

Synthesis and Characteristics of Organic Soluble Photoactive Polyimides

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SYNOPSIS

Soluble aromatic polyimides with inherent viscosities of 0.23–0.50 dL/g have been synthesized from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (BAPAF) and various aromatic tetracarboxylic dianhydrides. Almost all polyimides were soluble in a wide range of organic solvents, i.e., acetone, *m*-cresol, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, *N,N*-dimethylsulfoxide, *N*-methyl-2-pyrrolidone, methyl ethyl ketone, and tetrahydrofuran (except that polyimide derived from 3,3',4,4'-biphenyl tetracarboxylic dianhydride). Synthesized polyimides have a glass transition temperature in a range of 293 to 355°C, showing no appreciable weight loss up to 400°C in both air and nitrogen. These soluble polyimides exhibit high transparency in the UV visible region, with water absorption being between 3.6 to 5.7 wt %. They provide an aqueous base developable positive photoresist system when formulated with diazonaphthoquinone sensitizer. On the other hand, negative photoactive polyimides which are soluble in common organic solvents and optically transparent at a light of 365 nm wavelength, being obtained by reacting these soluble polyimides with methacryloyl chloride. Properties and characteristics of both positive and negative photoactive polyimides have been studied here. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides with a high thermal stability and low dielectric constant have been important organic materials in production of electronic devices. In recent years,¹ the extensive applications of photo-reactive polyimides and their precursors to passivation layer, alpha particle barrier, stress buffer, and interlayer dielectric are increasingly important in place of nonphotoreactive polyimides. A number of photoimaginable polyimides^{2,3} and their precursors^{4–6} have been reported, but most of them are not satisfactory for practical use. Novel photoreactive polyimide precursors that involve the hexafluoropropyl group within the chain structure have been studied.^{7–9} However, most of photoreactive polyimides and their precursors are negative working and the reports on positive-working photoreactive polyimides or precursors that are soluble in solvent

on exposure to the light is very limited. In recent years, a number of reports on positive-working polyimides^{10–14} have been investigated, which have been improved in transparency and solubility in common organic solvents.

In this article, soluble polyimides were synthesized from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (BAPAF) with various aromatic tetracarboxylic dianhydrides. These soluble polyimides have also been used here in developing a thermal stable positive and negative acting photoresist that could be processed like a conventional photoresist with improved physical, chemical, and lithographic characterizations.

EXPERIMENTAL

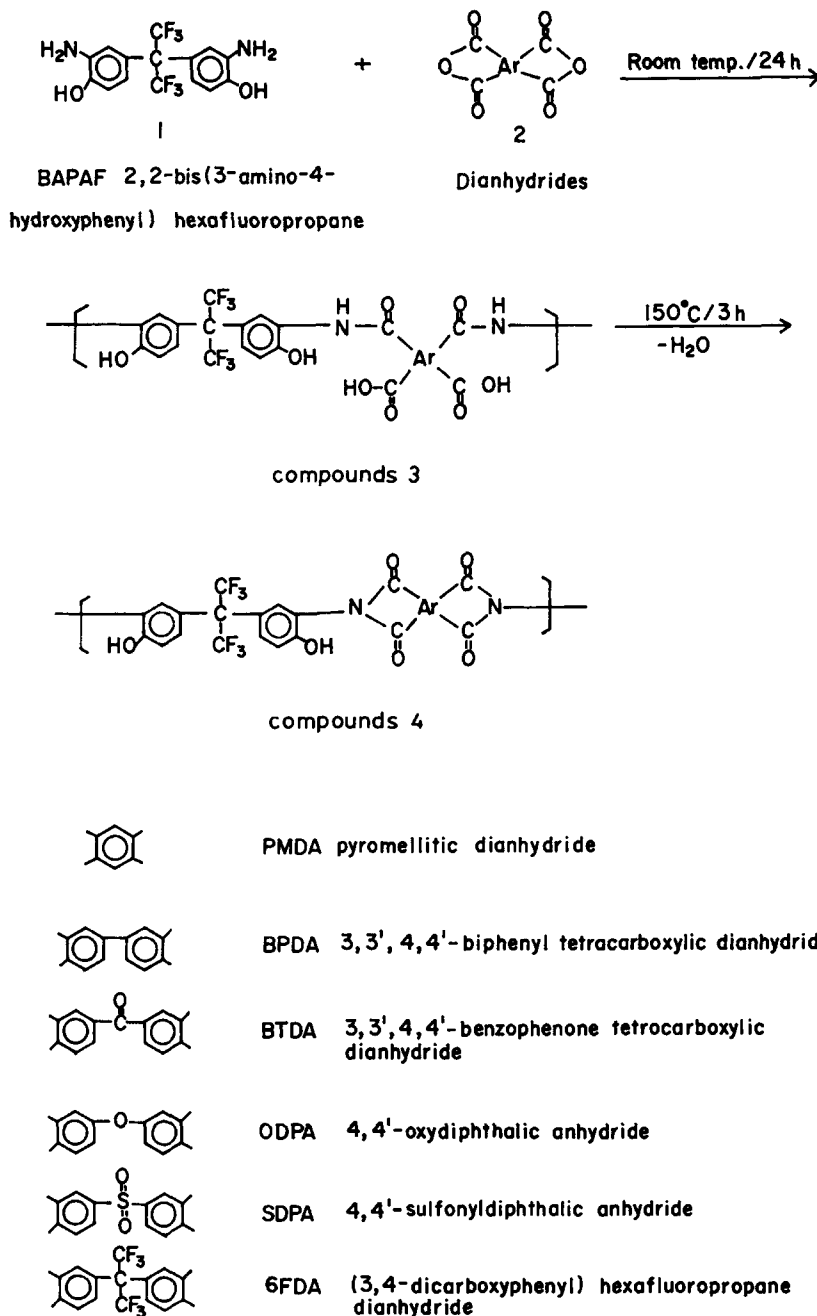
Materials

2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane (BAPAF, Central Glass) was purified by recrystallization from methyl alcohol. Pyromellitic dianhydride (PMDA, Merck) and 3,3',4,4'-benzo-

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phenoetetracarboxylic dianhydride (BTDA, Aldrich) were refluxed in acetic anhydride for 3 h, filtered, and then dried at 150°C for 3 h prior to being used. The other dianhydrides, used as received, included 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, Chriskev), 4,4'-oxydiphthalic anhydride (ODPA, Chriskev), 4,4'-sulfonyldiphthalic anhydride (SDPA, Chriskev), 4,4'-(hexafluoroisopro-

pylidene)-bis-(phthalic anhydride) (6FDA, Hoechst Celanese). *N,N*-Dimethylacetamide (DMAc, Merck) was dried over molecular sieve 4Å and fractionally distilled under vacuum from calcium hydride. Other solvents were obtained from Merck Company, Inc., and used as received. The structures for the monomers are listed in Scheme 1 and the abbreviations for solvents are listed in Table I.



