

A Novel Positive-Type Photosensitive Polyimide Having Excellent Transparency Based on Soluble Block Copolyimide with Hydroxyl Group and Diazonaphthoquinone

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ABSTRACT: A novel positive-type photosensitive polyimide having excellent transparency based on soluble block copolyimide (Bco-PI) with hydroxyl group and diazonaphthoquinone (DNQ) as a photoreactive compound was developed. The base Bco-PI A was prepared by a direct one-pot polycondensation of cyclohexanetetracarboxylic dianhydride (H-PMDA), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane) (Bis-AP-AF), and bis(4-(3-aminophenoxy)phenyl)sulfone (*m*-BAPS) in the presence of a γ -valerolactone and pyridine catalyst system by using dipolar aprotic solvent such as *N*-methyl-2-pyrrolidone (NMP). The wholly aromatic polyimides have strong absorptions in the visible regions, because of their charge-transfer complex forma-

tion. On the other hand, alicyclic dianhydride, H-PMDA, contributed to the resulting Bco-PI film with colorlessness and transparency, which are the important factors for a photosensitive polyimide. Photosensitive Bco-PI, containing 20 wt % 1,2-naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC5), showed a sensitivity of 250 mJ/cm² and a contrast of 2.56 when it was exposed to UV light, followed by development with 5% tetramethylammonium hydroxide (TMAH) aqueous solution at room temperature. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1619–1624, 2005

Key words: polyimides; transparency; lithography

INTRODUCTION

Since the first research of photosensitive polyimide (P-SPI) was reported by Rubner et al. in 1971, PSPIs have been widely used as protection and insulation layers of very large scale integrated circuit (VLSI), multichip modules for computers, telecommunications, and thermal heads because fabrication processes become simple and do not need a photoresist used in the microlithography or a toxic etchant such as hydrazine.¹

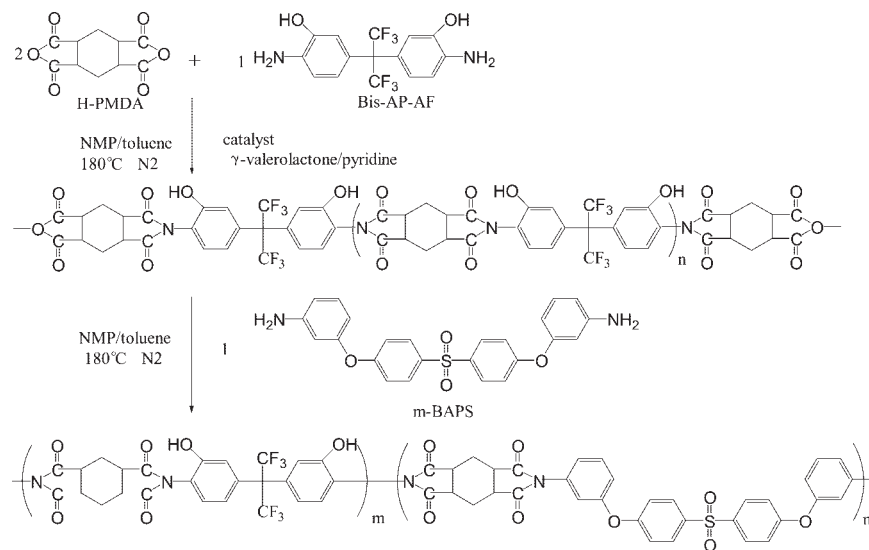
Most of the negative-type PSPIs are prepared from polyamic acid, where crosslink sites are introduced to amic acids through ester² and acid-amine ion linkages.³ Such negative-type PSPIs are commercially available; however, negative-type PSPI swells during development because the developer is an organic solvent. They also have several problems such as poor shelf life and shrinkage during curing.

