Synthesis and Characterization of a Positive-Working, Aqueous-Base-Developable Photosensitive Polyimide Precursor

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ABSTRACT: A positive-working, aqueous-base-developable photosensitive polyimide precursor based on poly(amic ester)-bearing phenolic hydroxyl groups and a diazonaphthoquinone photosensitive compound was developed. The poly(amic ester) was prepared from a direct polymerization of 2,2′-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane and bis(*n*-butyl)ester of pyromellitic acid in the presence of phenylphosphonic dichloride as an activator. Subsequently, the thermal imidization of the poly(amic ester) precursor at 300°C produced the corresponding polyimide. The inherent viscosity of the precursor polymer was 0.23 dL/g. The cyclized polyimide showed a glass-transition temperature at 356°C and a 5% weight loss at 474°C in nitrogen. The structures of the precursor polymer and the fully cyclized polymer were characterized by Fourier transform infrared spectroscopy and ^{1}H-NMR. The photosensitive polyimide precursor containing 25 wt % diazonaphthoquinone photoactive compound showed a sensitivity of 150 mJ/cm^2 and a contrast of 1.65 in a 3 μm film with 1.25 wt % tetramethylammonium hydroxide developer. A pattern with a resolution of 10 μm was obtained from this composition. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 352–358, 2002

Key words: polyimide; synthesis; photoresist

INTRODUCTION

Polyimides have been widely used in microelectronic devices as buffer coatings, passivation layers, α-particle barriers, interlayer insulation, and wafer scale packages, and so on.[1] Recently, photosensitive polyimides (PSPIs) have attracted a great deal of interest because they simplify processing steps and allow avoidance of the use of a photoresist to obtain the desired patterns.[2] Most PSPIs used in today's microelectronic industry are negative-working, organic-solvent-developable types. The demands for aqueous-base-developable PSPIs in integrated circuit (IC) fabs are increasing due to environmental and safety concerns and the desire to match the manufacturing processes of the currently used photoresists.

Varied attempts have been used to prepare aqueous-base-developable, positive-working PSPIs.[3–11] For example, U.S. patent 4,093,461 describes a positive resist composition, which is made simply by the addition of a diazonaphthoquinone (DNQ) compound to a poly(amic acid) solution.[7] However, the DNQ does not have enough power to inhibit the aqueous-base solubility of the poly(amic acid) before exposure. U.S. patent 5,399,655 discloses a positive-working PSPI precursor that makes use of chemical amplification on the basis of the photoacid-catalyzed cleavage of acid-labile poly(amic acetal esters),[8] but most photoacids are transparent in the G-line and I-line areas. Several articles have reported the use of fully imidized polyimides containing hydroxyl groups to prepare the PSPI.[9–11] However, the imidized polyimides usually do not have good solubility in aqueous bases, and some residue will remain after development.

In this article, we report on the preparation and properties of a novel positive-working aqueous-base-developable PSPI composition that consists of a polyimide precursor bearing phenolic hydroxyl groups, a DNQ photosensitizer, and a solvent. The polyimide precursor is a poly(amic ester), which can be totally dissolved in an aqueous base without residue after development. The phenolic hydroxyl groups in the polymer render the aqueous-base solubility, and the DNQ photosensitizer is added as the dissolution inhibitor for aqueous-base development.

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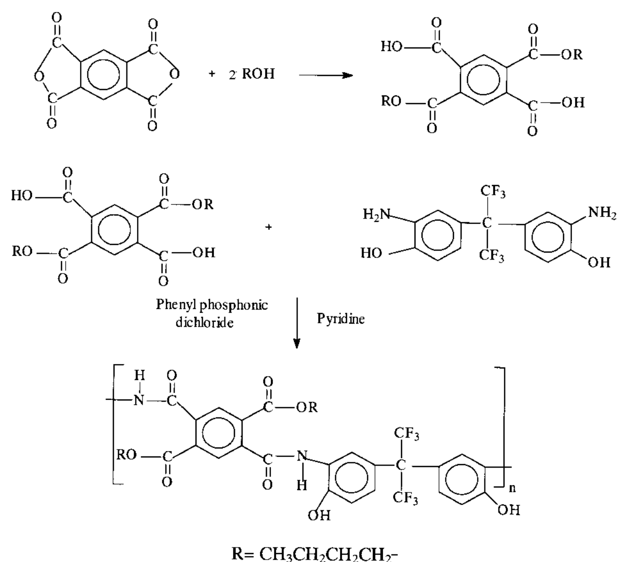


Scheme 1

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) and 2,2′-bis(3-amino-4-hydroxyphenol)hexafluoropropane (BisAPAF) were purchased from Chriskev (Leawood, KS). Anhydrous *N*-methyl-2-pyrrolidone (NMP) and pyridine were obtained from Aldrich (St. Louis, MO) and used without further purification. 2,3,4-Tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)-benzophenone (PIC-3), a photosensitive compound, was obtained from Koyo Chemicals (Osaka, Japan). Other chemicals were used as received.