Scheme 1

Table I The Solvent Abbreviations

Solvent	Abbreviations
Acetone	A
<i>m</i> -Cresol	C
Chloroform	CF
Cyclohexanone	CH
Dichloromethane	DCM
<i>N,N</i> -Dimethylacetamide	DMAc
<i>N,N</i> -Dimethylformamide	DMF
<i>N,N</i> -Dimethylsulfoxide	DMSO
Dioxane	DO
2-Ethoxyethanol	EE
Ethyl alcohol	EOH
Isoamyl acetate	IA
Methanol	MeOH
2-Methoxyethanol	ME
Methyl ethyl ketone	MEK
<i>N</i> -Methyl-2-pyrrolidone	NMP
Nitrobenzene	NB
Tetrahydrofuran	THF

Synthesis of the Organic Soluble Fluorine-Containing Polyimides

Fluorine-containing polyimides (Scheme 1, compound 4) were prepared according to a general reaction shown in Scheme 1. Polymerizations were conducted in a closed vessel at room temperature with a concentration of 15% solids by weight in DMAc. A stoichiometric amount of one of the dianhydrides was added to a solution of diamine BAPAF in DMAc. The container was flush with dry nitrogen and mechanically stirred overnight; it then obtained polyamic acid (Scheme 1, compound 3) solution and thermally cyclized at 150°C for 3 h. Water that was eliminated by its ring closure reaction, after this step, was separated as a *m*-xylene azeotrope at the same time. Compounds 4 were precipitated from the DMAc solution with water after reaction was completed, it was then dried overnight at 50°C in a vacuum oven.

Synthesis of the Negative Photoactive Fluorine-Containing Polyimides

Soluble compounds 4 were dissolved in DMAc, and then methacryloyl chloride and triethylamine being added (Scheme 2). Reaction was carried out at 0°C for 5 h. Reaction solution was poured into a large amount of water, with negative photoactive fluorine-containing polyimides having methacryloyl group (Scheme 2, compound 5) being obtained as the pre-

cipitate. It was purified by repeating reprecipitation, using DMAc and water. Then it was dried overnight at 50°C in a vacuum oven.

Measurements

IR spectra were recorded on a Perkin Elmer 842 spectrophotometer. ¹H NMR spectra were obtained on a Bruker MSL-400 spectrometer, using DMSO-d₆ as a solvent. Inherent viscosity was measured in a solution of 0.5 g of polyimide dissolved in 100 mL of DMAc at a temperature of 30°C. Wide angle x-ray diffraction patterns were obtained for powder specimens on a Rigaku XG x-ray diffraction apparatus with nickel-filtered radiation (30 kV, 20 mA). Thermal behaviors of polyimides were studied by using a DuPont 2100, equipped with 900 differential scanning calorimetry (DSC) and 910 thermogravimetric analyzer (TGA) modules. All measurements were made at a heating rate of 10°C/min in air or nitrogen, at a flow rate of 50 mL/min. Transmission UV-visible spectra were obtained on a Hitachi 320 UV-VIS spectrophotometer. Refractive index of compounds 4 were measured by an AutoEL-II automatic ellipometer with 589 nm wavelength. Water

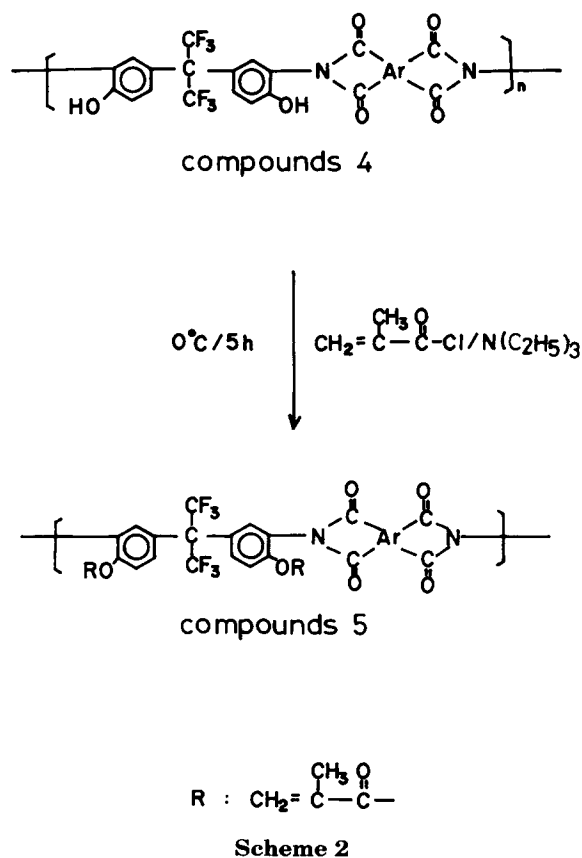


Table II Synthesis of Compounds 4

Diamine	Dianhydrides	Solvent (DMAc/g)	Compounds 4 ^a		
			Code	η_{inh}^b	Remark ^c
BAPAF	PMDA	66	BAPAF/PMDA	0.50	S
	BPDA	75	BAPAF/BPDA	—	S → P
	BTDA	78	BAPAF/BTDA	0.34	S
	ODPA	76	BAPAF/ODPA	0.27	S
	SDPA	83	BAPAF/SDPA	0.23	S
	6FDA	92	BAPAF/6FDA	0.23	S

^a Polymerization was carried out with 0.02 mol of each monomer in DMAc at room temperature for 24 h. The yields of compounds 4 were greater than 96%.

^b Measured at 0.5 g/dL in DMAc in 30°C.

^c P: Polymer Precipitation; S: Homogeneous solution.

absorptions were measured as followed: specimens were immersed in water of 30°C, with weight differences (after aging) being measured. Dissolution rate was measured by using laser interferometry. Film thickness were measured by Dektak IA surface profile.

Solubility Tests

Solubility tests of compounds 4 were carried out by following procedures. Specimens of 0.5000 ± 0.0005 g were immersed in 5 mL of liquid in sealed glass tubes. The tubes were placed in water bath at a tem-

perature of 30°C and continuously shaken for 24 h, then the samples were inspected.

Each of the negative photoactive compounds 5 was dissolved in DMAc in appropriate concentration followed by addition of Michler's ketone (MK) as an initiator. They were spin coated onto quartz substrate, prebaked at 90°C for 30 min, and then half the area of each sample was exposed at 365 nm wavelength to a filtered high pressure mercury lamp. They were developed in various solvents at a constant conditions. After that, both exposed and unexposed parts were observed.

