A Novel Positive-Type Photosensitive Polyimide Based on Soluble Block Copolyimide Showing Low Dielectric Constant with a Low-Temperature Curing Process

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ABSTRACT: A soluble block copolyimide (Bco-PI) was prepared by direct one-pot polycondensation of 2,2-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, and cyclohexane-tetracarboxylic dianhydride in the presence of γ-valerolactone and a pyridine catalyst system using γ-butyrolactone as the solvent. The thermal transmission temperature (T_g) of Bco-PI was 282°C. By having the curing process occur at 250°C, which was below the T_g, colorless and transparent films could be obtained. The film showed excellent optical characteristics. Such properties could not be attained by the conventional high-temperature thermal imidization process of poly(amic acid). The hydroxy groups in the polyimide backbone gave the Bco-PI the potential to become alkaline. To the Bco-PI was added 15 wt % ester of 2,3,4-trihydroxy-benzophenone with 1,2-naphthoquinone-(2) diazide-5-sulfonic acid (NT200) as the photoreactive compound. The system worked as a positive-type photosensitive polyimide (PSPI). The sensitivity and contrast of the PSPI system were 220 mJ/cm² and 1.27, respectively, when exposed to UV light, followed by development with a 5% tetramethylammonium hydroxide (TMAH) aqueous solution at room temperature. After curing at 250°C for 1 h, the average refractive index of Bco-PI with and without NT200 was 1.5543 and 1.5563, and the optically estimated dielectric constant of the polyimides was 2.66 and 2.67, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4240–4246, 2006

Key words: polyimides; lithography; refractive index; thermal properties

INTRODUCTION

Polyimides have been widely used as electric materials in large-scale integration (LSI) industries because of their outstanding characteristics such as high thermal stability, high mechanical strength, and excellent electric properties.

In recent years, the production of 300-mm wafers has been introduced to ultrathin chip packages for IC cards and related applications. As wafers have become bigger and thinner, a more serious problem has developed as a result of a mismatch in the coefficient of thermal expansion (CTE) between the wafer and poly(amic acid), which is the precursor of polyimide.[1] As the thermal imidization temperature is very high, usually more than 350°C, the stress between the wafer and polyimide from the mismatch of the CTE becomes more remarkable. Sometimes it causes the crack phenomenon in wafer or polyimide film. Moreover, the use of polyimide in areas of optics such as in light-guide material has been extensively studied recently.[2–4] The curing process has been investigated in detail for polyimide.[5] As the heating temperature rises, the for-mation of intermolecular change-transfer (CT) complexes is promoted. This causes strong absorption in the visible region, because of which the optical character of polyimide film deteriorates. This high-temperature thermal imidization process has restricted the use of polyimide. A curing process that could occur at a low temperature such as at 250°C is strongly needed.

Because polyimides that have a low dielectric constant (K) are desired for use in high-speed, high-frequency circuits, their development has been the focus of several recent investigations.

The dielectric constant of polyimide can be estimated by Clasius–Mosotti relationship, as shown in this equation:

$$K = (1 + 2(Pm/Vm))/(1 - (Pm - Vm))$$

where K is the dielectric constant of polyimide; Pm is the polarizability of the atom; and Vm is the free volume of the atom. As determined from the relationship of K, Pm, and Vm, the general method for how to reduce the dielectric constant of polyimide is to introduce low-molar-polarization atoms such as fluorine or bulky structures such as cardo or alicyclic moieties into the polyimide backbone. Thus, fluorinated polyimide,[6] cardo polyimide,[7] and alicyclic polyimide[8] have been synthesized to obtain a polyimide with a low K.

