

# Preparation and Properties of Soluble and Colorless Fluorine-Containing Photoreactive Polyimide Precursors

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## Synopsis

Photoreactive polyimide precursors, which are readily soluble in common organic solvents and optically transparent at light of 365 nm wavelength (*i*-line), similar to aliphatic polyimide precursors, were obtained by polycondensation of biphenyltetracarboxylic dianhydride (BPDA) and fluorine-containing diamine compounds. In particular, the polyimide precursor prepared from 2,2-*bis*(3-amino-4-methylphenyl)hexafluoropropane showed high solubility in common organic solvents and complete transparency at *i*-line wavelength. A 3  $\mu\text{m}$  thick film of the polyimide precursor on a silicon wafer was exposed and developed, and offered high resolution (0.5  $\mu\text{m}$  line) patterns with an aspect ratio of 6.0. This polyimide precursor swells very little in the developing solvent, resulting in the high resolution. Conversion of polyamic acid to polyimide at several curing temperatures was observed by infrared spectrophotometer and thermogravimetry.

## INTRODUCTION

Photoreactive polyimides and their precursors are increasingly replacing ordinary polyimides in extensive applications to passivation coatings (alpha particle barriers<sup>1</sup> interlayer dielectrics, etc.). The main advantages of using a photoreactive polyimide precursor are simplicity of the patterning process and the elimination of harmful agents like hydrazine hydrate.

In recent years, several photoreactive polyimides<sup>2,3</sup> and their precursors<sup>4,5</sup> have been reported, but most are not satisfactory in some characteristics required for practical use. For example, the negative types show lower resolution or reduction of initial film thickness because of swelling during development, caused by deficient density of photocrosslinking. On the other hand, the positive type,<sup>6</sup> which has been reported, still presents some problems.

Polyimide precursors of pyromellitic type that have been developed so far, absorb most of the light at 365 nm because of strong absorption of aromatic groups. The strong light absorption of a polyimide precursor film prevents incident light from transmitting to the bottom of the film layer, and results in insufficient crosslinking and difficulty in obtaining high sensitivity and resolution. Furthermore, most polyimide precursors are soluble only to strongly basic solvents that need a careful handling.

This article reports on properties of readily soluble and optically transparent fluorine-containing photoreactive polyimide precursors.

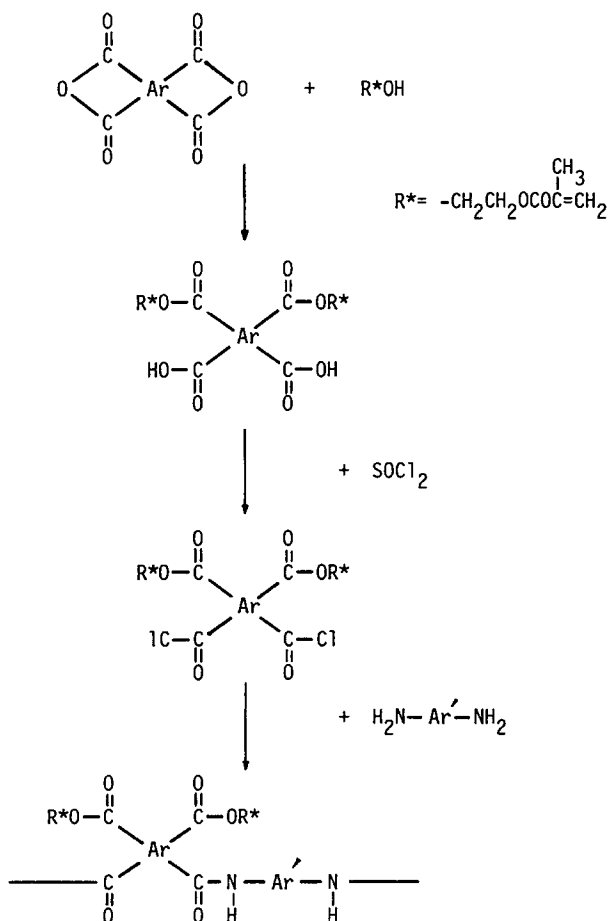
## EXPERIMENTAL

## Solvents and Reagents

All solvents were obtained from commercial sources and used after dehydration by molecular sieves (4A 1/16). Biphenyl tetracarboxylic dianhydride (BPDA) and diamines were also obtained from commercial sources. BPDA was used after drying at 120°C for 1 h, and diamines were purified by recrystallization from methylalcohol.

