Novel Photosensitive Polyimide Precursor Based on Polyisoimide Using an Amine Photogenerator

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ABSTRACT: A new amine photogenerator *N*-{[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl}-2,6-dimethylpiperidine (**3**) was prepared from 2,6-dimethylpiperidine and 4,5-dimethoxy-2-nitrobenzyl *p*-nitrophenylcarbonate. Compound **3** has a long wavelength band with an absorption maximum at 350 nm and the absorption tail extending out to 400 nm. **3** was found to be effective for the isomerization of polyisoimide (PII) to the corresponding polyimide (PI). The PII was prepared by the ring-opening polyaddition of oxydiphthalic anhydride (ODPA) and 3,3′-diaminodiphenyl sulfone (3,3′-DDS), followed by treatment with trifluoroacetic anhydride–triethylamine (TEA) in *N*-methyl-2-pyrrolidone (NMP). The PII film showed excellent UV transparency above 300 nm and a wide range of solubility in organic solvents. The isomerization behavior of the **PII** film containing 3–30 wt % of **3** after exposure and postexposure bake (PEB) has been studied and it was found that the isomerization ratio in the exposed area was 15–75%, while no obvious isomerization at the same PEB temperature was observed in the unexposed area. The PII containing 10 wt % of **3** functioned as a photosensitive resist, when it was postbaked at 150 °C for 5 min followed by development with cyclohexanone at 45 °C.

Introduction

Polyimides (PIs) have received considerable interest in the microelectronic industry due to their high thermal and chemical stabilities and low dielectric constants. In particular, photosensitive polyimide (PSPI) which can be directly patterned reduces the number of processing steps in microelectronic fabrication by eliminating the need for photoresists. Most of the photosensitive polyimides are prepared from poly(amic acid)s (polyimide precursor), where cross-linking sites are introduced to amic acids through ester[1] and acid–amine ion linkages.[2] These commercially available PSPIs are photochemically cross-linked, providing negative images.

Ito et al.[3,4] proposed and applied the concept of chemical amplification to the development of high-resolution, resist materials, that are based on acid-catalyzed cross-linking, depolymerization, and deprotection reactions.

Cameron and Fréchet reported[5] the photogeneration of organic base involving the protection of amines with photolabile [*o*-nitrobenzyl)oxy]carbonyl groups and provided a fundamental understanding of the factors that affect the quantum efficiency. These protected amines were confirmed to liberate free amines both in the solid state and in solution upon irradiation with UV light.

Mckean et al.[6,7] reported that the base-catalyzed imidization of poly(amic alkyl ester) provides a convenient pathway to the preparation of polyimide, and this chemistry was applied to the development of a new PSPI. This new PSPI system which contained an amine photogenerator in poly(amic alkyl esters) showed a high contrast and a lower level of shrinkage after the final cure treatment.

In the preceding paper,[8] we have reported the preparation and properties of polyisoimide (PII) as a polyimide precursor and found that the isomerization reaction of isoimide to imide is catalyzed by acid or base and that the solubility of PII in organic solvents is significantly different from that of the corresponding PI. This finding prompted us to employ the new approach to the development of a new photosensitive polyimide precursor.

This paper describes the development of a new approach to PSPI which is based chemically on the propensity for PII to imidize rapidly in the presence of a catalytic quantity of amines.

Experimental Section

Materials. Cyclohexanone, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), and triethylamine (TEA) were purified by vacuum distillation. Oxydiphthalic anhydride (ODPA) was obtained from Occidental Chem Corp. Other reagents and solvents were obtained commercially and used as received.

Preparation of 4,5-Dimethoxy-2-nitrobenzyl *p*-Nitrophenylcarbonate (2). 6-Nitroveratryl alcohol (**1**) was synthesized according to the method of Govindachari et al.[9] in 96% yield by the reduction of 4,5-dimethoxy-2-nitrobenzaldehyde in 2-propanol with aluminum isopropoxide. Mp: 146–147 °C. IR (KBr): ν 3490 (OH), 1520 (NO$_2$), 1350 cm^{-1} (NO$_2$). Anal. Calcd for $C_9H_{11}N_1O_5$: C, 50.71; H, 5.20; N, 6.57. Found: C, 50.90; H, 5.03; N, 6.59.

