

# Synthesis and Characterization of Negative-Type Photosensitive Polyimides Based on Cyclobutane-1,2,3,4-Tetracarboxylic Dianhydride

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**ABSTRACT:** A series of negative-type photosensitive polyamic acids (PAAs) with various molecular weights was synthesized from cyclobutane-1,2,3,4-tetracarboxylic dianhydride, 2-(methacryloyloxy)ethyl-3,5-diaminobenzoate, and 2-(methacryloyloxy)ethyl-4-aminobenzoate in *N*-methyl-2-pyrrolidone. We investigated the degree of planarity, transmittance, and thermal stability for the PAAs after the photoirradiation reaction at an exposure dose of 200 mJ/cm<sup>2</sup>. The films prepared from the PAA with the lowest molecular weight (PAA-1) exhibited a higher degree of planarity and transmittance compared with those of the film prepared

from the PAA with the highest molecular weight (PAA-4). The initial decomposition temperatures of the cured PAAs with different molecular weights were similar and were stable up to around 300°C. Further, the photosensitivity and transmittance of PAA-1 were investigated in the presence of photoinitiators at 365–400 nm with a high-pressure mercury lamp. The resolution of the photocured film was about 50 μm. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2300–2308, 2005

**Key words:** polyimides; synthesis

## INTRODUCTION

Alicyclic polyimides have been used widely in liquid crystal (LC) display devices because of their many desirable properties, including excellent transmittance, low dielectric constant, and high thermal stability.<sup>1–6</sup> In particular, photosensitive alicyclic polyimides<sup>7</sup> with direct patternability are favored because they can be used to simplify complicated processes and reduce processing costs in the manufacture of thin-film transistor liquid crystal displays (TFT-LCDs) or integrated circuits.<sup>8–11</sup>

Further, the degree of planarity (DOP) is an important property required for interlayer insulating materials in TFT-LCD devices with high aperture ratios.<sup>12,13</sup> The high DOP of interlayer insulating materials can suppress topography-induced LC disclination at the pixel edges, which affects the contrast ratio. Topography-induced LC disclination caused by a low DOP is shown in Scheme 1.

Insulating materials with a high DOP have several advantages: (1) no additional processing step is required for planarization, (2) there is low light leakage due to the reduced disclination of LCs, and (3) there is a more uniform cell gap between the two glass substrates.<sup>12,13</sup>

Therefore, many studies have been performed to improve the DOP of polymeric materials, which is affected by several factors, including the film thickness, surface topography (pattern width), solution viscosity, type of coating material, and molecular weight.<sup>14–16</sup>

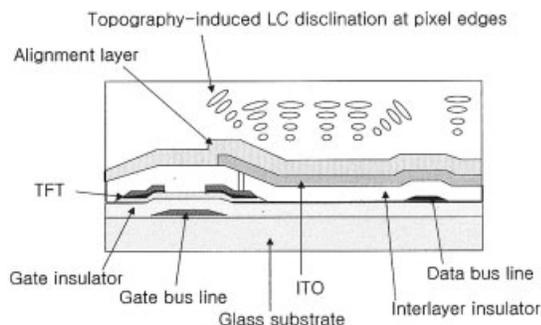
In this study, we synthesized a series of photosensitive polyamic acids (PAAs) with various molecular weights (PAA-1 to PAA-4) from cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA), 2-(methacryloyloxy)ethyl-3,5-diaminobenzoate (MEDAB), and 2-(methacryloyloxy)ethyl-4-aminobenzoate (MEAB) by controlling the molar ratios of these three monomers. An alicyclic dianhydride (CBDA), a diamine (MEDAB) containing a photocrosslinkable moiety, and a monoamine (MEAB) to control the molecular weights were introduced for high transmittance, photopatternability, and a high DOP, respectively. We investigated the effect of the molecular weights of these PAAs on the DOP, transmittance, and thermal properties, which are the typical properties required for the interlayer insulating materials in TFT-LCD devices. Further, a photolithographic study was performed for the PAA with the highest DOP and transmittance (PAA-1).

## EXPERIMENTAL

### Materials

Maleic anhydride (99%, mp = 54°C, Tokyo Kasei Kogyo Co., Ltd., Japan) was used without further puri-

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**Scheme 1** Topography-induced LC disclination caused by a low DOP. ITO: indium tin oxide coated glass.

fication for the synthesis of CBDA. 4-Nitrobenzoyl chloride (98%, mp = 72–74°C, Aldrich Chemical Co.), 3,5-dinitrobenzoyl chloride (98%, Acros Organics), 2-hydroxyethyl methacrylate (HEMA; 95%, Tokyo Kasei Kogyo Co., Ltd.), and *N*-methyl-2-pyrrolidone (NMP; 99%, bp = 202°C, Kanto Chemical Co., Inc., Japan) were used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (Irgacure 651) and 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione (CGI 124) were purchased from Ciba Specialty Chemicals, Inc. (Basel, Switzerland) and were used as received.