Lithographic Evaluation

Film Formation

Some initiators or sensitizers were added to a 20 wt % solution of photoactive polyimides in DMAc. Solution was then spread on silicon wafer or quartz substrate using a spincoater with a speed of 1500 rpm in forming a photosensitive layer; it was then prebaked at 90°C for 30 min.

Photosensitivity

Approximately 1 μm photosensitive polyimide film on a silicon wafer (or quartz substrate) was exposed at 365 nm wavelength to a filtered high pressure mercury lamp, being developed with an appropriate developer. Characteristic curve as obtained by a ratio of remained film thickness against exposure energy.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polyimides

Aromatic compounds 4 were synthesized by the standard two-step polymerization method using

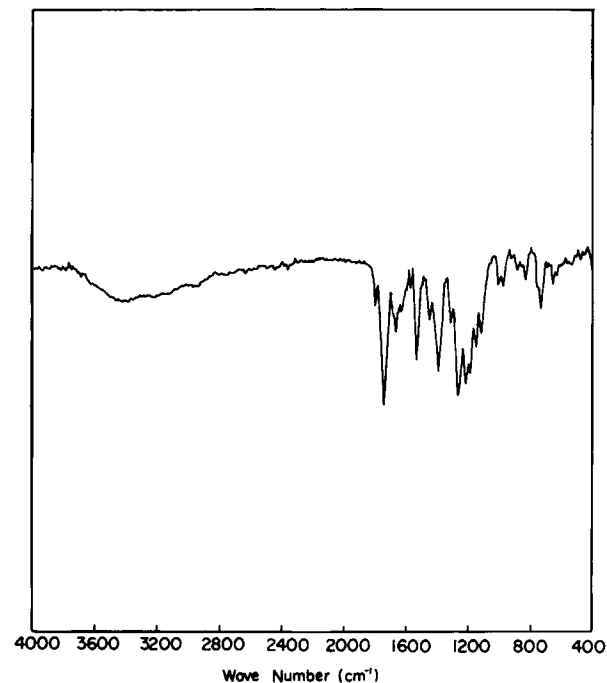


Figure 1 IR spectra of compound 4 BAPAF/6FDA.

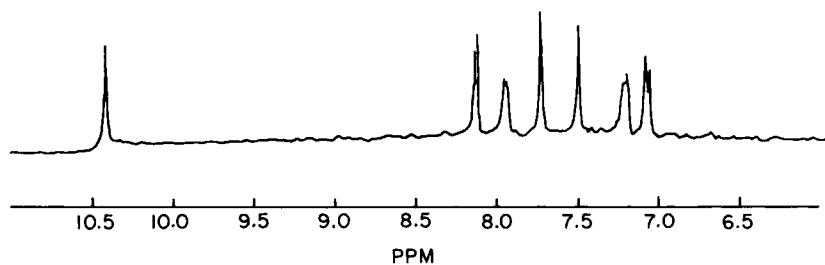


Figure 2 ^1H NMR spectra of compound 4 BAPAF/6FDA.

BAPAF and aromatic tetracarboxylic dianhydrides, which involved the ring-opening polymerization and subsequent cyclodehydration as shown in Scheme 1.

In the first step, the reaction of BAPAF and tetracarboxylic dianhydrides, were carried out in DMAc at room temperature and the resulted polyamide acid (compound 3) solutions were homogeneous, with no precipitation occurring. Thermal conversion of compounds 3 to compounds 4 (the second step of the imidization process) was accomplished by refluxing compound 3 solutions with m-xylene at 150°C for 3 h under nitrogen. These compounds 4 gave brown solutions, with no precipitation occurring. However, compound 4 BAPAF/BPDA precipitated during the course of cooling. It is probably due to its limited solubility in the lower temperature. Inherent viscosities of these compounds 4 were in range of 0.23 to 0.50 dL/g (Table II). The yield for the synthesized compounds 4 were greater than 96% (Table 2).

The identifications of compounds 4 were carried out by employing IR and ^1H NMR spectroscopies. Figure 1 is a typical IR spectrum of compound 4 BAPAF/6FDA. Similar results were observed for other polyimides. Absorption peaks are identified as

$\nu_{\text{O-H}}$ of hydroxyl group (3000 cm^{-1} to 3600 cm^{-1}), $\nu_{\text{C=O}}$ of imide carbonyl group (1775 cm^{-1} and 1715 cm^{-1}), $\nu_{\text{C-N}}$ of C—N (1355 cm^{-1}) and $\nu_{\text{C-F}}$ of perfluoromethyl group (1100 cm^{-1} to 1300 cm^{-1}) (Fig. 1). Structure for compound 4 BAPAF/6FDA was also determined by ^1H NMR (Fig. 2). Peaks at 10.4 ppm were due to a proton of hydroxyl group; and 7.0 ppm to 8.5 ppm due to a proton of benzene rings. From results of IR and ^1H NMR spectrum, the conversions of compounds 3 into compounds 4 by this imidization process are confirmed.

Compounds 4 synthesized from BAPAF with various aromatic tetracarboxylic dianhydrides, have a flexible linkage of 6F group in backbone and polar substituent of hydroxyl group along the polymer backbone. As a result, they will have good solubility in most organic solvents. Solubility tests of compounds 4 were carried out in 10 solvents, with results having been summarized in Table III. Compound 4 BAPAF/BPDA is insoluble in all solvents, whereas other compounds 4 derived from PMDA, BTDA, ODPA, SDPA, and 6FDA have good solubility in organic solvents except that in chloroform. It seems that the high solubility of compounds 4 derived from BAPAF achieved by that of the 6F group separates

Table III Solubility Tests for Compounds^{a,b}

Compound 4	Solvents									
	A	C	CF	DMAc	DMF	DMSO	MeOH	MEK	NMP	THF
BAPAF/PMDA	S	S	NS	S	S	S	S	S	S	S
BAPAF/BPDA	NS	NS	NS	SW	SW	SW	NS	NS	SW	NS
BAPAF/BTDA	S	S	SW	S	S	S	PS	S	S	S
BAPAF/ODPA	S	S	SW	S	S	S	S	S	S	S
BAPAF/SDPA	S	S	SW	S	S	S	PS	S	S	S
BAPAF/6FDA	S	S	SW	S	S	S	S	S	S	S

^a Solubility tests were carried out that compounds 4 of 0.5000 ± 0.0005 g were immersed in 5 mL liquid in sealed glass tubes at 30°C for 24 h.

^b S: Soluble, PS: Partial soluble, SW: Swelling, and NS: Nonsoluble.

the aromatic rings, and the trifluoromethyl group hinders the interaction between neighboring molecules.