A solution of **1** (4.26 g, 20.0 mmol) and TEA (5.6 mL, 40 mmol) in DMAc (85 mL) was cooled in an ice–water bath. To this solution was added *p*-nitrophenyl chloroformate (4.04 g, 20 mmol). The mixture was stirred at room temperature for 18 h. The solution wa poured into ice–water (500 mL). The precipitate was collected by filtration, washed with water, and dried *in vacuo*: yield 5.74 g (75%). Recrystallization from a mixture of benzene and cyclohexane (9:5) produced pale yellow needles. Mp: 158–160 °C. IR (KBr): ν 1750 (C=O), 1525 (NO$_2$), 1330 cm^{-1} (NO$_2$). Anal. Calcd for $C_{16}H_{14}N_2O_9$: C, 50.80; H, 3.73; N, 7.41. Found: C, 50.53; H, 3.74; N, 7.32.

Preparation of *N*-{[(4,5-Dimethoxy-2-nitrobenzyl)oxy]carbonyl}-2,6-dimethylpiperidine (3). A solution of **2** (7.56 g, 20.0 mmol), 2,6-dimethylpiperidine (10.8 mL, 80 mmol), and 1-hydroxybenzotriazole (0.8 g, 6 mmol) in DMAc (85 mL) was stirred at 90 °C for 24 h. The reaction mixture was then cooled to room temperature and poured into a 1% aqueous sodium hydrogen carbonate solution (2000 mL). The product was filtered off, washed with water, and dried *in vacuo*: yield 5.93 g (84%). Recrystallization from a mixture of benzene and *n*-hexane (1:8) produced pale yellow needles. Mp: 122–124 °C. IR (KBr): ν 1700 (C=O), 1525 (NO$_2$), 1320 cm^{-1} (NO$_2$). Anal. Calcd for $C_{17}H_{24}N_2O_6$: C, 57.94; H, 6.86; N, 7.94. Found: C, 57.76; H, 6.81; N, 7.9. ^{1}H NMR: δ 7.69 (s, Ph*H*,

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1H), 7.03 (s, Ph*H*, 1H), 5.52 (s, PhCH$_2$O*H*, 2H), 4.41 (m, dimethylpiperidino CH$-$*H*, 2H), 3.96 and 3.98 (two s, CH$_3$O-*H*, total 6H), 1.79$-$1.48 (m, dimethylpiperidino CH$_2$$-$*H*$-$, 6H), 1.29$-$1.26 (d, dimethylpiperidino CH$_3$$-$*H*$-$, 6H). ^{13}C NMR: δ 155.0 (C=O), 153.5 (C3), 147.9 (C4), 139.6 (C1), 128.8 (C2), 109.7 (C5), 63.8 (PhCH$_2$O), 55.3 (CH$_3$O), 46.32 (dimethylpiperidino C α to ring N), 30.12 (dimethylpiperidino C β to ring N), 20.97 (dimethylpiperidino CH$_3$), 13.7 (dimethylpiperidino C γ to ring N).

***N*-Phenylphthalisoimide (5a).** *N*-Phenylphthalamic acid (**4**) was prepared according to the literature method.[10] A solution of **4** (0.48 g, 4.0 mmol) and TEA (0.56 mL, 4.0 mmol) in dichloromethane (3 mL) was cooled with an ice$-$water bath. To this solution was added dropwise with stirring trifluoroacetic anhydride (0.28 mL, 2.2 mmol). The mixture was stirred at room temperature for 12 h. The precipitated triethylamine hydrochloride was removed by filtration. Then, the filtrate was evaporated under reduced pressure to give **5a**. The yield was 0.76 g (85%). Recrystallization from diethyl ether yielded pale yellow needles. Mp: 120 °C (lit.[11] mp 119$-$121 °C). IR (KBr): ν 1790 (C=O), 920 cm^{-1} (CO).