## Synthesis

It has been reported that the photoreactive polyimide precursors, which have (metha)acrylic groups, were obtained by the method presented in Scheme 1.<sup>1,7</sup> In the present study, soluble and transparent photoreactive polyimide precursors were also synthesized by this method. The structure and the molecular weight of polymers are shown in Table I. The molecular weight was measured by a high-speed liquid chromatograph (TOSO, Co. HLC-802UR).



Scheme 1.

TABLE I

Structure and Molecular Weight of Synthesized Photoreactive Polyimide Pre

Abbreviation	Structure
PMDA-4,4' DDE	
PMDA-BAPF	
BPDA-BAPF	
BPDA-AMHFP	

<sup>a</sup> Converted to polystyrene.

\*R  $\beta$ -oxyethyl-methacrylate.

The synthesized polymers were identified by means of infrared spectrophotometry, organic elemental analysis, and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ -NMR spectroscopy.

### Solubility and Transparency

Each of the photoreactive polyimide precursors was dissolved in *N*-methyl-2-pyrrolidone (NMP) in appropriate concentration, and next benzophenone (BP) and Michler's ketone (MK) were added as initiator and sensitizer, respectively. The solutions were spin-coated onto silicon wafers to form the photosensitive layer, 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.). The samples were developed in various solvents at a constant condition, after which the polymer layer in both exposed and unexposed parts was observed.

The 3  $\mu\text{m}$  photoreactive polyimide precursor films on quartz plates were measured for transparency by an ultraviolet (UV) spectrophotometer (Hitachi model 200-20).

### Lithographic Evaluation

#### *Film Formation*

BP and MK was added to the 40% solution of the polyimide precursor in cyclohexanone. Then the solution was spread on a silicon wafer using a spin-coater to form the photosensitive layer.

#### *Photosensitivity*

Photosensitivity was evaluated by the characteristic curve, which was obtained by a ratio of remained film thickness to initial film thickness after development (gel fraction) against each exposure energy.

The 1  $\mu\text{m}$  polyimide precursor films were exposed at 365 nm wavelength to the filtered super high-pressure mercury lamp, then developed for 90 s in the 1 : 2 mixed solvent of cyclohexanone and isoamyl acetate and rinsed for 20 s in isoamyl acetate. The film thickness was measured by the multiplet interference method using a Nikon surface finish microscope.

#### *Patterning*

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.

#### *Heat Resistance and Imidization*

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

## RESULTS AND DISCUSSION

### Solubility and Transparency

The four kinds of films of photoreactive polyimide precursors in Table I were examined for solubility in the unexposed areas and for resistance in the exposed areas to various solvents. The result is shown in Table II. Compared to the finding that PMDA-4,4' DDE is soluble only in strongly polar solvents containing nitrogen or sulfur, the polyimide precursors that contained trifluoromethyl ( $-\text{CF}_3$ ) substituents along the polymer backbone showed high solubility not only in those, but also in ketone-type solvents. In particular, BPDA-AMHFP polymer showed excellent solubility to all solvents which were tested, except methyl and ethylalcohol.

Judging from the finding that the solubility for PMDA-4,4' DDE ( $M_w = 10600$ ) and BPDA-AMHFP ( $M_w = 9800$ ) were quite different in spite of the similar molecular weight, the correlation between the solubility and the molecular weight of synthesized polyimide precursors is not significant. It seems that solubility of polyimide precursors is chiefly governed by the structural modification by introduction of bulky substituents ( $-\text{CF}_3$ ,  $-\text{CH}_3$ ) and nonsymmetrical linkage in polymer backbone.

