Novel Positive-Type Photosensitive Polyimide with Low Dielectric Constant

Xing Zhou Jin, Hiroyuki Ishii

PI R&D Company, Ltd., 12-5 Torihama, Kanazawa-ku, Yokohamashi 236-0002, Japan

ABSTRACT: A novel positive-type photosensitive polyimide (PSPI) with a low dielectric constant was developed. The PSPI system was composed of soluble block PI (Bco-PI) with a hydroxy group and diazonaphthoquinone as a photoreactive compound. The base Bco-PI was prepared by a direct one-pot polycondensation of 2,2-bis(3-amino-4-hydroxyphenylhexafluoropropane), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, and cyclohexanetetracarboxylic dianhydride in the presence of a γ-valerolactone and pyridine catalyst system using N-methyl-2-pyrrolidone as the solvent. The film of Bco-PI was colorless and transparent, both important factors for a PSPI. Photosensitive soluble block PI (Bco-PI), containing 20 wt % ester of 2,3,4-trihydroxybenzophenone with 1,2-naphthoquinone-(2)-diazide-5-sulfonic acid (NT200), showed a sensitivity of 350 mJ/cm^2 and a contrast of 1.20 when it was exposed to UV light, followed by development with 5% tetramethylammonium hydroxide aqueous solution at room temperature. The estimated optical dielectric constants of the PIs with and without NT200 were 2.68 and 2.75, respectively. These values were significantly lower than those of conventional aromatic PIs, such as Kapton film (50EN). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 15–21, 2005

Key words: polyimide; lithography; dielectric properties

INTRODUCTION

Polyimides (PIs) have been widely used as electronic materials in the large-scale integrated circuit industry, because of their outstanding characteristics such as high thermal stability, high mechanical strength, and excellent electronic properties.

The dielectric constant (K) is the ability of a material to store an electrical charge. Base PIs with low K are desirable for application in high-speed, high-frequency circuits. Hence, the development of PIs with lower dielectric constants has been the focus of several recent investigations.

The dielectric constant of PI can be estimated by the Clasius–Mosotti relationship as shown in the following equation:

$$K = [1 + 2(P_m/V_m)]/[1 - (P_m - V_m)]$$

where K is the dielectric constant of PI, P_m is the polarizability of an atom, and V_m is the free volume of an atom. From the relationship of K, P_m, and V_m, the general methods to reduce the K value of the PI are to introduce low molar polarization atoms, such as fluorine, or bulky structures, such as a cardo or alicyclic moiety, into the PI backbone. Thus, fluorinated PI (Scheme 1),[1] cardo PI (Scheme 2),[2] and alicyclic PI

(Scheme 3)[3] have been synthesized to obtain a PI with low K.

Furthermore, a direct photopatterning ability is necessary for a PI to reduce the number of processing steps in microelectronic fabrication by eliminating the need for photoresists.

Photosensitive PIs (PSPIs) are an environmental improvement because of the reduction of organic solvents and associated volatile organic compounds. They enable the process of using the industry standard tetramethylammonium hydroxide (TMAH) photoresist developer. Several attempts to use TMAH developable positive PSPIs in combination with o-diazonaphthoquinone (DNQ) have been reported.[4–7] Khanna and Muller[8] described PIs and polyamides containing hydroxyl groups for a positive working DNQ sensitized PSPI system. Upon exposure to UV light, DNQ is converted to indenecarboxylic acid, which increases the dissolution rate to the base aqueous solution. This PSPI system possesses good sensitivity and contrast. Hayase and coworkers[9] reported another DNQ sensitized approach, which was realized by polyamic acid esters with phenol moieties and DNQ. The PI precursors were synthesized from diamine and dicarboxylic acids that had phenol moieties through an ester linkage. By adjusting the dissolution rates in basic aqueous developers, they succeeded in achieving fine patterns. Watanabe et al.[10] reported a new PSPI with low K, and the PSPI was based on an alicyclic PI precursor. The PSPI system consisted of an alicyclic PI precursor, DNQ as a matrix, and a photo-
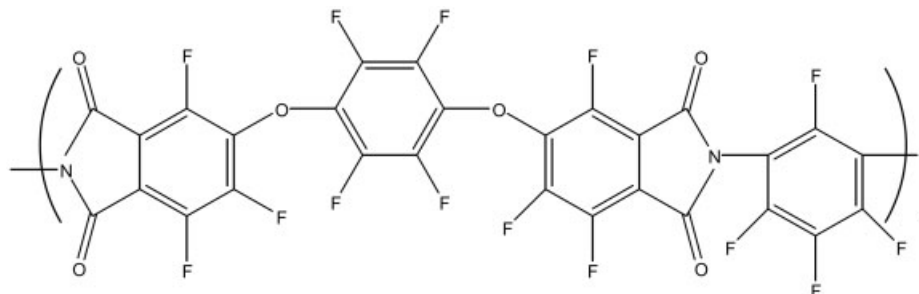
Scheme 1   The molecular structure of fluorinated polyimide.

