

Three-Component Negative-Type Photosensitive Polyimide Precursor Based on Poly(amic acid), a Cross-Linker, and a Photoacid Generator

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1. Introduction

Photosensitive polyimides (PSPIs) are widely used as protection and insulation materials because of their excellent properties such as thermal and chemical stabilities, a low dissipation factor, and a reasonably low dielectric constant. They are also attractive because they simplify processing and avoid the use of photoresist in the microelectric industry.¹

Most of the negative-type PSPIs are prepared from poly(amic acids) (PAAs), where cross-linking sites are introduced to PAAs through ester or acid amine ion linkages.^{2,3} On the other hand, the positive-type PSPIs consist of poly(hydroxyimide)s (PHIs) and diazonaphthoquinone (DNQ),⁴ *o*-nitrobenzyl esters of PAAs⁵, or poly(isoimide)s and DNQ.⁶

PAAs possessing hydrophilic carboxylic groups are conventional poly(imide) (PI) precursors, and they have a great possibility for application to PSPI precursors without partial imidization or functionalization. Several groups have reported the preparation of PSPIs consisting of PAAs and DNQ⁷⁻⁹. The dissolution rate of PAAs to 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution, however, is too high to get a sufficient dissolution contrast between unexposed and exposed areas. Although one report on the development of PSPI using PAA as a polymer matrix has been reported¹⁰, where 1,4-dihydropyridine was used as the photosensitive compound, the control of the post exposure baked (PEB) temperature is very critical for image formation. The PEB treatment at 150 °C gives a positive image. On the other hand, a negative image forms at 160 °C. Thus, it is important to develop a versatile method to formulate PSPIs based on PAAs.

In previous papers, we developed new PSPIs (from PHI)¹¹ and photosensitive poly(phenylene ether)¹² by combination of thermally stable polymer matrices with a cross-linker and a photoacid generator. These findings prompted us to develop PSPIs from PAAs.

This paper describes a simple PSPI formulation method based on PAA, 4,4'-methylenebis[2,6-bis(hydroxymethyl)]phenol (MBHP) as a cross-linker and a photoacid generator (5-propylsulfonyloxyimino-5H-thiophen-2-ylidene)-2-(methylphenyl)acetonitrile (PTMA).

2. Experiment Section

2.1. Materials.

N,N-Dimethylacetamide (DMAc) was stirred over powdered calcium hydride overnight, distilled under reduced pressure, and stored over 4A molecular sieves. PMDA was purified by recrystallization from acetic anhydride and dried at 150 °C for 12 h under vacuum before use. ODA was crystallized from tetrahydrofuran. A photoacid generator PTMA¹³ was donated by Chiba Specialty Chemicals K.K., and used without further purification. MBHP¹⁴ and 2,4-dimethyl-6-(hydroxymethyl)phenol (DHP)¹⁵ were prepared according to reported procedures. Other reagents were obtained commercially and used as received.

2.2 Preparation of PAA

To a solution of ODA (0.409 g, 2.04 mmol) in DMAc (3.6 mL) was added with stirring PMDA (0.446 g, 2.04 mmol). The mixture was stirred at room temperature for 4 h. The resulting viscous solution was diluted with DMAc (3.7 mL) and poured into methanol (100 mL). The PAA that precipitated was filtered off and dried *in vacuo* at 80 °C for 12 h. The inherent viscosity of the resulting polymer was 0.41 dL·g⁻¹ measured at a concentration of 0.5 dL·g⁻¹ in DMAc at 30 °C. IR (KBr): ν 1724 (C=O, carboxylic acid), 1658 cm⁻¹ (C=O, amide). 2.3. Dissolution Rate.

2.3. Model Reaction

PAA (52 wt%), DHP (38 wt%), and *p*-toluenesulfonic acid monohydrate (PTS) (10 wt%) were dissolved in DMSO. The solution was casted onto a glass plate, followed by heating at 80 °C for 15 min, and then at 120 °C for 15 min. The resulting film was dried at 100 °C for 1 h under reduced pressure to remove solvent. The sample was dissolved in DMSO-*d*₆ and analyzed by ¹H NMR spectroscopy.