Furthermore, it is necessary that polyimide have direct photopatterning ability for it to be able to reduce the number of processing steps in microelectronic fabrication by eliminating the need for photoresists. From an environmental standpoint, the use of organic solvents should be minimized. Patterning has to be carried out with the use of industrially standardized tetramethylammonium hydroxide (TMAH) photoresist developer. Several attempts to synthesize TMAH-developable positive PSPIs in combination with *o*-diazonaphthoquinone (DNQ) have been reported.[9–12]

Mochizuki et al.[13] reported the development of a positive-type PSPI based on polyisoimide as the precursor of polyimide and DNQ. The dissolution rate of the polyimide precursor was initially too high to obtain a sufficient dissolution contrast between the exposed and unexposed parts, which they succeeded in increasing with a high PEB temperature of more than 130°C. The curing temperature of the polyisoimide was 400°C. Hayase and coworkers[14] reported another approach to developing a DNQ-sensitized PSPI, which they accomplished by using poly(amic acid) esters with phenol moieties and DNQ. The polyimide precursors were synthesized from diamine and dicarboxylic acids that had phenol moieties through ester linkages. By adjusting the dissolution rates in basic aqueous developers, they succeeded in producing fine patterns. The curing temperature of the poly(amic acid) esters was 350°C.

In the present study, we developed the molecular design of a positive-type soluble Bco-PI with low K by using 2,2-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane (bis-AP-AF), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (HF-BAPP), and cyclohexanetetracarboxylic dianhydride (H-PMDA) as the key monomers. Alicyclic dianhydride (H-PMDA) and fluorinated monomers (bis-AP-AF and HF-BAPP) contributed to the preparation of Bco-PI film that was colorless, transparent, and had a low refractive index. The hydroxy groups in the polyimide backbone gave the Bco-PI alkaline development potential. Ester of 2,3,4-trihydroxybenzophenone with 1,2-naphthoquinone-(2) diazide-5-sulfonic acid (NT200) was used as a photoreactive compound. A 250°C curing process was attempted.

EXPERIMENTAL

Materials

Bis-AP-AF (Central Glass Co., Ltd., Japan) and HF-BAPP (Wakayamaseika Kogyo Co., Ltd., Japan) were commercially available, and H-PMDA was kindly donated by New Japan Chemical Co., Ltd. (Japan) and used without further purification. NT200 was purchased from Toyo Gosei Kogyo Co., Ltd. (Japan), and used without further purification.
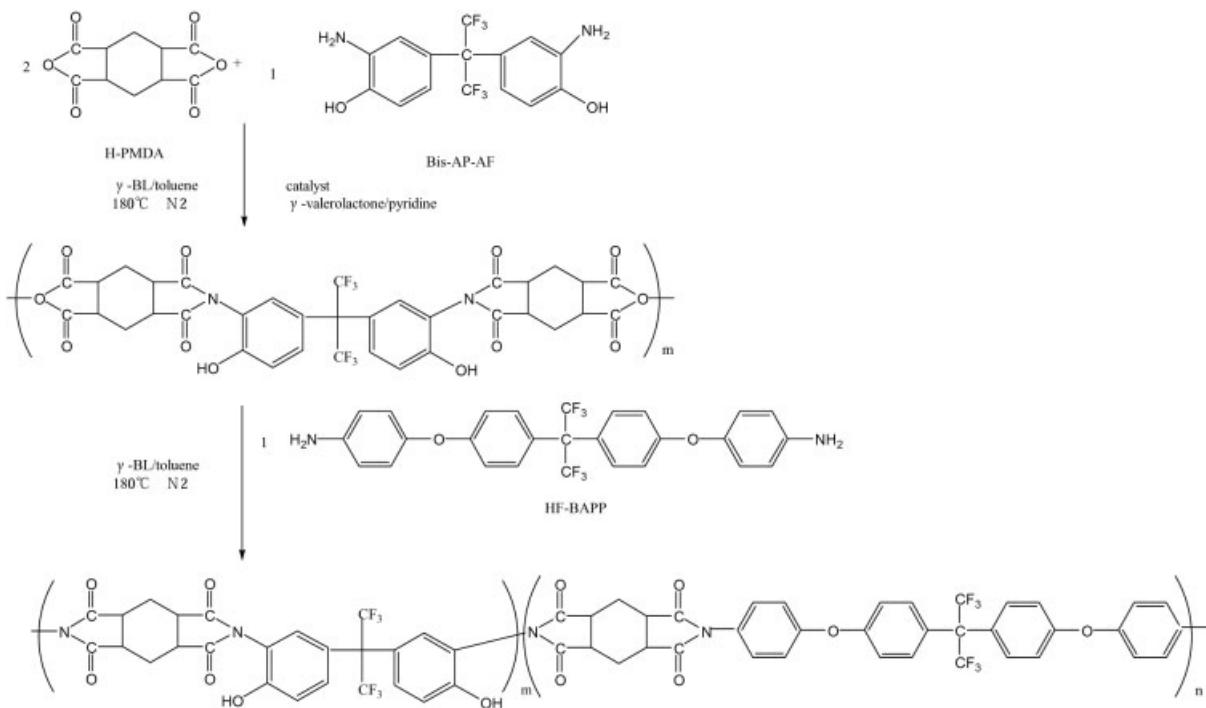
Synthesis of soluble Bco-PI and PAA