active compound. They succeeded in attaining a fine positive image.

In this study, we conducted the molecular design of a positive-type soluble Bco-PI with low K by using cyclohexanetetracarboxylic dianhydride (H-PMDA), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (HF-BAPP), and 2,2-bis(3-amino-4-hydroxy-phenyl-hexafluoropropane) (Bis-AP-AF) as the key monomers; alicyclic dianhydride (H-PMDA); and fluorinated monomers (Bis-AP-AF and HF-BAPP), which contributed to the resulting Bco-PI film with colorlessness, transparency, and low K. The hydroxy groups in the PI backbone gave the Bco-PI an alkaline developable potential. An ester of 2,3,4-trihydroxybenzophenone with 1,2-naphthoquinone-(2)-diazide-5-sulfonic acid (NT200) was used as the photoreactive compound.

EXPERIMENTAL

Materials

Bis-AP-AF (Central Glass Co., Ltd.) and HF-BAPP (Wakayamaseika Kogyo Co., Ltd.) were commercially available and H-PMDA was kindly donated by New Japan Chemical Co., Ltd. They were used without further purification. The ester of 2,3,4-trihydroxybenzophenone with NT200 was purchased from Toyo Gosei Kogyo Co., Ltd. and used without further purification.

Synthesis of soluble PI

Bco-PI was prepared by a one-pot polycondensation of H-PMDA, HF-BAPP, and Bis-AP-AF in the presence of a binary acid catalyst consisting of γ-valerolactone and pyridine (Scheme 4). *N*-Methyl-2-pyrrolidone (NMP) was used as a solvent, and toluene was used for distilling the water away from the reaction system.

A detailed procedure follows: 27.14 g of H-PMDA and 21.98 g of Bis-AP-AF were placed in a 500-mL four-necked flask fitted with a Dean–Stark trap, nitrogen gas inlet, and a stainless steel anchor agitator. The mixture was dissolved in 178 g of NMP and 30 g of toluene, and pyridine (1.89 g) and γ-valerolactone (1.20 g) were added to the solution. While nitrogen gas was introduced to the flask, the solution was heated at 180°C for 1 h with stirring. Then, the homogeneous solution of oligoimides was cooled to about 80°C, 31.11 g of HF-BAPP and 50 g of NMP were added to the solution, and the entire mix was stirred at room temperature for 1 h until it became a homogeneous solution. The solution was then heated to 180°C for 2.5 h under nitrogen. The solid concentration was maintained at approximately 25 wt %. The varnish that was obtained was used for a photosensitive polymer matrix without further purification.