To overcome these problems, positive-type PSPIs, which can be developed by base aqueous solution, have attracted great interest. Several attempts to alkaline-develop positive PSPIs in combinations with *o*-

diazonaphthoquinone (DNQ) were reported.^{4–7} Khanna et al.⁸ reported polyimide and polyamides containing hydroxyl groups for a positive working DNQ-sensitized PSPI system. Upon exposure to UV light, DNQ is converted to indenecarboxylic acid that increases the dissolution rate to the base aqueous solution. This PSPI system possesses good sensitivity and the contrast. Mochizuki et al.⁹ reported positive-type PSPIs on the basis of polyisoimide as the precursor of polyimide and DNQ because the dissolution rate of the polyimide precursor is essentially too high to obtain a sufficient dissolution contrast. They succeeded in increasing the dissolution contrast between the exposed and unexposed parts by a high post-exposure bake (PEB) temperature over 130°C. Hayase and coworkers¹⁰ reported another DNQ-sensitized approach which was realized by polyamic acid esters with phenol moieties and DNQ. The polyimide precursors were synthesized from diamine and dicarboxylic acids that had phenol moieties through ester linkage. By adjusting the dissolution rates in basic aqueous developers, they succeeded in realizing fine patterns.

In this article, we conducted a molecular design of a positive-type soluble block copolyimide (Bco-PI) A by using cyclohexanetetracarboxylic dianhydride (H-PMDA), bis(4-(3-aminophenoxy)phenyl)sulfone (*m*-BAPS), and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane) (Bis-AP-AF) as the key monomers. Viable based polyimide as a

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Scheme 1 Synthesis of soluble Bco-PI.

candidate for PSPIs must possess excellent solubility and good transmission in the UV region, as well as film properties. The wholly aromatic polyimides have strong absorptions in the visible region and in general they are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer (CT) complex formation.^{11–12} On the contrary, as alicyclic dianhydride, H-PMDA contributes to Bco-PI not only with good solubility in various solvents but also with excellent transparency. Another Bco-PI B was synthesized from pyromellitic dianhydride (PMDA), Bis-AP-AT, and *m*-BAPS. PMDA is the corresponding aromatic dianhydride of H-PMDA. Photosensitive properties of Bco-PI A and B and their UV spectrums were investigated and compared. In particular, diamines containing sulfone groups are effective in preparing transparent polyimide because the charge transfer interaction between the color-causing centers by reducing the electron density of the amine is hindered.^{13–16} The Bis-AP-AF-containing hydroxy group gives the polyimides an alkaline-developable potential. The soluble Bco-PI was synthesized by a one-pot process in which the polycondensation was prompted by a binary catalyst system consisting of γ -valerolactone and pyridine.^{17,18} This study deals with the PSPIs containing DNQ compound and Bco-PI.

EXPERIMENTAL

Materials

PMDA (Nippon Shokubai Co., Ltd., Tokyo, Japan), Bis-AP-AF (Central Glass Co., Ltd., Tokyo, Japan), and *m*-BAPS (Waka-yamaseika Kogyo Co., Ltd., Wakayama, Japan) were commercially available. H-PMDA was kindly donated by New Japan Chemical Co., Ltd. (Osaka, Japan) and used without further purification. 1,2-Naphthoquinonedia-

zide-5-sulfonic acid *p*-cresol ester (PC5) was purchased from Toyo Gosei Kogyo Co., Ltd. (Tokyo, Japan) and used without further purification.

Synthesis of the soluble polyimide

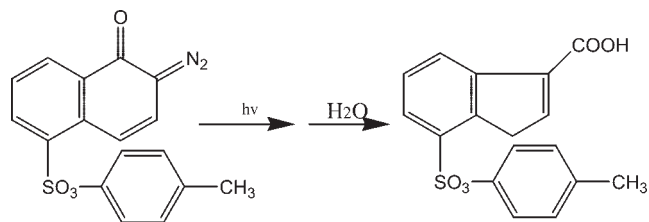
Bco-PI A (Scheme 1) was prepared by a one-pot polycondensation of H-PMDA, *m*-BAPS, and Bis-AP-AF in the presence of a binary acid catalyst consisting of γ -valerolactone and pyridine. *N*-methyl-2-pyrrolidone (NMP) was used as solvent, and toluene was used for distilling the formed water away from the reaction system.