On the other hand, the polyimide precursor in exposed areas become insoluble by photopolymerization of acryloyl groups in the polymer. PMDA-4,4' DDE and BPDA-AMHFP films in the exposed areas, as compared with the polymers containing BAPF, showed the higher resistance to various solvents. Especially, BPDA-AMHFP film in the exposed areas is insignificantly swelled in the solvents which dissolved easily the polymer in the unexposed areas. For this reason, it is considered that BPDA-AMHFP polymer in the exposed areas has a high crosslinking density.

Figure 1 shows UV-visible spectra of the  $3\ \mu\text{m}$  thick photoreactive polyimide precursor films. The fluorine-containing polymers are the more transparent in comparison with PMDA-4,4' DDE, as indicated by the shift of the absorption band to the shorter wavelengths. In particular, BPDA-AMHFP polymer showed the highest transmission of 90% at 365 nm wavelength, while that of PMDA-4,4' DDE was only 20%. It may be concluded that the complete transparency at 365 nm as well as the excellent solubility of BPDA-AMHFP polyimide precursor has been achieved by its structural modification.

### Lithographic Performance

The light intensity  $I_a$  which is absorbed by polymer film of thickness  $L\ \mu\text{m}$  is expressed as;

$$I_a = I_o(1 - e^{-\epsilon cL}) \quad (1)$$

where

$I_o$  = incident light intensity per unit area

$\epsilon$  = extinction coefficient of polymer

$c$  = concentration of absorption species

TABLE II  
Solubility in Unexposure (unexp.) Areas and Resistance in Exposure (exp.) Areas to Various Solvents of Photoreactive Polyimide Precursors

Solvent	PMDA-4,4 DDE		PMDA-BAPF		BPDA-BAPF		BPDA-AMHFP	
	exp.	unexp.	exp.	unexp.	exp.	unexp.	exp.	unexp.
Acetone	SW	PS	SW	S	SW	PS	SW	S
Methyl ethyl ketone	PSW	PS	SW	S	SW	S	SW	S
Cyclohexanone	UC	PS	SW	S	SW	S	UC	S
2-Methoxyethanol	SW	PS	SW	S	SW	S	SW	S
2-Ethoxyethanol	UC	PS	SW	S	SW	S	UC	S
2-Methoxyethyl acetate	UC	PS	SW	S	SW	PS	SW	S
2-Ethoxyethyl acetate	UC	IS	SW	S	UC	PS	UC	S
Dioxane	PSW	S	SW	S	SW	S	UC	S
Tetrahydrofuran	PSW	PS	SW	S	SW	S	SW	S
Diglym	UC	PS	SW	S	SW	S	SW	S
Dichloromethane	UC	IS	SW	PS	SW	PS	SW	S
Chloroform	UC	IS	SW	PS	SW	PS	SW	S
<i>m</i> -Cresol	UC	IS	SW	S	SW	PS	UC	S
Isoamyl acetate	UC	IS	UC	PS	UC	IS	UC	IS
$\gamma$ -butyrolactone	SW	S	SW	S	SW	PS	SW	S
Dimethyl sulfoxide	SW	S	SW	S	SW	S	SW	S
Dimethyl acetoamide	SW	S	SW	S	SW	S	SW	S
Dimethyl formamide	SW	S	SW	S	SW	S	SW	S
<i>N</i> -methyl-2-pyrrolidone	SW	S	SW	S	SW	S	SW	S
Nitrobenzene	UC	IS	SW	PS	UC	PS	UC	S
Methyl alcohol	SW	PS	SW	PS	SW	PS	SW	PS
Ethyl alcohol	UC	IS	SW	PS	UC	IS	UC	PS

Abbreviations: exp: UC: unchanged PSW: partly swelling SW: swelling unexp: S: soluble ps: partly soluble IS: insoluble.