### Measurements

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were taken on a Bruker AMX-300 MHz spectrometer (Switzerland) with *N,N*-dimethylformamide (DMF)- $d_7$ , dimethyl sulfoxide (DMSO)- $d_6$ , or  $\text{CDCl}_3$  as the solvent. Fourier transform infrared spectra were recorded on KBr pellets with a Bio-Rad Digilab Division FTS-165 spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument 2950 at a heating rate of 10°C/min under a nitrogen flow up to 800°C. The molecular weights of the PAAs were determined with a Spectro-Physics SP 8450 gel permeation chromatograph in a mixture of DMF (2 L) and tetrahydrofuran (20 mL) containing lithium bromide (5.21 g) and phosphoric acid (11.76 g) as an eluent. Mass spectra and elemental analysis were measured with a Jeol JMS-DX 303 mass spectrometer (Japan) and a FISON Instruments EA-1108, respectively. Film thickness was determined with a KLA-Tencor Alpha-Step 500 instrument. Ultraviolet-visible spectra were recorded on quartz plates with a Scinco UV S-2100. The photoirradiation reaction was performed at 365–400 nm with a 350-W high-pressure mercury lamp, and exposure dose was measured at 365 nm.

### Synthesis of the monomers

#### Synthesis of CBDA

A solution of maleic anhydride (100 g, 1.02 mol,  $\lambda_{\text{max}}$  = 280 nm) in 150 mL of chloroform was photoirradi-

ated at 300 nm for 2 weeks at room temperature. The crude CBDA was precipitated from the solution and collected by filtration and was then purified by recrystallization from acetic anhydride to give a white solid product [yield = 40.0%, mp = 112°C, mass spectrometry mass-to-charge ratio = 196 ( $\text{M}^+$ )].

$^1\text{H-NMR}$  (DMF- $d_7$ ,  $\delta$ , ppm): 4.01 (s, cyclobutane ring, CH, endo form), 4.13 (s, cyclobutane ring, CH, exo form).

$^{13}\text{C-NMR}$  (DMF- $d_7$ ,  $\delta$ , ppm): 39.8 (cyclobutane ring, CH), 172.1 (C=O).

ANAL. Calcd for  $\text{C}_8\text{H}_4\text{O}_6$ : C, 48.99%; H, 2.06%. Found: C, 48.30%; H, 2.07%.

#### Synthesis of 2-(methacryloyloxy)ethyl-3,5-dinitrobenzoate (MEDNB)

MEDNB was prepared by the condensation reaction of 3,5-dinitrobenzoyl chloride (100.0 g, 0.43 mol) and HEMA (56.9 g, 0.43 mol) according to a previously reported method (yield = 86%).<sup>17</sup>

$^1\text{H-NMR}$  (DMSO- $d_6$ ,  $\delta$ , ppm): 9.04 (t, phenyl ring, 1H), 8.89 (d, phenyl ring, 2H), 6.05 (d, vinyl, 1H), 5.70 (d, vinyl, 1H), 4.65 (m, methylene, 2H), 4.51 (m, methylene, 2H), 1.87 (s, methyl, 3H).

#### Synthesis of MEDAB

MEDAB was prepared by the reduction of MEDNB with hydrochloric acid and iron powder according to a previously reported method (yield = 59%, mp = 93°C).<sup>17</sup>

$^1\text{H-NMR}$  (DMSO- $d_6$ ,  $\delta$ , ppm): 6.41 (d, phenyl ring, 2H), 6.02 (d, phenyl ring, 1H), 6.01 (d, vinyl, 1H), 5.68 (d, vinyl, 1H), 4.99 (d, amine protons, 4H), 4.42 (m, methylene, 2H), 4.36 (m, methylene, 2H), 1.85 (s, methyl, 3H).

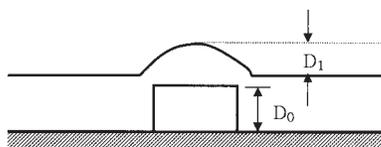
#### Synthesis of 2-(methacryloyloxy)ethyl-4-nitrobenzoate (MENB)

MENB was synthesized by the condensation of 4-dinitrobenzoyl chloride (40.0 g, 0.216 mol) and HEMA (17.04 g, 0.216 mol) with a similar method to that used for the synthesis of MEDNB (yield = 85%).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.35 (d, phenyl ring, 2H), 8.27 (d, phenyl ring, 2H), 6.20 (d, vinyl, 1H), 5.67 (d, vinyl, 1H), 4.69 (m, methylene, 2H), 4.58 (m, methylene, 2H), 2.00 (s, methyl, 3H).

#### Synthesis of MEAB

MEAB was prepared by the reduction of MENB with hydrochloric acid and iron powder with a similar method to that used for the synthesis of MEDAB (yield = 79%, mp = 130°C).



$$\text{DOP (\%)} = (1 - D_1/D_0) \times 100$$

Scheme 2 Definition of DOP.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.83 (d, phenyl ring, 2H), 6.61 (d, phenyl ring, 2H), 6.12 (d, vinyl, 1H), 5.55 (d, vinyl, 1H), 4.06 (s, amine protons, 2H), 4.48 (m, methylene, 2H), 4.44 (m, methylene, 2H), 1.94 (s, methyl, 3H).

ANAL. Calcd for  $\text{C}_{13}\text{H}_{15}\text{NO}_4$ : C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.53%; H, 6.11%; N, 5.62%.

### Synthesis of PAAs

A typical procedure for the synthesis of PAA-1 was as follows: to a solution of MEDAB (10.57 g, 40 mmol) in 76 g of NMP containing 2 mg of hydroquinone (0.02 mmol) as a polymerization inhibitor, 11.77 g of CBDA (60 mmol) and 9.97 g of MEAB (40 mmol) were added slowly at 0–10°C at a concentration of 30 wt %. The reaction mixture was stirred at 0–10°C for 24 h. The molar ratios of the three monomers (CBDA:MEDAB:MEAB) were controlled at 3:2:2 (PAA-1), 10:9:2 (PAA-2), 15:14:2 (PAA-3), and 1:1:0 (PAA-4) to obtain PAAs with different molecular weights.

