Fluorine-Containing Photoreactive Polyimide. II. Preparation and Properties of Self-Sensitized Polyimide Precursors

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Synopsis

Two series of polyimide precursors that have benzophenone (BP) segments in addition to methacryloyl groups and perfluoromethyl groups in the main chain are described. These fluorinated polyimide precursors offered remarkable improvement in solubility in common organic solvents and self-sensitivity at 365-nm light (*i*-line). It was also found that the sensitivity is extremely enhanced by the aid of a small amount of photoinitiators, and the effective initiators for sensitivity enhancement were different for each series of the precursors. These self-sensitized polyimide precursors offered high resolution with good pattern profile of aspect ratio over 1.5. The temperatures for 10% weight loss of the imidized films were nearly 500°C from thermogravimetry analysis (TGA), indicating high thermal stability.

INTRODUCTION

Recently, a great deal of attention has been focused on the use of polyimide in the fabrication of microelectronic devices such as a passivation coating, alpha particle barriers, and interlayer dielectric and of large-scale integrated circuits, primarily as an insulating dielectric layer, because of the high thermal stability and the low dielectric constant. In particular, photoreactive polyimides[1-3] and their precursors[4-6] are increasingly important in place of nonphotoreactive ones for the simplicity of the patterning process and the elimination of harmful agents like hydrazine hydrate. However, the use of photoreactive polyimides or their precursors has been limited by lack of photospeed, excessive volume contraction, and low resolution. In order to improve the sensitivity required for practical use, some sensitizers and photoreactive monomers are added to photoreactive polyimides or their precursors in some cases. However, excessive volume contraction in the thermal curing process due to the use of these additives would still remain a serious problem.

Authors have reported fluorine-containing polyimide precursors that offered good pattern profile as well as high resolution.[7] In the present article, we report two series of self-sensitized fluorine-containing polyimide precursors, BTDA–AMHFP and 6FDA–DAB, which involve BP structure within the main chains. The precursors were molecular designed in order to improve the sensitivity of the previously reported polyimide precursor (BPDA–AMHFP) without excessive volume contraction. BTDA–AMHFP was prepared by polycondensation of benzophenonetetracarboxylic acid diester with the fluorinated diamine, and

6FDA–DAB was prepared by polycondensation of the fluorinated tetracarboxylic acid diester with diaminobenzophenone. The effect of the position and the concentration in the polymers of BP group on the sensitivity was investigated.

EXPERIMENTAL

Solvents and Reagents

All of the solvents were obtained from commercial sources and used after dehydration by molecular sieves (4A 1/16). Tetracarboxylic dianhydrides, diamines, and 2-hydroxyethyl methacrylate were also obtained from commercial sources. Tetracarboxylic dianhydride was used after refluxing with acetic anhydride followed by drying at 150°C for 3 h. Diamines were purified by recrystallization from methyl or ethyl alcohol. The p,p'-tetramethyl diaminobenzophenone (Michler's ketone: Wako Pure Chemical Industries, Ltd.) was also recrystallized from methyl alcohol three times and 3,3',4,4'-tetrakis(t-butyldioxycarbonyl)benzophenone (BTTB: Nippon Oil & Fats Co., Ltd.) was recrystallized from diethylether twice. N-Phenylglycine (NPG: Eastman Kodak Company) was sublimed at vacuum (10^{-3} torr at 60°C).

Synthesis

Preparation of Tetracalboxylic Diesters

A mixture of 10 g of tetracarboxylic dianhydride, 40 mL of 2-hydroxyethyl methacrylate, and 0.01 g of hydroquinone was combined in a 100-mL round flask equipped with a condenser and stirred at 120°C for 4 h. This reaction mixture was poured into 100 mL of 0.5% NaOH aqueous solution and extracted with diethyl ether. Then, the diethyl ether phase was poured into a separatory funnel to wash with 0.5% acetic acid aqueous solution and with water three times. The diethyl ether phase was dried with sodium sulfate anhydride over night. Evaporation of the filtrate gave the diester as a viscous liquid residue. These were identified by means of infrared spectrophotometry, elemental analysis, and ^{1}H-NMR spectroscopy.

Chlorination of Tetracarboxylic Diesters

A 5-g solution of tetracarboxylic diester was reacted with 30 g of SOCl$_2$ and a slight amount of DMF (two drops) at 70°C for 4 h. The reaction mixture was evaporated and dried under reduced pressure, and the small amount of residual SOCl$_2$ was separated as the dichloromethane azeotrope.

Polymerization

Into a 3-necked 100-mL round-bottle flask equipped with nitrogen inlet and outlet, 3 g of diamine was dissolved in 10 mL N-methyl-2-pyrrolidon (NMP) and vigorously stirred. Equivalent moles of chlorinated diester were added to the diamine with 15 mL NMP dropped slowly in it under cooling with ice. After dropping, the reaction mixture was stirred for 24 h at room temperature under nitrogen. The polymer was precipitated in water and in a mixture of

water and methyl alcohol (1 : 1) and dried at vacuum at 20°C for over two days (see Scheme 1). Various synthesized polymers were identified by means of infrared spectrophotometry and ^{1}H, ^{13}C, ^{19}F-NMR spectroscopy.