Synthesis of poly(amic ester)

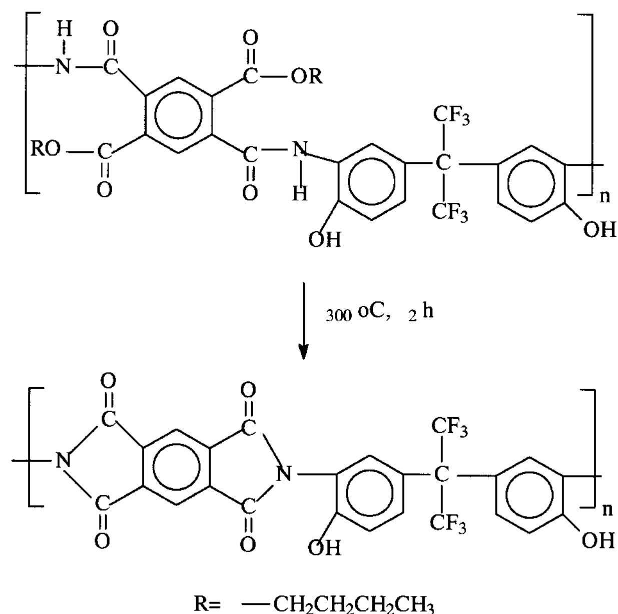
We added 10.91 g (50 mmol) of PMDA, 7.40 g (100 mmol) of *n*-butanol, and 50 g of anhydrous NMP to a 250-mL three-necked round-bottom flask equipped with a mechanical stirrer and a condenser. The mixture was heated to 80°C and stirred at this temperature for 4 h. The solution was cooled to ambient temperature, and 16.63 g (200 mmol) of pyridine and 65 g of NMP were added. The reaction mixture was cooled to 0–4°C with an ice bath, and 19.50 g (100 mmol) of phenylphosphonic dichloride was added slowly with an addition funnel. The solution was then stirred at ambient temperature for 2 h and then cooled to 0–4°C again. After that, 18.30 g (50 mmol) of hexafluoro-2,2-bis(3-amino-4-hydroxyphenyl)propane was added. The reaction mixture was stirred at 0–4°C for 1 h and at ambient temperature for 8 h. The resulting viscous solution was precipitated in 1000 mL of methanol. The polymer was collected by filtration and washed with deionized water three times. The polymer was dried under vacuum at 80°C for 24 h. The yield was almost quantitative, and the inherent viscosity of the polymer was 0.23 dL/g, measured in NMP at a concentration of 0.5 g/dL at 30°C. The synthesis steps are illustrated in Scheme 1.

Preparation of the poly(amic ester) film and thermal conversion to polyimide

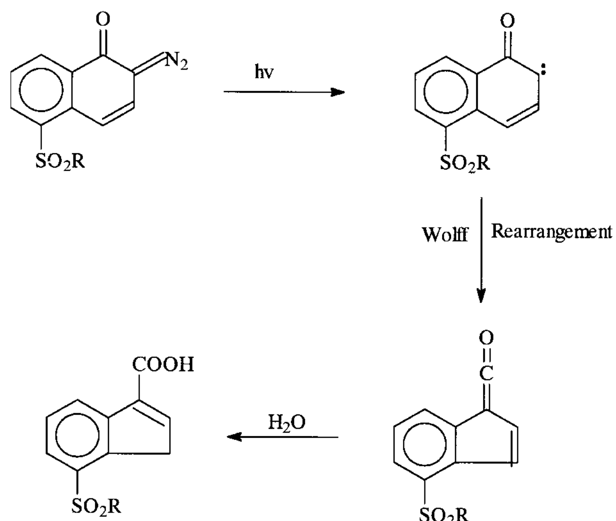
Poly(amic ester) powder (5 g) was dissolved in 20 g of dimethylacetamide (DMAC) to make a 20% (w/w) solution. A film was cast from the viscous solution on a glass plate with a doctor's knife. The film was dried at 100°C for 1 h, 200°C for 1 h, and 300°C for 2 h in a heating oven to convert the poly(amic ester) to a polyimide as shown in Scheme 2. The film was yellow and transparent.

