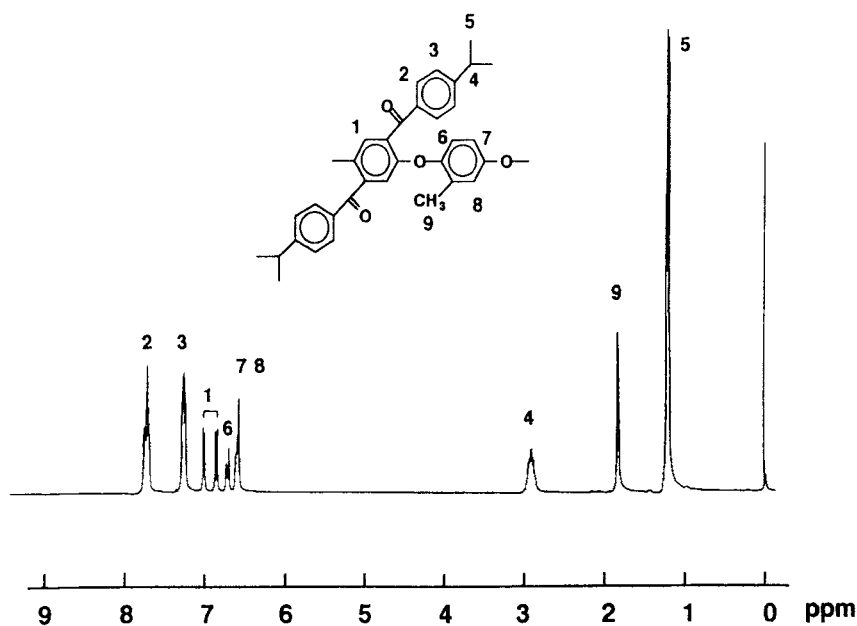


SCHEME 1.



SCHEME 2.

respectively. Elemental analysis also supported the formation of the expected polymer. Figure 1 shows the  $^1\text{H-NMR}$  spectrum of **3**, in which all signals correspond to the structure of **3**. The  $^1\text{H NMR}$  of Polymer **3** showed methyl and isopropyl groups at  $\delta = 1.8$  and  $1.3$ ,  $2.8\text{--}3.0$  ppm, and two multiplet signals at  $\delta = 6.52\text{--}6.72$  and  $7.65\text{--}7.78$  ppm for the methylhydroquinone and benzoyl units. The  $^{13}\text{C-NMR}$  spectrum of Polymer **3** is presented in Fig. 2, together with assignments of the observed resonances. The observed and calculated chemical shifts listed in Table 1 are all within  $\pm 3$  ppm. We can see several splittings of resonances (Fig. 2) that are derived from regio-irregular structures (Scheme 3). Because the methylhydroquinone monomer is nonsymmetric, it would be expected to give the four regio-selective polymers (A: head-to-head; B: head-to-tail; C: tail-to-tail; D: tail-to-tail), considering triads of monomer units. These findings clearly indicate the formation of the expected

FIG. 1.  $^1\text{H-NMR}$  spectrum of Polymer **3** ( $\text{CDCl}_3$ ).

