

A Positive-Type Alkaline-Developable Photosensitive Polyimide Based on the Poly(amic acid) from 2,2',6,6'-Biphenyltetracarboxylic Dianhydride and 1,3-Bis(4-aminophenoxy)benzene, and a Diazonaphthoquinone

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Photosensitive polyimides (PSPIs) have been indispensable materials for the field of semiconductors as insulation layers because of their high thermal stability, insulating properties, and good productivities.^{1,2} Because polyimides (PIs) often show the low solubilities, poly(amic acid)s (PAAs) as precursors of PIs are used instead and subsequently are transformed into PIs by thermal treatment. Recently, PSPIs have been applied as protective layers for circuit wiring on printed circuit boards. This new application requires high sensitivity, solution stability, and the ability to be developed by using aqueous alkaline solution. The sensitivity of PSPIs depends on the transmittance of PAAs and the quantum yield of photosensitive additives at the exposure wavelength.

In general, aromatic PAAs have strong absorptions at wavelengths near 365 nm because of their extended π conjugation. To overcome this problem, 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride and 4,4'-biphthalic dianhydride (BPDA) are used to shift the absorptions to shorter wavelengths by the decrease of the conjugation length.¹ Another approach is the introduction of alicyclic moieties into the PAAs.³

The molecular weight of conventional PAAs, which are derived from five-membered cyclic acid anhydride such as pyromellitic dianhydride (PMDA) and BPDA, decreases rapidly under the ambient condition as a result of an intramolecular acidolysis.^{4,5} The change of the molecular weight has a direct effect on the solution viscosity and causes the coating irregularities in the manufacturing process. Thus, the solution stability of PAAs is an important factor in the formulation of PSPIs.

In a preceding paper,⁶ we reported that PAAs derived from 2,2',6,6'-biphenyltetracarboxylic dianhydride (2,2',6,6'-BPDA) show good solution stability at room temperature and excellent transparency at 365 nm because of their twisted conformation. The twisted conformation inhibits the intramolecular acidolysis reaction and the conjugation of the π -electrons of two phenyl rings in the biphenyl structure. These findings prompted us to develop a new PSPI based on PAAs derived from 2,2',6,6'-BPDA.

We describe here an alkaline-developable PSPI based on a PAA (PAA-BB) derived from 2,2',6,6'-BPDA and 4,4'-(1,3-phenylenedioxy)dianiline (1,3-APB), with a diazonaphthoquinone derivatives (DNQ-1) as a dissolution inhibitor. Furthermore, PAA-BB has a high solution stability and is transparent at 365 nm.

EXPERIMENTAL

Materials

1-Methyl-2-pyrrolidinone (NMP) was purchased from Kanto Kagaku Organics Co., Ltd., and used as received. 1,3-APB was purchased from Wakayama Seika Kogyo Co., Ltd. and used as received. 2,2',6,6'-BPDA was prepared according to the literature⁷ in 26% yield after vacuum sublimation at 250 °C and 1 mmHg. PA-6 (α,α,α -Tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene trisubstituted with (6-diazo-5-oxo-5,6-dihydronaphthalene-1-yl)sulfonyl groups) (DNQ-1) was purchased from Daito Chemix Corporation and used as received.

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Synthesis of PAA-BB from 2,2',6,6'-BPDA and 1,3-APB

2,2',6,6'-BPDA (2.94 g, 10.0 mmol) was slowly added to a solution of 1,3-APB (2.92 g, 10.0 mmol) in dry NMP (32 mL) cooled in an ice bath under nitrogen at such a rate that the temperature was kept below 0 °C. The mixture was stirred at 0 °C for 5 h, and then was poured into dry diethyl ether (1000 mL). The precipitate was dried *in vacuo* at 23 °C for 14 h. The yield was 5.51 g (94%), the number-averaged molecular weight (M_n) was 17,400, and the molecular weight distribution (M_w/M_n) 4.7 (determined by GPC)