Bco-PI was prepared by 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.[15,16,18] The solvent used was γ-butyrolactone (γ-BL), and toluene was used for distilling the water synthesized during the reaction from the reaction system.

A detailed description of the procedure follows. First, 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, a nitrogen gas inlet, and a stainless-steel anchor agitator. The mixture was dissolved in 178 g of γ-BL and 30 g of toluene. 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, after which 31.11 g of HF-BAPP and 50 g of γ-BL were added, and the entire mixture was stirred at room temperature for 1 h, until the mixture became homogeneous. Then the solution was heated to 180°C for 2.5 h under nitrogen. The concentration of the solids was maintained at approximately 25 wt %. The polyimide varnish obtained was poured into methanol in great excess in order to precipitate out the product, Bco-PI. The precipitate was filtered, washed twice with methanol, and dried at 50°C for 8 h by vacuum-drying. Powder of the Bco-PI obtained above was dissolved in γ-BL to a concentration of 16 wt %. The polyimide varnish obtained was used for the photosensitive polymer matrix.

For comparison with Bco-PI, poly(amic acid) (PAA) also was synthesized by random polymerization using the same monomers.

Measurement

The molecular weight of the polyimide was determined on a Tosoh gel permeation chromatograph (GPC), with dimethylformamide (DMF) containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) as the elution solvent; a TSK-GEl-type gel column; and a flow rate of 0.8 mL/min at room temperature. Polystyrene was used as the calibrating standard. Infrared spectra were recorded on a Perkin–Eilmer spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL-500NMR spectrometer (500 mHz, and tetramethylsilane as an internal standard), with dimethyl sulfoxide (DMSO-d6) as the solvent. The UV-visible absorption spectra of polyimide were measured with quartz cells on a Shimadzu UV-VIS-NIR scanning spectrophotometer (UV-3150). Thermal mechanical analysis (TMA) and thermogravimetric analysis (TGA) were performed with polyimide films on a Mac Sciences instrument (MTC 1000s) at a heating speed of 10°C/min

Scheme 1 Synthesis of soluble Bco-PI.

under nitrogen. Irradiation was carried out with a UV exposure apparatus (ORC JP-2000-EXC) by a contact technique through a mask. The refractive indexes of Bco-PI were measured by a Metricon model PC-2010 prism couple at room temperature in air at a wavelength of 633 nm.

Photosensitivity

The PSPI was formulated by the Bco-PI as matrix resins and the DNQ compound, NT200 (Scheme 2), as a photosensitive agent (15 wt % for polyimide) dissolved in γ-BL. The PSPI was spin-coated onto a silicon wafer, prebaked at 90°C for 5 min, and exposed on an ORC JP-2000EXC through a mask by a contact technique in the wavelength range of 300–450 nm to a super-high-pressure mercury lamp without a filter. The dose was measured with an ORC UV-331AP2 in the wavelength range of 320–390 nm. The exposed PSPI films were developed in an aqueous TMAH solution at room temperature and subsequently were rinsed with pure water containing 30 wt % isopropyl alcohol (IPA).