Measurement

The molecular weight of PI was determined on a Tosoh gel permeation chromatography (GPC) appara-
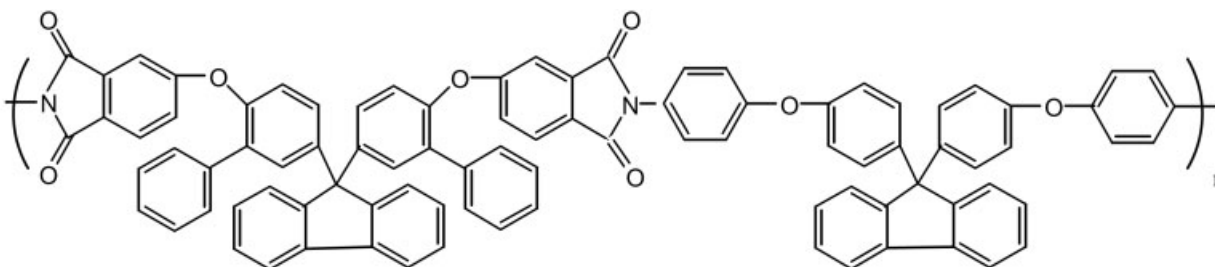
**Scheme 2**   The molecular structure of cardo polyimide.
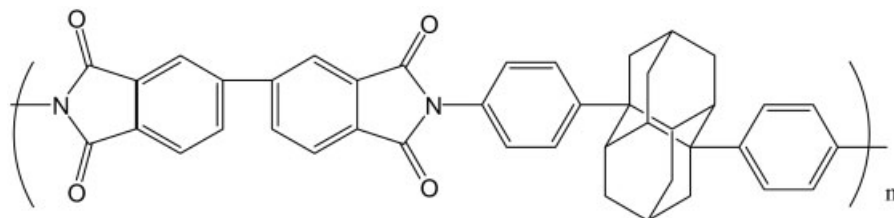
Scheme 3 The molecular structure of alicyclic polyimide.

tus. The instrument conditions were an elution solvent (dimethylformamide) containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) in a TSK-GEI type gel column at a flow rate of 0.8 mL/min at room temperature. Polystyrene was used as the calibrating standard. The IR spectra were recorded on a Perkin–Elmer spectrophotometer, and the ^{1}H-NMR spectra were recorded on a Jeol 500 NMR spectrometer (500 MHz, with tetramethylsilane as an internal standard). Dimethylsulfoxide (DMSO-d_6) was used as a solvent. The UV–visible absorption spectra of the PIs were measured with quartz cells on a Shimadzu UV–visible–near IR spectrophotometer (UV-3150). Thermogravimetric analyses (TGA) were performed on a Mac Sciences MTC 1000s at a heating rate of 10°C/min under nitrogen with PI films. Irradiation was carried out with a UV exposure apparatus (ORC JP-2000-EXC) by a contact technique through a mask that had the pattern information to be transferred. A reduced value of the dose was measured at the wavelengths of 320–390 nm (ORC UV-

331AP2). The film thickness was measured by a Nanometrics Nanospec/AFT model 3000 noncontact-type optical film-thickness analyzer. The refractive indices of Bco-PI were measured by a Nikon NPDM-1000 at room temperature in open air. The measurements were carried out at a wavelength of 633 nm.