IR (attenuated total reflection, ν): 3278 (COO–H), 3066 (C–H: aromatic), 1716 and 1678 (C=O), 1605 (aromatic), 1537 (N–H), 1505 and 1479 (aromatic), 1214 (–C–O–C–), 762 cm^{-1} (C–H: aromatic). ^1H NMR (DMSO- d_6 , δ , ppm): 12.58 (2H, –COOH) 10.53 (1H, NH), 10.04 (1H, NH), 7.95 (d, $J = 8.0$ Hz, 1H, Ar), 7.86 (d, $J = 7.6$ Hz, 1H, Ar), 7.72 (d, $J = 7.4$ Hz, 1H, Ar), 7.70 (d, $J = 7.4$ Hz, 1H, Ar), 7.59 (t, $J = 7.4$ Hz, 0.5H, Ar), 7.49 (t, $J = 8.0$ Hz, 1H, Ar), 7.43 (t, $J = 8.0$ Hz, 1H, Ar), 7.40 (d, $J = 8.0$ Hz, 2H, Ar), 7.39 (d, $J = 8.0$ Hz, 2H, Ar), 7.26 (t, $J = 8.0$ Hz, 1H, Ar), 6.95 (d, $J = 7.6$ Hz, 4H, Ar), 6.58 (d, $J = 7.8$ Hz, 2H, Ar), 6.53 (s, 1sH, Ar). ^{13}C NMR (CDCl_3 , δ , ppm): 168.68, 167.29, 166.96, 166.18, 158.67, 158.63, 151.62, 151.44, 137.69, 137.42, 136.53, 135.88, 134.81, 134.57, 133.30, 131.43, 131.20, 130.88, 130.09, 128.67, 127.71, 127.40, 121.46, 121.29, 119.65, 111.83, 107.57, and 107.53. E_{LEM} . A_{NAL} . Calcd for ($\text{C}_{34}\text{H}_{22}\text{N}_2\text{O}_8 + 0.2\text{H}_2\text{O}$): C, 69.20%; H, 3.83%; N, 4.75%. Found: C, 69.38%; H, 4.55%; N, 4.93%. (The PAA is so hygroscopic that it takes up water during weighing).

Synthesis of PI from PAA-BB by Thermal Treatment

The 20 wt % solution of PAA-BB in NMP was spin coated on a glass, and dried at 100 °C for 10 min. The glass coated with PAA-BB was heated in nitrogen atmosphere up to 300 °C at the heating rate of 10 °C/min, and held the temperature at 300 °C for 1 h. After the cooling, the substrate was dipped in the distilled water for 2 d, and the film of PI was peeled off from the glass.

Measurements

Number- and weight-average molecular weight (M_n and M_w), and M_w/M_n values were determined by gel permeation chromatography (GPC), calibrated with standard polystyrenes, on a Tosoh HLC-8120 GPC system equipped with polystyrene gel columns (TSK gels α -M \times 2), at 40 °C in NMP (containing 0.03 M of lithium bromide and 0.03 M of H_3PO_4 ; flow rate = 0.5 mL/min). Thermal analysis (TG-DTA) was performed on a RIGAKU TG8120 at a heating rate of

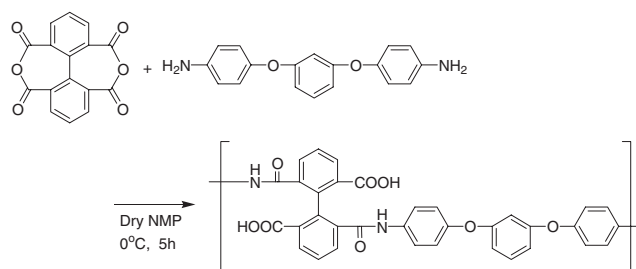
10 °C/min under nitrogen. Thermal mechanical analysis (TMA) was performed on a RIGAKU TMA8310 at a heating rate of 10 °C/min under nitrogen. Dynamic mechanical analysis (DMA) was performed on a Rheometric Science RSA2 at a heating rate of 5 °C/min under air. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400WB spectrometer. Samples were analyzed in DMSO- d_6 , and the chemical shift values were expressed relative to Me_4Si as an internal standard. UV-visible spectra were obtained on a SHIMADZU UV-2550GLP spectrometer, and samples, which were cast on the glass, were analyzed at 23 °C. Infrared spectra for identification were recorded on a JASCO FT-IR 610 infrared spectrophotometer using a SensIR Technologies Durascope diamond ATR unit, and samples were analyzed at 23 °C. Lithographic evaluation was performed by the contact type proximity one-shot exposure system MA-1200 (Japan Science Engineering Co., Ltd.). The film thickness was measured by a Dectak 3030 (Veeco Instruments Inc.).