2.4. Dissolution Rate

MBHP and PTMA were added to a PAA solution (13 wt% in 2-methoxyethanol) to construct a photosensitive polymer. The polymer film spin-cast on a silicon wafer was pre-baked at 80 °C for 5 min, and then exposed to a filtered super-high pressure mercury lamp. The exposed film was developed with 2.38 wt% aqueous TMAH solution at 25 °C for 40 sec. The changes in the film thickness against the exposure energy were measured with a Dektak³ surface profiler (Veeco Instrument Inc.).

2.5. Photosensitivity.

A 1.8 μ m-thick polymer film on a silicon wafer was exposed to radiation at a wavelength of 436 nm through the filtered super high-pressure mercury lamp, developed with 2.38 wt% aqueous TMAH solution at 25 °C, and rinsed with water. A characteristic curve was obtained by a normalized film thickness against exposure energy.

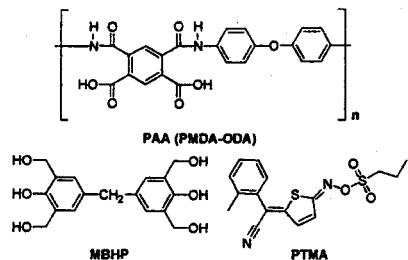
2.6. Measurements.

Infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ¹H NMR spectra were obtained using a BRUKER DPX300 (300 MHz) spectrometer. Thermogravimetry (TG) was performed with a Seiko TG/DTA 6300. The film thickness was measured by a Dektak³ surface profiler (Veeco Instrument Inc). Field emission scanning electron microscope (SEM) was taken with a HITACHI S-800 scanning electron microscope with 15 kV accelerating voltage for imaging.

3. Results and Discussion

3.1. Fabrication of PSPI

The PAA from PMDA and ODA was selected as a typical PAA to demonstrate the usefulness of the proposed method. The photoacid generator PTMA and the cross-linker MBHP were chosen due to their availability and high reactivity. The PSPI formulation is shown in Scheme 1. The ring-opening polyaddition of PMDA with ODA was carried out in DMAc at room temperature for 4 h, giving the PAA with an inherent viscosity of 0.41 dL·g⁻¹.



Scheme 1. Poly(amic acid), cross-linker, and photoacid generator.

3.2. Lithographic Evaluation.

To clarify the dissolution behavior of the exposed and unexposed areas (436 nm light), the effect of MBHP loading and post exposure baked (PEB) temperature on the dissolution rate in 2.38 wt% aqueous TMAH solution was investigated. The dissolution rate was estimated by measuring the film thickness after development. The effect of MBHP loading after exposure of 100 mJ·cm⁻² with 436 nm light and PEB temperature of 130 °C for 3 min was studied, and the results are shown in Figure 1. The dissolution rate of the unexposed area decreases with increasing MBHP contents, while the exposed areas are not dissolved in the developer even in a 20wt% MBHP loading. However, the exposed area is swelled at this loading. These findings indicate that a 25 wt% MBHP loading is appropriate to achieve a good dissolution contrast.

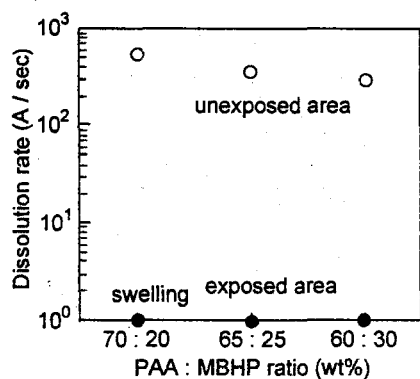


Figure 1. Effect of MBHP loading on the dissolution rate of the film consisting of PAA, MBHP, and PTMA (10 wt%) to 2.38 wt% aqueous TMAH solution after exposure 100 mJ·cm⁻² with 436 nm light and PEB temperature at 130 °C for 3 min

To investigate the PEB temperature effect on the dissolution rate, the dissolution rates of both exposed and unexposed areas at various PEB temperatures were measured. The results in the case of the resist formulated by mixing PAA (65 wt%), MBHP (25 wt%), and PTMA (10 wt%) in 2-methoxyethanol are shown in Figure 2, where the film was exposed to 436 nm light with 100 mJ·cm⁻², post-baked at elevated temperature from 110 to 140 °C for 3 min, and developed with 2.38 wt% aqueous TMAH solution at 25 °C for 40 sec. The dissolution rate of unexposed region decreases with an increase of PEB temperature, and

suddenly becomes zero at 140 °C because of thermal cross-linking. On the other hand, the exposed areas are insoluble in the developer, and a little swelling is observed at PEB temperature of 110 °C. Thus, the suitable PEB temperature was determined to be around 120-130 °C.