Photosensitivity

The PSPI was formulated with the Bco-PI as the matrix resin and the NT200 DNQ compound (Scheme 5) as a photosensitive agent (20 wt % for PI) dissolved in NMP. The PSPI was spin coated onto a silicon wafer, prebaked at 90°C for 10 min, and exposed on an ORC JP-2000EXC through a mask using the contact technique at 300–450 nm wavelengths with a super-high-pressure mercury lamp without a filter. The dose was measured with an ORC UV-331AP2 at wavelengths of 320–390 nm. The exposed PSPI films were developed
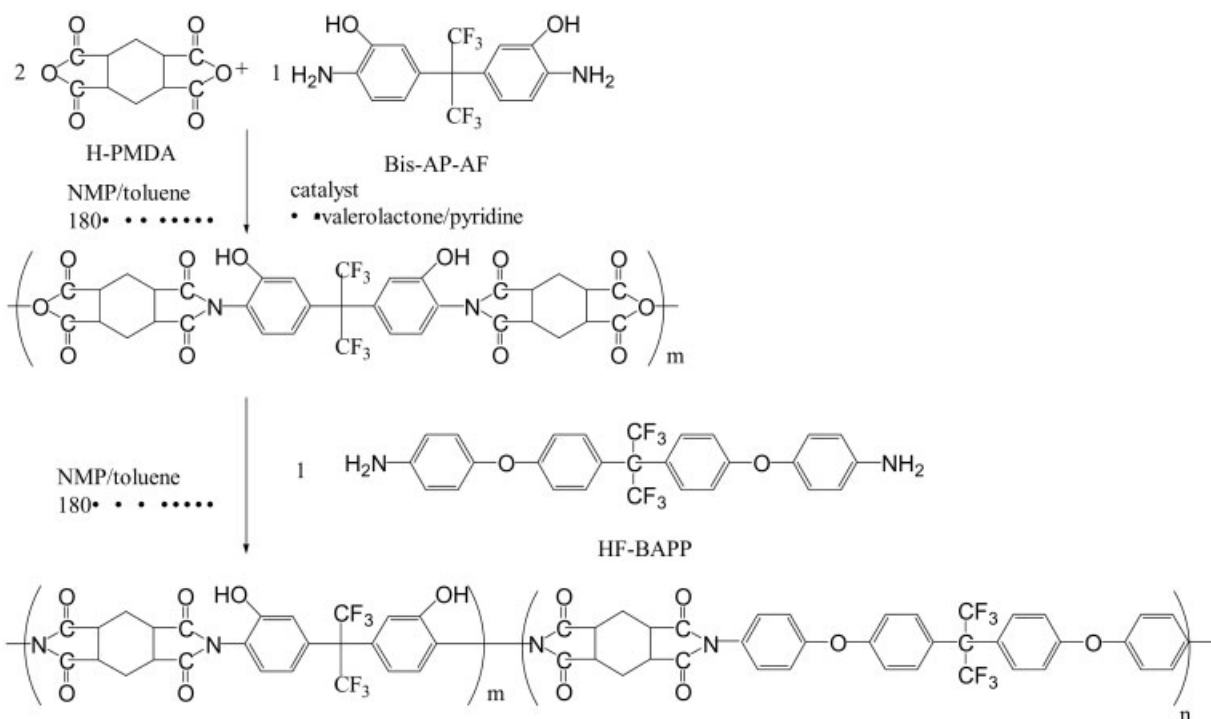
Scheme 4 The synthesis of soluble Bco-PI.
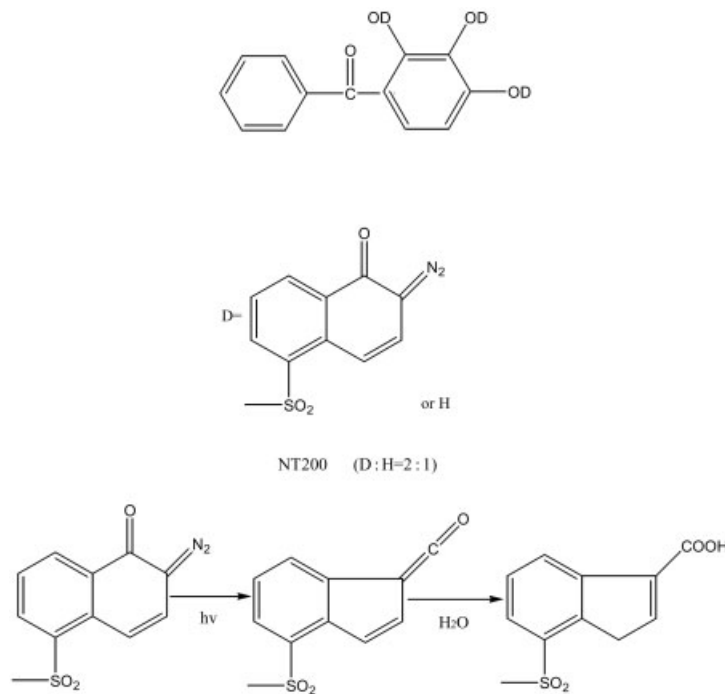
Scheme 5 The structure of NT200.

in an aqueous TMAH solution at room temperature and subsequently rinsed with pure water containing 30 wt % IPA (isopropanol).

The characteristic exposure curve was obtained by plotting the normalized film thickness against the exposure energy.

RESULTS AND DISCUSSION

Polymer synthesis and characterization

Using the catalyst system of γ-valerolactone and pyridine (Scheme 4), a soluble Bco-PI was easily prepared by polycondensation on the basis of the sequential addition technique without any special isolation process of the precursor polyamic acid.

The first step was polycondensation of excess H-PMDA with Bis-AP-AF (molar ratio of H-PMDA/Bis-AP-AF = 2 : 1), and it afforded oligoimides. The second step was polycondensation of the oligoimides with HF-BAPP, and it gave a Bco-PI with a high molecular weight. This Bco-PI containing H-PMDA, Bis-AP-AF, and HF-BAPP was composed of two kinds of blocks: block A(H-PMDA–Bis-AP-AF) and block B(H-PMDA–HF-BAPP). The weight-average molecular weight (M_w) and polydispersity (M_w/M_w) of Bco-PI as determined by GPC were 79,000 and 1.91, respectively, relative to polystrene standards.