### Measurement of DOP

Silicone wafers (20 × 30 mm) with topographies consisting of isolated line patterns were prepared for the measurement of DOP. The width of the uncoated lines was in the range 8–50  $\mu\text{m}$ , and the step height was fixed at 1.0  $\mu\text{m}$ . PAA solutions containing 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione (3 wt % to PAA) were coated on the silicone wafers and cured under the following processing conditions: they were (1) prebaked at 90°C for 2 min, (2) photoirradiated with an exposure dose of 200  $\text{mJ}/\text{cm}^2$  at 365 nm, (3) postexposure baked at 190°C for 10 min, and (4) imidized at 250°C for 60 min. The thickness of the cured films was controlled at 2.0–2.2  $\mu\text{m}$ , and the DOP was calculated from the difference of the step height of the dry film ( $D_1$ ) and the step height of the uncoated substrate ( $D_0$ ), as shown in Scheme 2.

### Measurement of transmittance

PAA solutions containing 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione (3 wt % to PAA) were coated on quartz plates (30 × 30 mm) to produce

thin films. The transmittance of the PAA films was measured after they were cured under the following conditions: they were (1) prebaked at 90°C for 2 min, (2) photoirradiated with an exposure dose of 200  $\text{mJ}/\text{cm}^2$ , (3) postexposure baked at 190°C for 10 min, and (4) imidized at 250°C for 60 min. The thickness of the cured films was controlled at 2.0–2.2  $\mu\text{m}$ .

### Measurement of the thermal properties

The thermal decomposition temperatures of the PAAs containing 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione (3 wt % to PAA) after curing were measured by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

### Determination of the normalized film thickness

The normalized film thickness was determined by the division of the remaining thickness of the exposed film after development ( $d_1$ ) by the film thickness before development ( $d_0$ ).

### Lithographic imaging of PAA-1

The PAA-1 containing 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione (3 wt %) was spin-coated on a silicone wafer and prebaked at 90°C for 2 min. Exposure, with a dose of 200  $\text{mJ}/\text{cm}^2$ , was performed at 365 nm with a 350-W, high-pressure mercury lamp through a photomask with patterns of different sizes and was followed by postexposure baking at 190°C for 10 min. The resulting film was developed by immersion in a 2.38 wt % aqueous solution of tetramethylammonium hydroxide (TMAH) for 30 s at room temperature and was rinsed with deionized water several times. Finally, the patterned film was thermally cured at 250°C for 60 min in a convection oven. The resolution of the pattern was evaluated by scanning electron microscopy (SEM) and the Alpha-Step 500 instrument.

## RESULTS AND DISCUSSION

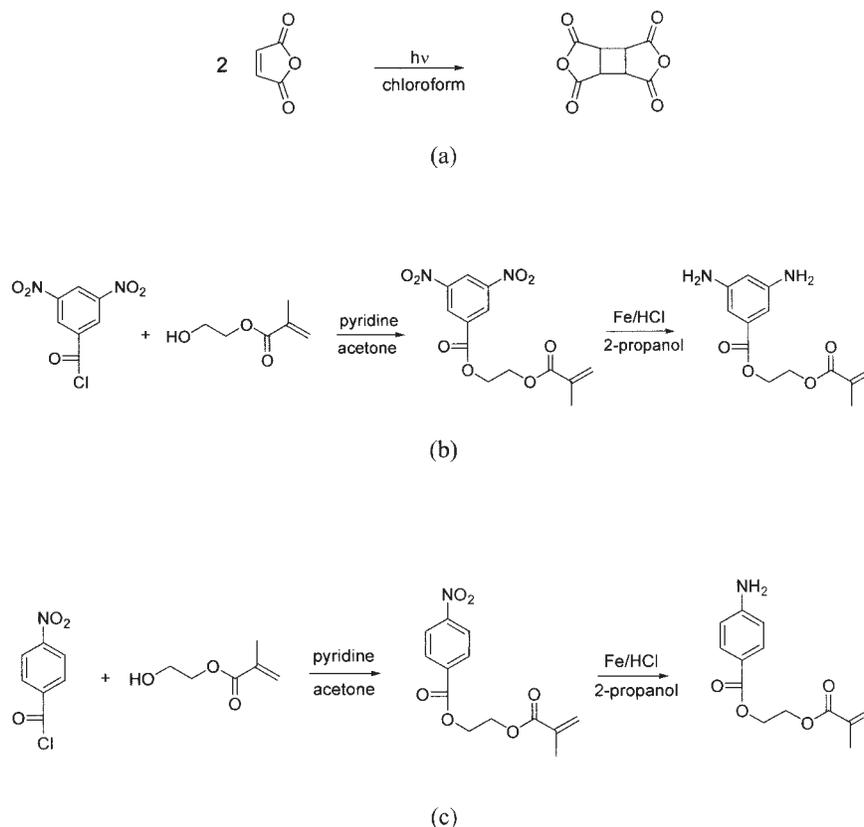
### Synthesis of the monomers

The alicyclic dianhydride CBDA was synthesized by the [2 + 2] cycloaddition of maleic anhydride, as shown in Scheme 3(a), and the yield was about 40%. The structure of CBDA was identified by elemental analysis and  $^1\text{H-NMR}$  spectroscopy as follows:

ANAL. Calcd for  $\text{C}_8\text{H}_4\text{O}_6$ : C, 48.99%; H, 2.06%. Found: C, 48.30%; H, 2.07%.