Solubility

Each of the photoreactive polyimide precursors was dissolved in NMP in appropriate concentration followed by addition of a initiator, and Michler's ketone (MK) was also added as a sensitizer. These were spin-coated onto silicon wafers, prebaked at 90°C for 30 min, and then half the area of each sample was exposed to super high pressure mercury lamp (Ushio Electric Inc.). These were developed in various solvents at a constant condition. After that, both exposed and unexposed parts were observed.

Lithographic Evaluation

Film Formation

To the 30% solution of the polyimide precursor in cyclohexanone some initiators were added. Then, the solution was spread on silicon wafers by using a spin coater to form the photosensitive layer.
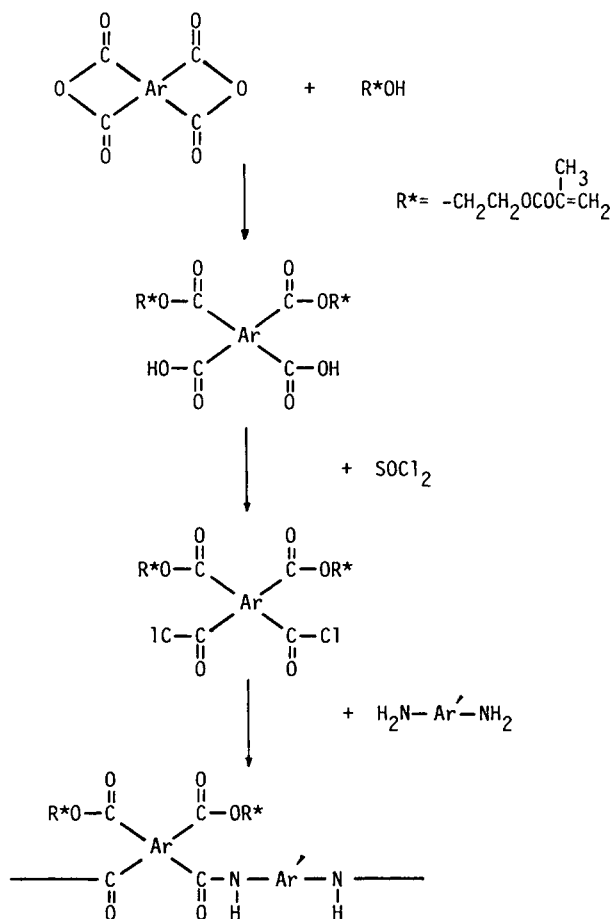
Scheme 1

Photosensitivity

The 1-μm polyimide precursor films on a wafer were exposed at 365-nm wavelength to the filtered super high pressure mercury lamp, developed for 90 s in the 1 : 2 mixed solvent of cyclohexanone and isoamile acetate, and rinsed for 20 s in isoamile acetate. The characteristic curve was obtained by a ratio of remained film thickness (gel fraction) against exposure energy. The film thickness was measured by the multiplet interference method using a Nikon surface finish microscope.

Resolution

The polyimide precursor films were exposed to the super high pressure mercury lamp through a chromium negative mask on a quartz substrate in contact. These irradiated films were developed in the mixed solvent of cyclohexanone and isoamyl acetate (1 : 2) and rinsed in isoamyl acetate.

Imidization and Heat Resistance

The heat resistance of the polyimides and their imidization were observed by means of thermogravimetry (Rigaku Denki, Co. TGA). A infrared spectrophotometer (Hitachi, Model 260-10) was used to confirm a ring closure reaction.

RESULTS AND DISCUSSION

Solubility

Table I shows the structures and molecular weights of the synthesized polyimide precursors. The unexposed and the exposed films of these polymers were

TABLE I
Structures and Molecular Weights of Synthesized Polyimide Precursors[a]

Abbreviation	Structure	$\bar{M}_w{}^{[b]}$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
BTDA–AMHFP		16,100	8500	1.9
6FDA–DAB		10,400	7100	1.5
PMDA–4,4'DDE		10,600	5100	2.1

[a] R = β-oxyethyl methacrylate.
[b] Converted to polystylene.

evaluated for solubility and resistance to various organic solvents, respectively (Table II). PMDA-4,4'DDE, reported by Rubner et al.,[4] was also synthesized to compare the effect of the structural modification on solubility to organic solvents. These polyimide precursors, which have BP segment in the polymer main chain, showed high solubility to most of the solvents tested in this study. Because the molecular weight of BTDA–AMHFP and 6FDA–DAB are almost similar to that of PMDA-4,4'DDE, it seems that the high solubility of these polyimide precursors was achieved by a decrease in the intermolecular cohesive force due to their bended structure accomplished by the introduction of hexafluoropropylene unit and the kinked m,m'-linkage in the polymer backbone. On the other hand, the exposed films of the precursors were insoluble by photopolymerization of the methacryloyl groups in the polymer and were hardly swelled even in the solvents that dissolved the unexposed films easily, due to the high crosslinking density.

