Polymer Bulletin 50, 295–302 (2003)
DOI 10.1007/s00289-003-0171-y

Polymer Bulletin

A novel positive photosensitive polybenzoxazole based on a tetrahydropyranyl (THP) protected polyhydroxyamide

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Received: 10 March 2003/Revised version: 1 May 2003/ Accepted: 16 May 2003

Summary

A new positive working, aqueous base developable photosensitive polybenzoxazole (PBO) precursor composition based on a partially tetrahydropyranyl (THP) protected PBO precursor and a Bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4) photosensitive compound has been developed. The polymer was prepared from a low temperature polymerization of 2，2'-bis-(3-amino-4-hydroxyphenyl) hexafluoropropane (BisAPAF) and isophthaloyl chloride (IC), followed by reacting with 3,4-Dihydro-2H-pyran in the presence of p-toluenesulfonic acid monohydrate as a catalyst. The photosensitive PBO precursor containing 20wt % DNQ-4 photosensitive compound showed a sensitivity of 221 mJ/cm^2 and a contrast of 1.44 in a 3μm film with a 0.6wt % tetramethylammonium hydroxide (TMAH) developer. A pattern with a resolution of 10 μm was obtained from this composition. The novel PBO precursor photosensitive composition showed a significant improvement in dark film loss after development, which can and could be used to make a thick film resist.

Introduction

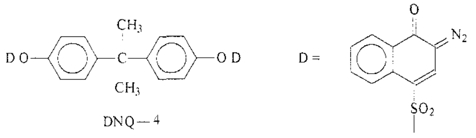
Polybenzoxazoles (PBOs) are a kind of high temperature polymers, which possess physical and chemical properties similar to polyimides. Unlike polyimides, PBOs have no polar groups in the polymer backbone, thus having a lower water absorption and dielectric constant. They are better suited for microelectronic applications than polyimides, and have received increasing interest in recent years [1-6]. Aside from those characteristics, polyhydroxyamide (PHA), the precursor of PBO, bears phenolic hydroxyl groups in the polymer backbone, which render the polymer soluble in the aqueous base. Similar to the novolak resin used in the commercial g-line (436 nm) or i-line (365 nm) photoresists, the aqueous base solubility of the precursor can be inhibited by the addition of diazonaphthoquinone (DNQ) photoactive compound. After exposure, the DNQ is converted to indene carboxylic acid, which restores the aqueous base solubility of the precursor [7]. Based on this principle, the PBO precursors have been used to prepare positive working photosensitive materials for microelectronic applications [8-9].

Although the conventional photosensitive PBO has good lithographic performance, its high dark film loss is due to the high solubility of the PBO precursor in the aqueous base developer. Therefore, it is difficult to obtain a thick film photoresist from positive working photosensitive PBO. In a previous paper [10], we have reported the use of trimethylsilyl (TMS) group to partially protect the phenolic hydroxyl groups in the PBO precursor, which is used to reduce the dark film loss of PBO photoresist. In the present study, we report the use of another effective protecting group, tetrahydropyranyl (THP), to prepare a low dark film loss PBO photoresist. The THP protected PBO precursor in the photoresist can be easily deprotected by the acid generated from a DNQ photoactive compound after exposure to UV light, obtaining a high dissolution rate contrast in an aqueous base developer.

Experimental

Materials

2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) was purchased from Chriskev Company. Isophthaloyl chloride (IC) was obtained from Aldrich and dried under vacuum at 60 °C for 24 h before use. Anhydrous N-methylpyrrolidone (NMP), diglyme, triethylamine, and Bisphenol A were obtained from Aldrich and used without further purification. Naphthoquinone-1,2-diazide-4-sulfonic acid chloride (S-214) was purchased from TCI Co. (Japan). 3,4-Dihydro-2H-pyran was obtained from ACROS. Tetramethylammonium hydroxide (TMAH) in 25wt % solution were obtained from Lancaster. P-toluenesulfonic acid monohydrate was received from Showa Chemical Inc. The Bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4) photoacid generator was synthesized by reacting Bisphenol A with S-214 according to the literature [11]. Its structure is shown in Scheme 1.