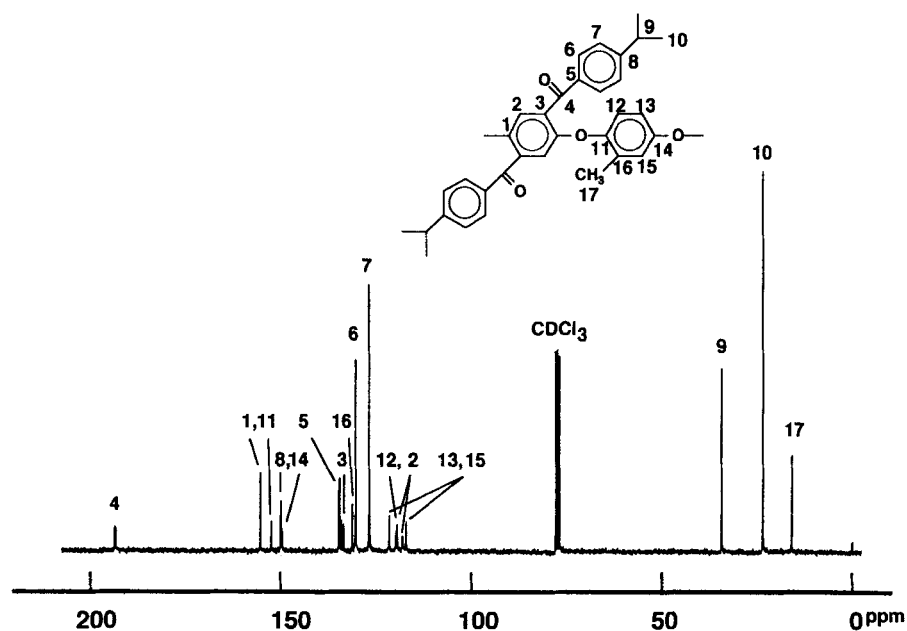
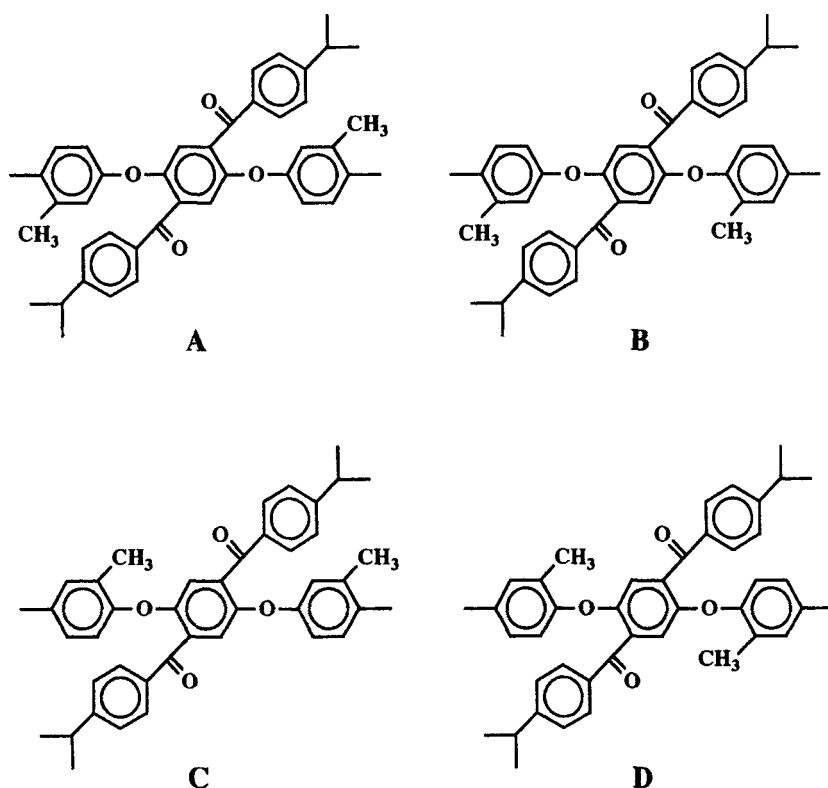


FIG. 2. <sup>13</sup>C-NMR spectrum of Polymer 3 (CDCl<sub>3</sub>).

TABLE 1. Assignment of <sup>13</sup>C-NMR Signals of 3

Carbon	Calculated, ppm	Observed, ppm
1	154.1	155.2
2	122.2	117.7, 118.0, and 119.5
3	133.7	133.2 and 133.8
4	—	193.5, 193.6, and 193.9
5	135.5	134.3 and 134.5
6	130.2	130.0
7	126.3	126.5
8	152.1	1149.9
9	—	34.2
10	—	23.5
11	153.3	152.3
12	120.6	119.2 and 119.3
13	117.8	116.9
14	152.5	149.4 and 149.5
15	121.4	121.3
16	129.6	130.9 and 130.1
17	—	16.0



SCHEME 3.

Polymer 3. Similar splitting effects have been observed in the  $^{13}\text{C}$ -NMR spectrum of PEEK which was prepared from methylhydroquinone [12].

### Polymer Properties

The new Polymer 3 is quite soluble in a wide range of organic solvents including chlorinated solvents, THF, and DMAc. The molecular weight of Polymer 3, which has an inherent viscosity of 0.93 dL/g, was determined by SEC to be unimodal with the relative  $\bar{M}_n$  and  $\bar{M}_w$  values of 86,000 and 220,000, respectively, relative to polystyrene standards. The  $\bar{M}_w/\bar{M}_n$  was 2.5, as expected for step-growth polymerizations.

In thermal analysis (Fig. 3), Polymer 3 exhibited a clear endothermic peak at 140°C due to a glass transition, but no melting endothermic peaks were observed. This is in agreement with x-ray diffraction patterns of Polymer 3 obtained with nickel-filtered  $\text{CuK}\alpha$  radiation, which showed very little crystallinity. Polymer 3 showed a 10% weight loss temperature at 430°C in nitrogen.