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

RESULTS AND DISCUSSION

Polymer synthesis and characterization

With the catalyst system of γ-valerolactone and pyridine (Scheme 1), a soluble Bco-PI was prepared easily

by polycondensation according to the sequential addition technique without performing any special isolation process of the precursor poly(amic acid).

The first step, polycondensation of excess H-PMDA with bis-AP-AF (the molar ration of H-PMDA and Bis-AP-AF was 2:1), afforded oligoimides. The second step, polycondensation of the oligoimides with HF-BAPP, produced a high-molecular-weight Bco-PI. This Bco-PI, which contained 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 molecular weight (M_w) and polydispersion (M_w/M_n) of Bco-PI were determined by GPC to be 158,000 and 2.05, respectively.

FTIR spectra of Bco-PI showed characteristic absorptions at 1780 and 1720 cm^{-1}, because of the imide carbonyl (C=O sym stretch), and at 1380 cm^{-1} (C—N stretch). Furthermore, the characteristic absorption of OH stretching was observed at about 3400 cm^{-1}, and amide bands attributed to poly(amic acid) [1660 cm^{-1} (C=O)] were not observed.

The ^{1}H-NMR spectra of Bco-PI revealed a signal at 10.5 ppm, according to the hydroxy group from bis-AP-AF, and 10.5 ppm (s, OH, 2H) and a signal at 7.00–7.60 ppm according to the aromatic protons.

Lithographic evaluation

Figure 1 shows the changes in the UV-visible spectra corresponding to the PSPI films of Bco-PI containing 15 wt % NT200 upon UV irradiation. The absorption bands at 350 and 400 nm decreased rapidly upon
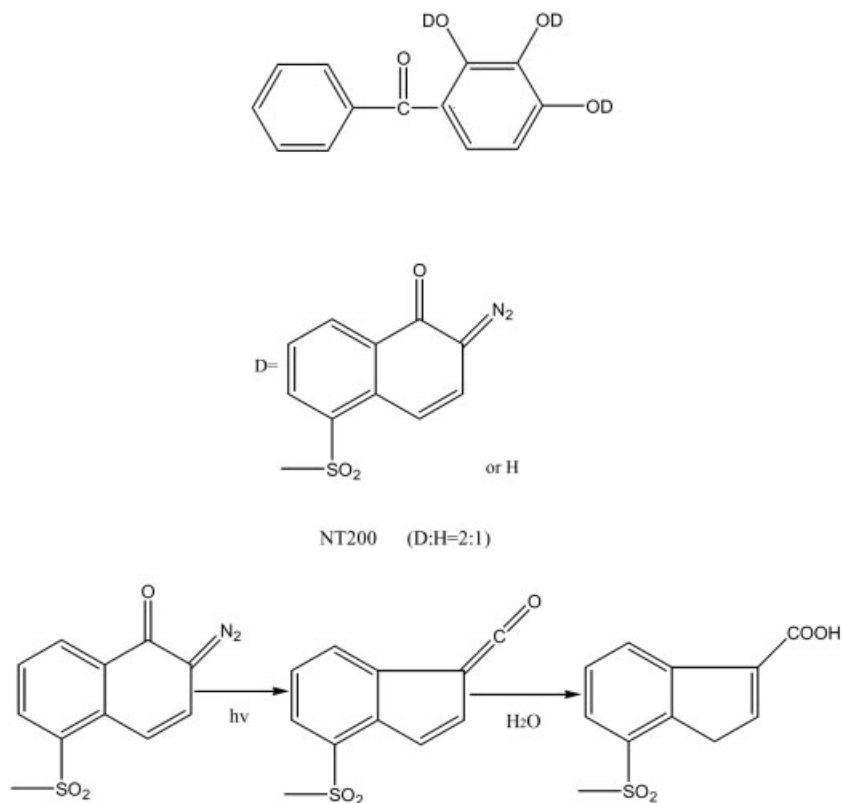
Scheme 2 NT200.

irradiation. After 220 mJ/cm^2 was irradiated, the absorption band in the range of 350–400 nm disappeared completely.