$^1\text{H-NMR}$  ( $\text{DMF-}d_7$ ,  $\delta$ , ppm): 3.89–4.01 (m, cyclobutane, endo form), 4.13 (s, cyclobutane, exo form).

Cyclobutane ring proton peaks appeared at 3.89–4.01 and 4.13 ppm; the appearance of these peaks was



**Scheme 3** Synthesis of the monomers: (a) CBDA, (b) MEDAB, and (c) MEAB.

attributed to the endo and exo forms, respectively. The double-bond proton peaks of maleic anhydride disappeared during the photoirradiation reaction.

MEDAB was synthesized as shown in Scheme 3(b), and the yield was 59%. The structure of MEDAB was identified by  $^1\text{H-NMR}$  spectroscopy as follows:

$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ,  $\delta$ , ppm): 6.41 (d, phenyl ring, 2H), 6.02 (d, phenyl ring, 1H), 6.01 (d, vinyl, 1H), 5.68 (d, vinyl, 1H), 4.99 (d, amine protons, 4H), 4.42 (m, methylene, 2H), 4.36 (m, methylene, 2H), 1.85 (s, methyl, 3H).

New amine proton peaks of the MEDAB appeared at 4.99 ppm.

MEAB was synthesized as shown in Scheme 3(c), and the yield was 79%. The structure of MEAB was identified by  $^1\text{H-NMR}$  spectroscopy as follows:

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.83 (d, phenyl ring, 2H), 6.61 (d, phenyl ring, 2H), 6.12 (d, vinyl, 1H), 5.55 (d, vinyl, 1H), 4.06 (s, amine protons, 2H), 4.48 (m, methylene, 2H), 4.44 (m, methylene, 2H), 1.94 (s, methyl, 3H).

New amine proton peaks of MEAB that did not exist in MENB appeared at 4.06 ppm.

### Synthesis of PAAs

Negative-type photosensitive PAAs were synthesized from CBDA, MEDAB, and MEAB in NMP as shown in

Scheme 4. We controlled the weight-average molecular weights ( $M_w$ 's) of the PAAs (PAA-1 to PAA-4) by changing the molar ratios of the monomers, which ranged from 17,900 to 101,200 g/mol.  $M_w$  decreased with increasing molar ratio of MEAB, as shown in Table I. The structural identification of the representative PAA (PAA-1) was confirmed by  $^1\text{H-NMR}$  spectroscopy, as shown in Figure 1.

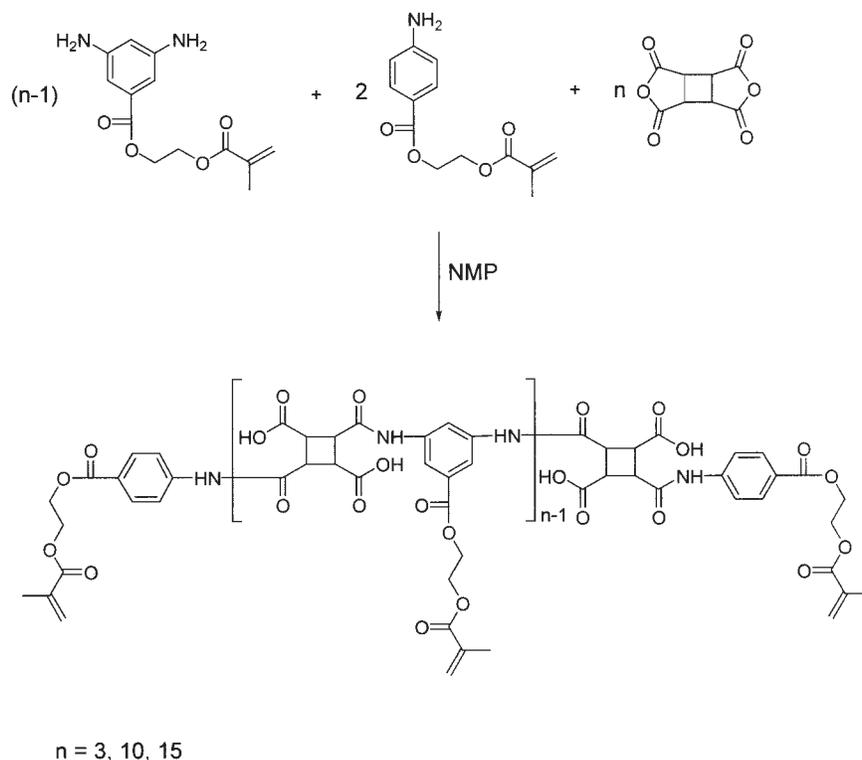
$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ,  $\delta$ , ppm): 12.6–12.4 (b, carboxylic acid protons, 6H), 10.5–10.4 (m, amide protons, 6H), 8.2–7.5 (m, phenyl ring, 14H), 6.0 (d, vinyl, 4H), 5.6 (d, vinyl, 4H), 4.6–4.4 (m, methylene, 16H), 3.8–3.5 (m, cyclobutane ring, 12H), 1.8 (s, methyl, 12H).