RESULTS AND DISCUSSION

Synthesis and Transparency of PAA-BB

The conversion into PIs of PAAs derived from 2,2',6,6'-BPDA and aromatic diamines such as 4,4'-oxydianiline, 4,4'-(1,4-phenylenedioxy)dianiline, and 1,3-APB was successfully carried out by chemical treatment, which was carried out in a mixture of trifluoroacetic anhydride, pyridine, and toluene (molar ratio, 1:1:20) solution at room temperature for 24 h, then the resulting film was cured at 300 °C for 1 h. However, most of PAAs did not form PIs on thermal treatment, and only the PAA-BB from 2,2',6,6'-BPDA and 1,3-APB was converted to the correspondent PI by thermal treatment. Thus, PAA-BB was selected as a PSPI precursor. PAA-BB with a M_n of 17,400 and a M_w/M_n of 4.7 was prepared by polymerization of 2,2',6,6'-BPDA with 1,3-APB in NMP (Scheme 1).

Figure 1 shows the transmittance of the 3.5 μm thickness film of PAA-BB and those of conventional PAAs such as PMDA/ODA and BPDA/ODA (Scheme 2). The films were prepared by heating at



Scheme 1. Synthesis of PAA-BB.

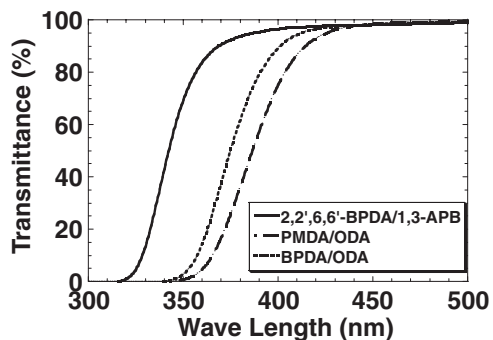
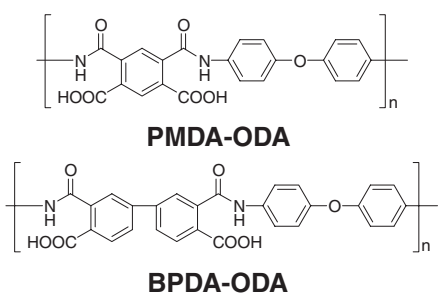
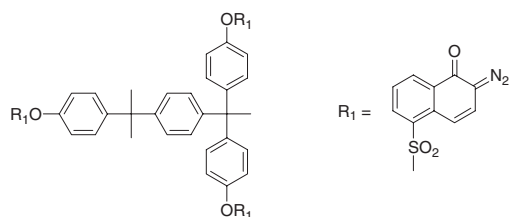


Figure 1. Transmittance of the films of PAA-BB, PMDA/ODA, and BPDA/ODA (The film thickness was 3.5 μm).



Scheme 2. Structure of PMDA/ODA and BPDA/ODA.



Scheme 3. Structure of DNQ-1.

100 $^{\circ}\text{C}$ for 10 min after spin coating on a glass sheet. PAA-BB exhibited an excellent transmittance of about 88% at 365 nm as a result of its twisted conformation.

Lithographic Evaluation

PAAs possessing hydrophilic carboxylic groups have a great promise for application as PSPI precursors without partial imidization or functionalization. The dissolution rate of PAAs in 2.38 wt% aqueous tetramethylammonium hydroxide (TMAHaq) solution is, however, too high to get a sufficient contrast in dissolution rates between unexposed and exposed areas when combined with DNQ derivatives. In a previous paper,⁸ we reported the preparation of PSPIs consisting of highly hydrophobic PAAs and DNQ derivatives. PAA-BB is very high hydrophobic: a high dissolution contrast between unexposed and exposed areas could, therefore, be obtained by using DNQ-1, a highly hydrophobic DNQ derivative (Scheme 3).

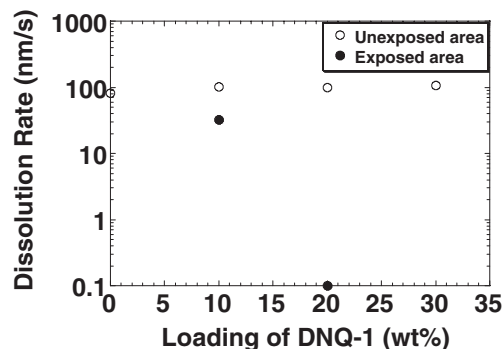


Figure 2. Dissolution rate of PSPI based on PAA-BB and DNQ-1. The film thickness was 3.5 μm . The film was developed by using 0.1% TMAHaq solution at 23 $^{\circ}\text{C}$. The film was exposed to light from an un-filtered high-pressure mercury arc lamp at 2 J/ cm^2 .