Wide angle x-ray diffractions of compounds 4 are shown in Figure 3. All compounds 4 showed amorphous pattern.

Thermal properties of compounds 4 were evaluated by means of a differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA). Representative thermogram of compound 4 BAPAF/6FDA, similar results were observed for other polyimides, is shown in Figure 4. Compounds 4 had a relatively high glass transition temperature (T_g) between 293°C and 355°C, depending on structure of composition. Compounds 4 derived from PMDA and BPDA (with hard units) had a higher T_g than other compounds 4 with flexible units. An increase in T_g was observed according to the following series: ODPa < BTDA < 6FDA < DSPA < BPDA < PMDA. Compounds 4 exhibited a good resistance to thermal and thermooxidative degradation up to 400°C, as reflected by results of TGA in both air and nitrogen atmospheres. Data of thermal properties of compounds 4 are summarized in Table IV.

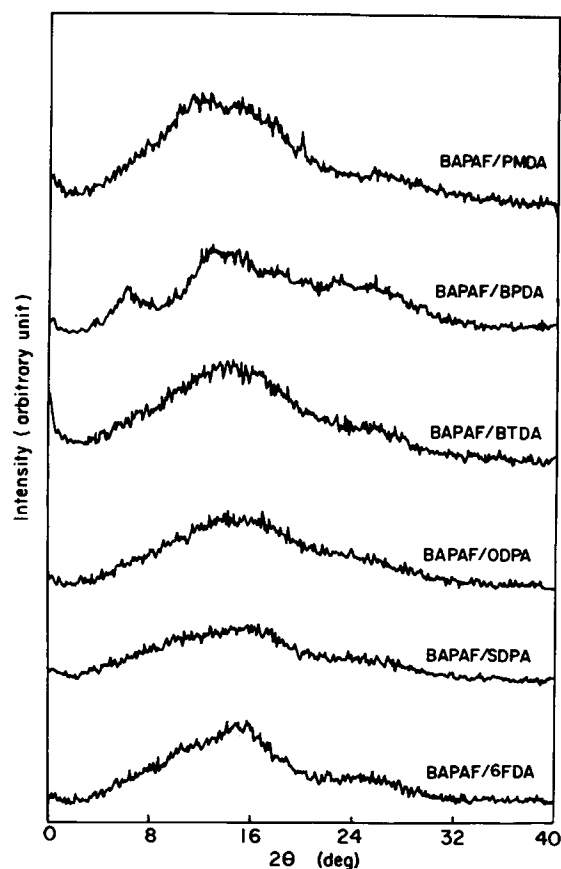


Figure 3 X-Ray diffractograms of compounds 4.

Table IV Thermal Properties of Compounds 4

Compound 4	T_g (°C) ^a	Decomposition Temperature (°C) ^b	
		Air	Nitrogen
BAPAF/PMDA	353	443	447
BAPAF/BPDA	335	476	471
BAPAF/BTDA	304	473	471
BAPAF/ODPA	293	483	445
BAPAF/SDPA	313	483	431
BAPAF/6FDA	306	482	456

^a T_g (glass transition temperature) were determined by DSC in nitrogen at a heating rate of 10°C/min.

^b Temperature at which 10% weight loss were recorded by TGA at a heating rate of 10°C/min.

Tetracarboxylic dianhydrides had a significant influence on thermal and thermooxidative stability of compounds 4. Following relative order of thermal stability based on a 10% weight loss temperature in nitrogen, was observed: BPDA > BTDA > 6FDA > ODPa > PMDA > SDPA. Relative order of thermooxidative stability in air was observed as: ODPa > SDPA, 6FDA > BPDA, BTDA > PMDA.

Transmission UV-visible spectra of THF solution of compounds 4 with concentration of 1×10^{-3} mol/L in 250–600 nm wavelength are shown in Figure 5. Strong absorptions, with a cutoff located between 300 and 400 nm, are observed. No distinct peak maximum was obtainable. Molar extinction coefficients of these compounds 4 at 365 nm were 60 to 387 L/mol cm (Table V), they indicate a high transparency in this wavelength region.

Refractive index decreases from 1.59 to 1.52 in compounds 4 as fluorine content increases (Fig. 6). Introduction of 6F group directly lead to a decrease in reflective index of compounds 4.

Table V Transmittance ($T\%$) and Mol Extinction Coefficient (ϵ) of Compounds 4 at 365 nm Wavelength

Compound 4	$T(\%)$ ^a	$\epsilon(\text{L/mol cm})$ ^b
BAPAF/PMDA	59	229
BAPAF/BTDA	41	387
BAPAF/ODPA	87	60
BAPAF/SDPA	67	174
BAPAF/6FDA	87	60

^a Obtained from UV-visible spectra of 1×10^{-3} mol/L THF solution of compounds 4 at 365 nm wavelength.

^b Calculated from the equation: $\text{LOG}_{10}(100/T) = \epsilon c l$.