As shown in Figure 1, the peaks due to the carboxylic acid and amide protons appeared at 12.6–12.4 and 10.5–10.4 ppm, respectively. Amine proton peaks of MEDAB and MEAB did not appear.

### Characterization of PAAs

#### DOP

In this study, the molecular weights of the PAAs were controlled with an end-capping agent (MEAB) to investigate the effect of the molecular weights of the PAAs on DOP. We also investigated the relationship of the pattern width and DOP. As shown in Figure 2, DOP increased with decreasing molecular weight of



**Scheme 4** Synthesis of the PAAs.

the PAAs. Polymers with low molecular weights were expected to reduce the viscosity of the solution at the same solid content, which resulted in a high DOP. The cured PAA-1 film with a 2.2.  $\mu\text{m}$  thickness showed the highest DOP, above 70% on the isolated line pattern with a 10  $\mu\text{m}$  width, which could be used for the interlayer insulating materials in a TFT-LCD array.<sup>13</sup> Further, Figure 2 shows that DOP decreased with increasing line width, which was similar to the results of a previous study.<sup>13</sup>

#### Transmittance

We investigated the effect of the molecular weights of the PAAs and processing conditions on the transmittance.

The transmittance of the PAA-1 films was measured after the films were processed under the following conditions: they were (1) prebaked at 90°C for 2 min, (2) photoirradiated with a dose of 200 mJ/cm<sup>2</sup> at 365 nm, (3) postexposure baked at 190°C for 10 min, and (4) imidized at 250°C for 60 min. The thickness of the cured films was controlled at 2.0–2.2  $\mu\text{m}$ .

As shown in Figure 3, the transmittance of PAA-1 decreased with photoirradiation and with heat treatment at 250°C. The initial transmittance of the PAA-1 film was about 97% at 400 nm, but this decreased to 85% after the postexposure baking process at 250°C for 60 min. This was attributed to the change in film composition from the PAA to the polyimide at a high temperature of 250°C, which was similar to results

**TABLE I**  
Synthetic Results of the PAAs with Various Molecular Weights

PAA	Molar ratio of monomers (CBDA:MEAB) <sup>b</sup>	Molecular weight (g/mol) <sup>c</sup>			Inherent viscosity (dL/g) <sup>c</sup>
		$M_w$	$M_n$	MWD	
PAA-1 <sup>a</sup>	3:2:2	17,900	14,600	1.23	0.16
PAA-2	10:9:2	43,600	27,100	1.61	0.31
PAA-3	15:14:2	49,900	31,800	1.56	0.38
PAA-4	1:1:0	101,200	81,600	1.24	0.61

$M_n$  = number-average molecular weight; MWD = molecular weight distribution.

<sup>a</sup> PAA-1 was synthesized from CBDA (11.77 g, 60 mmol), MEDAB (10.57 g, 40 mmol) and MEAB (9.97 g, 40 mmol) in NMP (75.4 g).

<sup>b</sup> Measured by gel permeation chromatography in a mixture of DMF (2 L) and tetrahydrofuran (20 mL) containing lithium bromide (5.21 g) and phosphoric acid (11:76 g) as an eluent.

<sup>c</sup> Measured at a concentration of 0.5 g/dL in NMP at 30°C.

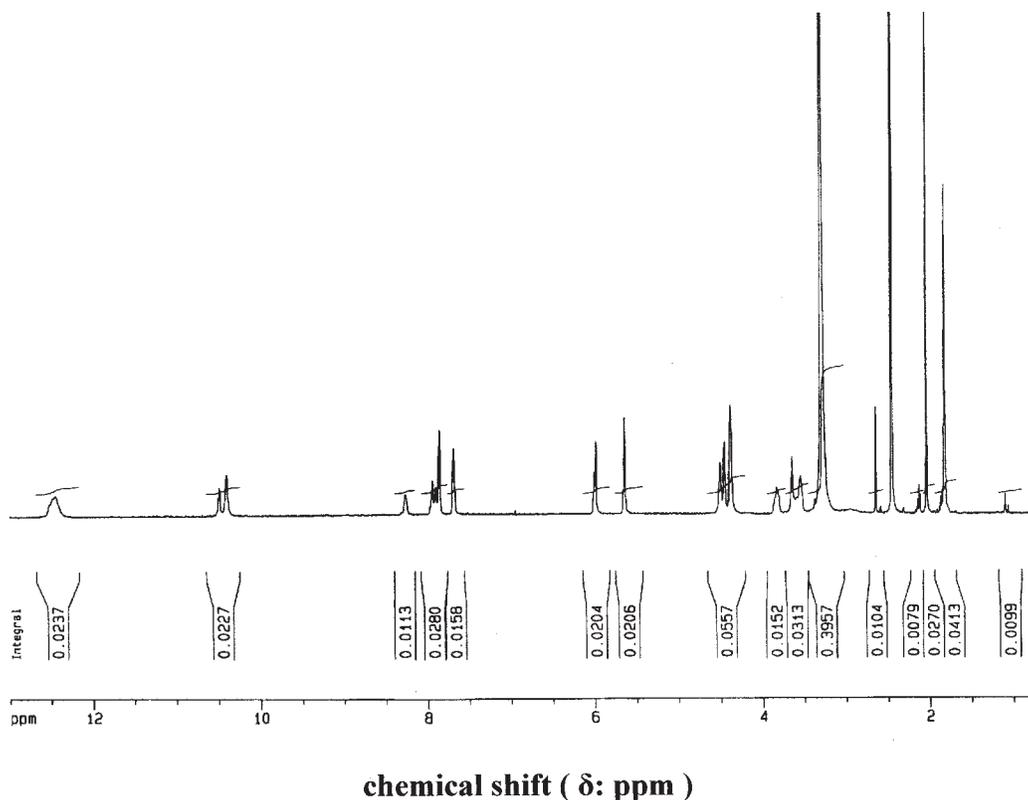


Figure 1 <sup>1</sup>H-NMR spectrum of PAA-1.