Characterization

The IR spectra were recorded on a Jasco 460 Fourier transform infrared spectrometer (Tokyo, Japan). ^{1}H-NMR spectra were recorded on a Brucker Advance 600 spectrometer (Rheinstetten, Germany). Inherent viscosity was measured with a Cannon-Ubblehode No. 100 viscometer (State College, PA) at a concentration of 0.5 g/dL in NMP at 30°C. Thermal stability was analyzed with a TA Instruments Q500 thermogravimetric analyzer (New Castle, DE) at a heating rate of 10°C/min under nitrogen. The glass-transition temperature (T_g) and the in-plane coefficient of thermal expansion (CTE) of cured BisAPAF–PMDA polyimide film were determined with a TA Instruments thermal



Scheme 2



Scheme 3

mechanical analyzer 2940 with a extension probe under 0.05 N tension force on the film and at a heating rate of 5°C /min under nitrogen. The ultraviolet–visible (UV–vis) spectrum was obtained on a Varian Cary 100 UV–vis spectrophotometer (Palo Alto, CA).

Preparation of the photoresist formulation and lithographic evaluation

Poly(amic ester) (5 g) was dissolved in 20 g of γ)-butyrolactone (GBL) and 1.25 g of a DNQ photoactive compound was added to prepare the photoresist solution. The solution was filtered through a 5-μm Teflon filter. It was then spin-coated onto a silicon wafer and soft baked on an airflow clean room oven at 105°C for 40 min to obtain a film of about 3 μm thick. The film was exposed to an unfiltered mercury arc lamp measured at 250–400 nm. The wafer was developed in a 1.25 wt % tetramethylammonium hydroxide (TMAH) developer. The film thickness was measured with a Tenco α-step instrument (San Jose, CA). The characteristic curve was obtained by plotting the normalized film thickness against the exposure energy.

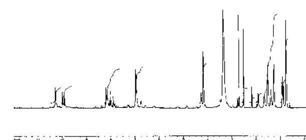


Figure 2 ^{1}H-NMR spectrum of BisAPAF-PMDA poly(amic acid)-*n*-butyl ester.

RESULTS AND DISCUSSION

Synthesis of poly(amic ester)

Conventional G-line and I-line photoresists are based on the novolac/DNQ systems. The phenolic hydroxyl groups in the novolac resin render the resin aqueous-base solubility. Although it is a molecular interaction, probably a hydrogen bond between the diazo group of DNQ and novolac resin, the aqueous base solubility of novolac can be inhibited by DNQ.[12,13] After exposure to UV light, DNQ is converted to indenecarboxylic compounds that promote dissolution as shown in Scheme 3.

The distinct discrimination of the dissolution rate between the exposed and the unexposed areas makes the novolac/DNQ an ideal photoresist system. Based on the same concept, we designed the molecular structure of a poly(amic ester) containing phenolic hydroxyl groups and expected it to have the similar photoresist performance as that of novolac/DNQ.

In general, poly(amic esters) can be prepared from diester diacid chloride[1] and diamine or from the direct

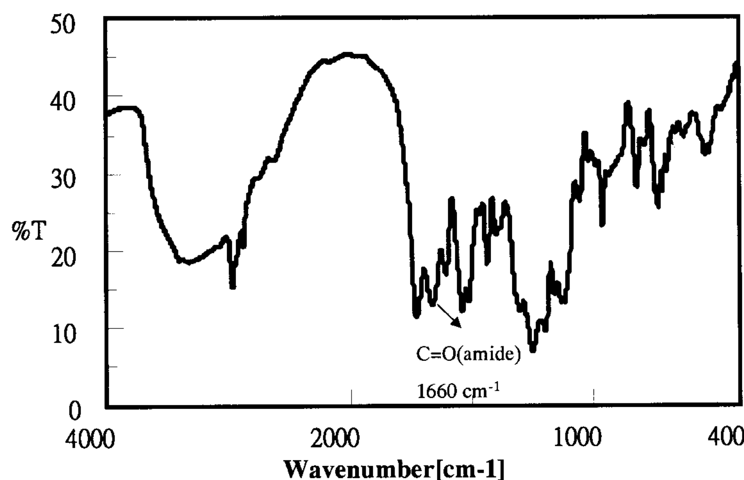


Figure 1 IR spectrum of BisAPAF–PMDA poly(amic acid)-*n*-butyl ester.