A detail procedure is as follows: 27.16 g H-PMDA and 21.98 g 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 125 g NMP and 30 g toluene. γ -Valerolactone (1.20 g) and pyridine (1.89 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. Added to the solution were 25.95 g *m*-BAPS and 40 g NMP, and the mixture was stirred at room temperature for 1 h, until the mix became a homogeneous solution. Then, the solution was heated to 180°C for 2.5 h under nitrogen. The solid concentration was maintained at ~ 30 wt %. The obtained varnish was used for photosensitive polymer matrix without further purification.

Bco-PI B was prepared from PMDA, *m*-BAPS, and Bis-AP-AF by the same synthesis process as Bco-PI A.

Measurement

The molecular weight of polyimide was determined with a Tosoh gel permeation chromatographer (GPC)



Scheme 2 PC5.

equipped with gel column TSK-GEI-type. Dimethylformamide (DMF) containing LiBr (30 mM) and phosphoric acid (60 mM) was employed as the eluant and the flow rate was 0.8 mL/min at room temperature. Polystyrene was used as the calibrating standard. The infrared spectra were recorded with a Perkin-Elmer spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on a JEOL-500 NMR spectrometer (500 MHz, with tetramethylsilane as an internal standard), and dimethylsulfoxide (DMSO-d_6) was used as solvent. UV-visible absorption spectra of polyimide were measured with the use of quartz cells on a Shimadzu UV-Vis NIR Spectrophotometer (UV-3150). Thermogravimetric analyses were performed by use of Mac Sciences (MTC 1000s) thermogravimetric analyzer at a heating speed of $10^\circ\text{C}/\text{min}$ under nitrogen. Irradiation was carried out with a UV exposure apparatus (ORC JP-2000-EXC) by a contact technique through a mask. 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 non-contact-type optical film-thickness analyzer.

Photosensitivity

The PSPI was formulated by the Bco-PI A as matrix resins and DNQ compound, PC5 (Scheme 2), as a photosensitive agent (20 wt % for polyimide) dissolved in NMP. The PSPI was spin-coated onto a silicon wafer and was prebaked at 90°C for 5 min. This was exposed on an ORC JP-2000EXC equipped with a super high-pressure mercury lamp through a mask in contact technique. The light contains the wavelength from 300 to 450 nm. The dose was measured with an ORC UV-331AP2 at the wavelength range of 320–390 nm. The exposed PSPI films were developed in aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature and subsequent rinsing with pure water.

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

RESULTS AND DISCUSSION

Polymer synthesis and characterization

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

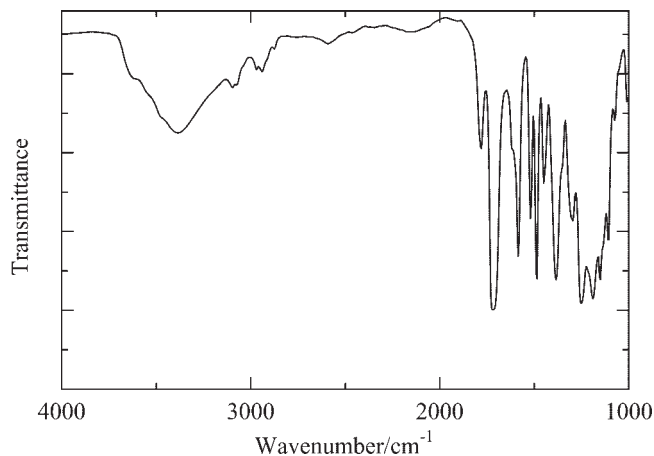
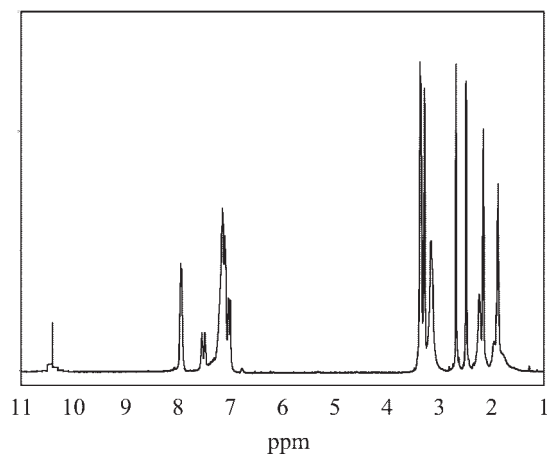


Figure 1 IR spectrum of Bco-PI A film.

polycondensation on the basis of the sequential addition technique without any special isolation process of precursor polyamic acid.