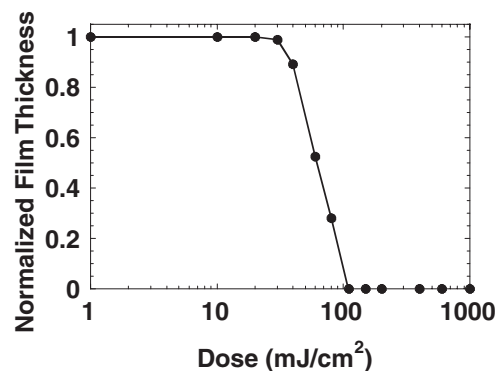


Figure 3. Photosensitive curve for PSPI based on PAA-BB and 20 wt% of DNQ-1. The film thickness was 1.3 μm . The film was developed with 0.1% TMAHaq solution at 23 $^{\circ}\text{C}$. The film was exposed to i-line light through a filter.

Figure 2 shows the relationship between the loadings of DNQ-1 in PAA-BB and the dissolution rates in 0.1 wt% TMAHaq solution. The films were prepared by heating at 100 $^{\circ}\text{C}$ for 10 min after spin coat on the chrome-plated glass, and the film thickness was 3.5 μm . The exposed area was irradiated with 2.0 J/ cm^2 by an unfiltered high-pressure mercury arc lamp. The dissolution rate of PAA-BB in the 0.1 wt% TMAHaq solution was about 90 nm/s, and became almost zero with a 20 wt% loading of DNQ-1: a large dissolution contrast (900-fold) between the exposed area and the nonexposed area was thus obtained. The dissolution rate of the exposed film containing a 30 wt% loading of DNQ-1 was not determined because of swelling of the film during development.

The sensitivity curve of the 1.3 μm thickness film containing 20 wt% DNQ-1 exposed at 365 nm (i-line) is shown in Figure 3. The sensitivity (D^0) and contrast (γ^0) were 110 mJ/ cm^2 and 2.0, respectively.

Figure 4 represents an image obtained by scanning

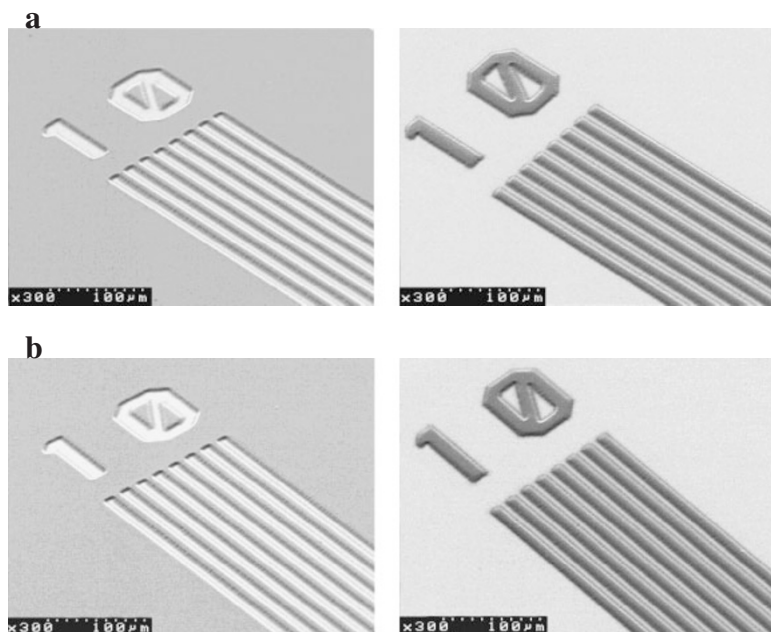


Figure 4. The SEM images of PSPI containing PAA-BB and 20 wt % of DNQ-1 after development (a) and after imidization (b). The film thickness was 2.0 μm . The film was developed with 0.1% TMAHq solution at 23 $^{\circ}\text{C}$. The film was exposed to i-line light with 250 mJ/cm^2 through the filter.