***N*-Phenylphthalimide (5b).** This compound was prepared by reaction of phthalic anhydride with aniline in boiling acetic acid, purified by recrystallization from acetic acid. Mp: 211 °C (lit.[11] mp 209 °C). IR (KBr): ν 1700 (C=O), 1380 cm^{-1} (C=N).

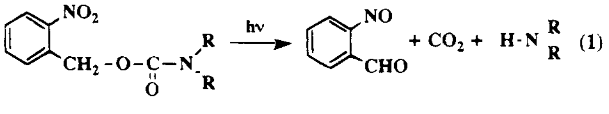
Polyisoimide (PII) Synthesis. A solution of 3,3′-DDS (1.24 g, 5.0 mmol) in NMP (11.3 mL) was cooled with an ice$-$water bath. To this solution was added with stirring ODPA (1.55 g, 5.0 mmol). The mixture was stirred at room temperature for 4 h. The resulting viscous solution was diluted with NMP (41.8 mL), and TEA (1.4 mL, 10.0 mmol) was added dropwise with stirring. Then, the reaction mixture was cooled with an ice$-$water bath, and trifluoroacetic anhydride (2.1 mL, 15.0 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 4 h and poured into 2-propanol (1000 mL). The precipitated polymer was filtered off and dried *in vacuo* at 40 °C. The yield was 2.56 g (98%). The inherent viscosity of the polymer in DMAc was 0.36 dL/g at a concentration of 0.5 g/dL at 30 °C. IR (KBr): ν 1800 (C=O), 920 cm^{-1} (CO). Anal. Calcd for $(C_{28}H_{14}N_2O_7S\cdot{}^1/_2H_2O)_n$: C, 63.27; H, 2.84; N, 5.27. Found: C, 63.04; H, 3.15; N, 5.24.

Photosensitivity. Three-micron-thick PII films on a silicone wafer were exposed to 365-nm radiation using a filtered super-high-pressure mercury lamp. Exposed films were postbaked at 150 °C for 5 min, developed in cyclohexanone at 45 °C, and subsequently rinsed with 2-propanol. The characteristic sensitivity curve was obtained by plotting a normalized film thickness against the logarithmic exposure energy.

Measurements. The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer and UV$-$visible spectra on a Shimadzu UV-2200 spectrophotometer. The NMR spectra were obtained on a JEOL EX270 (270 MHz) spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10 °C/min for (TGA) and a Seiko SSS 5000-DSC220 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen. Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a Jasco HPLC system equipped with a Shodex KD-80M column at 40 °C in dimethylformamide (DMF). The film thickness was measured on a Dektak 3030 system (Veeco Instruments Inc.).

Results and Discussion

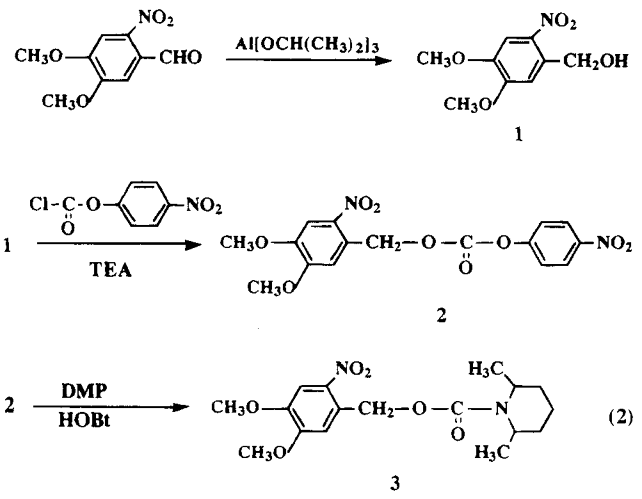
Synthesis of *N*-{[(4,5-Dimethoxy-2-nitrobenzyl)oxy]carbonyl}-2,6-dimethylpiperidine (3). It is well-known that aromatic nitro compounds containing benzylic hydrogens ortho to the nitro group are light sensitive.[12] This reaction was used for designing photosensitive protecting groups for amino compounds, and the use of these photosensitive protecting groups is of potential importance to many areas of synthetic chemistry[13] and formulation of resist materials.[14-16] The photochemical cleavage of these photosensitive protecting groups is illustrated in eq 1. A requirement for the imaging of PII using base-catalyzed PSPI is that the amine photogenerators must be capable of functioning at long wavelengths. This is due to the high absorbance of most PII at wavelengths less than 350 nm.