Figure 1 shows the UV visible spectra of these polyimide precursors in 2-ethoxyethanol in the 450–250 nm wavelength. The molar extinction coefficients of BTDA–AMHFP and 6FDA–DAB at 365 nm were 150 and 350 L/mol cm, respectively, indicating the high transparency in this wavelength region.

TABLE II
Solubility of Unexposed Films and Resistance of Exposed Films
to Various Solvents of Photoreactive Polyimide Precursors[a]

	PMDA-4,4'DDE		BTDA–AMHFP		6FDA–DAB	
Solvent	Exp.	Unexp.	Exp.	Unexp.	Exp.	Unexp.
Acetone	SW	PS	SW	S	PSW	S
Methyl ethyl ketone	PSW	PS	SW	S	PSW	S
Cyclohexanone	UC	PS	UC	S	UC	S
2-Methoxyethanol	SW	PS	UC	S	PSW	S
2-Ethoxyethanol	UC	PS	UC	S	PSW	S
2-Methoxyethyl acetate	UC	PS	SW	S	PSW	S
2-Ethoxyethyl acetate	UC	IS	UC	S	UC	S
Dioxane	PSW	S	UC	S	UC	S
Tetrahydrofurane	PSW	PS	SW	S	UC	S
Diglym	UC	PS	UC	S	SW	S
Dichloromethane	UC	IS	SW	S	UC	S
Chloroform	UC	IS	SW	S	SW	S
m-Cresol	UC	IS	SW	S	SW	S
Isoamyl acetate	UC	IS	UC	IS	UC	IS
γ-Butyrolactone	SW	S	SW	S	SW	S
Dimethyl sulfoxide	SW	S	SW	S	SW	S
Dimethyl acetoamide	SW	S	SW	S	SW	S
Dimethylformamide	SW	S	SW	S	SW	S
N-methyl-2-pyrrolidone	SW	S	SW	S	SW	S
Nitro benzene	UC	IS	UC	S	UC	S
Methyl alcohol	SW	PS	UC	PS	UC	PS
Ethyl alcohol	UC	IS	UC	PS	UC	PS

[a] Exp.—UC: unchanged, PSW: partially swelling, SW: swelling; unexp.—S: soluble, PS: partially soluble, IS: insoluble.
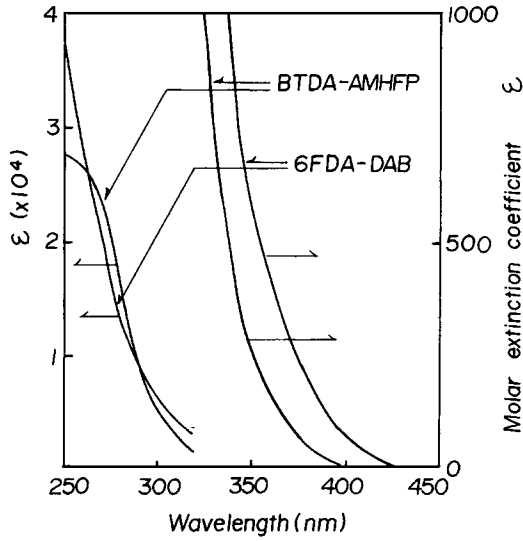
Fig. 1.   Electronic spectra of the self-sensitive polyimide precursors in 2-ethoxyethanol.

Photosensitivities

Photosensitization

The photosensitivities of these polyimide precursors were evaluated by the characteristic curves in Fig. 2. BTDA–AMHFP and 6FDA–DAB offered the sensitivities of 2 and 5 J/cm^2 at 365 nm, respectively, without any initiators or sensitizers. In spite of the low self-sensitivities, remarkable enhancement of the sensitivity was achieved by the use of 5 wt % MK as an additional initiator.
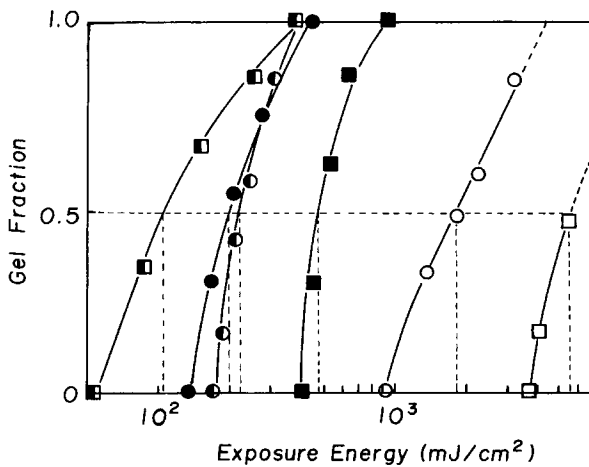

Fig. 2.   Characteristic curves of BTDA–AMHFP and 6FDA–DAB: (○) BTDA–AMHFP only; (□) 6FDA–DAB only; (●) BTDA–AMHFP with 5 wt % MK; (■) 6FDA–DAB with 5 wt % MK; (◐) BTDA–AMHFP with 5 wt % NPG; (◧) 6FDA–DAB with 5 wt % BTTB.