The structure of the obtained Bco-PI was confirmed by IR spectroscopy, and Figure 1 shows the results. The IR spectrum (attenuated total reflectance) shows characteristic absorptions at 1780 and 1720 cm^{-1} that

are due to the imide carbonyl. Furthermore, the characteristic absorption of —OH stretching was observed at about 3400 cm^{-1}, and amide bands attributed to polyamic acids (1660 cm^{-1} for C=O, 1559 cm^{-1} for C—NH) were not observed.

The ^{1}H-NMR spectrum of Bco-PI revealed a signal at 10.5 ppm according to the hydroxy group from Bis-AP-AF (s, OH, 2H) and a signal at 7.00–7.60 ppm according to the aromatic protons (Fig. 2). However, the signals of amide (NH) protons ($\sim$10.5 ppm)[11,12] relating to the unreacted polyamic acid as a precursor were not observed in the spectrum. Hence, complete imidization was effected in this polycondensation.
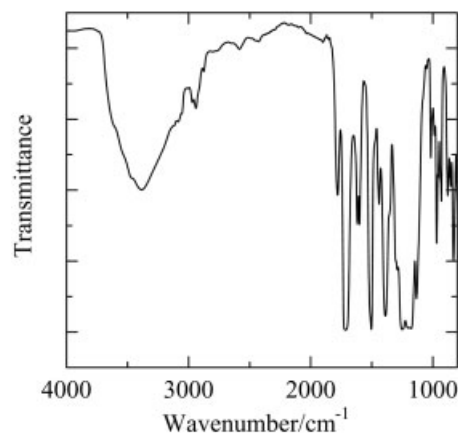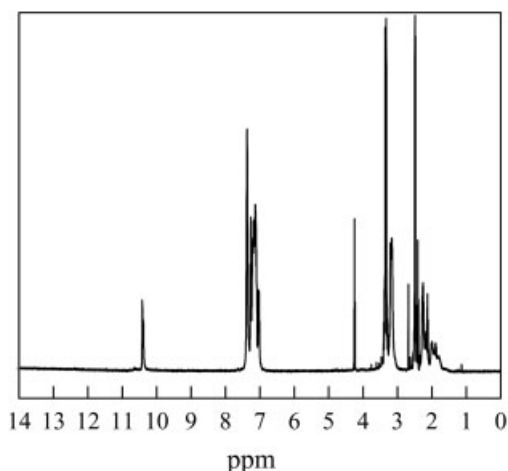

Figure 1 The IR spectrum of Bco-PI film.

Figure 2 The ^{1}H-NMR spectrum of Bco-PI in DMSO-d_6 at 25°C.

Figure 4 The dissolution rates of the exposed and unexposed parts of Bco-PI containing 20 wt % NT200 and Bco-PI.

Lithographic evaluation

Figure 3 shows the UV–visible spectrum of Bco-PI. The thickness of the film was 7.5 μm. The film of Bco-PI was entirely colorless and transparent. It exhibited a cutoff at a wavelength of about 290 nm, and the film was entirely transparent in the region over 350 nm. The transmittance of the Bco-PI at 365 nm was 95%.

We chose NT200 as the photoactive DNQ compound.