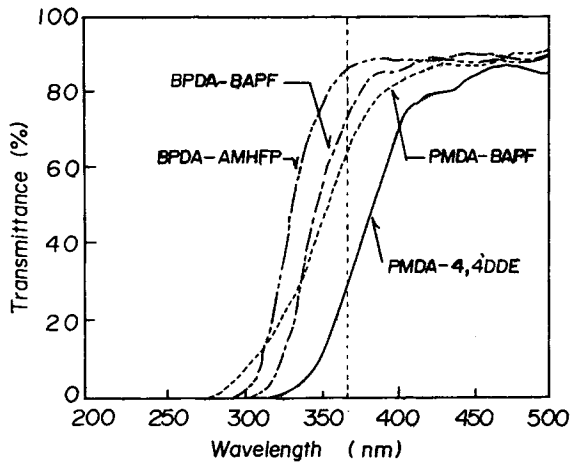


Fig. 1. UV-visible spectra of the 3  $\mu\text{m}$  thick photoreactive polyimide precursor films.

It is clear from Eq. (1) that the light intensity  $I_a$ , which is absorbed by polymer film exponentially increases with the increase in  $L$  and  $\epsilon c$ . Figure 2 shows the relationship between  $I_a/I_o$  and  $L$  of each photoreactive polyimide precursor, which was calculated by substituting  $\epsilon c$  at 365 nm wavelength of each polymer in Figure 1 into Eq. (1). Due to the strong absorption at 365 nm of PMDA-4,4' DDE, only 14% of the incident light ( $I_o$ ) is transmitted at the depth 10  $\mu\text{m}$  from the polymer surface. This means that the photoreactive polyimide precursor with strong absorption at 365 nm can show neither high sensitivity nor good pattern profile, especially in the case of a thick layer. As the light absorption by BPDA-AMHFP polyimide precursor at 365 nm is very small, which is only 5% at the depth 10  $\mu\text{m}$  from surface, it is expected that BPDA-AMHFP may show good patterning characteristics, even with a thick layer.

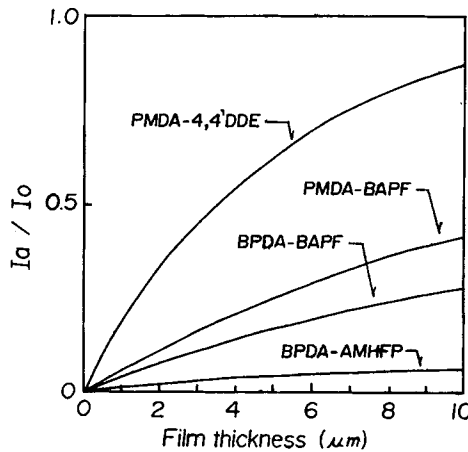


Fig. 2. Ratio of absorbed light intensity to incident light intensity at each depth from film surface.

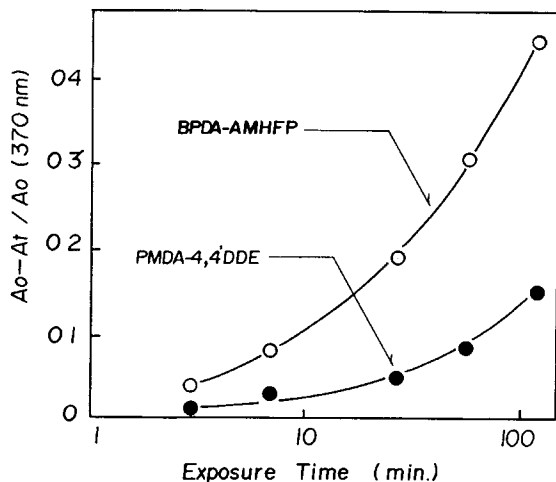


Fig. 3. Dependence of exposure time on a photodecomposition of MK in PMDA-4,4' DDE and BPDA-AMHFP films.