Further, the radical generators NPG and BTTB, as shown in formulas I and II, were also effective in improving the sensitivities of BTDA–AMHFP and 6FDA–DAB, respectively. The exposure energy to attain 0.5 gel fraction $(D_g^{0.5})$ at 365 nm was 220 mJ/cm^2 for BTDA–AMHFP with NPG and 112 mJ/cm^2 for 6FDA–DAB with BTTB.
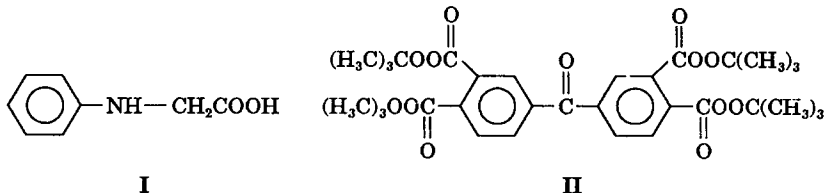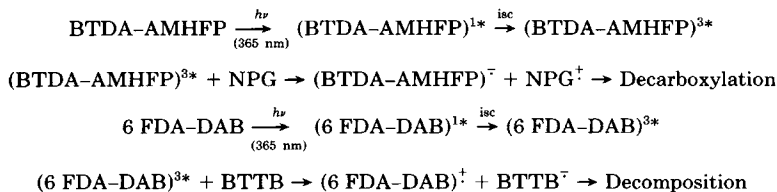

However, it is worth noticing that when the combination of the precursor and the radical generator were reversed, no sensitivity enhancement was observed. That is, BTDA–AMHFP is not improved in the sensitivity with BTTB, and 6FDA–DAB is also not improved with NPG. NPG and BTTB have been reported as the radical generators of the composite initiators in which the radical generators are sensitized with some organic dyes.[8-10] The dye-sensitized decomposition process of NPG and BTTB follows:
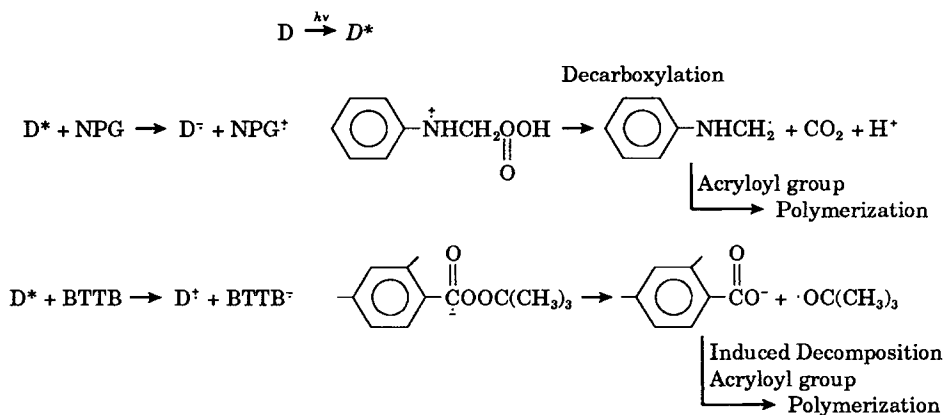
Here, the dye, which is excited by the light of a 488-nm wavelength, interacts with electron-donative NPG or electron-acceptable BTTB through a redox reaction. The sensitization system of the precursors by NPG or BTTB may be also explained by the photoinduced electron transfer mechanism similar to that of NPG–dye or peroxide–dye system. The electron-acceptable BP groups in BTDA–AMHFP and the electron-donative diamino BP groups in 6FDA–DAB are first excited by the light of a 365-nm wavelength because NPG and BTTB hardly absorb the light at wavelengths longer than 365 nm. Although it is not clear whether the excited states can be singlet or triplet states, it is considered that the BP groups and the diamino BP groups in excited singlet states are converted to the triplet states through intersystem crossing, in view of the general behavior of BP. The triplet states of BP groups in BTDA–AMHFP and the diamino BP groups in 6FDA–DAB interact with the ground states of NPG and BTTB, respectively. Then the reducing agent NPG is oxidized by the excited BP group in BTDA–AMHFP, and the oxidizing agent BTTB is