In order to investigate the effect of NT200 during development, the dissolution behavior of the exposed (500 mJ/cm^{-2}) and unexposed parts of Bco-PI containing 20 wt % NT200 and Bco-PI according to the prebake temperature was studied. The results are shown in Figure 4. The dissolution rate was estimated by measuring the film thickness after development. This was performed at room temperature by using 5 wt % TMAH as a developer. Upon exposure to UV light,
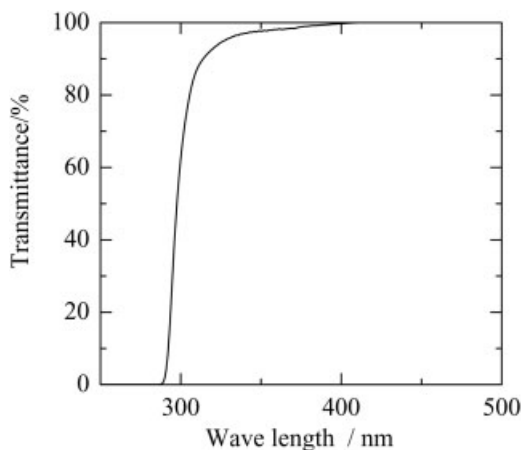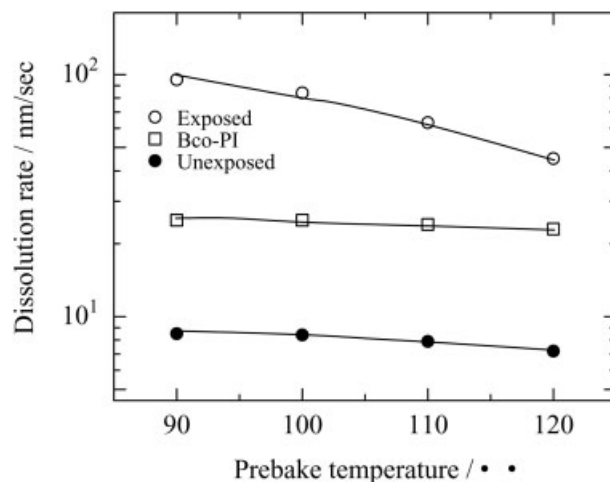
DNQ is converted to indene carboxylic acid, which is extremely soluble in TMAH by virtue of the carboxylic acid functionality. As a result, the exposed part containing 20 wt % NT200 dissolved faster than the Bco-PI, at all prebake temperatures. The unexposed part containing 20 wt % NT200 dissolved slower than the Bco-PI, which meant that the DNQ worked as a dissolution inhibitor during development. In the case of prebaking at 90°C for 10 min, the dissolution contrasts between the exposed and unexposed parts were enough to obtain a good pattern image.

Figure 5 provides the changes of the UV–visible spectra corresponding to the PSPI films of Bco-PI containing 20 wt % NT200 upon UV irradiation. The absorption bands at 350 and 400 nm decreased rapidly

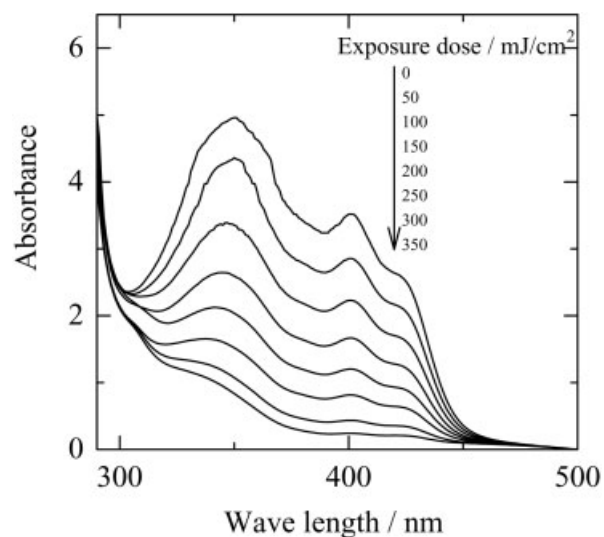**Figure 3** The UV–visible spectrum of Bco-PI film.

Figure 5 The changes of the UV–visible spectra of PSPI films consisting of Bco-PI and 20 wt % NT200 after UV irradiation.

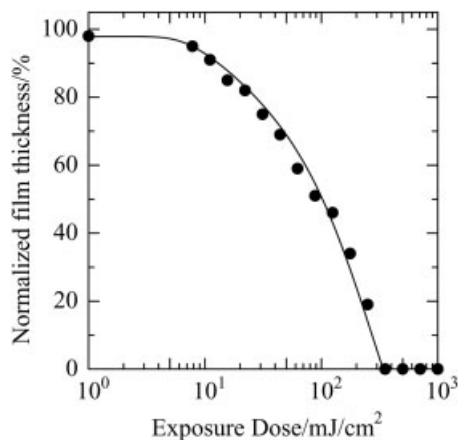**Figure 6** A photosensitivity curve for the PSPI film consisting of Bco-PI and 20 wt % NT200.