To confirm the effect of transparency at 365 nm, photodecomposition ratio of MK in PMDA-4,4' DDE on exposure time was compared to that in BPDA-AMHFP film. The polymer films were exposed at 365 nm to the filtered super high pressure mercury lamp (250 W) and the photodecomposition ratio of MK was measured spectroscopically by monitoring the absorption peak of MK at 370 nm. Figure 3 shows the decomposition ratio ( $A_0 - A_t / A_0$ ) of MK plotted against the irradiation time. MK in BPDA-AMHFP polymer was photodecomposed 3–4 times faster than in PMDA-4,4' DDE polymer, and this result agrees with the difference of transmittance at 365 nm for these polymers (Fig. 1). It is understood from this result that transparency of the polymer film allows for the high sensitivity and the high resolution.

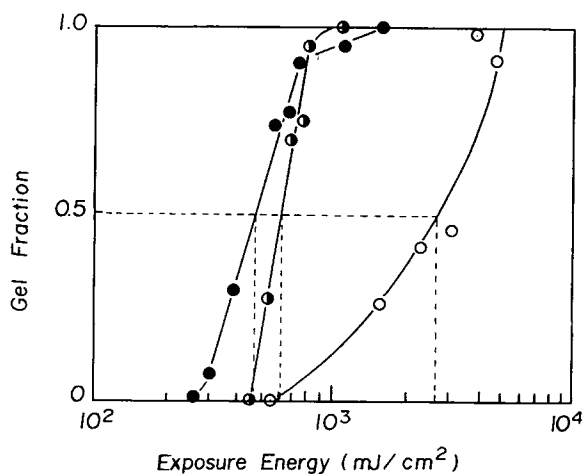
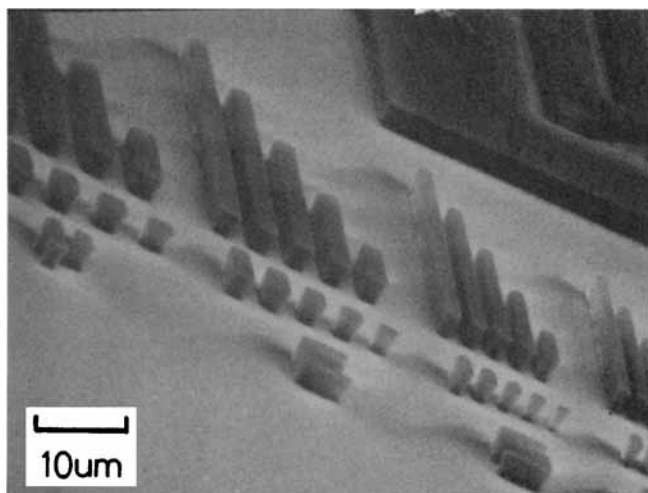


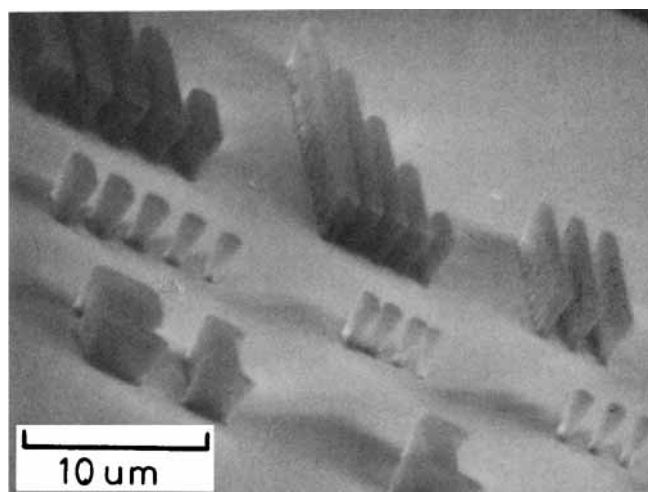
Fig. 4. Characteristic curve for BPDA-AMHFP initiated by BP and MK combination for super high-pressure mercury lamp (365 nm): (O) 1 phr of BP and MK; (●) 5 phr of BP and MK; (⊙) 1 phr of BP and 5 phr of MK.