Figure 2 shows the sensitivity curves of PSPI films consisting of Bco-PI with 15 wt % NT200. The thickness of films was 3.75 μm. After development of the

5% TMAH aqueous solution at room temperature for 1.5 min, the substrate was rinsed by pure water containing 30 wt % IPA. The sensitivity and contrast were 220 mJ/cm^2 and 1.27, respectively.

Figure 3 shows the typical pattern of the scanning electron micrograph of the contact-printed image for the PSPI film containing Bco-PI and NT200 after ex-
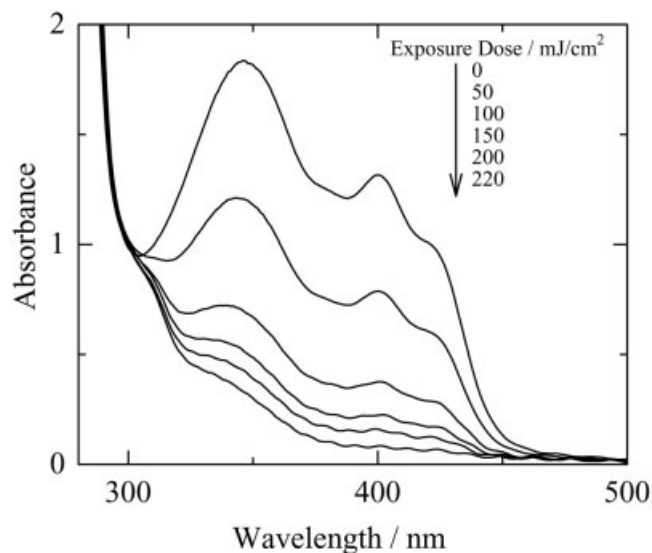

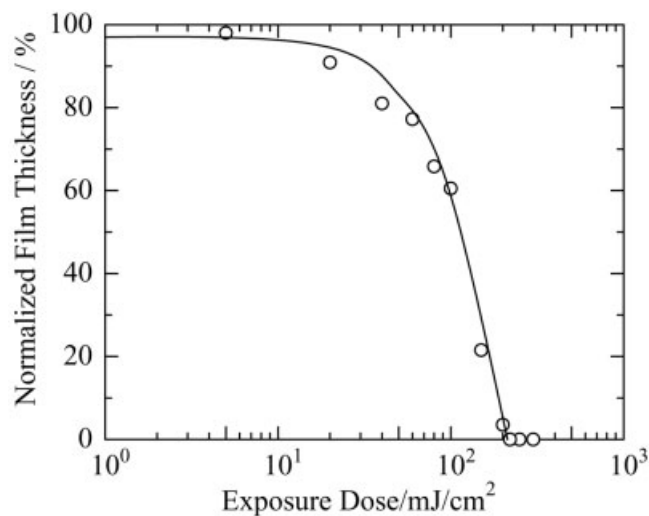**Figure 1** Changes in UV-visible spectra of PSPI films consisting of Bco-PI and 15 wt % NT200 after UV irradiation.