Figure 8 The TGA curves of Bco-PI film.

upon irradiation. After 350 mJ/cm^2 of energy was irradiated, the absorption band in the range of 350–400 nm disappeared completely. Therefore, the PSPI system consisting of Bco-PI and NT200 as a matrix and a photoactive compound would be expected to be an excellent photoresist of i and g line sensitivity.

Figure 6 shows the sensitivity curves of PSPI films consisting of Bco-PI with 20 wt % NT200. The thickness of the films was 7.5 μm. After development of the 5% TMAH aqueous solution at room temperature for 3 min, it was rinsed with pure water containing 30 wt % IPA. The sensitivity and contrast were 350 mJ/cm^2 and 1.20, respectively.

Figure 7 displays a typical pattern of a scanning electron micrograph of the contact printed image for the PSPI film containing Bco-PI and NT200 after an exposure of 350 mJ/cm^2. This PSPI film was also de-
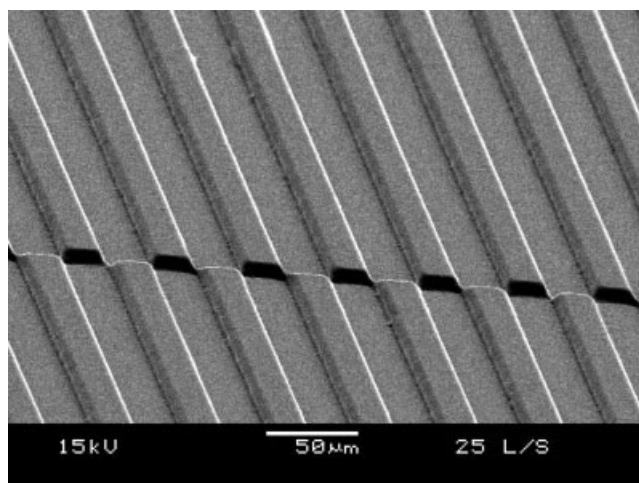

Figure 7 A scanning electron microscopy photo of 25 L/S patterns for the PSPI film of Bco-PI containing 20 wt % NT200 with 5% TMAH aqueous solution as the developer with an exposure of 350 mJ/cm^2 for 3 min.
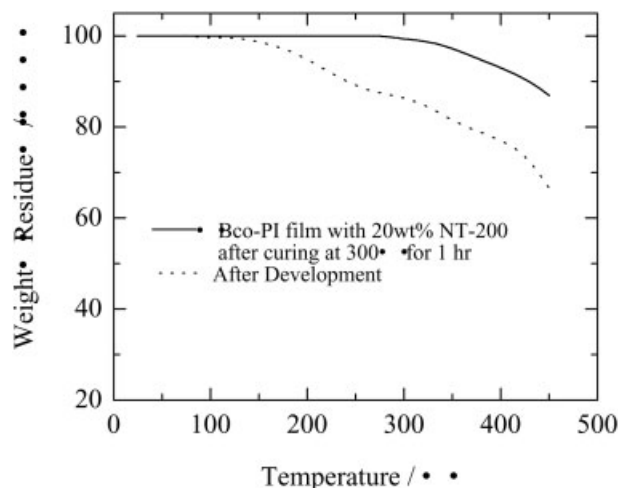
veloped with 5% TMAH aqueous solution at room temperature for 3 min and rinsing with water containing 30 wt % IPA.

Thermal properties of PSPI film

Figure 8 presents the TGA curves of PSPI films consisting of Bco-PI and NT200 after development with 5% TMAH aqueous solution at room temperature and curing at 300°C for 1 h. The TGA curve of the PSPI film after development showed two steps of weight loss; the first one started at about 100°C and indicated both vaporization of residual solvent and the degradation of NT200 beginning at this temperature. The first step of weight loss continued to about 300°C. Over 300°C, the second step of weight loss started, which was due to the decomposition of the PI.

After curing at 300°C for 1 h, the PSPI film containing 20 wt % NT200 showed no weight loss below 300°C. This indicated that NT200 as the photoreactive compound can be removed from the PSPI film by high temperature treatment after the development process, and the thermal properties of the resulting PI film were not damaged by the addition of NT200.