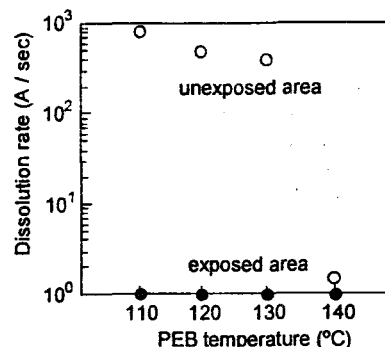


Figure 2. Effect of PEB temperature on the dissolution rate of the film consisting of PAA (65 wt%), MBHP (25 wt%), and PTMA (10 wt%) to 2.38 wt% aqueous TMAH solution after exposure 100 mJ·cm⁻².

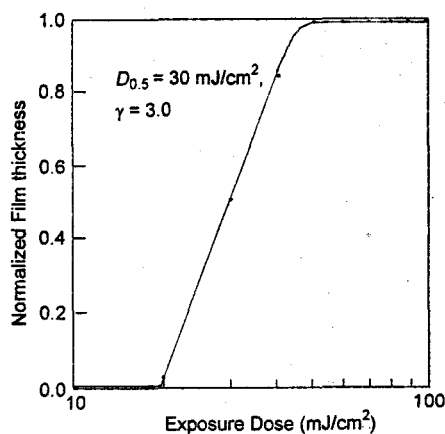


Figure 3. Exposure characteristic curve of the film consisting of PAA (65 wt%), MBHP (25 wt%), and PTMA (10 wt%) with 2.38 wt% aqueous TMAH solution after PEB temperature at 130 °C for 3 min.

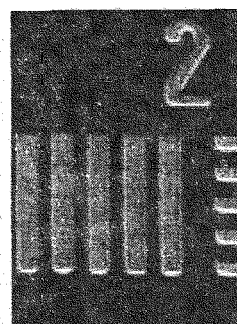


Figure 4. Scanning electron micrograph of a negative contact-printed image. The film was exposed to 436 nm light with 100 mJ·cm⁻², post-baked at 130 °C for 3 min, developed with 2.38 wt% aqueous TMAH solution at 25 °C for 40 sec, and rinsed in water.

Figure 4 presents a scanning electron micrograph of the contact-printed image that was obtained using the system described above after exposure to 436 nm light with 100 mJ·cm⁻², developed with 2.38 wt% aqueous TMAH solution at 25 °C, and rinsed in water.

After these preliminary optimization studies involving MBHP contents and PEB temperatures, we formulated a PSPI precursor consisting of 65 wt% of PAA, 25 wt% MBHP and 10 wt% of PTMA. The sensitivity curve of the PSPI precursor film with 1.8 μm thickness is shown in Figure 3, indicating that the sensitivity ($D_{0.5}$) and contrast ($\gamma_{0.5}$) were 30 $\text{mJ}\cdot\text{cm}^{-2}$ and 3.0, respectively, with 436 nm light.

The clear positive pattern with a 10 μm resolution is obtained.

3.3 Thermal Stability of Polymer Films.

Figure 5 shows a TG curve of the film after exposure of 100 $\text{mJ}\cdot\text{cm}^{-2}$, post-baking at 130 $^{\circ}\text{C}$ for 3 min, developing with 2.38 wt% aqueous TMAH solution at 25 $^{\circ}\text{C}$ and curing 350 $^{\circ}\text{C}$ for 2 h. A 5% weight loss temperature of the film is observed at 485 $^{\circ}\text{C}$, which is a little lower than that of corresponding PI. This behavior would be attributed to decomposition of MBHP residues.