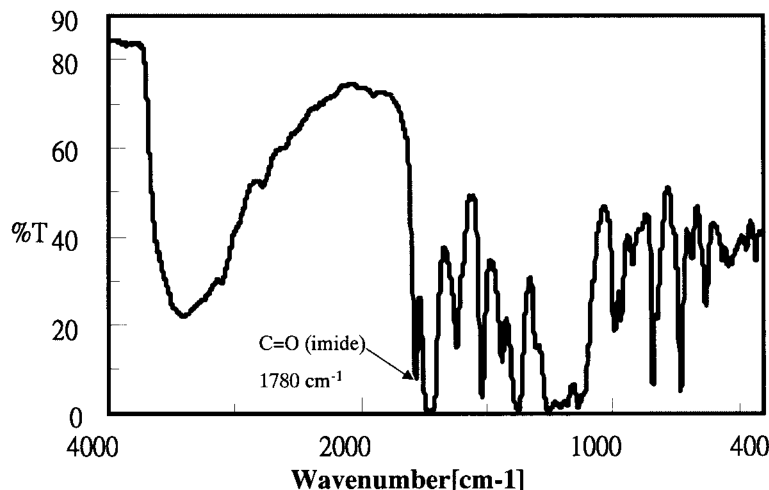


Figure 3 IR spectrum of BisAPAF–PMDA polyimide.

polymerization of diacid diester with diamine with an activator such as diphenyl(2,3-dihydro-2-thixo-3-benzoxazoyl)phosphonate, 3,3′-(phenyl phosphinylidene)bis[2(3H)-benzothiazolone], dicyclohexylcarbodimide, phenyl phosphonic dichloride, and so on.[14–17] Due to the simplicity in practice, we chose direct polymerization to prepare the poly(amic ester). First, PMDA was reacted with *n*-butanol to form bis(*n*-butyl)ester of pyromellitic acid. The diester diacid was directly polymerized with BisAPAF with phenyl phosphonic dichloride as an activator to give BisAPAF–PMDA poly(amic acid)-*n*-butyl ester. The inherent viscosity of this polyimide precursor was 0.23 dL/g. Cured at 300°C, the film prepared from the poly(amic ester) was transparent and tough, which indicated that the polymer had enough molecular weight. The IR spectrum of the poly(amic ester) (Fig. 1) showed a broad absorption band at 3400–3100 cm^{-1}, due to the amino (N—H) and hydroxyl (OH) groups, and an amide carbonyl absorption at 1660 cm^{-1}. The ^{1}H-NMR spectrum of the poly(amic ester) (Fig. 2) exhibited the signals of hydroxyl proton (10.3 ppm), amino proton (9.8 ppm), and *n*-butyl protons (0.8, 1.3, 1.5, and 4.2 ppm). The appearance of a strong imide absorption at 1780 cm^{-1} and the disappearance of the amide carbonyl absorption at 1660 cm^{-1} in the IR spectrum (Fig. 3) of the film prepared from the poly(amic ester) and cured at 300°C indicated the conversion from poly(amic ester) to polyimide. Thermogravimetric analysis (TGA) of the poly(amic ester) under the imidization condition (100°C, 1 h; 200°C, 1 h; and 300°C, 2 h) showed a weight loss of 20.80%, which corresponded to a degree of imidization of 98% as calculated from the theoretical weight loss (21.26 wt %) due to vaporization of *n*-butanol. The degree of imidization obtained from TGA might have been higher than the actual value because the polymer might have contained trace amounts of water and NMP.

Polymer characterization

Table I summarizes the qualitative solubility of the BisAPAF–PMDA poly(amic acid)-*n*-butyl ester and the corresponding BisAPAF–PMDA polyimde. The poly(amic ester) was soluble in a lot of solvents, but the polyimde did not dissolve in any organic solvents. The thermal mechanical analysis (TMA) curve (Fig. 4) of the cured BisAPAF–PMDA polyimide film showed a T_g at 356°C and an in-plane CTE of 47 ppm/°C. The cured BisAPAF–PMDA polyimide displayed good thermal stability. Its TGA thermogram, which was obtained at a heating rate of 10°C/min, showed 5% weight loss at 474°C in nitrogen (Fig. 5).