(1)

Recently, we found that the isomerization reaction of isoimide to imide was accelerated by a catalytic amount of base.[8] This finding led us to synthesize a new amine photogenerator, *N*-{[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl}-2,6-dimethylpiperidine (**3**). As a photogenerated base, 2,6-dimethylpiperidine (DMP) was chosen in order to avoid the nucleophilic addition of amine to isoimide, because isoimides tend to react with nucleophiles such as amines or alcohols.[17,18]

The new amine photogenerator **3** was prepared by the reactions shown in the eq 2. The reduction of 4,5-dimethoxy-2-nitrobenzaldehyde gave 6-nitroveratryl alcohol (**1**).[9] Compound **1** was converted to 4,5-dimethoxy-2-nitrobenzyl *p*-nitrophenylcarbonate (**2**) by treatment with *p*-nitrophenyl chloroformate. Then, the reaction of **2** with DMP in the presence of 1-hydroxybenzotriazole (HOBt)[19] yielded the new amine photogenerator **3**. Recrystallization from a mixture of benzene and *n*-hexane gave pale yellow needles. The structure of amine photogenerator **3** was confirmed to be the corresponding carbamate by means of infrared spectroscopy and elemental analyses. The IR spectra exhibited characteristic absorptions at 1700, 1525, and 1320 cm^{-1} due to carbamate carbonyl, nitro asymmetric, and nitro symmetric stretching vibrations, respectively.



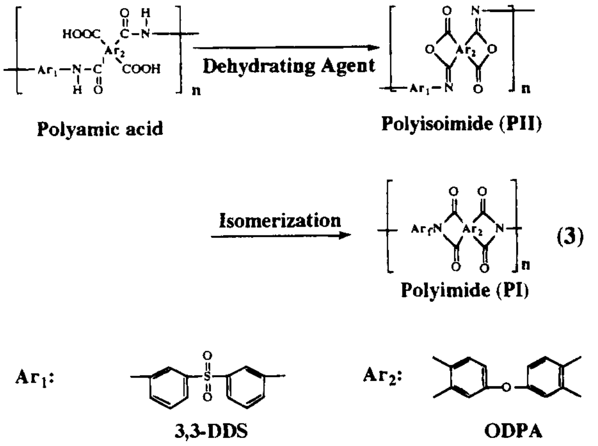
(2)

Elemental analyses also supported the formation of the expected structure. The most conclusive spectral evidence for the proposed structure was provided by ^{13}C NMR spectroscopy. Four peaks at 46.3, 30.1, 13.7, and 21.0 ppm are attributed to the α, β, γ, and methyl carbons of the DMP moiety. Furthermore, carbamate, *o*-nitrobenzyl, and methoxy carbons appeared at 155.0, 63.8, and 55.3 ppm. Six lower field peaks at 153.5, 147.9, 139.6, 128,8, 109.7, and 108.1 ppm are assigned to the aromatic carbons. Thus, no unaccounted peaks were found, clearly indicating the formation of the expected structure of **3**.