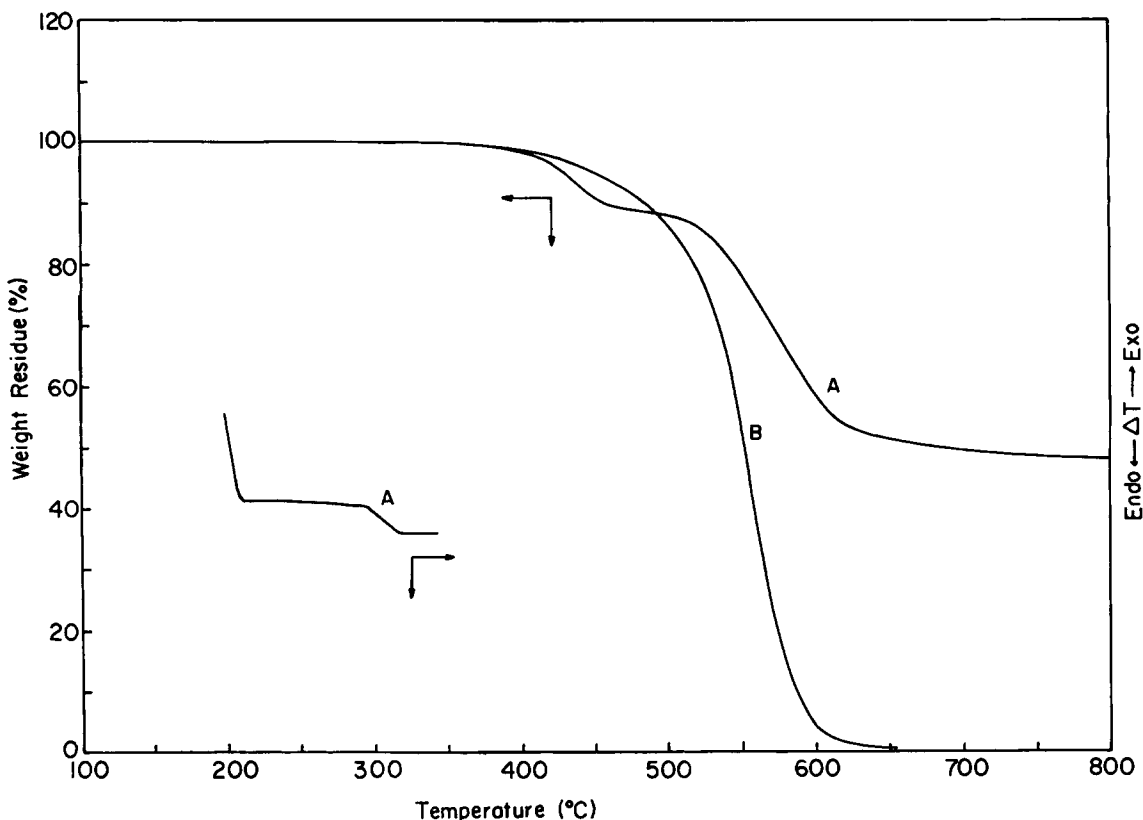


Figure 4 TGA and DSC curves for compound 4 BAPAF/6FDA measured at a heating rate of 10°C/min: (A) in nitrogen, (B) in air.

Water absorption of compounds 4 are compared with those of reference polyimides prepared from *m*-phenylenediamine (MPD)¹⁶ in Figure 7. Since compounds 4 contained a hydroxyl group along polymer backbone, which could form H-bonding with water, therefore, values of water absorption ra-

Table VI Dissolution Rate of Compounds 4

Compound 4	Dissolution Rate of Compounds 4 ($\mu\text{m}/\text{min}$) ^{a,b}				
	R ₁	R ₂	R ₃	R ₁ /R ₂	R ₃ /R ₂
BAPAF/PMDA	5.44	4.00	6.74	1.35	1.68
BAPAF/BTDA	6.57	3.45	4.95	1.90	1.43
BAPAF/ODPA	4.60	2.12	4.52	2.17	2.34
BAPAF/SDPA	4.63	2.90	5.06	1.60	1.74
BAPAF/6FDA	0.92	0.19	2.64	4.92	14.15

^a Dissolution rate of compounds 4 were measured in 0.05N NaOH base solution at 25°C by using laser interferometry.

^b R₁: Dissolution rate of compounds 4. R₂: Dissolution rate of compounds 4 + 20 wt % PAC (unexposed). R₃: Dissolution rate of compounds 4 + 20 wt % PAC (exposed).

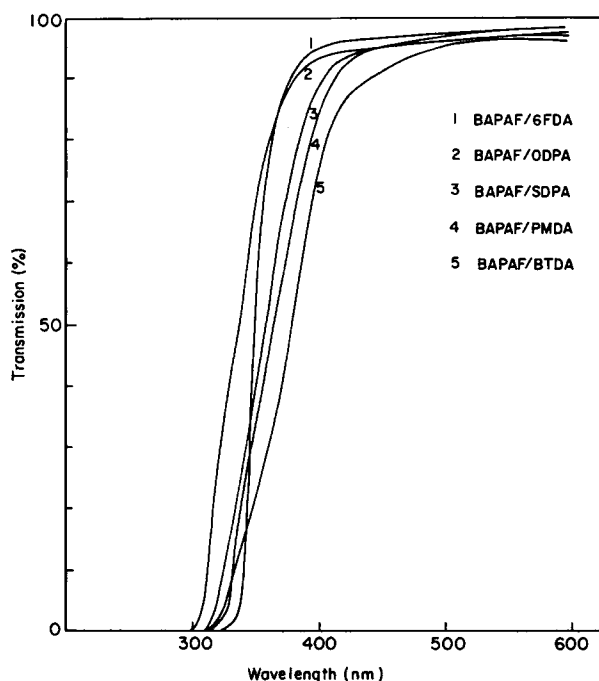


Figure 5 UV-visible spectra of compounds 4 solution in THF at concentration of 1×10^{-3} mol/L.

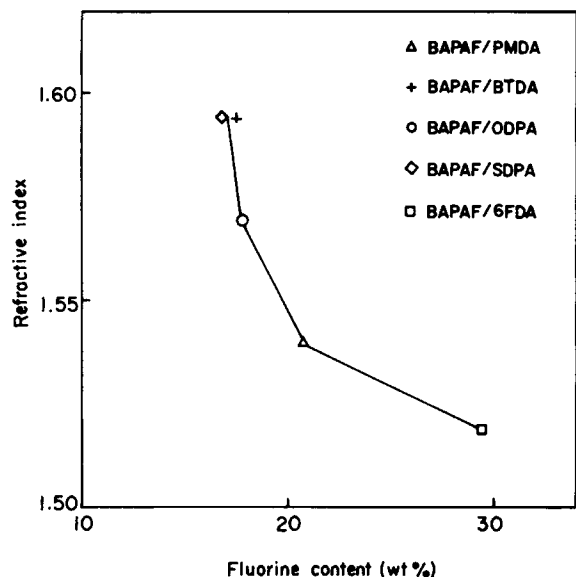


Figure 6 Relationship between refractive index and fluorine content of compounds 4 (the 589 nm wavelength was used to measure the refractive index).

tio of compounds 4 are between 3.6 to 5.7 wt %, being higher than reference polyimides (which are in a range of 1.6 to 3.1 wt %).¹⁶

Polyimides as Positive Resists

The performances of compounds 4 as positive photoresists were studied, which were processed simi-

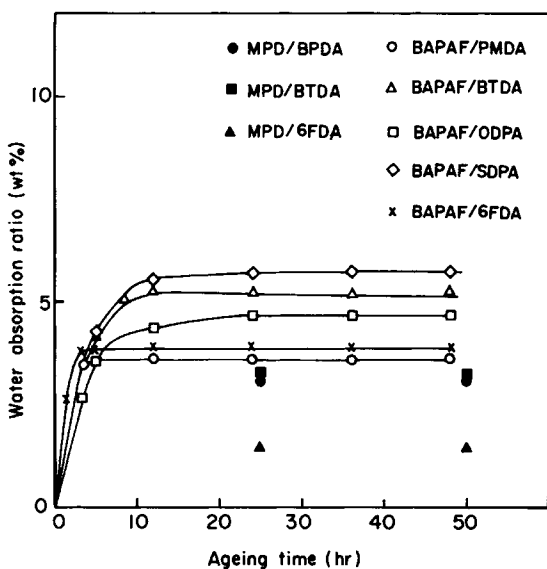
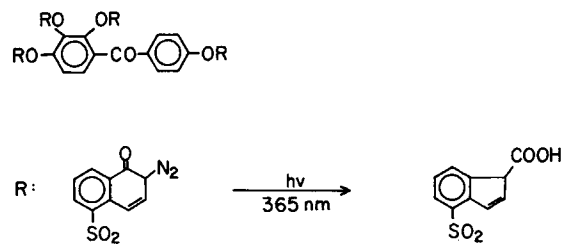