Figure 2 Photosensitivity curve of PSPI film consisting of Bco-PI and 15 wt % NT200.
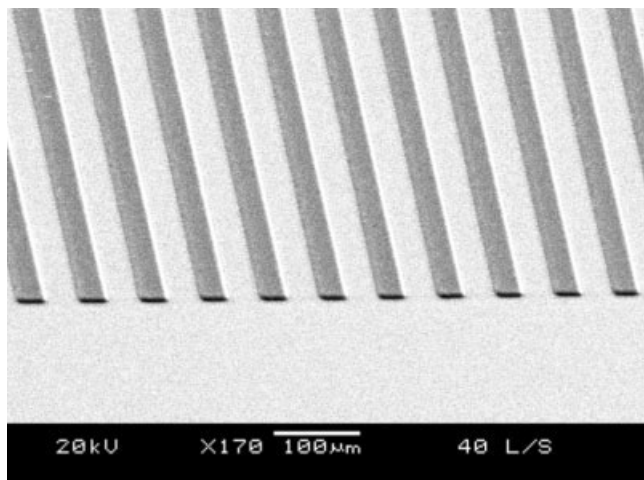
Figure 3 SEM photo of 40 L/S patterns of PSPI film of Bco-PI containing 15 wt % NT200 (exposure: 220 mJ/cm^2; developer: 5% TMAH aqueous solution; time: 1.5 min).

Figure 5 UV spectra of Bco-PI films from different curing processes.

posure to 220 mJ/cm^2. This PSPI film was developed with a 5% TMAH aqueous solution at room temperature for 1.5 min and rinsed by water containing 30 wt % IPA.

Changes in characteristics of Bco-PI by thermal treatment

PAA was cast on a wafer, and the changes of FT-IR spectra are summarized in Figure 4 after thermal treatment. After curing at 300°C for 1 h, characteristic imide absorptions of 1780, 1720, and 1380 cm^{-1} were observed. The absorption at 1660 cm^{-1} because of the amide group completely disappeared. In agreement
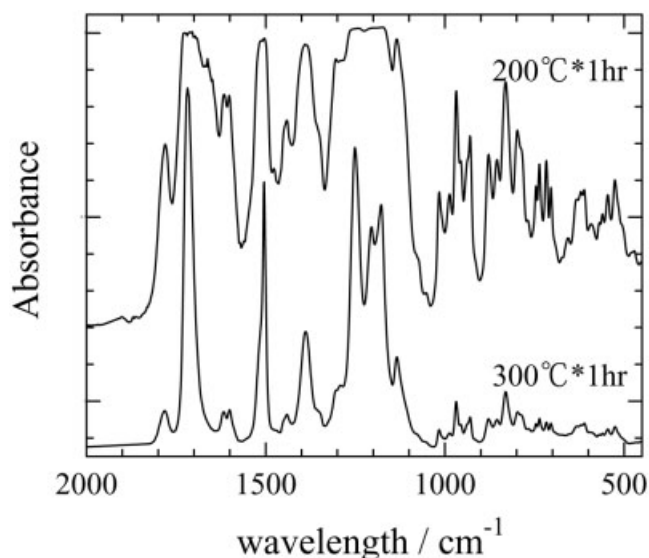
with results reported in the literature,[17] the results indicated that high-temperature thermal treatment, at 300°C or higher, was necessary for the entire imidization of poly(amic acid).

As reported previously,[18] the characteristics of polyimide [poly(amic acid)] changed according to curing temperature. In the study, the optical and thermal properties of Bco-PI films with different curing temperatures were investigated.

Figure 5 shows the changes in the UV spectra of Bco-PI films because of different curing temperatures. After curing at 250°C for 1 h, the film was transparent and colorless and showed a cutoff at about 290 nm. However, after curing at 300°C for 1 h, the film was somewhat yellow, and after curing at 350°C for 1 h, the film became reddish yellow. As shown in Figure 5, the transmittance at 365 nm of the three Bco-PI films cured at 250°C, 300°C, and 350°C was 98%, 75%, and 3%, respectively.

The refractive indexes of the Bco-PI films changed according to the curing temperature. The results are listed in Table I. The refractive indexes were deter-

Figure 4 FTIR spectra of PAA from different thermal treatments.