The first-step polycondensation of excess H-PMDA with Bis-AP-AF (the molar ratio of H-PMDA and Bis-AP-AF was 2 : 1) afforded oligoimides. The second-step polycondensation of the oligoimides with *m*-BAPS gives Bco-PI with a high molecular weight. This Bco-PI A, containing H-PMDA, Bis-AP-AF, and *m*-BAPS, was composed of two kinds of blocks: block A (H-PMDA—Bis-AP-AF) and block B (H-PMDA—*m*-BAPS). The molecular weight (MW) and polydispersity (MW/M_n) of Bco-PI were determined by GPC as 79,000 and 1.91, relative to standard polystyrene, respectively.

The structure of the obtained Bco-PI A was confirmed by IR spectroscopy. Figure 1 shows the result. The IR spectrum (ATR) showed characteristic absorptions at 1780 and 1720 cm^{-1} because of the imide carbonyl. Furthermore, the characteristic absorption of O—H stretching was observed at $\sim 3400\text{ cm}^{-1}$ and amide bands attributed to polyamic acids [1660 cm^{-1} (C=O), 1559 cm^{-1} (C—NH)] were not observed.

Figure 2 ^1H spectrum of Bco-PI A in DMSO-d_6 at 25°C .

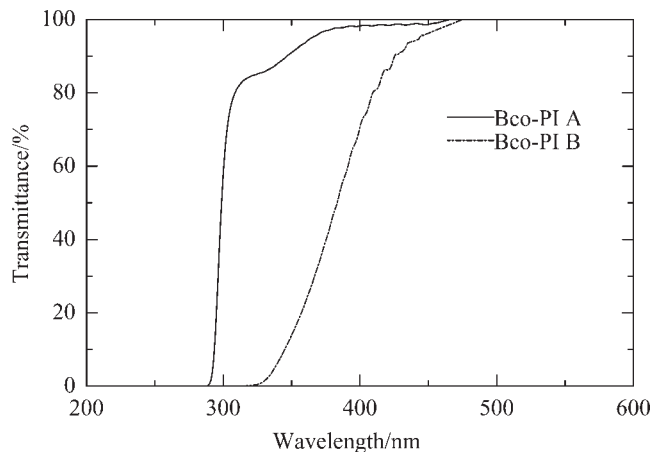


Figure 3 UV-visible spectrum of Bco-PI A and B.

The $^1\text{H-NMR}$ spectrum of Bco-PI revealed the signal at 10.5 ppm (s, OH, 2H), associated with the hydroxy group from Bis-AP-AF, and the signal at 6.90–8.10 ppm due to the aromatic protons. However, the signals of amide (NH) protons (~ 10.5 ppm)¹⁹ were not observed in the spectrum; hence, the complete imidization was supported.

Lithographic evaluation

Figure 3 showed the UV-visible spectrums of Bco-PI A and B. The thicknesses of both films were $4.8 \mu\text{m}$. The film of Bco-PI A was entirely colorless and transparent. It exhibited cutoffs at wavelength ~ 290 nm, and the film was entirely transparent in the region over 350 nm. The transmittance of the Bco-PI A at 365 nm was 95%.

Compared with the Bco-PI A, the film of Bco-PI B was pale yellow. It exhibited cutoffs at a wavelength about 320 nm, and the transmittance of the Bco-PI B at 365 nm was 28%.