Lithographic evaluation

The DNQ compound used in this study was PIC-3. The structure of PIC-3 is shown in Scheme 4.

The UV–vis spectrum of the tetrahydrofuran (THF) solution of BisAPAF–PMDA poly(amic acid)-*n*-butyl ester with a concentration of 1×10^{-3} mol/L in the 250–600 nm wavelength is shown in Figure 6. Due to the presence of the hexafluoroisopropylidene (6F) group in the polymer backbone that can separate chro-

TABLE I
Solubility of BisAPAF–PMDA Poly(amic acid)-*n*-butyl Ester and BisAPAF–PMDA Polyimide

Solvent	BisAPAF–PMDA poly(amic acid)-*n*-butyl ester	BisAPAF–PMDA polyimide
NMP	+	−
DMAC	+	−
DMF	+	−
THF	+	−
Acetone	+	−
Ethanol	−	−

+ = soluble; − = insoluble.

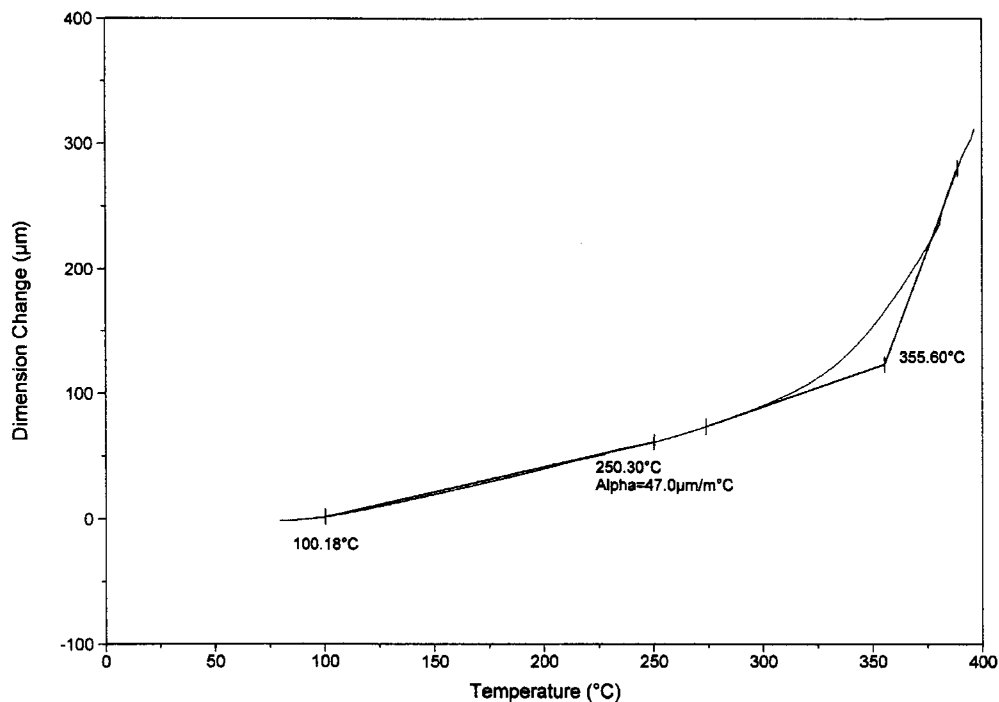


Figure 4 TMA curve of the cured BisAPAF–PMDA polyimide film.

mophoric groups, the polymer has a high transmittance above 360 nm. Therefore, the PIC-3, having a strong absorption in the range of 320–450 nm, could be used as the photosensitive compound in the resist formulation.