The contrast and the sensitivity of BPDA-AMHFP polymer were evaluated by the characteristic curves in Figure 4. In the case of 1 phr of BP and MK, both contrast and the sensitivity were low indicating that crosslinking was insufficient. On the other hand, the film which contained 1 phr of BP and 5 phr of MK showed higher contrast and sensitivity; the contrast at 0.5 gel fraction ( $\gamma^{0.5}$ ) was 3.9, and the exposure energy to attain 0.5 gel fraction ( $D_g^{0.5}$ ) was 480 mJ/cm<sup>2</sup>. Further, in the case of 5 phr BP and MK, the contrast was



A

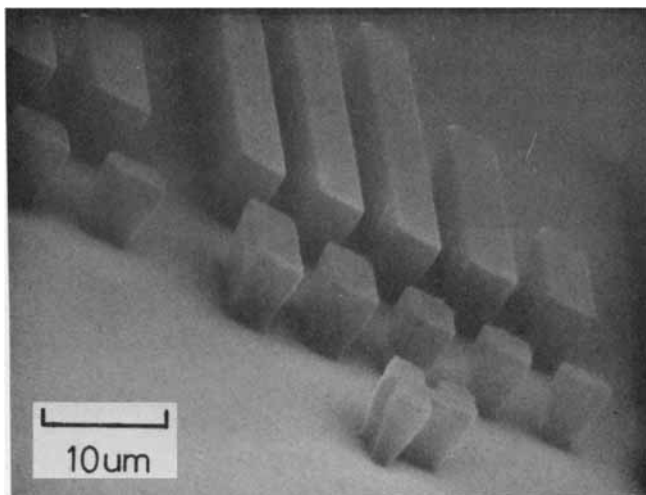


B

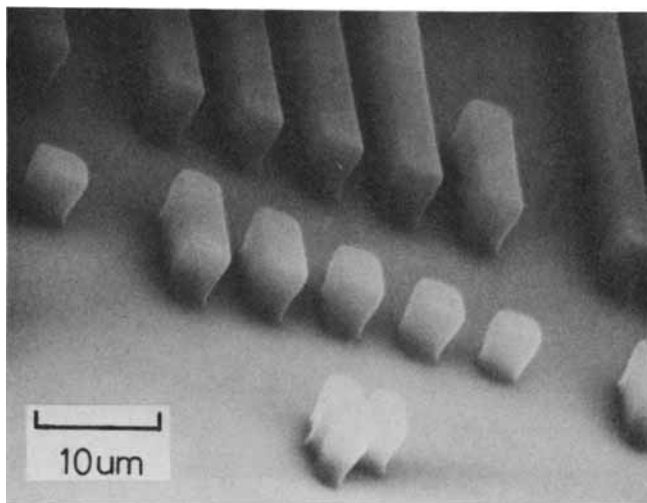
Fig. 5. SEM photographs of pattern from 3  $\mu\text{m}$  thick BPDA-AMHFP film; A from 1.5  $\mu\text{m}$  to 4  $\mu\text{m}$  lines; B from 0.5  $\mu\text{m}$  to 1.5  $\mu\text{m}$  lines.

lower than in the case of 1 phr of BP and 5 phr of MK while the photosensitivity was slightly higher.

Based on the results described above, the evaluation of patterning characteristics of BPDA-AMHFP polyimide precursor was carried out by adding 1 phr of BP and 5 phr of MK as the initiator. A 40 wt% cyclohexanone solution of BPDA-AMHFP was spin-coated onto silicon wafers to form about 3 and 8  $\mu\text{m}$  thick films and were imagewise exposed to the super high-pressure mercury lamp (250 W) for 10 and 20 min. The developer used was 1 : 2 mixed solvent of cyclohexanone and isoamyl acetate, which dissolved unexposed



A



B

Fig. 6. SEM photographs of pattern from 8  $\mu\text{m}$  thick BPDA-AMHFP film: *A* before curing; *B* after curing at 350°C for 30 min.