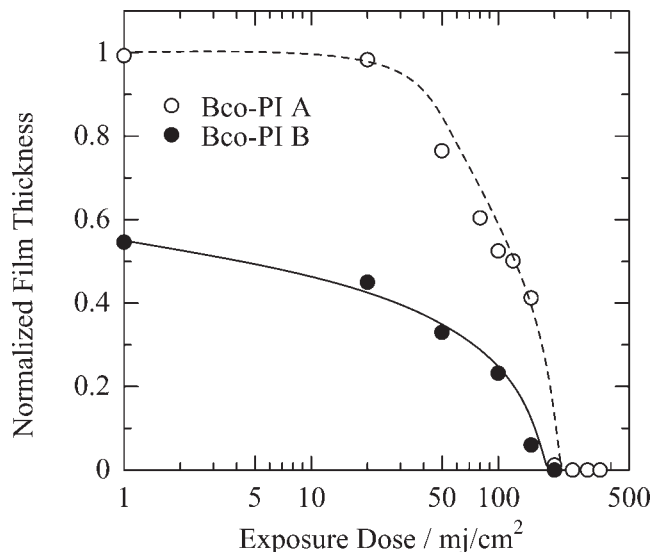


Figure 5 Photosensitivity curves for the PIPI films of Bco-PI A and B consisting of 20 wt % PC5.

We have chosen PC5 as the photoactive DNQ compound.

Figure 4 showed the changes of the UV-visible spectrums corresponding to the PSPI film of Bco-PI A containing 20 wt % of PC5 upon UV irradiation. The absorption band at 350 and 400 nm decreased rapidly upon irradiation. After 250 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 A and PC5 as a matrix and a photoactive compound would be expected to be excellent photoresists sensitive to the I and G line.

Figure 5 showed the sensitivity curves of PSPIs films consisting of Bco-PI A with 20 wt % PC5 and Bco-PI B with 20 wt % PC5 each. The thickness of both were $4.8 \mu\text{m}$. After development of 5% TMAH aque-

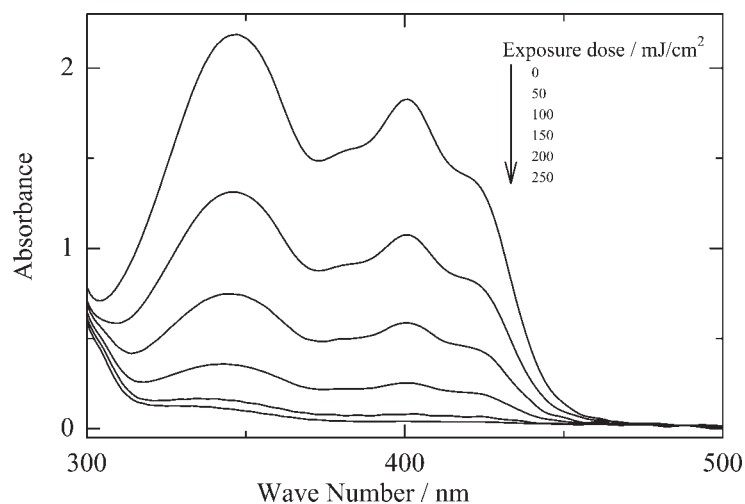


Figure 4 Changes of UV-visible spectra of 20 wt % PC5 in Bco-PI A film after UV irradiation.

ous solution at room temperature, the sensitivity and contrast were 250 mJ/cm^2 and 2.56, respectively. In the case of Bco-PI B using PMDA, which is the corresponding aromatic dianhydride of H-PMDA, after development of 5% TMAH aqueous solution at room temperature, the sensitivity and contrast were 250 mJ/cm^2 and 1.08, respectively.

After development, the residual film thickness of PSPI consisting of Bco-PI B and PC5 is only 55% of the original thickness. However, in the case of Bco-PI A, after development, the film thickness hardly decreased. Compared with Bco-PI B, the dissolution rate of the unexposed part of Bco-PI A was drastically low. This result indicated that H-PMDA as the alicyclic dianhydride was effective for dissolution inhibitor much more than PMDA, which was the corresponding aromatic dianhydride of H-PMDA.

Figure 6 showed the typical pattern of the scanning electron micrograph of the contact printed image for the PSPI film containing Bco-PI A and PC5 after exposure of 250 mJ/cm^2 . This PSPI film was developed with 5% TMAH aqueous solution at room temperature for 135 s.