reduced by the excited diamino BP group in 6FDA–DAB. The reaction scheme of decarboxylation of NPG and decomposition of BTTB by the precursors is as follows:

$$\text{BTDA–AMHFP} \xrightarrow[\text{(365 nm)}]{h\nu} \text{(BTDA–AMHFP)}^{1*} \xrightarrow{\text{isc}} \text{(BTDA–AMHFP)}^{3*}$$

$$\text{(BTDA–AMHFP)}^{3*} + \text{NPG} \rightarrow \text{(BTDA–AMHFP)}^{-} + \text{NPG}^{+} \rightarrow \text{Decarboxylation}$$

$$6\,\text{FDA–DAB} \xrightarrow[\text{(365 nm)}]{h\nu} \text{(6 FDA–DAB)}^{1*} \xrightarrow{\text{isc}} \text{(6 FDA–DAB)}^{3*}$$

$$\text{(6 FDA–DAB)}^{3*} + \text{BTTB} \rightarrow \text{(6 FDA–DAB)}^{+} + \text{BTTB}^{-} \rightarrow \text{Decomposition}$$

Dependence of Molecular Weight

Figure 3 shows the dependence of the sensitivity on the molecular weight (M_w) to 365-nm light for BTDA–AMHFP sensitized with MK. The polymers, which have different molecular weights, were synthesized by controlling the feeding ratio of molar concentration of benzophenone tetracarboxylic diester and fulorinated diamine in the polymerization reaction. Among the polymers whose molecular weight were from 10,000 to 26,000, no remarkable dependence of the sensitivity and the contrast on the molecular weight was observed from characteristic curves, although there is apparently a relationship between molecular weight and sensitivity in theory.

The Dependence of BP Concentration

In order to further confirm the effect of benzophenone groups in the polymer main chain, the sensitivities ($D_g^{0.5}$) and contrasts ($\gamma^{0.5}$) of the various polymers, including different concentration of BP in the main chain, were evaluated by the characteristic curve (Fig. 4). The structure of the polymers are shown in Fig. 5. The molecular weights of these precursors were between 10,000 and 30,000, and the concentration of BP groups was determined from the ratio of
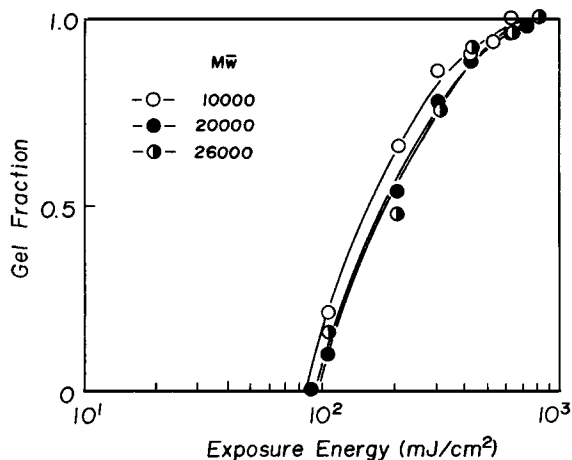

Fig. 3. Characteristic curves of BTDA–AMHFP polymers that have different molecular weight with 5 wt % MK.
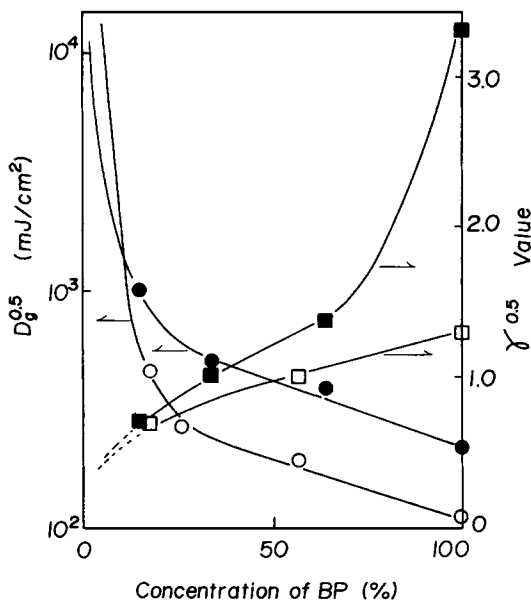
Fig. 4.   The dependences of sensitivity and contrast on the concentration of BP group in the precursors: (●, ■) BTDA base polyimide precursors; (○, □) DAB base polyimide precursors.

IR absorption intensity of the polyimide precursors. As the sensitivity was not influenced by the molecular weight in this region from the preceding results, it was noticed that the polymers containing BP and diamino BP groups in the main chains effectively act as macromolecular photosensitizers, and the sensitivity and contrast at 365-nm wavelength were increased with increasing BP and diamino BP concentration in the polymers.