TABLE I
Refactive Indexes and Estimated Dielectric Constants of Bco-PI Films

Item	Curing process	d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	ε[e]
Bco-PI	250°C for 1 h	3.6590	1.5573	1.5483	1.5543	2.66
Bco-PI	300°C for 1 h	3.6144	1.5577	1.5556	1.5570	2.67
Bco-PI	350°C for 1 h	3.5205	1.5902	1.5858	1.5887	2.78

[a] Film thickness.
[b] In-plane refractive index.
[c] Out-of-plane refractive index.
[d] Average refractive index.
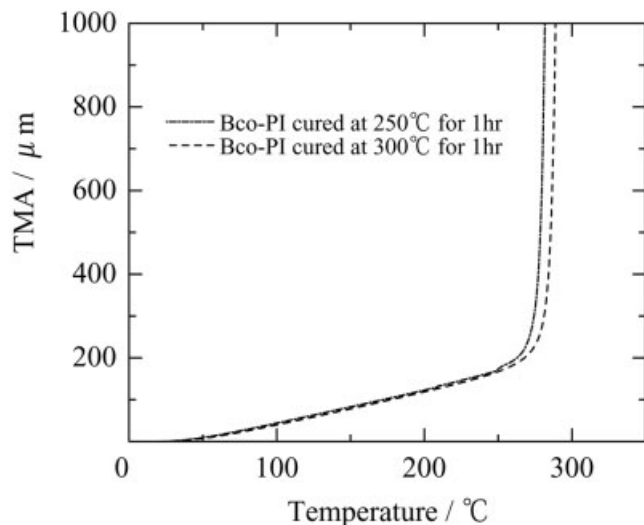[e] Estimated optical dielectric constant; $\varepsilon = 1.10\, n_{AV}^2$.

Figure 6 TMA curves of Bco-PI films cured at 250°C and 300°C.

Figure 7 FTIR spectra of PSPI films at each thermal treatment step.

mined by a prism coupler method. The in-plane (n_{TE}) and our-of-plane refractive indexes of the sample films could be determined using polarized laser light. The average refractive index (n_{AV}) could be calculated using the equation $n_{AV} = (2n_{TE} + n_{TM})/3$. Optical anisotropy ($\Delta n$) is given as the difference between n_{TE} and n_{TM}. The dielectric constants of the material at optical frequencies could be estimated from the refractive index, n, according to Maxwell's equation[17,19]: $\varepsilon \cdot n^2$. The value of ε, around 1 MHz, was evaluated as $\varepsilon \cdot 1.10\, n_{AV}^2$, including an additional contribution from the infrared absorption of approximately 10%.

The refractive index of Bco-PI film increased with an increasing curing temperature. After curing at 250°C for 1 h, the n_{AV} was 1.5543. However, after curing at 350°C for 1 h, the refractive index increased to 1.5661. The dielectric constants estimated from the refractive indexes at the two temperatures were 2.66 and 2.78, respectively.

This result indicated that an improved optical property of Bco-PI film could be obtained by lowering the curing temperature. TMA measurement of the Bco-PI films cured at 250°C,300°C was carried out (Fig. 6). When the curing temperature was increased, the glass-transition temperature (T_g) of the corresponding Bco-PI film rose. The T_g of the Bco-PI films cured at 250°C and 300°C was 282°C and 289°C, respectively, and the average coefficient thermal expansion (CTE) was 40 and 36 ppm, respectively. In the 250°C curing process, it was considered an amorphous phase. Because the heating temperature was below the T_g of Bco-PI, the space produced when the solvent evolved from the Bco-PI film remained as it was. Bco-PI film cured at 250°C had a structure of large intermolecular free volume and showed excellent optical characteristics and high CTE.
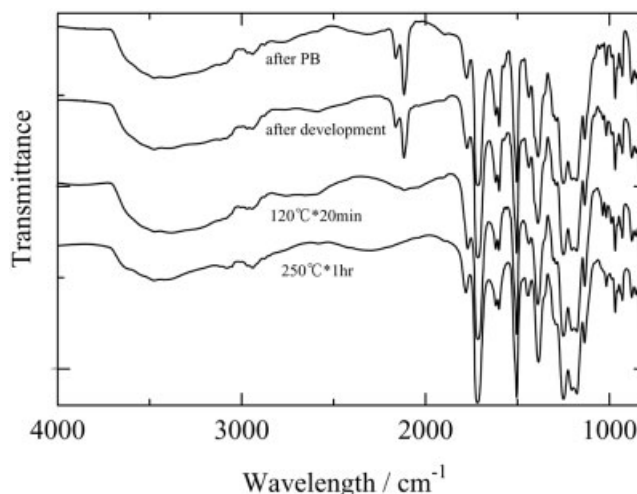
On the other hand, when the Bco-PI film was cured at 300°C which was above the T_g of Bco-PI, spontaneous orientation behavior occurred. As a result, Bco-PI film cured at 300°C showed a CTE with comparatively low transparency and a high refractive index.