reported by Mo et al.<sup>18</sup> However, the reduction in the transmittance of the PAA-1 film synthesized from the alicyclic dianhydride CBDA was much lower than that of the aromatic polyimide prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride and *p*-phenylenediamine, which decreased from 90 to 55% with hard baking.<sup>18</sup>

Figure 4 also shows the effect of the molecular weight of the PAAs on transmittance. The transmittance of the PAAs with different molecular weights (PAA-1 and PAA-4) after they were cured at 250°C for

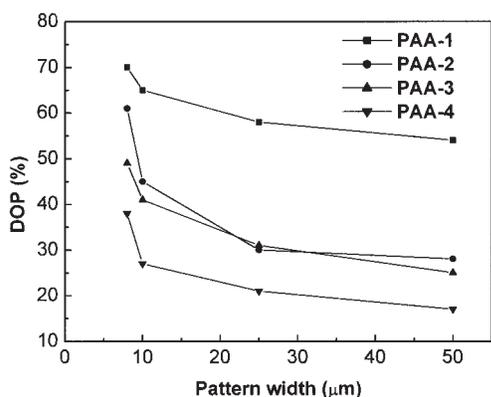


Figure 2 Effect of molecular weight and pattern width on DOP.

60 min were compared, which revealed that the PAA end-capped with MEAB (PAA-1) exhibited a slightly higher transmittance than the PAA with a higher molecular weight (PAA-4). Possibly, the transmittance of the cured PAA-4 decreased because of the presence of a terminal free amine group, which could have been oxidized during the high-temperature curing process.

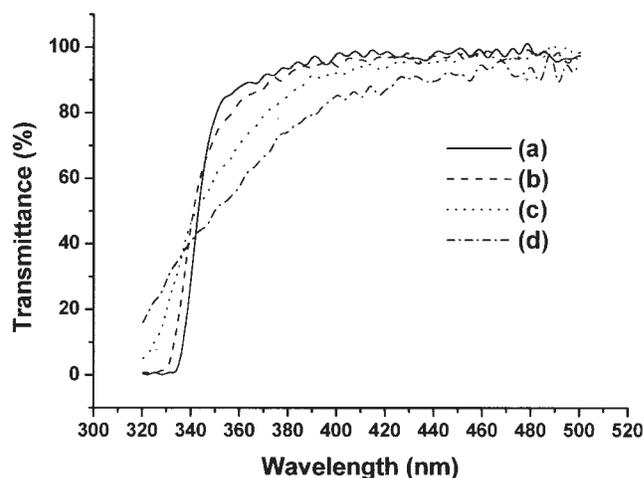
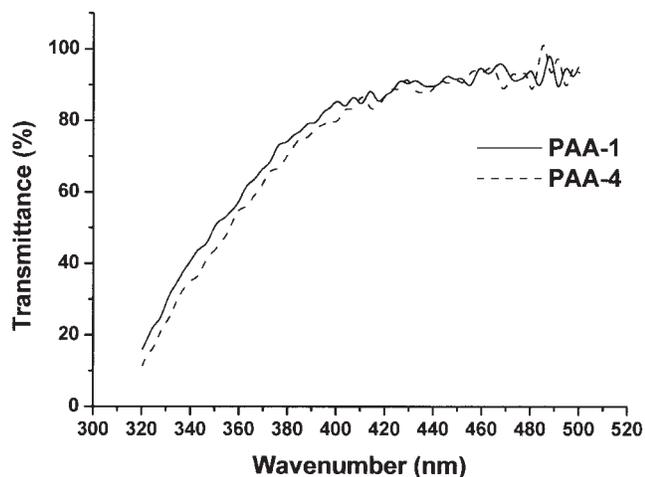


Figure 3 Effect of processing conditions and molecular weight on the transmittance of PAA-1. Processing conditions: (a) prebaking at 90°C for 2 min, (b) exposure dose of 200 mJ/cm<sup>2</sup>, (c) postexposure baking at 190°C for 10 min, and (d) curing at 250°C for 60 min.



**Figure 4** Effects of molecular weight on the transmittance after curing at 250°C for 60 min.

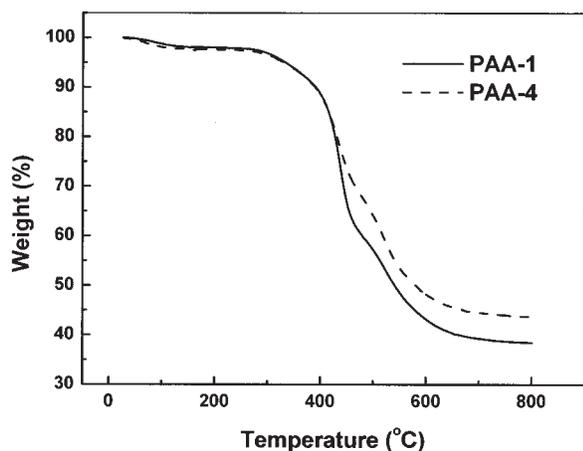
As a result, the PAA with a lower molecular weight produced a higher transmittance, about 85% at 400 nm, after photoirradiation followed by the heat treatment at 250°C, which was much higher than that of aromatic photosensitive polyimides.