The UV–visible spectrum showed that compound **3** has a strong absorption centered at approximated 350 nm and is almost transparent above 450 nm. Therefore, the resist formulated from compound **3** and PII would be expected to be lithographically sensitive to the 365-nm mercury emission line.

Thermal Stability of the Amine Photogenerator 3. Since the standard processing steps of the PSPI system involving prebake or postexposure bake (PEB) require thermostable amine photogenerators, the thermal stability of **3** was examined by thermogravimetry. Compound **3** was found to be stable up to 250 °C.

Synthesis of Polyisoimide (PII). When PII as a polymer matrix is considered for a photosensitive polyimide precursor, the PII should have a low absorption above 350 nm and the solubility of the polymer should be changed significantly after the isomerization. PIIs generally exhibit a lower optical transparency than those of the corresponding PIs and have intense yellow color. St. Clair et al.[20] reported that a less colored polyimide film can be prepared by separation of chromophoric centers and the reduction in conjunction on the structure of PII. Therefore, the introduction of the 3,3′-linkage to the diamine moiety could be expected to prevent conjugation between the aromatic moieties. Considering the transparency and solubility of PII, we have selected the PII from oxydiphathlic anhydride (ODPA) and 3,3′-diaminodiphenyl sulfone (3,3′-DDS) as a polymer matrix. The PII was prepared by ring-opening polyaddition of ODPA and 3,3′-DDS, followed by treatment of trifluoroacetic anhydride–TEA in NMP (eq 3). The PII was isolated by precipitation into 2-propanol, and the structure of PII was confirmed to be the corresponding PII by means of infrared spectroscopy and elemental analyses. The IR spectra showed characteristic absorptions at 1800 cm^{-1} due to the isoimide carbonyl. The imide content determined by IR spectroscopy was less than 5%. Elemental analyses also supported the formation of the expected polymer. The molecular weight of the polymer having an inherent viscosity of 0.36 dL/g was determined by GPC. The GPC trace was unimodal with a polydispersity of 1.6. The chromatogram indicated that the $\bar{M}_n$ and $\bar{M}_w$ values were 39 000 and 62 000, respectively, relative to standard polystyrene. The polymer was a white powder, and a transparent flexible film was obtained by casting the polymer solution. The UV spectrum of a 3-μm-thick film of the PII indicates that the film is transparent in the region above 360 nm (Figure 1). Table 1 shows the results of the qualitative solubility of the PII and corresponding PI.



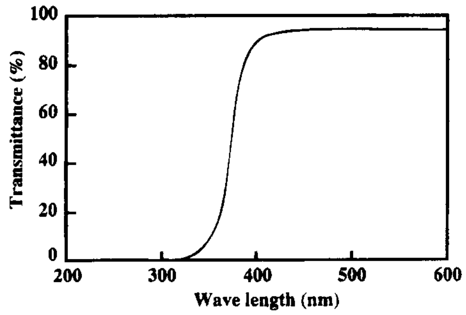


Figure 1. UV–visible spectrum of PII.

Table 1. Solubility of Polyisoimide (PII) and Polyimide (PI)[a]

	solubility			solubility	
solvent	PII	PI	solvent	PII	PI
acetone	±	–	1,2-dichloroethane	±	–
methyl ethyl ketone	–	–	*N,N*-dimethylformamide	++	++
cyclohexanone	++	–	*N*-methyl-2-pyrrolidone	++	++
isoamyl acetate	–	–	*N,N*-dimethylacetamide	++	++
tetrahydrofuran	++	–	methanol	–	–
dioxane	++	–	2-propanol	–	–
chloroform	±	–	2-methoxyethanol	–	–

[a] ++: soluble at room temperature. +: soluble by heating. ±: partially soluble or swelling. –: insoluble.