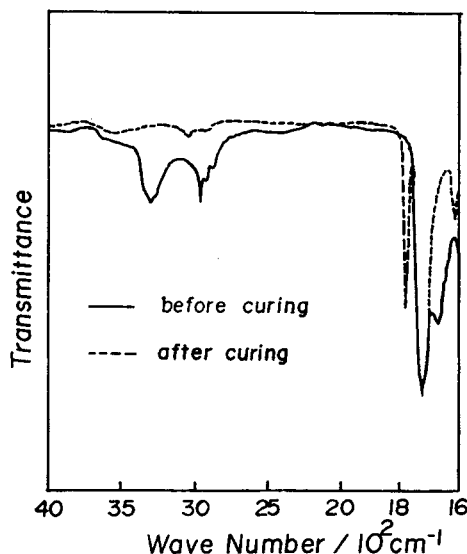


Fig. 7. IR spectral change of BPDA-AMHFP after curing at 350°C for 30 min.

areas completely without damaging the exposed areas, and isoamyl acetate was used as the rinse solution since it did not damage the exposed areas. Figure 5(A) and (B) show the scanning electron micrograph (SEM) of the patterns obtained from the films of 3  $\mu\text{m}$  thickness. From these photographs, it was confirmed that the 3  $\mu\text{m}$  thick films of BPDA-AMHFP polyimide precursor offered the high resolution of 0.5  $\mu\text{m}$  line patterns with the aspect ratio of 6.0. The high resolution patterns of BPDA-AMHFP may be offered by the property whereby this polymer in the exposed areas is hardly swell in the developer by the formation of high crosslinking density.

Figure 6(A) and (B) show the change of the pattern profile before and after curing at 350°C for 30 min. The reduction of film thickness by curing was only 15–20%.

### Thermal Stability and Imidization

Figure 7 shows infrared (IR) spectra of BPDA-AMHFP polymer films after curing for 30 min at 200°C and at 350°C, respectively. The spectrum of the film after curing at 200°C was almost similar to that of uncured film. However, in the spectrum after being cured at 350°C, the absorption due to ( $\text{>N-H}$ ) of aromatic amide acid at 3300  $\text{cm}^{-1}$  and the absorption due to ( $\text{>C=O}$ ) of amide acid at 1660  $\text{cm}^{-1}$  disappear, while the typical absorption due to ( $\text{>C=O}$ ) of imide at 1785  $\text{cm}^{-1}$  appears anew. From these spectral behavior, it was recognized that the heat-resistant polyimide is formed by the cyclization of amide acid in the temperature range from 200°C to 350°C.

The thermogravimetric (TGA) curves of BPDA-AMHFP and PMDA-4,4'-DDE polymers are shown in Figure 8. The curves showed slopes of two steps. It seems that the first weight loss starting at 225°C was assigned to the imidization from comparison with the IR spectral changes given in Figure 7. The weight loss between 225 and 517°C agreed well with the value of the

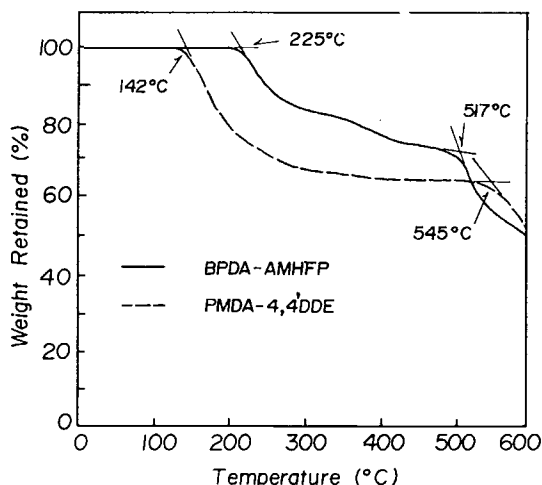


Fig. 8. TGA curves of PMDA-4,4' DDE and BPDA-AMHFP in  $N_2$  gas.

weight loss calculated by attributing it to the elimination of  $\beta$ -oxyethylmethacrylate. This result also supports the explanation that the first slope of the TGA curve was due to a reaction of cyclization. The thermal degradation of BPDA-AMHFP polyimide precursor started at 517°C, the initial point of the second slope of the TGA curve, indicating that the thermal stability of BPDA-AMHFP polyimide is as high as that of PMDA-4,4' DDE polyimide.