Scheme 1. Structure of DNQ-4

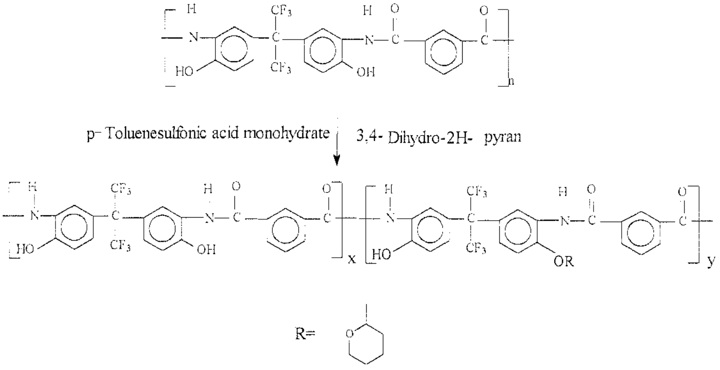
Synthesis of PBO Precursor

The preparation of BisAPAF-IC poly(hydroxyamide) (PHA) precursor was described in our previous paper[10].

Synthesis of PBO Precursor Partially Protected by A Tetrahydropyranyl (THP) Group

A 35% THP protected BisAPAF-IC PBO precursor was prepared as follows.

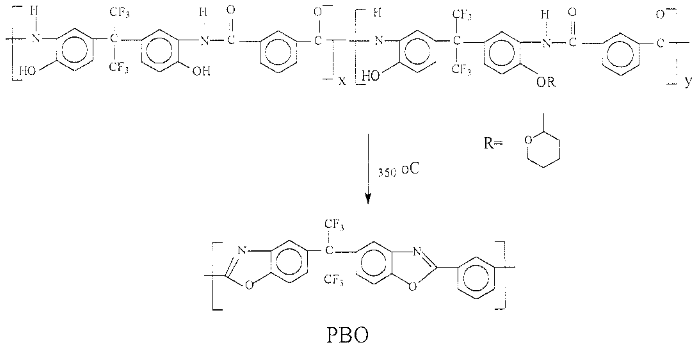
To a 250mL three-necked round bottom flask equipped with a mechanical stirrer and a nitrogen inlet, 7.5 g (15 mmol) of BisAPAF-IC poly(hydroxyamide) and 67.5 g of diglyme were added. The mixture was cooled to 0-5 °C by using an ice-bath and then 1.26 g (15 mmol) of 3,4-dihydro-2H-pyran was added. After stirring for 10 min, 0.15g (0.79 mmol) of p-Toluenesulfonic acid monohydrate in 4.0 g of diglyme was added slowly using an addition funnel. The reaction mixture was stirred at room temperature for 6 h, and then 0.3 g of triethylamine in 3 g of diglyme was added to quench the reaction. The reaction mixture was precipitated in 1.5 L of de-ionized water. The polymer was collected by filtration and washed with de-ionized water twice. The polymer was dried under vacuum at 80 °C for 24 h. The synthesis procedure is shown in Scheme 2.



Scheme 2. Synthesis of partially THP protected PBO precursor

Preparation of THP Protected PBO Precursor Film and Thermal Conversion to PBO

Five grams of 35% THP protected PBO precursor powder was dissolved in 20 g of dimethylacetamide (DMAC) to make a 20 % (w/w) solution. A film was cast from the viscous solution on a glass plate with a doctor's knife. The film was dried at 100 °C for 1 h, 200 °C for 1 h, and 350 °C for 1 h in a heating oven to convert the THP protected PBO precursor to a PBO as shown in Scheme 3. The film was transparent yellow.



Scheme 3. Thermal cyclization of partially THP protected PBO precursor

Characterization

The IR spectra were recorded on a Jasco 460 FTIR Spectrometer. ^{1}H-NMR spectra were recorded on a Brucker Advance 600 Spectrometer using dimethyl sulfoxide-d_6 as solvent. The inherent viscosity of BisAPAF-IC PBO precursor was measured using a Cannon-Ubbelohde No. 100 viscometer at a concentration of 0.5 g/dL in NMP at 30 °C. Thermal stability was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) Q500 at a heating rate of 10 °C/min under nitrogen. The UV-visible spectrum was obtained on a Hitachi U-2001 UV-VIS spectrophotometer.