Figure 7 Water absorptions of compounds 4 after immersing in water of 30°C and the reference polyimides prepared from *m*-phenylenediamine (MPD).¹⁶



Scheme 3

larly to a conventional positive photoresist when they were formulated with a diazonaphthoquinone sensitizer. Table VI contains dissolution rate data for compounds 4 and for the compounds 4 containing 20 wt % of diazonaphthoquinone sensitizer (Scheme 3). Using a 0.05*N* solution of sodium hydroxide as the developer, the dissolution rate of the compounds 4 were measured. Rate of compounds 4 dissolution in 0.05*N* NaOH solution was in a range of 0.92 to 6.57 $\mu\text{m}/\text{min}$, depending on the structure of polyimide. Effect of compounds 4 structure on dissolution rate in base solution is still not clear. The addition of the diazonaphthoquinone sensitizer decreases this rate to 0.19–4.00 $\mu\text{m}/\text{min}$. However, upon the exposure under UV light (365 nm) the rate of dissolution is increased to 2.64–6.74 $\mu\text{m}/\text{min}$, a rate substantially faster than the original compounds 4. The

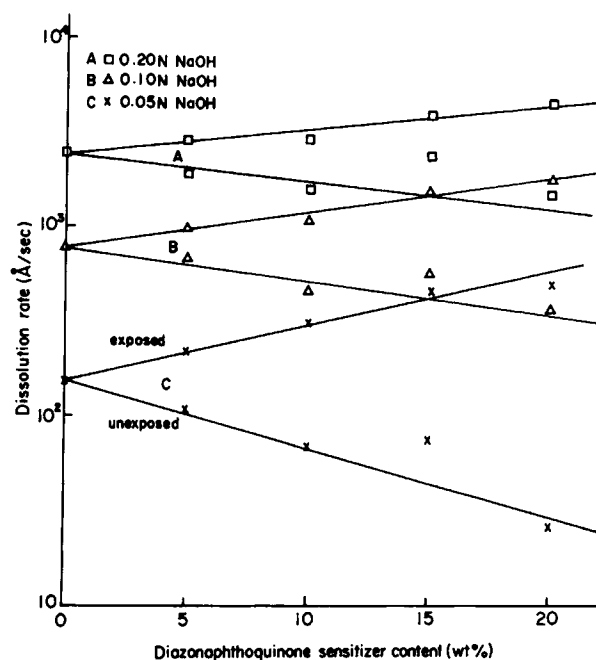


Figure 8 Dissolution rates of unexposed and exposed resist made from compound 4 BAPAF/6FDA and diazonaphthoquinone sensitizer.

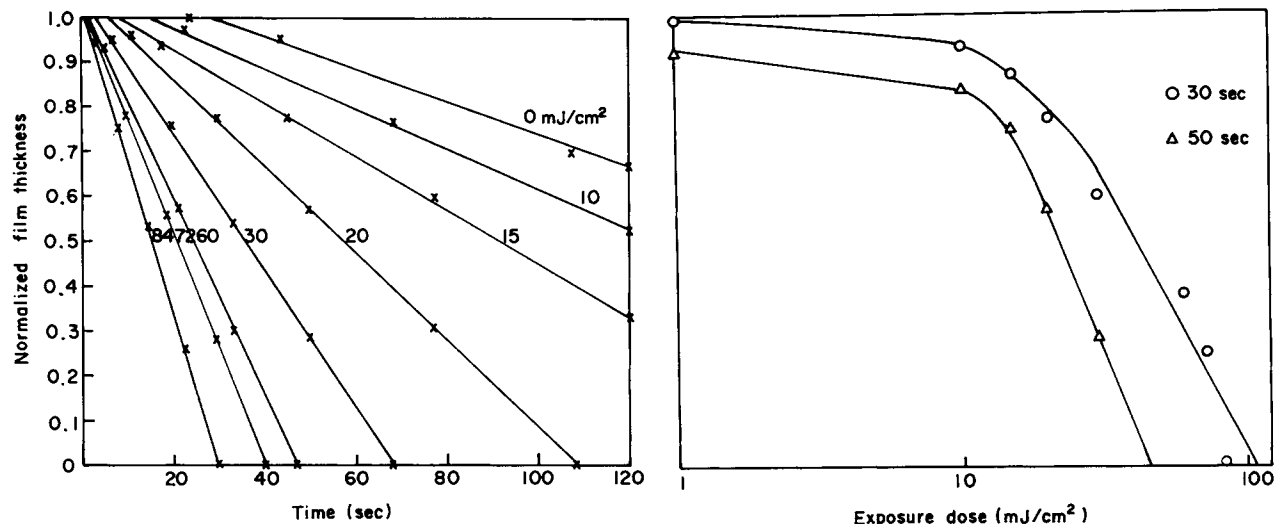


Figure 9 (a) Normalized film thickness vs. time developer curves for compound BAPAF/6FDA with 20 wt % diazonaphthoquinone sensitizer that received different exposure doses. (b) Normalized film thickness vs. exposure dose curve derived from (a).

developer discrimination between exposed and unexposed compounds 4 containing diazonaphthoquinone sensitizer are not high except for the compound 4 (BAPAF/6FDA) which has a better discrimination/dissolution rate ratio of 14.15. The discrimination/dissolution rate ratio of most compounds 4 are lower than that for the conventional novolac positive photoresist.¹⁷ It is difficult to formulate the compounds 4 (except compound 4 BAPAF/6FDA) into a simple resist because there is too much thickness lost in the unexposed areas when a developer is used to develop the exposed areas in a reasonable time. From above results, only the compound 4 BAPAF/6FDA can be used as a positive photoresist.