Influence of NT200 on properties of PSPI films

The influence of NT200 on the properties of PSPI films was investigated. After development, the curing process of PSPI films was carried out at various temperatures. The FTIR spectra of PSPIs at each step are summarized in Figure 7. After development, an absorbance peak at 2200 cm^{-1} was observed because of the NT200. This absorbance peak became very weak after a heating treatment at 120°C for 20 min, indicating that the NT200 was almost completely decomposed at this temperature. After a heating treatment at 250°C for 1 h, the peak at 2200 cm^{-1} from NT200 disappeared completely, which indicates the NT200 was decomposed completely.

The influence of NT200 on the properties of PSPI films is summarized in Table II. Compared with Bco-

TABLE II
Influence of NT200 on Properties of Bco-PI Films

Item	T_g[b] (°C)	CIE[c] (ppm/°C)	T_5[a] (°C) in N$_2$	n_{AV}	ε
Bco-PI	282	40	420	1.5543	2.66
Bco-PI +15 wt % NT200	273	43	380	1.5563	2.67

[a] Temperature of 5% weight loss measured by TGA at a heating rate of 10°C/min in N$_2$.
[b] Measured by TMA at a heating rate of 10°C/min in N$_2$.
[c] Measured by TMA in a temperature range of 50°C–200°C.

PI films, PSPI films composed of Bco-PI with 15 wt % NT200 showed a higher CTE and a lower T_g. After being cured at 250°C for 1 h, both the Bco-PI and the PSPI films showed no weight loss below 300°C, and the thermal decomposition temperature (T_5) was 420°C and 380°C, respectively. The addition of 15 wt % NT200 to Bco-PI did not affect the refractive index much. After the same curing process at 250°C for 1 h, the n_{AV} of the Bco-PI and PSPI films were 1.5543 and 1.5563, respectively, and the optically estimated dielectric constants were 2.66 and 2.67, respectively. These values were significantly lower than those of conventional aromatic polyimides.

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. The Bco-PI containing 15 wt % NT200 was found to be a positive-type PSPI after UV irradiation and subsequent development with a 5% TMAH aqueous solution at room temperature. The sensitivity and contrast of the PSPI were 220 mJ/cm² and 1.27, respectively.

In conventional PAA process, the thermal imidization temperature should be 350°C or higher. The influence of curing temperature on the properties of Bco-PI films was investigated in this study. With curing at 250°C, which was below the T_g, the Bco-PI was considered an amorphous phase. The space produced when the solvent evolved from the Bco-PI film remained as it was. The corresponding Bco-PI film showed excellent optical properties. In contrast, when the Bco-PI was cured at 300°C, the optical property deteriorated.

Compared with the conventional PAA process, Bco-PI has the advantage of yielding polyimide films with excellent optical characteristics by a 250°C curing process. The optically estimated dielectric constants of the films of Bco-PI and Bco-PI containing 15 wt % NT200 were 2.66 and 2.67, respectively. The value of Bco-PI was significantly lower than the conventional aromatic polyimide film.

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