Preparation of Photoresist Formulation and Lithographic Evaluation

Two grams of the 35% THP protected BisAPAF-IC PBO precursor were dissolved in 10 g of NMP and 0.4 g of DNQ-4 photoactive compound was added to prepare the photoresist solution. The solution was filtered through a 1 μm Teflon filter. It was then spin-coated onto a silicon wafer, and softbaked on an airflow clean room oven at 105 °C for 40 min to obtain a film around 3 μm thick. The film was exposed to an unfiltered mercury arc lamp measured @ 250-400nm. The wafer was developed in a 0.6 wt % TMAH developer. The film thickness was measured with a Tenco instrument Alpha-Step 200. The dissolution rates were calculated from the resist thickness before and after immersing in the TMAH solution, followed by dividing the decreased thickness by the immersing time. The characteristic curve was obtained by plotting the normalized film thickness against the exposure energy.

Results and Discussion

Synthesis of PBO Precursor

The soluble polyhydroxyamide was synthesized from the reaction of isophthaloyl chloride (IC) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) at 5 °C in anhydrous NMP. The inherent viscosity of the polymer was 0.35 dL/g measured at 30 °C in NMP at a concentration of 0.5 g/dL. The polymer exhibited a broad absorption band at 3400~3100 cm^{-1} due to amino (N-H) and hydroxyl (OH) groups, and a strong carbonyl absorption at 1650 cm^{-1} in IR spectrum [12]. The ^{1}H-NMR spectrum of the polymer also showed the hydroxyl (10.4 ppm) and amino (9.8 ppm) groups [13].

Synthesis of PBO Precursor Partially Protected by A Tetrahydropyranyl Group

Tetrahydropyranyl group is known as an effective hydroxyl or phenolic protecting group in organic synthesis [14-15]. It is an acid labile group and is easily deprotected from hydroxyl or phenolic group by acids. THP has been used to prepare photoresists through a chemical amplification process [16-20]. Based on the same concept, we synthesized a partially THP protected PBO precursor by the reaction of PBO precursor with 3,4-Dihydro-2H-pyran in the presence of p-toluenesulfonic acid monohydrate as a catalyst. The ^{1}H-NMR spectrum of THP protected polymer showed the THP peaks at 1.4~1.8 ppm ($-CH_2-CH_2CH_2-$), 2.8 ppm ($-O-CH_2-$) and 4.8 ppm (-O-CH-O-). The protecting level was estimated to be 35 % from ^{1}H-NMR by comparing the ratio of methylene protons in THP to the aromatic protons on the polymer.

Polymer Characterization

Table 1 summarizes the qualitative solubility of the BisAPAF-IC PBO precursor, 35% THP protected BisAPAF-IC PBO precursor, and the corresponding BisAPAF-IC PBO. The BisAPAF-IC PBO precursor and the 35 % THP protected BisAPAF-IC PBO precursor were soluble in many solvents, but the cured PBO did not dissolve in any organic solvents. The cured BisAPAF-IC PBO film displayed good thermal stability. Its TGA thermogram, which was obtained with a heating rate of 10 °C/min, showed 5% weight loss at 550 °C in nitrogen. The IR spectrum of the cured PBO film appeared a new characteristic absorption of benzoxazole ring at 1620 cm^{-1} and disappearance of the broad absorption of 3400~3100 cm^{-1} (OH groups) and 1650 cm^{-1}(carbonyl groups of polyhydroxyamide).