#### Thermal properties

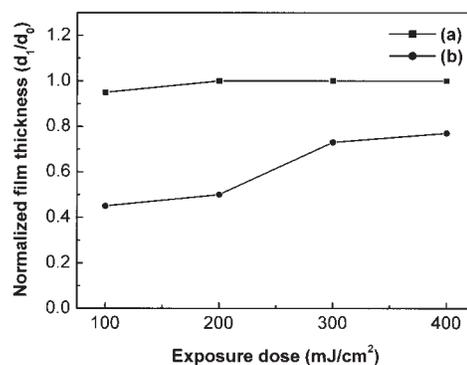
We investigated the thermal properties of the PAAs with different molecular weights (PAA-1 to PAA-4) after they were cured at 250°C for 60 min by differential scanning calorimetry and TGA. As shown in Figure 5, the initial decomposition temperatures of PAA-1 and PAA-4 were around 300°C, and their residual weights were 38 and 44%, respectively. However, glass-transition temperatures were not detected.

#### Lithographic imaging of PAA-1

We performed a photolithographic study of PAA-1, which showed the highest DOP and transmittance. In



**Figure 5** TGA curves of PAA-1 and PAA-4 after curing at 250°C for 60 min.

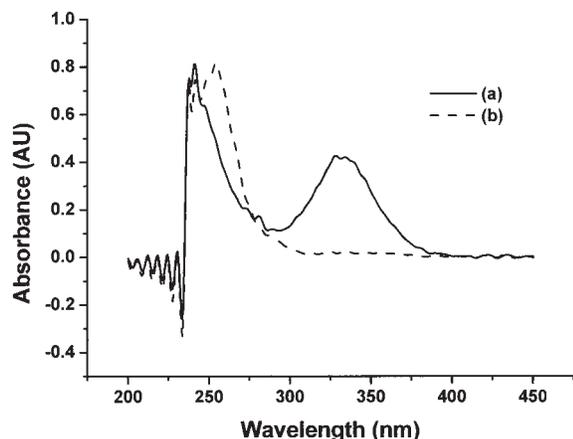


**Figure 6** Effect of the type of photoinitiator on the exposure characteristics of PAA-1. Photoinitiators (5 wt % to PAA-1): (a) 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione and (b) 2,2-dimethoxy-2-phenylacetophenone. PAAs were postexposure baked at 190°C for 10 min and cured at 250°C for 60 min. They were developed by immersion in 2.38 wt % aqueous TMAH for 30 s.

the lithographic evaluation of PAA-1, the film thickness was fixed at 2.0–2.2  $\mu$ , and a 2.38 wt % aqueous solution of TMAH was used as the developer.

#### Effect of the photoinitiator and the exposure dose

The photosensitivity of PAA-1 itself was very low, which resulted in good solubility with the 2.38 wt % aqueous solution of TMAH, even after exposure with a dose of 400 mJ/cm<sup>2</sup>. Therefore, two kinds of photoinitiators were added to increase the photosensitivity of PAA-1. The effects of the photoinitiators on the exposure characteristics are shown in Figure 6, in which the normalized film thickness with respect to the exposure energy is plotted. In this study, the photosensitivity was defined as the irradiated energy required to crosslink the PAA-1 such that the exposed area retained 50% of its original thickness after development. As shown in Figure 6, the photosensitivity of PAA-1 containing 5 wt % 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione, was below 100 mJ/cm<sup>2</sup>. However, the photosensitivity of PAA-1 containing 5 wt % 2,2-dimethoxy-2-phenylacetophenone was about 200 mJ/cm<sup>2</sup>. The addition of 2,2-dimethoxy-2-phenylacetophenone increased the photosensitivity of PAA-1 only a little, whereas the addition of 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione resulted in a more than twofold increase in the remaining film thickness at an exposure dose of 100–200 mJ/cm<sup>2</sup>; that is, the photosensitivity of 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione was superior to that of 2,2-dimethoxy-2-phenylacetophenone. We concluded that 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione generated more radicals than 2,2-dimethoxy-2-phenylacetophenone due to its strong absorption at 365 nm, as shown in Figure 7.

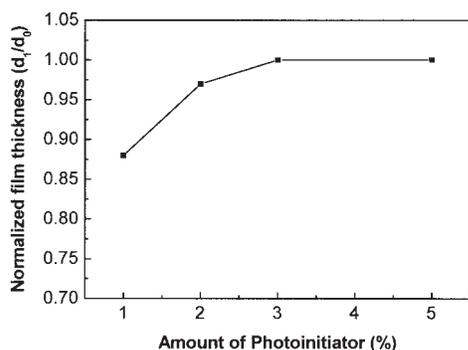


**Figure 7** Comparison of the ultraviolet absorption of the photoinitiators at a concentration of  $4.0 \times 10^{-5} M$  in dichloromethane: (a) 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione and (b) 2,2-dimethoxy-2-phenylacetophenone.