The photosensitive poly(amic ester) composition consisted of 25 wt % PIC-3 photosensitizer in GBL. Using a 1.25 wt % TMAH solution as the developer, we estimated the dissolution rate by measuring the film thickness after development. The dissolution rate

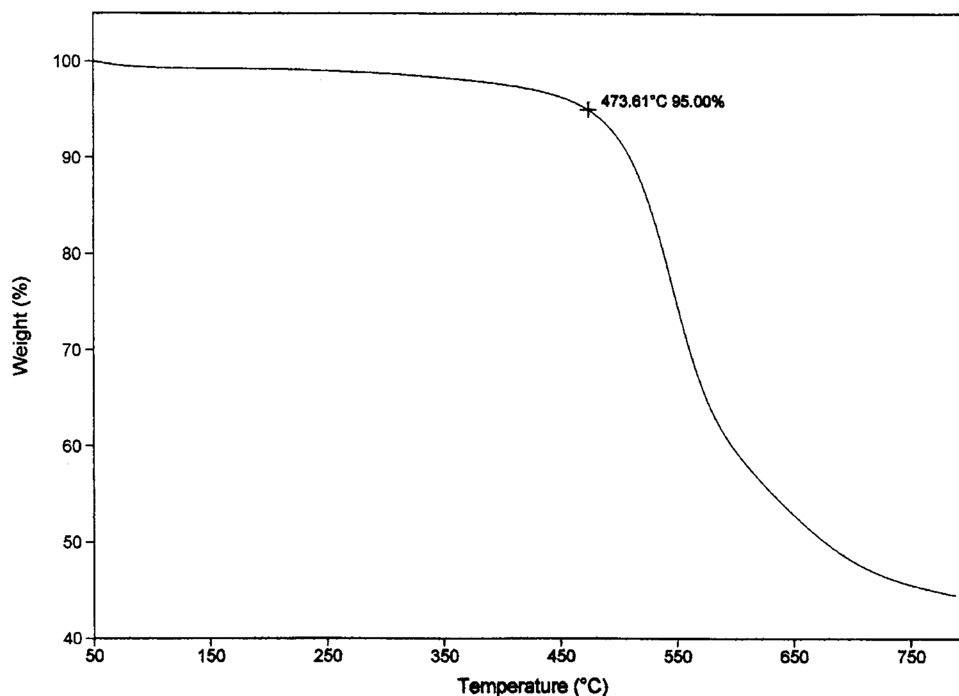
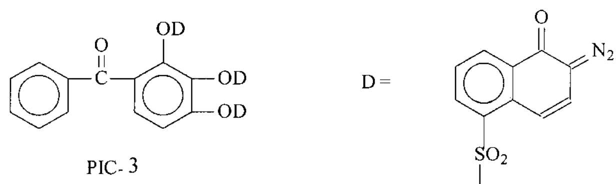


Figure 5 TGA thermogram of the cured BisAPAF–PMDA polyimide film.



Scheme 4

of BisAPAF–PMDA poly(amic acid)-*n*-butyl ester and the poly(amic ester) containing 25 wt % PIC-3, before and after exposure, is shown in Table II. The high dissolution rate contrast between the exposed and the unexposed areas was expected to have a high resolution. The exposure characteristic curve of a film (3 μm) for the BisAPAF–PMDA poly(amic acid)-*n*-butyl ester/PIC-3 system developed by a 1.25 wt % TMAH solution is shown in Figure 7. The system's sensitivity was 150 mJ/cm^2, and the contrast was 1.65. A resolution of 10 μm pattern was obtained in a 3-μm film, as shown in Figure 8. The poly(amic ester) pattern was finally cured at 300°C for 2 h to give the polyimide pattern (Fig. 9). After thermal cure, the film thickness was reduced 38.54% compared to the precursor film. The reason for the film shrinkage was the vaporization

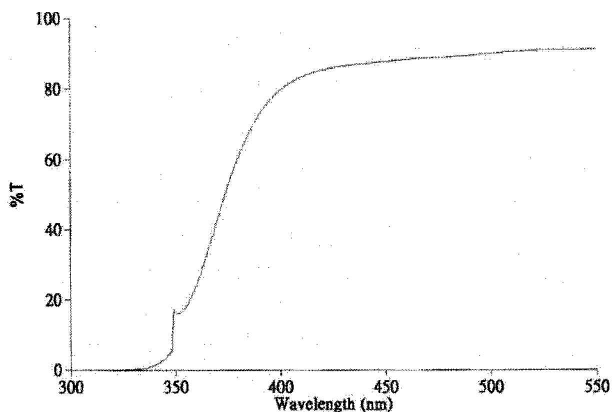


Figure 6 UV–vis spectrum of the THF solution of BisAPAF–PMDA poly(amic acid)-*n*-butyl ester.