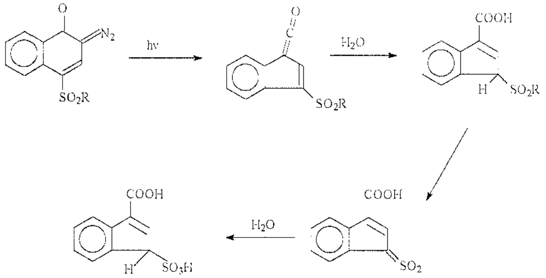
Table 1. Solubility of BisAPAF-IC PBO precursor, 35% THP protected BisAPAF-IC PBO precursor and cured PBO

Solvent	BisAPAF-IC PBO Precursor	35% THP Protected BisAPAF-IC PBO Precursor	Cured BisAPAF-IC PBO
NMP	+	+	-
DMAC[a]	+	+	-
DMF[b]	+	+	-
THF[c]	+	+	-
Acetone	+	+	-
Ethanol	+	+	-

+: soluble, -: insoluble [a] DMAC : Dimethylacetamide
[b] DMF : Dimethylformamide [c] THF : Tetrahydrofuran

Lithographic evaluation

A photosensitive PBO photoresist was prepared by the addition of a photoacid generator to the THP protected PBO precursor. Because PBO precursors are not transparent in the deep UV area, most photoacid generators used in 254nm and 193nm photoresists, such as onium salts, nitro benzyl esters and halogenated organic compounds, are not suitable in the PBO system because they only have absorption in the deep UV area and are transparent in the g-line and I-line area. The photoacid used in this study was Bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4). Unlike the 1,2-naphthoquinone diazide-5-sulfonate (DNQ-5), which only produces weak carboxylic acid after irradiation, the DNQ-4 generates both carboxylic acid and strong sulfonic acid according to Scheme 4 [21]. The strong sulfonic acid is able to deblock the tetrahydropyranyl group from THP protected PBO precursor, enabling the restoration of its aqueous base solubility. Hayase et al. have reported using DNQ-4 as a photoacid generator to prepare a photoresist based on partially t-butoxycarbonylmethylared poly(4-hydroxystyrene) [22].



Scheme 4. Photoreaction Mechanism of DNQ-4

The 35 % THP protected BisAPAF-IC PBO precursor has a high transmittance above 360 nm as shown in the UV-visible spectrum (Figure 1). This is due to the presence of the hexafluoroisopropylidene (6F) group in the polymer backbone, which can separate chromophoric groups. Therefore the DNQ-4, having a strong absorption in the range of 320~450 nm, can be used as the photosensitive compound in the resist formulation. Figures 2 displays the absorption spectra of 35% THP protected PBO precursor with 20% DNQ-4 before and after exposure. It is clear that the absorption peak at 365 nm of DNQ-4 is bleached. That ensures the bottom of the resist layer can also be exposed and obtain good lithographic results.

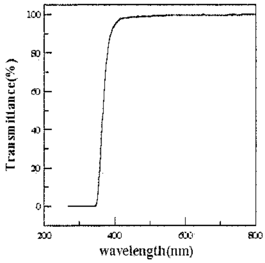


Figure 1. UV-visible spectrum of THF solution of 20% THP protected BisAPAF-IC PBO precursor

Hattori et al. have reported that the photoresist derived from a fully THP protected poly(4-hydroxystyrene) suffered from poor developability, and 30% protection was enough to inhibit the aqueous base dissolution of the polymer [23]. In the present study, a 35% THP protected PBO precursor was used as the base polymer. Using a 0.6 wt % TMAH solution as the developer, the dissolution rate was estimated by measuring the film thickness after development. The dissolution rates of the BisAPAF-IC PBO precursor, the 35% THP protected BisAPAF-IC PBO precursor, and the 35% THP protected BisAPAF-IC PBO precursor with 20% DNQ-4 before and after exposure, are shown in Table 2. Due to the THP protecting groups, the dissolution rate of 35 % THP protected PBO precursor decreased from 0.148 μ m/s to 0.015 μ m/s. The ratio of dissolution rate of 35 % THP protected PBO precursor before and after exposure is about 46. The high dissolution rate contrast is expected to have a high resolution. The exposure characteristic curve of a 3 μm film for the 35% THP protected BisAPAF-IC PBO precursor/DNQ-4 system developed by a 0.6 wt % TMAH solution is shown in Figure 3. The system's sensitivity is 221 mJ/cm^2 and the contrast is 1.44. A resolution of 10 μm pattern can be obtained in a 3μm film. The 35% THP protected BisAPAF-IC PBO precursor was finally cured at 350 °C for 1h to give the thermally stable PBO pattern (Figure 4). The most important contribution of the THP protecting group on the photosensitive PBO precursor composition is reducing the dark film loss after development. Compared to the unprotected PBO precursor/DNQ-4 system, which has a high dark film loss of 36.5%, the THP protected PBO precursor/DNQ-4 system only has a 8.92% dark film loss after development that can be attributed to the considerable decrease in the dissolution rate of the 35 % THP protected PBO precursor. It is expected that the low dark film loss could help in making thick films photoresist for use in microelectronic applications.