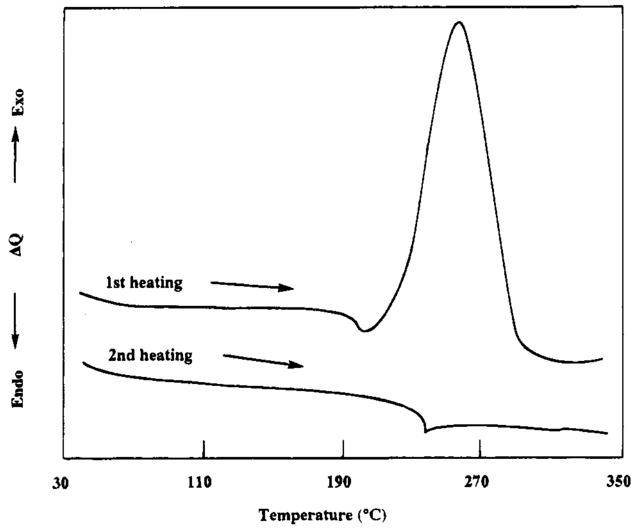


Figure 2. DSC curves of PII in nitrogen.

The PI was prepared by chemical cyclization of poly(amic acid) using an acetic anhydride–pyridine dehydrating agent for comparison. The PII showed excellent solubility toward a wide range of solvents, whereas the solubility of the corresponding PI was very poor and PI was soluble only in polar aprotic solvents such as DMAc or NMP (Table 1). These large differences in solubility between the PII and corresponding PI could be applied to the development of the new PSPI system.

Thermal Properties of PII. It is very important to clarify the thermal behavior of the PII because the isomerization reaction of PII to PI also occurs by high thermal treatment. DSC on a powder sample was performed, and the results are shown in Figure 2. The PII exhibited an endotherm at 190 °C and a large exothermic peak at around 260 °C in the first heating process. In the second heating process, these peaks were not observed and a new endothermic peak appeared at 230 °C. The IR spectrum after the large

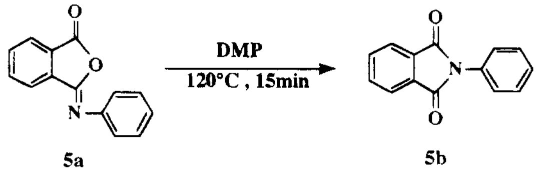
Table 2. 2,6-Dimethylpiperidine (DMP) Catalyzed Isomerization of 5a to 5b[a]

DMP (wt %)	yield (%)	convn (%)
0	99	12
10	95	73

[a] Isomerization reaction was carried out in sealed tube at 120 °C for 15 min.

exothermic peak showed strong imide cabonyl absorptions at 1780 and 1725 cm^{-1}. On the basis of these studies, the first endotherm at 190 °C and the large exothermic peak at around 260 °C observed in the first heating process are assigned to the glass transition temperature (T_g) and the thermal isomerization temperature of the PII, respectively. The endothermic peak at 260 °C in the second heating process reflects the T_g of the corresponding PI which was isomerized from the PII. The thermal stability of the PII was examined by TGA. The polymer showed a 10% weight loss at 550 °C in nitrogen but no weight loss at 260 °C.

Model Reaction. In order to clarify the effect of DMP on the isomerization of isoimide to imide, we studied the base-catalyzed isomerization of *N*-phenylphthalisoimide (**5a**) in the presence of DMP. The reaction was carried out in a sealed tube at 120 °C above the melting point of **5a** for 15 min in the presence of 10 wt % of DMP (eq 4). The reaction products were a mixture of **5a** and *N*-phenylphthalimide (**5b**), whose molar ratios were determined by comparing the absorptions of isoimide (920 cm^{-1}) and internal standard compound *p*-dicyanobenzene (2200 cm^{-1}). The results summarized in Table 2 indicate that DMP was effective in the isomerization reaction of **5a** to **5b**. Furthermore, no other reaction products were observed in the isomerization reaction.