Based on the comparison of TGA curves for PMDA-4,4' DDE and BPDA-AMHFP polyimide precursors, the thermal characteristics of the two polymers were summarized as follows:

1. The weight loss % due to imidization was less for BPDA-AMHFP polymer than for PMDA-4,4' DDE polymer.
2. The starting temperature of weight loss of BPDA-AMHFP is about 80°C higher than that of PMDA-4,4' DDE.

The difference described in item 1 occurred because the concentration of  $\beta$ -oxyethylmethacrylate in BPDA-AMHFP polymer was less than in PMDA-4,4' -DDE. The higher temperature for imidization of BPDA-AMHFP may be attributed to the requirement of the higher temperature in the imidization reaction due to the steric hindrance of methyl groups on orthoposition, although not conclusive.

Figure 9 shows the imidization ratio determined by TGA curves of BPDA-AMHFP polymer films which were cured at different temperatures for 30 min. The imidization ratio ( $R$ ) can be expressed by the following equation.

$$R(\%) = (G_o - G_t)/G_o \times 100$$

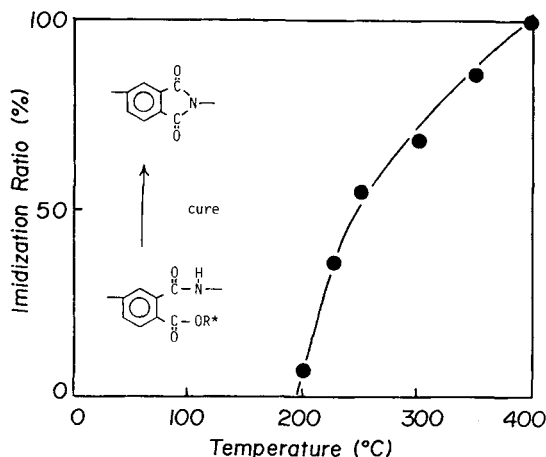


Fig. 9. Dependence of cure temperature for 30 min on imidization ratio.

where

$G_o$  = The percentage of weight loss for cyclization of an uncured film

$G_t$  = The percentage of weight loss for cyclization of a cured film at  $t^\circ\text{C}$

Imidization was slight until  $200^\circ\text{C}$ , and BPDA-AMHFP polyimide precursor was converted completely to the thermally stable polyimide by curing at  $400^\circ\text{C}$  for 30 min. This result was similar to that of ordinary polyimide precursors.

### CONCLUSION

Soluble and transparent fluorine-containing photoreactive polyimide precursors have been described. The features of these polyimide precursors are as follows:

1. The precursors showed good solubility in various common solvents, and especially the polyimide precursor based on AMHFP diamine showed excellent solubility to all solvents which were tested, except methyl and ethylalcohol.
2. The transmittance at 365 nm (*i*-line) by these fluorine-containing polyimide precursors was higher than that of other polyimide precursors which were reported so far. In particular, BPDA-AMHFP polyimide precursor showed almost complete transparency at 365 nm wavelength.
3. BPDA-AMHFP photoreactive polyimide precursor showed the high resolution as well as the high aspect ratio of 6.0 ( $0.5\ \mu\text{m}$  line with  $3\ \mu\text{m}$  thick layer).
4. BPDA-AMHFP polyimide produced by curing the precursor at  $400^\circ\text{C}$  for 30 min exhibited the excellent thermal stability comparable to those of other polyimide like PMDA-4,4' DDE which are presently in practical use.

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