Table 2. Dissolution rates of BisAPAF-IC PBO precursor, the 35% THP protected BisAPAF-IC PBO precursor, the 35% THP protected BisAPAF-IC PBO precursor/20% DNQ-4 before and after exposure

Polymer	Dissolution rate (μm / s)
BisAPAF-IC PBO precursor	0.148
35% THP protected BisAPAF-IC PBO precursor	0.015
35% THP protected BisAPAF-IC PBO precursor +20% DNQ-4 (before exposure)	0.003
35% THP protected BisAPAF-IC PBO precursor +20% DNQ-4 (after exposure)	0.140

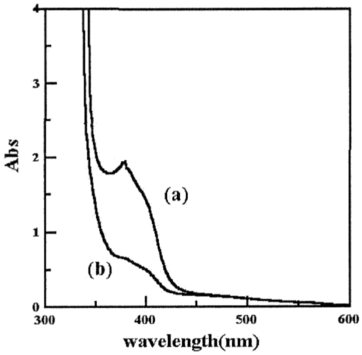


Figure 2. UV-visible spectra of 35 % THP protected BisAPAF-IC PBO precursor film with 20 wt % DNQ-4

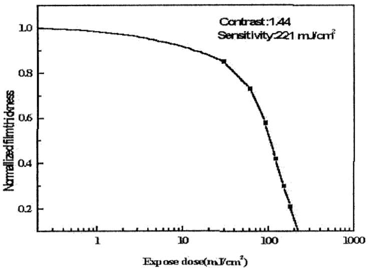


Figure 3. Characteristic exposure curve of 35 % THP protected BisAPAF-IC with 20 wt % DNQ-4 system

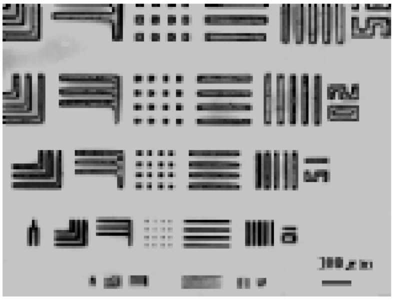


Figure 4. Optical micrograph of a pattern from 35 % THP protected BisAPAF-IC /DNQ-4 system and cured at 350 °C for 1h

Conclusions

A partially THP protected BisAPAF-IC PBO precursor was prepared from the low temperature polymerization of 2，2'-bis-(3-amino-4-hydroxyphenyl) hexafluoropropane (BisAPAF) and isophthaloyl chloride (IC) followed by reacting with 3,4-Dihydro-2H-pyran in the presence of p-toluenesulfonic acid monohydrate as a catalyst. A novel positive-working, aqueous base developable photosensitive resin composition was prepared from this polymer and a Bisphenol A based 1,2-naphthoquinpne diazide-4-sulfonate (DNQ-4) photoacid generator. The partially THP protected photosensitive PBO precursor containing 20 wt% DNQ-4 photoacid generator showed a sensitivity of 221 mJ/cm^2 and a contrast of 1.44 in a 3μm film. A pattern with a resolution of 10 μm was obtained from this composition. Due to the decrease of THP protected polymer's dissolution rate, the novel PBO precursor photosensitive composition showed a significant decrease in dark film loss after development and has the potential to make a thick film resist.

Acknowledgements. The financial support provided by the National Science Council (Taiwan, ROC) through project NSC 90-2216-E-006-028 is greatly appreciated.

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