A series of experiments were done here in knowing the effect of content of diazonaphthoquinone sensitizer and concentration of NaOH base solution on the dissolution rate of compound 4 BAPAF/6FDA before and after exposure. Results are summarized in Figure 8. Dissolution rate of compound 4 BAPAF/6FDA is increased as concentration of NaOH base solution increased (Fig. 8). The dissolution rate is decreased with the increasing of the content of diazonaphthoquinone sensitizer while the compound is unexposed. Results, however, are opposite for after exposure. It is because the diazonaphthoquinone sensitizer which acts as dissolution inhibitor before exposure does not dissolve in NaOH base solution. Upon irradiation, diazonaphthoquinone sensitizer turns into an acid (Scheme 3) which is soluble in NaOH base solution and no longer acts

as a dissolution inhibitor and, instead, promotes the dissolution rate. From the study shown in Figure 8, the best discrimination/dissolution rate ratio of BAPAF/6FDA polyimide is obtained under the

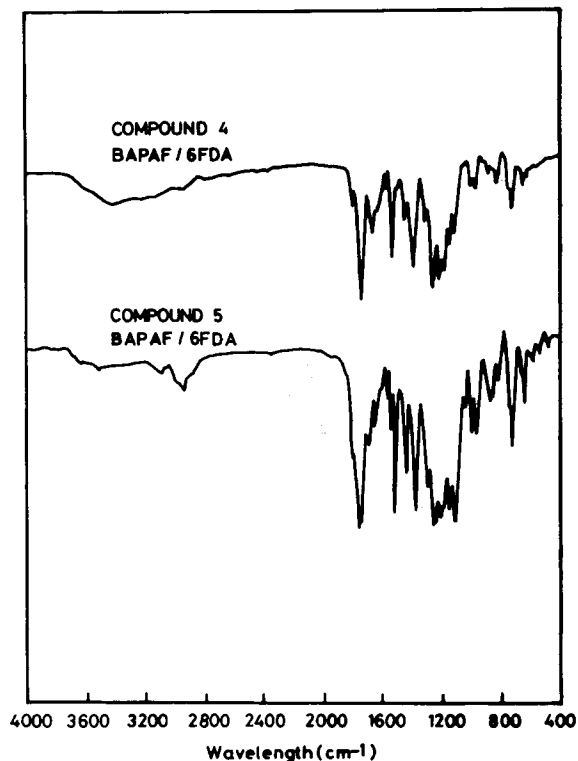


Figure 10 IR spectra of compound 4 and compound 5 BAPAF/6FDA.

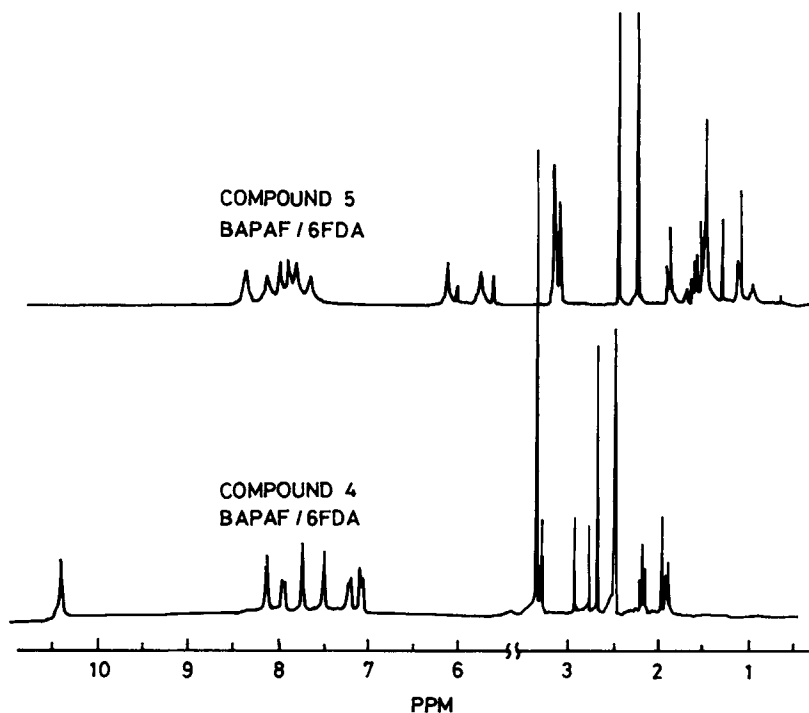


Figure 11 ^1H NMR spectra of compound 4 and compound 5 BAPAF/6FDA.

conditions of high content of diazonaphthoquinone sensitizer and low concentration of NaOH base solution.

Figure 9 shows the results of exposure characteristic for compound 4 BAPAF/6FDA with 20 wt % diazonaphthoquinone sensitizer while it was devel-

Table VII Solubility in Unexposure (Unexp) Areas and Exposure (Exp) Areas to Various Solvents of Photoactive Compounds 5

Solvent	PMDA		BTDA		ODPA		SDPA		6FDA	
	Unexp	Exp	Unexp	Exp	Unexp	Exp	Unexp	Exp	Unexp	Exp
A	S	SW	S	IS	S	IS	S	IS	S	IS
MEK	S	IS	S	IS	S	IS	S	IS	S	IS
CH	S	IS	S	IS	S	IS	S	IS	S	IS
ME	S	SW	S	SW	S	IS	S	IS	S	PSW
EE	S	PSW	PS	PSW	PS	IS	IS	IS	S	IS
DO	S	IS	S	IS	S	IS	S	IS	S	IS
THF	S	SW	S	PSW	S	IS	S	IS	S	SW
DCM	S	IS	S	IS	S	IS	S	IS	S	IS
CF	S	IS	S	IS	S	IS	S	IS	S	IS
C	S	SW	S	SW	S	SW	S	SW	S	SW
IA	S	IS	PS	IS	PS	IS	PS	IS	S	IS
DMSO	S	SW	S	SW	S	SW	S	SW	S	SW
DMAc	S	SW	S	SW	S	SW	S	SW	S	SW
DMF	S	SW	S	SW	S	SW	S	SW	S	SW
NMP	S	SW	S	SW	S	SW	S	SW	S	SW
NB	S	IS	S	SW	S	SW	S	SW	S	SW
MeOH	PS	IS	PS	IS	PS	IS	PS	IS	S	IS
EOH	PS	IS	IS	IS	PSW	IS	PSW	IS	SW	IS

Abbreviations: S: Soluble, PS: Partial Soluble, PSW: Partial Swelling, SW: Swelling, and IS: Insoluble.