Refractive indices and estimated dielectric constants

The refractive indices of the films of Bco-PI and Bco-PI containing 20 wt % NT200 were determined.[13,14] The refractive indices of the sample films can be determined using polarized laser light. Measurements were carried out at a wavelength of 633 nm. The refractive indices (n_{AV}) of the films of Bco-PI and Bco-PI, containing 20 wt % NT200 cured at 300°C for 1 h, were 1.56 and 1.58, respectively. The dielectric constants of the material at optical frequencies can be estimated from the refractive index according to the Maxwell

TABLE I
Refractive Indices and Estimated Dielectric Constants of Polyimide (PI) Films

PI	d (μm)	n_{AV}	ε
Bco-PI	7.9	1.56	2.67
Bco-PI + NT200	8.6	1.58	2.75
Kapton 50EN	12.5	1.77	3.44

d, film thickness; n_{AV}, average refractive index; ε, optical estimated dielectric constant, $\varepsilon = 1.10 n_{AV}^{2}$.

equation, $\eta \doteqdot n^2$. The value of η around 1 MHz has been evaluated as $\eta \doteqdot 1.10 n_{AV}^2$, including an additional contribution of approximately 10% from the IR absorption. The refractive indices of 1.56 and 1.58 translated into dielectric constants of 2.67 and 2.75, respectively. As a reference, the refractive index of a commercially available Kapton film (50EN) was also measured, and it was 1.77. According to the Maxwell equation, the estimated value of the dielectric constant of Kapton 50EN was 3.44. Compared with Kapton 50EN, which is the conventional aromatic PI film, Bco-PI consisting of alicyclic dianhydride and fluorinated monomers showed better dielectric properties (Table I).

CONCLUSIONS

A soluble Bco-PI was synthesized from H-PMDA, Bis-AP-AF, and HF-BAPP in the presence of a γ-valerolactone and pyridine catalyst system. It showed excellent transparency in the UV region above 300 nm. The Bco-PI containing 20 wt % NT200 was found to be a positive-type PSPI by UV irradiation. Following development with a 5% TMAH aqueous solution at room temperature, the sensitivity and contrast of the PSPI were 350 mJ/cm^2 and 1.20, respectively. After the development process, a high temperature treatment such as 300°C for 1 h removed the NT200 from the PSPI film, so that the thermal properties of the resulting PI film were not damaged. The optically estimated dielectric constants of the films of Bco-PI and Bco-PI containing 20 wt % NT200 were 2.67 and 2.75, respectively. The value of Bco-PI was significantly lower than a conventional aromatic PI film such as Kapton 50EN.

References

1. Chern, Y. T. Macromolecules 1998, 31, 1898.
2. Goto, K.; Inoue, Y.; Matsubara, M. J Photopolym Sci Technol 2001, 14, 33.
3. Ando, S.; Matsuura, T.; Sasaki, S. Macromolecules 1992, 25, 5858.
4. Nakayama, T.; Mochizuki, A.; Ueda, M. React Funct Polym 1996, 30, 109.
5. Seino, H.; Mochizuki, A.; Haba, O.; Ueda, M. J Polym Sci Part A: Polym Chem 1998, 36, 2261.
6. Ueno, T.; Okabe, Y.; Maekawa, Y.; Rames-Lang-Lade, G. ACS Symposium Series 706; American Chemical Society: Washington, DC, 1998; p 358.
7. Jin, X. Z.; Ishii, H. J Photopolym Sci Technol 2004, 17, 201.
8. Khanna, D. K.; Muller, W. H. In Regional Technical Conference on Photopolymers: Principles, Process and Material; Ellenville, NY; Society of Plastics Engineers: Brookfield, CT, 1988; p 429.
9. Hayase, R.; Kihara, N.; Oyasato, N.; Matake, S.; Oba, M. J Appl Polym Sci 1994, 51, 1971.
10. Watanabe, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. Chem Mater 2002, 14, 1762.
11. Kailani, M. H.; Sung, C. S. P. Macromolecules 1998, 31, 5771.
12. Fukushima, T.; Oyama, T.; Iijima, T.; Tomoi, M.; Itatani, H. J Polym Sci Part A: Polym Chem 2001, 39, 3451.
13. Matsumoto, T. Macromolecules 1999, 32, 4933.
14. Matsumoto, T.; Feger, C. J Photopolym Sci Technol 1998, 11, 231.