### Lithographic Evaluation

The UV-visible spectrum of a film of Polymer 3 (Fig. 4) showed absorption due to  $\pi \rightarrow \pi^*$  of the aromatic ring and  $n \rightarrow \pi^*$  transition of the carbonyl of the



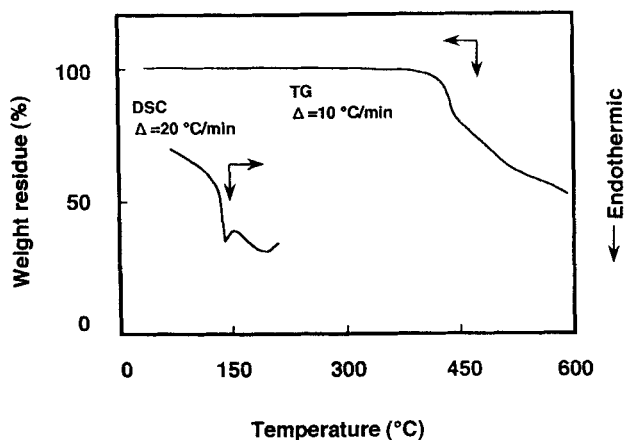


FIG. 3. TG and DSC traces of Polymer 3; N<sub>2</sub> purge.

benzophenone moiety in the 250–390 nm range. Therefore, Polymer 3 would be expected to be photosensitive between 240 and 400 nm UV irradiation.

After a preliminary of optimization study involving developing solvent and prebake and postbake temperatures, the photosensitivity of Polymer 3 was estimated by the following process. The polymer was dissolved in cyclohexanone and a film was spin-cast. This film was prebaked at 100°C for 15 minutes, exposed to 365 nm irradiation with 500 mJ/cm<sup>2</sup>, postbaked at 150°C for 10 minutes, developed with toluene/2-propanol (1:1, vol%) for 40 seconds, and rinsed with 2-propanol.

The sensitivity curve of Polymer 3 exhibited in Fig. 5 indicates that the part which was exposed to UV becomes totally soluble in toluene/2-propanol, and the sensitivity and the contrast were 300 mJ/cm<sup>2</sup> and 0.67, respectively. Polymer 3 was a positive-type resist, contrary to our prediction. In Fig. 6 a scanning electron micrograph of positive images contact-printed in polymer at 500 mJ/cm<sup>2</sup> using toluene/2-propanol (1:1, vol %) as developer is presented. This polymer was capable 10 μm features when a 3-μm thick film was used.

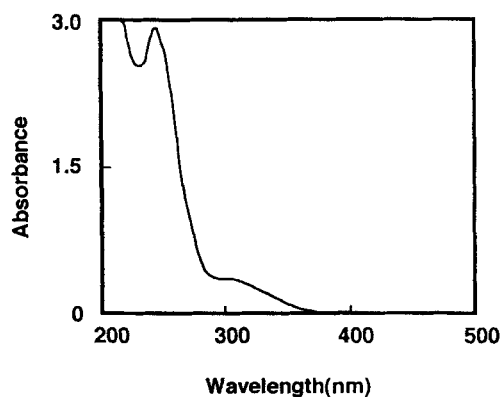


FIG. 4. UV spectrum of Polymer film 3.

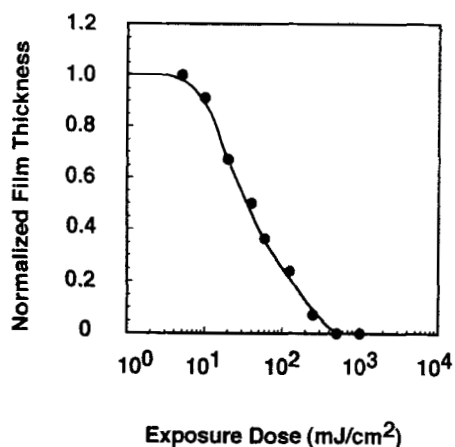


FIG. 5. Sensitivity curve of the system of Polymer 3.

### Mechanism for Positive Image

In many cases, polymers containing a benzophenone skeleton and alkyl groups are crosslinkable with UV irradiation and result in negative-type resist materials. However, Polymer 3 acted as a positive-type resist with UV irradiation. We must address the fundamental question as to why crosslinking did not occur in Polymer 3. Figure 7 shows the IR spectra of polymer 3 film before and after exposure to UV. Compared with the unexposed film of Polymer 3, it was found that OH absorption appeared and the intensity of carbonyl was decreased in the exposed sample. These

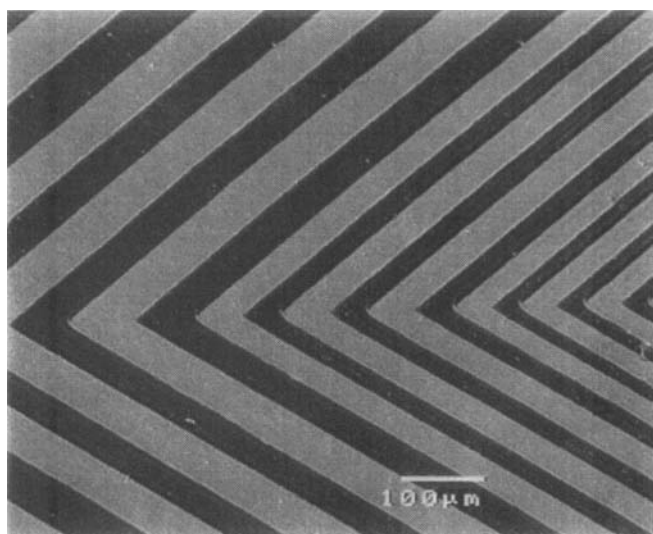


FIG. 6. Scanning electron micrograph of a pattern printed from the system of Polymer 3.