IR spectral changes of BTDA–AMHFP with MK and 6FDA–DAB with BTTB before and after exposure with 365-nm light are shown in Fig. 6. After irradiation of 500 mJ/cm^2 with 365-nm light, the absorption peak of 3500 cm^{-1} due to —OH increases, while the peak of 2950 cm^{-1} due to —CH$_3$ decrease in the case of BTDA–AMHFP with MK. From these spectral changes, it seems that BP group abstracted hydrogen from —CH$_3$ groups of MK or from —CH$_3$ groups at ortho position of the aromatic main chain of BTDA–AMHFP. On the other hand, the broad peak in the vicinity of 2500–3200 cm^{-1} due to —COOH appears after irradiation in the case of 6FDA–DAB with BTTB. The IR spectral changes may indicate that the carboxyl radical generated by decomposition of BTTB was converted to carboxylic acid through hydrogen abstraction, although not conclusive.

Patterning Property

In the cases of BTDA–AMHFP with 5 wt % NPG and 6FDA–DAB with 5 wt % BTTB, patterning characteristics were evaluated. Figures 7(A) and (B) show the scanning electron micrograph (SEM) of the patterns obtained from 5-μm-thick film of BTDA–AMHFP and 3 μm thick film of 6FDA–DAB, respectively. From these photographs, it was confirmed that both precursors pro-

BTDA base polyimide precursor

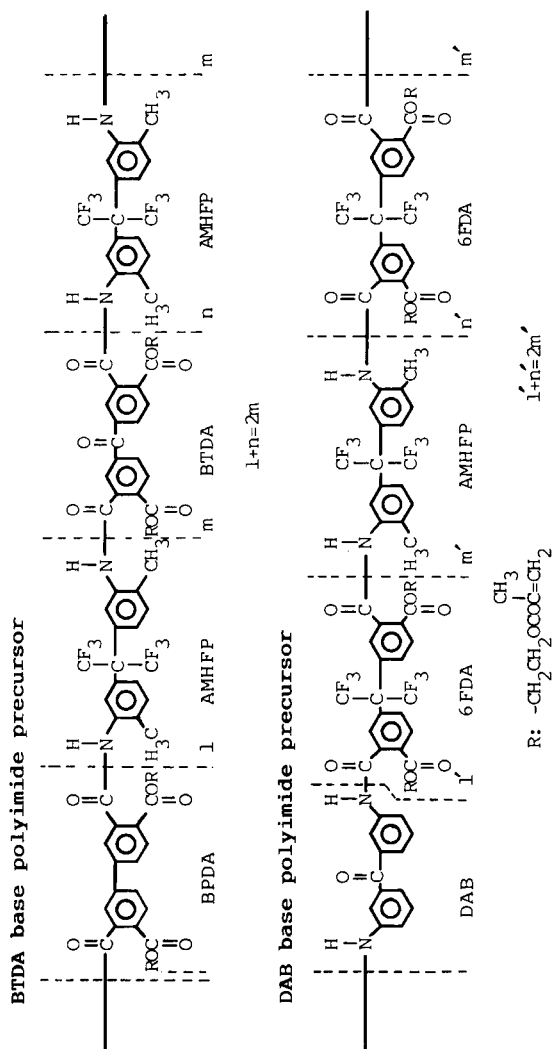DAB base polyimide precursor

Fig. 5. Structures of the precursors including different concentration of BP group in the main chain.
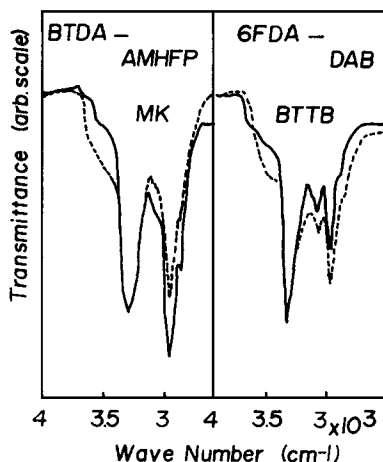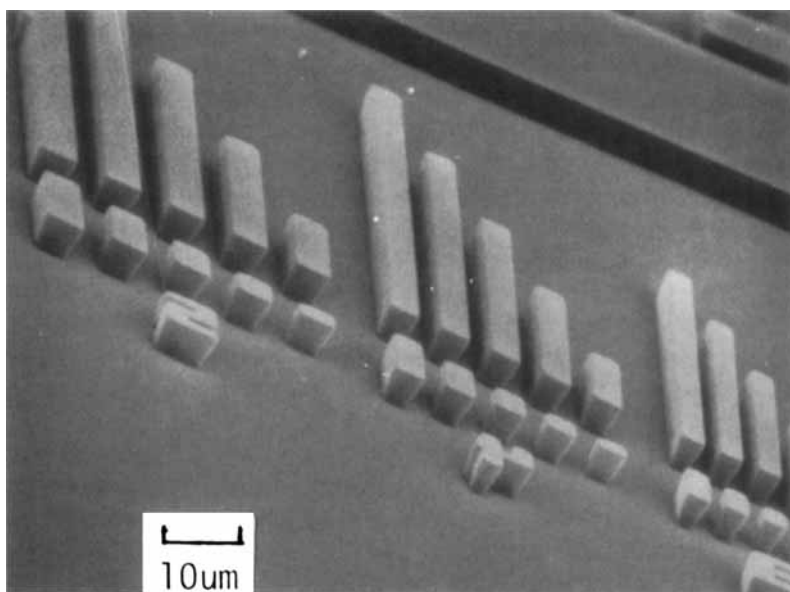
Fig. 6.   IR spectral changes of the precursors before and after exposure with 365-nm light.