This negative image in the PAA film was successfully converted to that of the polyimide film by high-temperature treatment (350 $^{\circ}\text{C}$ for 2 h) in air. The IR spectra of films before and after thermal treatment are shown in Figure 6, where characteristic imide absorptions at 1778 and 1728 cm^{-1} appear and the absorptions due to the carboxylic acid, amide I and II groups at 1724, 1658 cm^{-1} , and 1542 cm^{-1} respectively, are disappeared. On the other hand, the absorption bands at 3100-3600 and 1670 cm^{-1} assigned to O-H and C=O stretchings, respectively indicate the presence of MBHP residues.

The negative pattern obtained was heated at 350 $^{\circ}\text{C}$ for 2 h under air, and a scanning electron micrograph of the heated pattern was presented in Figure 7. Although some reduction of the film thickness was observed (from 1.8 μm to 1.1 μm), there was no deformation of the pattern. This indicates the high thermal stability of the polymer.

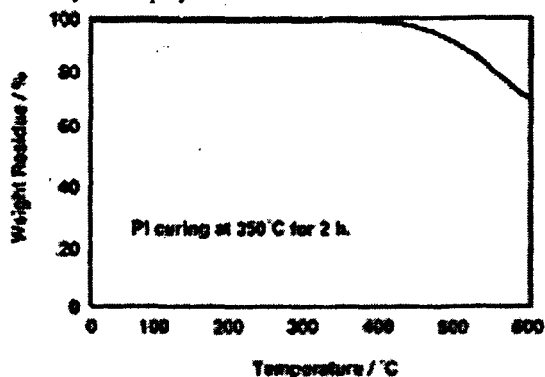


Figure 5. TG curve of the film after exposure of 100 $\text{mJ}\cdot\text{cm}^{-2}$, post-baking at 130 $^{\circ}\text{C}$ for 3 min, developing with 2.38 wt% aqueous TMAH solution at 25 $^{\circ}\text{C}$ and curing 350 $^{\circ}\text{C}$ for 2 h.

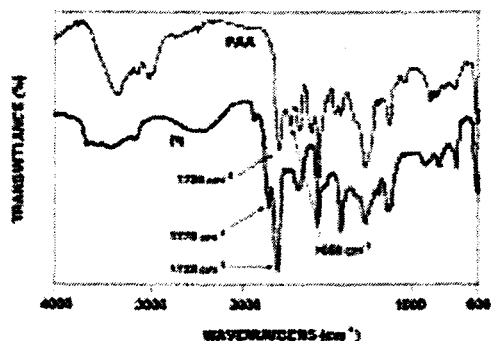


Figure 6. IR spectra of films before and after thermal treatment

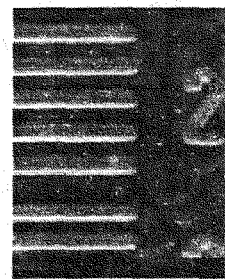
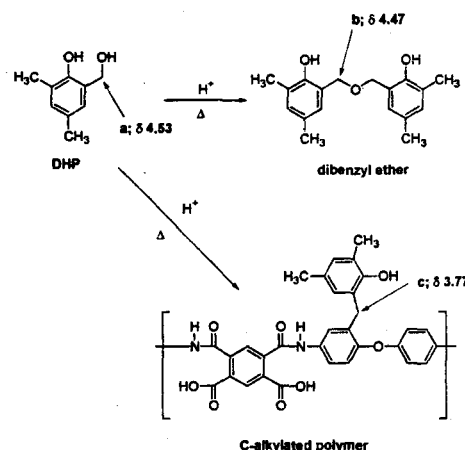


Figure 7. Scanning electron micrograph of the heated pattern (350 $^{\circ}\text{C}$ for 2 h).