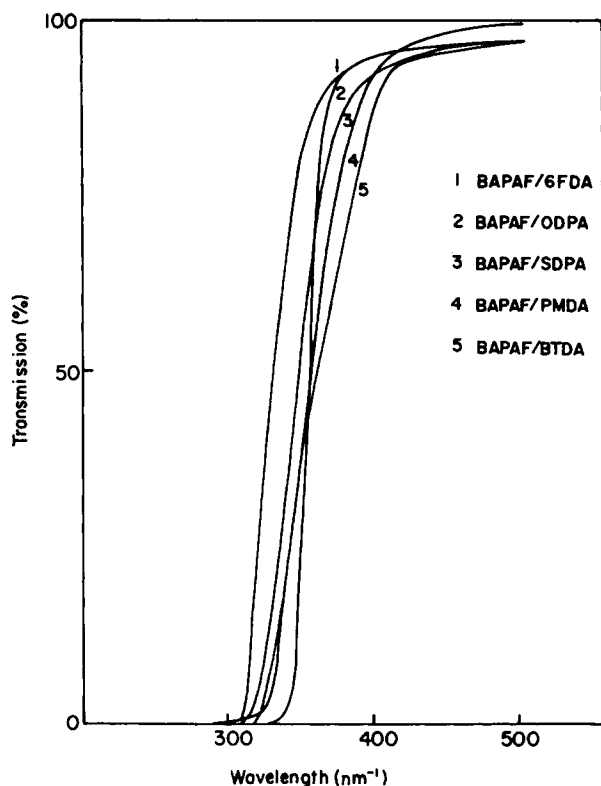


Figure 12 UV-visible spectra of compounds 5 solution in THF at concentration of 1×10^{-3} mol/L.

oped in 0.05N NaOH base solution. Sensitivity of this system is approximately 105 and 46 mJ/cm^2 , with the contrast being 1.18 and 1.53 (which is ob-

tained at a development time of 30 s and 50 s, respectively).

Photoactive Polyimides as Negative Resists

Negative photoactive compounds 5 were obtained from the reaction of compounds 4 with methacryloyl chloride (as shown in Scheme 2). Figure 10 is the IR spectra of compound 5 BAPAF/6FDA compared with compound 4 BAPAF/6FDA. A peak of $\nu_{\text{O-H}}$ in hydroxyl group (3000 to 3600 cm^{-1}) disappears after reaction; peaks due to $\nu_{\text{C=O}}$ of methacryloyl group (1760 cm^{-1}), $\nu_{\text{C=C}}$ of methacryloyl group (1650 cm^{-1}) appear. Structure and content of methacryloyl group for compounds 5 were determined by $^1\text{H-NMR}$ (Fig. 11). Peak of proton in hydroxyl group (10.4 ppm) disappeared after reaction, resulting with the appearance of new peaks at 5.8 ppm and 6.1 ppm; this is due to a proton of $-\text{C}=\text{CH}_2$, and at 1.5 ppm due to proton of $-\text{CH}_3$ (Fig. 11). The content of introduced methacryloyl group was estimated from the ratio of the absorption intensity of the $^1\text{H-NMR}$ between aromatic protons (7.0 ppm to 8.5 ppm) and methacryloyl's protons ($-\text{C}=\text{CH}_2$, 5.8 ppm and 6.1 ppm). Methacryloyl group, from IR and $^1\text{H-NMR}$ spectrum, was proved to have been introduced into hydroxyl group as 100%.

Five kinds of films in photoactive compounds 5, with 5 wt % initiator (Michler's ketone, MK), were investigated for solubility and resistance to various organic solvents. Approximately $1 \mu\text{m}$ thick films of photoactive compounds 5 were coated on a wafer.

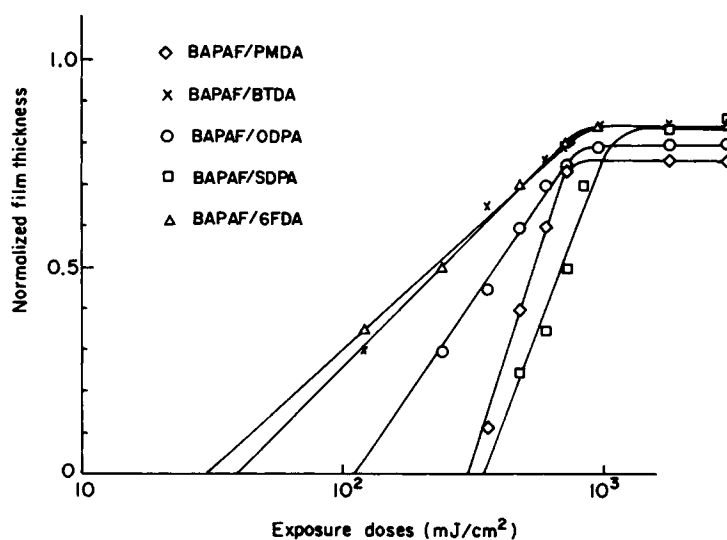


Figure 13 Effects of exposure doses on compounds 5 (with 5 wt % MK). All samples were developed in MEK for 30 s.

Table VIII The Sensitivity and Contrast of Compounds 5

Compound 5	Sensitivity (mJ/cm ²)	Contrast
BAPAF/PMDA	540	1.91
BAPAF/BTDA	280	0.68
BAPAF/ODPA	380	0.93
BAPAF/SDPA	680	1.63
BAPAF/6FDA	240	0.53

After half of which being exposed to UV light, the films were immersed in various solvents. Results of the dissolution tests of films at various solvents are listed in Table VII. Compounds 5, which have 6F group in polymer backbone, show a high solubility in most solvents. UV irradiation will induce the photopolymerization of methacryloyl group in polymer. Therefore, exposed films of photoactive compounds 5, on the other hand, are insoluble in all of the solvents. They are hardly swelled, even in solvents that are easily dissolved the unexposed films.

UV-visible spectra of compounds 5 in THF solution, in a range 250 to 500 nm wavelength, are shown in Figure 12. Compounds 5 have a high transparency in this wavelength region. Compounds 5 BAPAF/6FDA and BAPAF/ODPA in particular, showed the highest transmission of 90% at 365 nm wavelength.

Figure 13 show the characteristic curves of a series of photoactive compounds 5, being sensitized with 5 wt % MK, which are exposed to 365 nm light and developed in MEK for 30 s. Sensitivities of these system are in a range from 240 to 700 mJ/cm² and contrast are in a range from 0.53 to 1.91. The results are summarized in Table VIII.

CONCLUSIONS

Soluble aromatic polyimides have been synthesized from BAPAF and various aromatic tetracarboxylic dianhydrides. These polyimides have good soluble characteristics and maintain their high thermal stability. In these soluble polyimides, only compound 4 BAPAF/6FDA provides a positive photoresist

when formulated with a diazonaphthoquinone sensitizer. It shows a high sensitivity about 46 mJ/cm² and with the contrast being 1.53. Negative photoactive polyimides derived from reacting with methacryloyl chloride had the sensitivity in a range from 240 to 700 mJ/cm² and the contrast in a range of 0.53 to 1.91.

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Received November 29, 1993

Accepted February 24, 1994