vided the high resolution patterns with the high aspect ratio over 2.0, because of the high transmittance at 365-nm light and the high γ value. Furthermore, patterning properties of BTDA–AMHFP polymer films having different $\bar{M}_w$ from 10,000 to 26,000 were almost similar in resolution and pattern profile. From this observation, it seems that the dependence of $\bar{M}_w$ on patterning properties is not remarkable, as is not in the case of sensitivity.

Imidization and Thermal Stability

Figures 8(A) and (B) show IR spectral changes of BTDA–AMHFP and 6FDA–DAB polymers after thermal curing at 400°C for 1 h *in vacuo*. The spectra show the disappearance of the absorption peaks at 3300 and 1670 cm^{-1} assigned to N—H bondings of amide groups and the appearance of new absorption peaks at 1790, 1350, and 720 cm^{-1} assigned to the imide structure, respectively. These facts indicate that the precursors are completely converted into polyimide by the cyclization of amide acid at these curing conditions.

The TGA curves shown in Figures 9(A) and (B) indicate the thermal behavior of the photocrosslinkable precursors. The curves exhibit slopes with two steps. The first weight loss starts at 150°C for 6FDA–DAB and at 215°C for BTDA–AMHFP, indicating that imidization begins at these temperatures. The imidization continues up to 500°C, and decomposition of polyimide occurs at temperatures higher than 500°C in both air and N$_2$ atmospheres. The higher temperature at which imidization starts for BTDA–AMHFP may be also caused by the steric hindrance of the methyl group, which is substituted on the phenyl group in a manner similar to that of BPDA–AMHFP reported so far. The solid lines in Fig. 9 show TGA curves of the polyimide films prepared from the corresponding precursors under the condition of 400°C for 1 h. From these curves, the temperatures of 10% weight loss are nearly 500°C, indicating high thermal stability of the both polyimides. And the change of the pattern profile before and after thermal curing in this condition was observed by SEM. The contraction in volume of the pattern was consequently very slight, and the reduction of film thickness by thermal curing was only 7–8%.

(A)
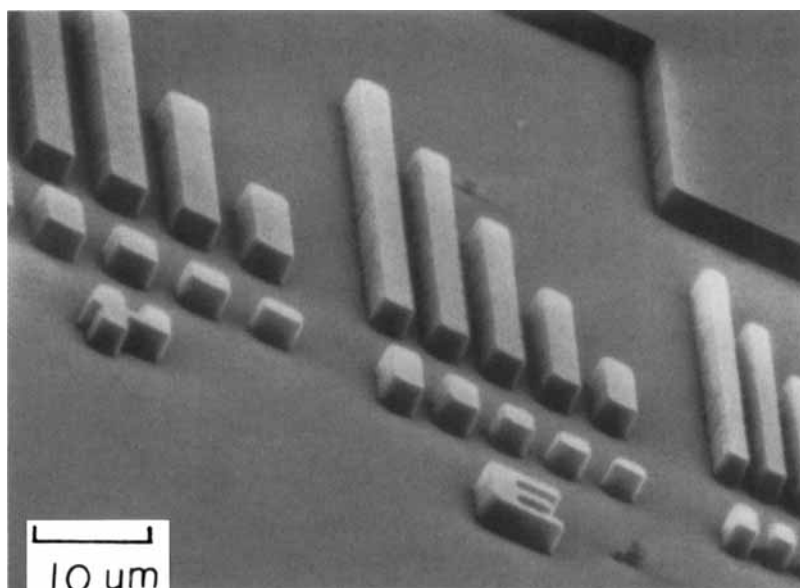
(B)