3.4. Mechanism of the Acid-Catalyzed Cross-Linking.

To clarify the mechanism of the acid-catalyzed cross-linking, a model reaction was carried out using the PAA, a monofunctional benzyl alcohol, DHP, and PTS (Scheme 2). This mixture in 2-methoxyethanol was spin-coated onto a glass plate, followed by heating at 80 $^{\circ}\text{C}$ for 15 min and then at 120 $^{\circ}\text{C}$ (postbaking) for 15 min to mimic the prebaking and postbaking steps in resist processing. Figure 8a and 8b show the ^1H NMR spectra obtained from a solution of PAA and DHP in DMSO-d_6 , and the post-cured film consisting PAA, DHP and PTS, respectively. In the former sample, the peak due to the methylene protons of DHP is observed at 4.53 ppm. In the latter post-curing film, a new a small peak at 3.77 and a large peak at 4.47 ppm are observed. Two peaks are assigned to the methylene protons in the C-alkylated product and the methylene protons in dibenzyl ether formed by the selfcondensation of DHP, respectively. The appearance of new peaks is accompanied by a decrease in the amount of starting materials in the presence of *p*-toluenesulfonic acid monohydrate. On the other hand, the amount of dibenzyl ether increases rapidly. These experiments shows that a photogenerated acid catalyzes the formation of benzylic carbocation species, which undergo the nucleophilic attack of benzyl alcohol moiety to produce mainly the self-condensation product and the electrophilic aromatic substitution to form the C-alkylated polymer as the minor product. These experiments show that an acid catalyzes the formation of benzylic carbocation species, which undergo the nucleophilic attack of benzyl alcohol moiety to produce mainly the self-condensation product and the electrophilic aromatic substitution to form the C-alkylated polymer as the minor product.



Scheme 2. Model reaction using PAA, DHP, and PTS.

To confirm the self-condensation reaction, another model reaction was carried out using MBHP and PTS. This mixture

was heated in DMSO at 130 °C for 3 min, then the solution became gel. This means crosslinking reaction occurred. This mechanism is different from one proposed for negative-type photosensitive polyimide based on PHI, MBHP, and a photoacid generator, where C-alkylated polymers and dibenzyl ether are produced in almost equal amount. This difference is explained by lower nucleophilicity of PAA compared to PHIs. The negative-type pattern formation in this resist system is mainly attributed to the cross-linking reaction of MBHP induced by the photogenerated acid.

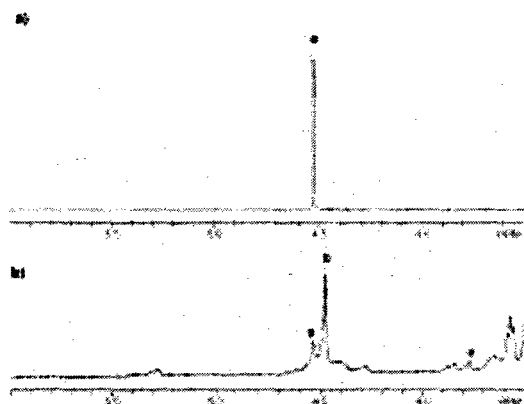
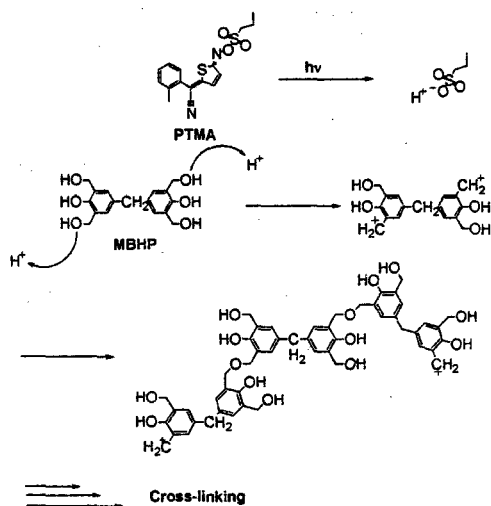


Figure 8. ¹H NMR spectra of (a) PAA and DHP mixture in DMSO-*d*₆ at 40 °C, and (b) the solution of PAA, DHP, and PTS after curing.



Scheme 3. Proposed mechanism of the negative image formation.

4. Conclusions

PAA (65 wt%) from PMDA and ODA containing MBHP (25 wt%), and PTMA (10 wt%) functioned as a negative-type alkaline developable PSPI, and its sensitivity and contrast were 30 mJ·cm⁻² and 3.0 with 436 nm light, respectively, and the suitable PEB temperature was around 120-130 °C.

The negative image of PAA film after development was converted to the corresponding PI image by thermal treatment. A 5 % weight loss temperature of the corresponding PI under nitrogen was 485 °C. The cross-linking reaction of MBHP induced by the photogenerated acid is main reason for the negative-type pattern formation in this resist system. The three-component resist system based on PAA proposed here is a versatile, promising and straightforward route for the formulation of PSPIs using PAAs as a polymer matrix.

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