(4)

Base-Catalyzed Isomerization of PII. On the basis of the model reaction, the base-catalyzed isomerization of PII to the corresponding PI was carried out by irradiating PII films containing 10 wt % of **3**. PII is significantly converted to the corresponding PI upon exposure to 1000 mJ/cm^2 of 365-nm irradiation followed by postexposure bake (PEB) at 150 °C, as evidenced by strong absorptions due to imide C=O at 1780 cm^{-1} and imide CO at 1380 cm^{-1}. On the other hand, the unexposed PII film containing 10 wt % of **3** was quite stable under thermal treatment at 150 °C for 5 min.

In order to determine the isomerization ratio of the exposed PII film containing **3**, the effect of a UV dose on the isomerization rate was studied and the results are shown in Figure 3. The PII films containing 3–30 wt % of **3**, spin-coated on a NaCl plate, were exposed to 365-nm UV irradiation and subsequently postbaked at 150 °C for 5 min. The conversion of PII to PI was determined by comparing the absorptions of imide (1380 cm^{-1}) and the internal standard peak at 1500 cm^{-1}. The results are represented as a normalized conversion value because PII contained approximately 5% of the imide form. At 4 J/cm^2 of the exposure dose, the PII film containing 3 wt % of **3** only isomerized less than 20%. On the contrary, the film containing 30 wt % of **3** isomerized more than 70%. This result indicates that **3** acts as the amine photogenerator in the PII film and the 10 wt % of **3** was necessary to obtain a high degree of isomerization. Figure 4 shows the relationship between the PEB temperature and the conversion of the PII containing 10 wt % of **3**. The isomerization reaction of the exposed (1000 mJ/cm^2) films containing 10 wt % of **3** proceeded smoothly, giving the corresponding PI. However, no significant isomerization was observed in the unexposed film even at a PEB temperature of 170 °C.

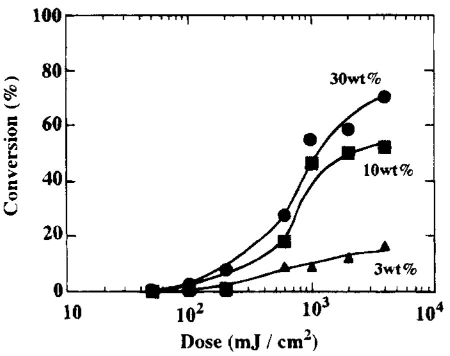


Figure 3. Thermal isomerization of PII in the presence of **3** after UV exposure followed by postbake at 150 °C for 5 min.

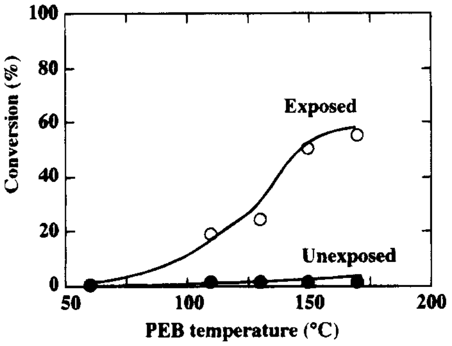


Figure 4. Thermal isomerization of PII in the presence of 10 wt % of **3**.

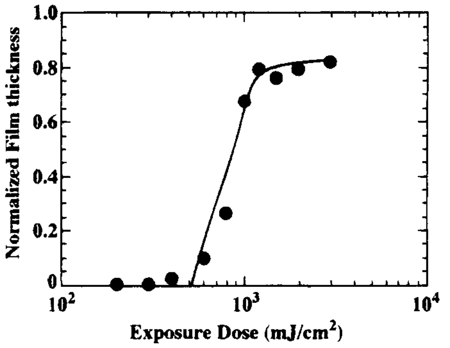


Figure 5. Exposure characteristic curves for the system of PII and 10 wt % of **3**.

Lithographic Evaluation. After preliminary optimization studies involving the loading of **3**, postbaking temperature, developer, and developing temperature, we formulated a photosensitive polyimide precursor system consisting of PII and 10 wt % of **3**. The PII films (ca. 3 μm thick) containing 10 wt % of **3** were exposed to 365-nm UV irradiation, postbaked at 150 °C for 5 min, and developed with cyclohexanone at 45 °C.