Fig. 7. SEM photographs of the patterns from the precursors: (A) BTDA–AMHFP with 5 wt % NPG; (B) 6FDA–DAB with 5 wt % BTTB.
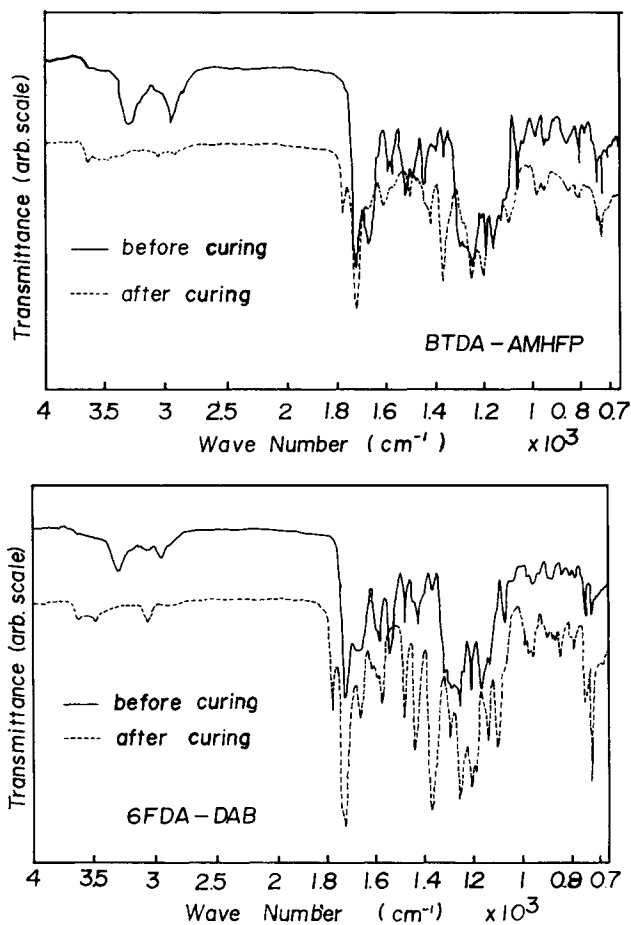
Fig. 8.   IR spectral change of the precursors before and after thermal curing at 400°C for 1 h *in vacuo:* (A) BTDA–AMHFP; (B) 6FDA–DAB.

CONCLUSION

In this study, the polyimide precursors, which have BP segment in the chain structure, in addition to methacryloyl groups and perfluoromethyl group have been studied. The features of these polyimide precursors are as follows:

1. The precursors showed excellent solubility in the various common solvents tested, except methyl alcohol, ethyl alcohol, and isoamile acetate.

2. The precursors BTDA–AMHFP and 6FDA–DAB have absorption with low extinction coefficients, which are 150 and 350 (L/mol cm) at 365-nm wavelength, respectively.

3. The precursors offered self-sensitive characteristics at 365 nm due to the presence of BP group in the polymer structure. Further, remarkable enhancement of the sensitivity in this region of wavelength is achieved by
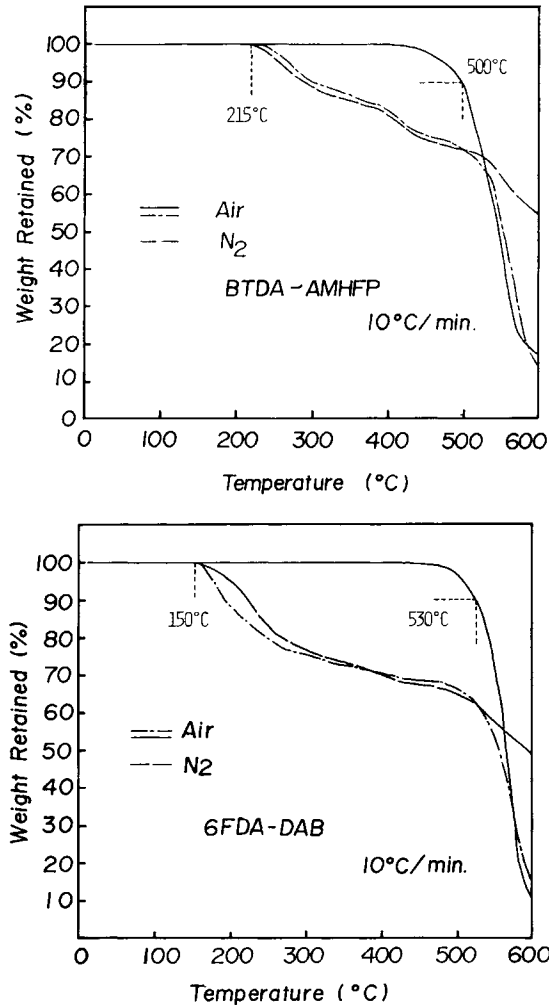
Fig. 9. TGA curves of the precursors: (A) BTDA–AMHFP, (B) 6FDA–DAB.

the use of a small amount of additional radical generator, such as NPG and BTTB.

4. The polyimide precursors showed good patterns of high resolution with the high aspect ratio over 2.0 from 3 to 5 μm thick films. And the reduction of film thickness of the precursor patterns by thermal curing at 400°C for 30 min was only 7–8%.

5. The polyimides are produced completely from their precursors by thermal curing at 400°C for 30 min. And they exhibited the high thermal stability over 500°C at the point of 10% weight loss from TGA curves.

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