Thermal properties of the PSPIs film

Figure 7 shows the TG curves of PSPI films consisting of Bco-PI A and PC5 after development with 5% TMAH at room temperature (dashed line), and after curing at 300°C for 1 h (solid line). The former curve (dashed line) exhibited slopes with two steps being evident. The first weight loss starts at $\sim 150^\circ\text{C}$. It indicated that both vaporization of residual solvent and degradation of the PC5 begin at this temperature. The first step of weight loss continues to $\sim 300^\circ\text{C}$. The second step of weight loss associated with the degradation of Bco-PI A began at around 350°C . On the other hand, the solid line shows no weight loss until 350°C with the 10% weight loss

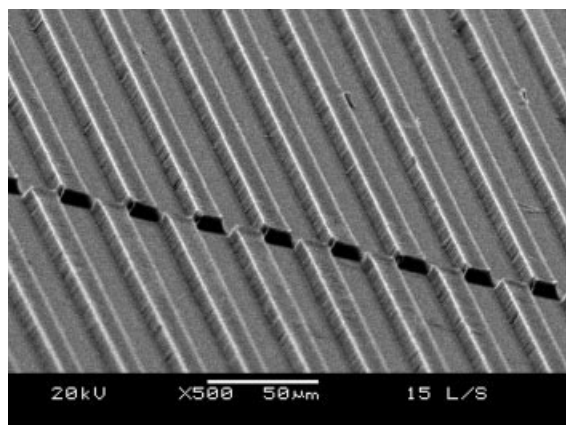


Figure 6 SEM photograph of L/S patterns for positive PSPI of Bco-PI A containing 20 wt % PC5. Development: 5% TMAH in water; time: 135 s; exposure: 250 mJ/cm^2 .

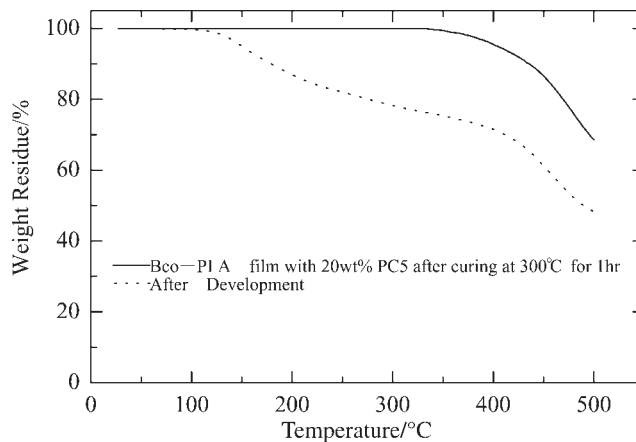


Figure 7 TG curves of Bco-PI A film.

temperature being 445°C , which indicated that PC5 as the photoreactive compound can be removed from the PSPI film by high-temperature treatment after the development process, and that the thermal properties of the resulting polyimide film were not damaged by the addition of PC5.

CONCLUSIONS

A soluble Bco-PI A was synthesized from H-PMDA, Bis-AP-AF, and *m*-BAPS in the presence of a γ -valerolactone and pyridine catalyst system. Compared with Bco-PI B using PMDA, which is the corresponding aromatic dianhydride of H-PMDA, Bco-PI A showed excellent transparency in the UV region above 350 nm. The Bco-PI A containing 20 wt % of PC5 was found to be a positive-type PSPI by UV irradiation followed by development with 5% TMAH at room temperature. The sensitivity and contrast of the PSPI were 250 mJ/cm^2 and 2.56, respectively. After development, the residual film thickness of PSPI film consisting of Bco-PI A and PC5 was much higher than that for Bco-PI B using PMDA. Therefore, as alicyclic dianhydride, H-PMDA showed an excellent effect of dissolution inhibitor. After the development process, high-temperature treatment such as 300°C for 1 h can remove the PC5 from the PSPI film. Therefore, the thermal properties of the resulting polyimide film were not damaged.

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