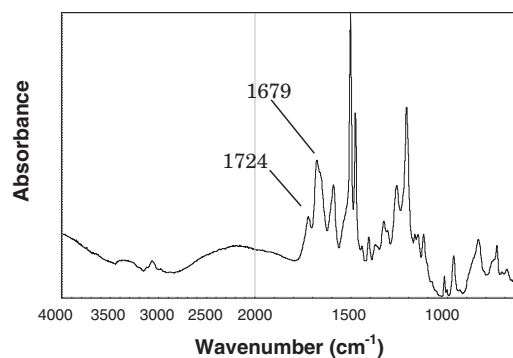


Figure 5. IR spectra of the PI from PAA-BB containing 20 wt % DNQ-1 after heating at 300 $^{\circ}\text{C}$ for 1 h.

electron microscopy (SEM) image of a contact-printed pattern obtained from a 2.0 μm resist film exposed to i-line irradiation with 250 mJ/cm^2 , and subsequently developed with 0.1 wt % TMAHq for 60 s at room temperature, and cured at 300 $^{\circ}\text{C}$ for 1 h under nitrogen. A clear positive tone image with a 10 μm line and space resolution was obtained. Additionally, the pattern maintained its shape without flow after curing. The film thicknesses before and after the post-bake were 2.0 μm and 1.45 μm , respectively.

The IR spectrum of the thermally imidized film of PAA-BB containing 20 wt % DNQ after UV-exposure is shown in Figure 5. This film has same spectrum to that of the thermally imidized film of PAA-BB. Figure 6 shows the TG curves of PAA-BB containing 20 wt % DNQ-1 and that of the corresponding PI. The weight loss of the former was about 20% in the range

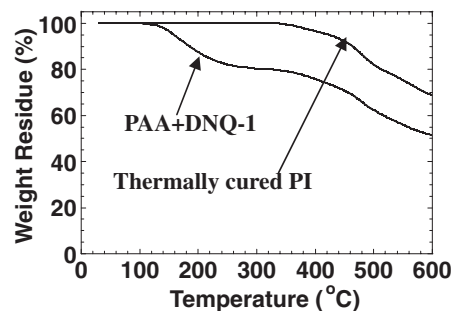


Figure 6. TGA traces of PAA-BB containing DNQ-1 and the PI at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen.

of 200–300 $^{\circ}\text{C}$, indicating that the residues from the decomposition of DNQ-1 remained within the film because the theoretical total weight loss due to degradation of DNQ-1 (20 wt %) and dehydration (6 wt %) is 26%.

The thermal properties of PAA-BB containing 20 wt % DNQ-1 were examined with TMA and DMA. The average of the coefficient of thermal expansion (CTE) of the thermally cured film of PSPI containing PAA-BB and 20 wt % DNQ-1 from 50 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$ was 63.9 ppm, which is almost same to that of thermally cured PAA-BB (61.6 ppm).⁶ The temperature dependence of the dynamic mechanical storage modulus (E') and dynamic mechanical loss modulus (E'') of PAA-BB containing 20 wt % DNQ-1 cured at 300 $^{\circ}\text{C}$ for 1 h is illustrated in Figure 7. The E' value was around 2.4 GPa at room temperature, and started to decrease at 330 $^{\circ}\text{C}$. 1 GPa of E' value, however, retained

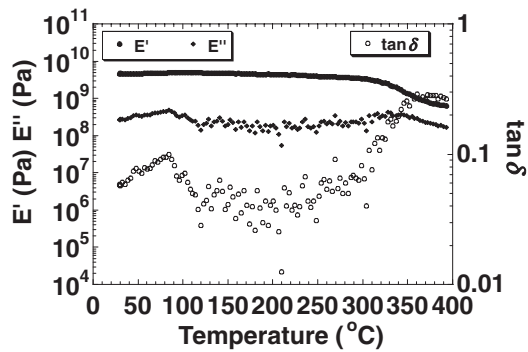


Figure 7. Dynamic mechanical spectroscopy of PAA-BB containing 20 wt % DNQ-1 after heating at 300 °C for 1 h.

at up to 400 °C. The peak value of $\tan \delta$ for the PI from PAA-BB occurred at around 280 °C, which corresponds to its glass-transition temperature T_g .⁶ On the other hand, clear E'' and $\tan \delta$ peaks were not observed for PI containing DNQ-1, indicating that the cross-linking was induced by decomposition of DNQ-1.

CONCLUSIONS

A positive PSPI was formulated from PAA-BB and the dissolution inhibitor DNQ-1. The photosensitivity and contrast of 1.3 μm thick resist film consisting of

PAA-BB (80 wt %) and DNQ-1 (20 wt %) were 110 mJ/cm^2 and 2.0, respectively. This PSPI produced a clear positive image with a 10 μm line and space feature in a 2 μm thickness. This pattern could be converted into the corresponding PI by heating at 300 °C for 1 h. As PAA-BB has excellent solution stability and transparency in the i-line region, this PSPI system would have a high potential for a practical usage.

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