The sensitivity curve for a 3-μm-thick PII film shown in Figure 5 is consistent with the isomerization study, indicating that the sensitivity ($D^{0.5}$) and contrast ($\gamma^{0.5}$) were 900 mJ/cm^2 and 3.4, respectively. In Figure 6 are

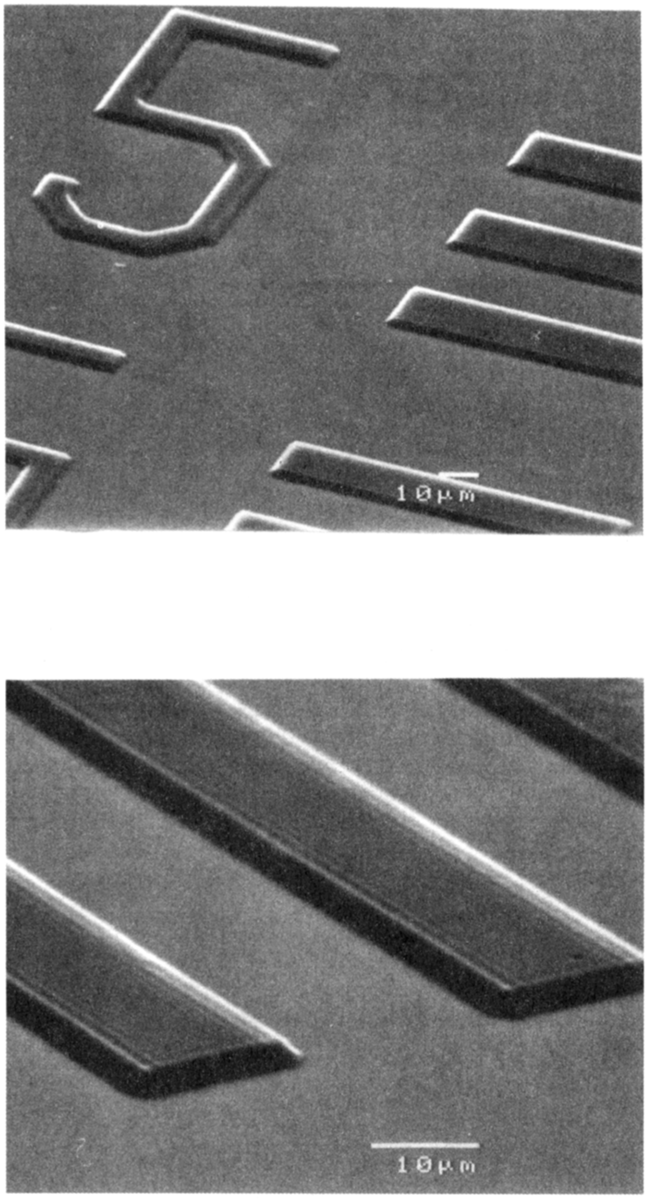


Figure 6. Scanning electron micrograph of the pattern from PII containing **3** (after development with cyclohexanone).

presented scanning electron micrographs of negative images projection-printed in PII by postbaking at 150 °C for 5 min after exposure to 1000 mJ/cm^2.

Summary

The new amine photogenerator **3** was effective for the isomerization of PII to PI. The isomerization degree of the exposed PII film containing 30 wt % of **3** reached to 70% at the PEB temperature of 150 °C (5 min), while no significant isomerization was observed in the unexposed film. **3** is a crystalline compound having strong absorptions in the 300−400-nm region and an excellent thermal stability. PII containing 10 wt % of **3** functioned as a negative type PSPI with a good contrast due to the large difference of solubility between PII and PI. Its sensitivity and contrast were 900 mJ/cm^2 and 3.4 at 365 nm, respectively.

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