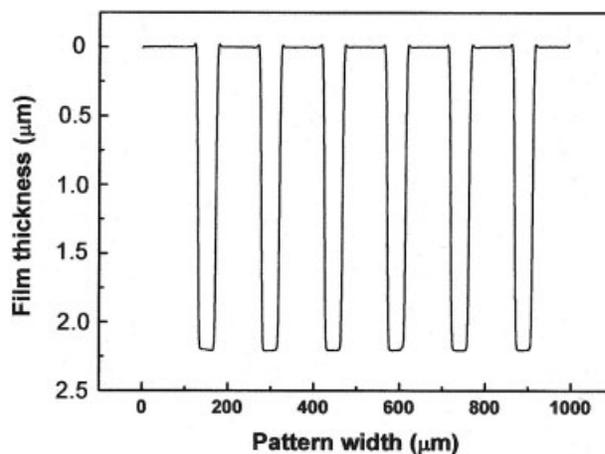
Figure 6 shows the effect of exposure dose (100–400  $\text{mJ}/\text{cm}^2$ ) on the remaining film thickness of PAA-1. The remaining film thickness increased with increasing exposure energy in the presence of the photoinitiators. PAA-1 containing 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione [Fig. 6(a)] showed a 100% remaining film thickness at an exposure dose of 200  $\text{mJ}/\text{cm}^2$ .

#### Effect of photoinitiator amount

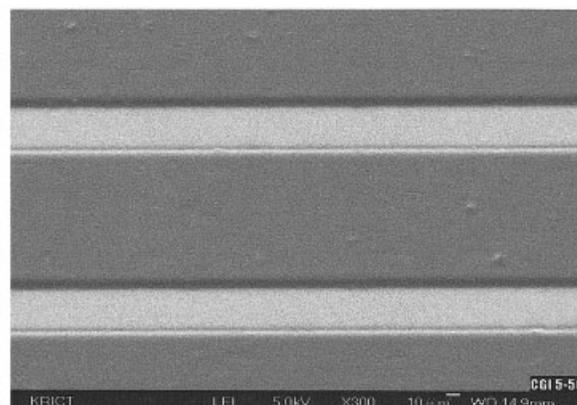
Figure 8 shows the effect of the amount of 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione on the normalized film thickness at an exposure dose of 200  $\text{mJ}/\text{cm}^2$ . As shown in Figure 8, the normalized film thickness increased with increasing amount of 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione, and the optimum amount for the addition of 1-[4-



**Figure 8** Effect of the amount of photoinitiator (CGI 124) on the normalized film thickness of PAA-1. PAAs were postexposure baked at 190°C for 10 min and cured at 250°C for 60 min. They were developed by immersion in 2.38 wt % aqueous TMAH for 30 s. Exposure dose = 200  $\text{mJ}/\text{cm}^2$ .



(a)



(b)

**Figure 9** (a) Negative pattern of the PAA-1 film surface profile measured by the Alpha-Step instrument and (b) an SEM photograph (the photoinitiator was CGI 124 at 3 wt % to PAA-1). PAAs were postexposure baked at 190°C for 10 min and cured at 250°C for 60 min. They were developed by immersion in 2.38 wt % aqueous TMAH for 30 s. Exposure dose = 200  $\text{mJ}/\text{cm}^2$ .

(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione was 3 wt % to PAA-1. The photosensitivity of this composition would be adequate for most microelectronic device applications.

#### Lithographic imaging of PAA-1

The PAA-1 film was soluble in the 2.38 wt % aqueous solution of TMAH, and photoirradiation gave rise to a solubility change at exposed areas of the film. The photolithography evaluation was performed under previously optimized exposure conditions. The PAA containing 3 wt % 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione (PAA-1) was spin-coated

on a silicone wafer and prebaked at 90°C for 2 min. Exposure, with a dose of 200 mJ/cm<sup>2</sup>, was performed at 365 nm and was followed by postexposure baking at 190°C for 10 min. The PAA was finally cured at 250°C in a convection oven. The resolution of the patterns was evaluated from SEM with the Alpha-Step 500 instrument. Figure 9 shows the representative line-pattern profile obtained by the Alpha-Step and SEM image. The resulting pattern of PAA-1 exhibited a 50- $\mu$ m resolution with a film thickness of about 2.2  $\mu$ m.

### CONCLUSIONS

A series of photosensitive PAAs was synthesized from CBDA, MEDAB, and MEAB in NMP. The PAA with the lowest molecular weight (PAA-1) gave the highest DOP and transmittance compared to that of the PAA with the highest molecular weight (PAA-4). The initial decomposition temperatures of the cured PAAs were above 300°C. Photolithographic studies were conducted for PAA-1 in the presence of 1-[4-(phenylthio)phenyl]-2-(*O*-benzoyloxime)-1,2-octanedione as a photoinitiator. PAA-1 was found to be an excellent negative-type photosensitive material precursor with an exposure dose of 200 mJ/cm<sup>2</sup> and was easily developed with a 2.38 wt % TMAH aqueous solution. The resulting pattern of the photocured PAA-1 exhibited a 50- $\mu$ m resolution. PAA-1 showed excellent characteristics, including a high transmittance, above 85% at 400 nm; a high DOP of 70%; and photopatternability, with a resolution of 50  $\mu$ m, and could be applied to insulating materials in TFT-LCD devices.

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