TABLE II
Dissolution Rate of BisAPAF–PMDA Poly(amic acid)-*n*-butyl Ester and the BisAPAF–PMDA Poly(amic acid)-*n*-butyl Ester/PIC-3 System

	Dissolution rate (μm/min)
BisAPAF-PMDA poly(amic acid)-*n*-butyl ester	2.03
BisAPAF-PMDA poly(amic acid)-*n*-butyl ester/PIC-3 system before exposure	1.34
BisAPAF-PMDA poly(amic acid)-*n*-butyl ester/PIC-3 system after exposure	8.41

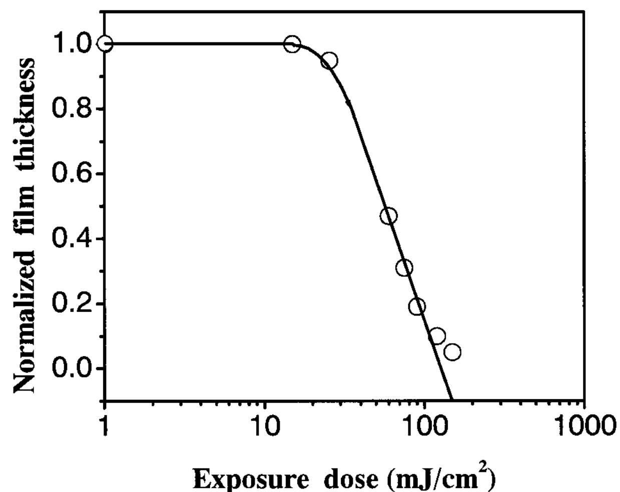


Figure 7 Characteristic exposure curve of the BisAPAF–PMDA poly(amic acid)-*n*-butyl ester/PIC-3 system.

of *n*-butanol and the decomposition of the DNQ photosensitive compound.

CONCLUSIONS

A BisAPAF–PMDA poly(amic acid)-*n*-butyl ester was prepared from BisAPAF and bis(*n*-butyl)ester of pyromellitic acid by direct polymerization in the presence of phenylphosphonic dichloride as an activator. A positive-working, aqueous-base-developable photosensitive resin composition was prepared from this polymer and the PIC-3 photosensitive compound. The PSPI precursor, containing a 25 wt % DNQ photoactive compound, showed a sensitivity of 150 mJ/cm^2 and a contrast of 1.65 in a 3-μm film. A pattern with a resolution of 10 μm was obtained from this composition.

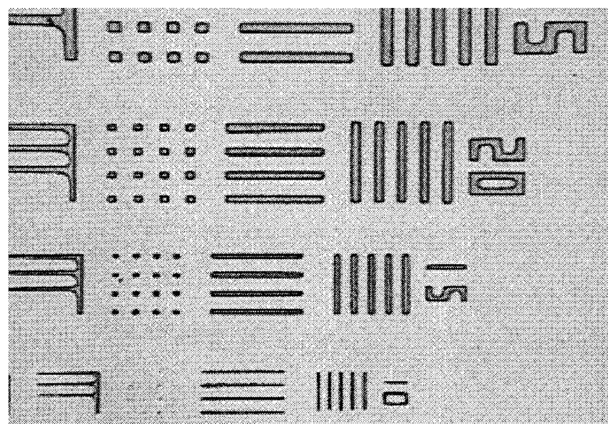


Figure 8 Optical micrograph of a pattern from the BisAPAF–PMDA poly(amic acid)-*n*-butyl ester/PIC-3 system after development with 1.25 wt % TMAH solution.

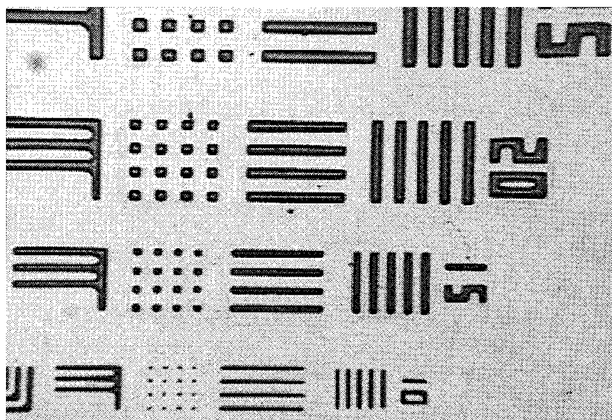


Figure 9 Optical micrograph of a pattern from the Bis-APAF–PMDA poly(amic acid)-*n*-butyl ester/PIC-3 system after development and curing at 300°C for 2 h.

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