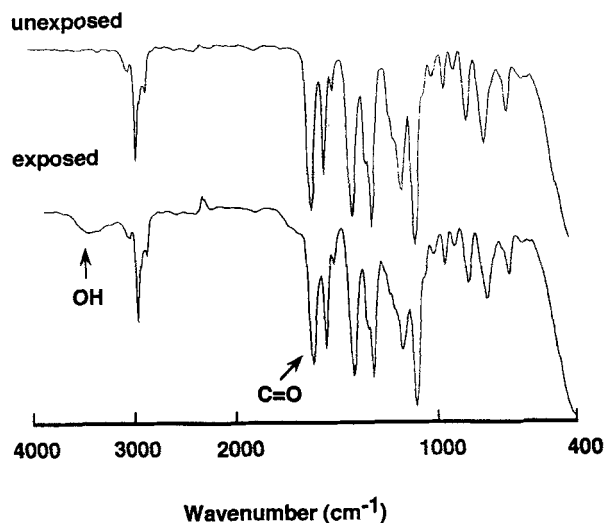
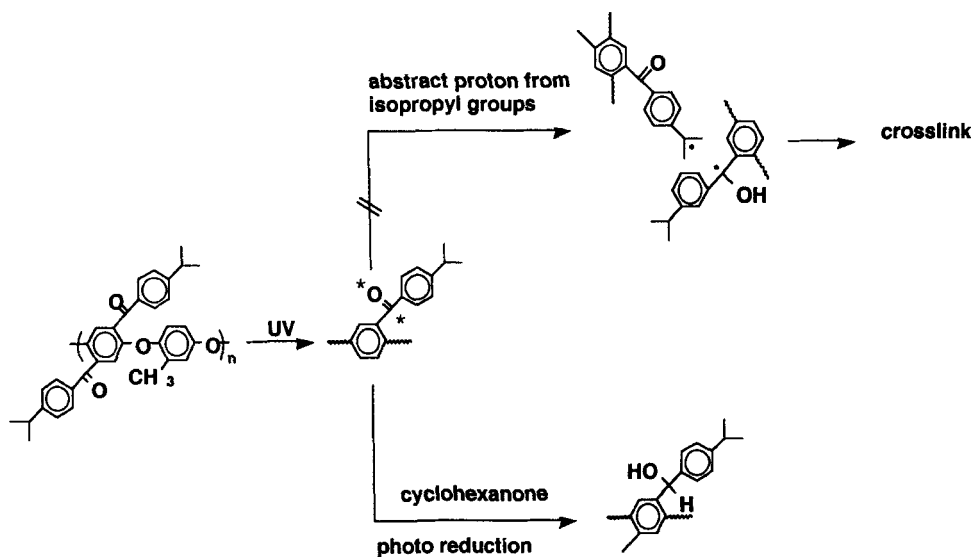


FIG. 7. IR spectrum of Polymer film 3.

facts indicate that crosslinking did not occur but that hydrogen was abstracted from the residual solvent (cyclohexanone) to give a tertiary alcohol (Scheme 4). This is probably due to the following reasons. The two pendant benzoyl groups provide a long conjugated system and would delocalize the oxygen lone pair in the triplet state of Polymer 3. This kind of triplet state would be of low activity with regard to hydrogen abstraction from isopropyl groups on the polymer. When electron-donating groups such as isopropyl groups are substituted *para* to the carbonyl



SCHEME 4.

group, the lifetime of the triplet state would become longer, which means the ratio of  $\pi \rightarrow \pi^*$  to  $n \rightarrow \pi^*$  in the triplet state is large. Thus, the reactivity of hydrogen abstraction from the isopropyl group in the rigid polymer compared to the more mobile solvent would decrease. Furthermore, it is known that the abstraction from the hydrogen on isopropyl groups which are substituted on the *p*-position of an electron-withdrawing group such as a carbonyl group is relatively difficult [13].

## CONCLUSIONS

Poly(arylene ether) containing 4-isopropylbenzoyl groups with a high molecular weight was successfully prepared by the nucleophilic substitution reaction of 1,4-bis(4-isopropylbenzoyl)-2,5-difluorobenzene with methylhydroquinone. Polymer 3 was amorphous and showed good thermal properties. It functioned as a positive-type photosensitive polymer with UV irradiation (240–400 nm).

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