

A novel kind of photosensitive polyimides

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Abstract

Polyimides PI-OH containing hydroxyl group were synthesized by condensation of 4,6-diaminoresocinol hydrochloric (DAR), 4, 4'-oxydianiline (ODA) and 4,4'-oxydiphthalic anhydride (ODPA). The positive photoresist consisting of PI-OH and 20 wt% 1,2-naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC-5) shows a sensitivity (D^0) of 225 mJ/cm² and a resolution of about 4 μm with development in 2% tetramethylammonium hydroxide (TMAH) aqueous solution. PI-OH can be further acrylated to introduce the methylacrylate groups into polyimide chain to obtain the negative PSPI PI-A, which shows good photolithographic properties, with a line width about 8 μm and a sensitivity ($D^{0.5}$) of 250 mJ/cm².

Key words:

Polyimide; Photosensitive; Positive; Negative

1. Introduction

As high performance polymer materials with exceptional thermal stability, mechanical and electrical properties, polyimides (PIs) have been widely used in many fields such as aerospace, electrical and microelectronics industries [1-7]. Photosensitive polyimides (PSPIs) have recently obtained much attention and played very important roles in the field of semiconductor manufacturing as protection and insulation layer because of much simplified and safer processing steps required for getting a desired pattern [8-17]. In generally, photosensitive polyimide includes two types: one is the positive and the other is negative. Because of their poor solubility, photosensitive polyimides are usually used in the form of poly (amic acid) precursors, which requires thermal imidization after patterning. In some cases, it is difficult to make them suitable for practical processing because thermal imidization requires a high temperature and causes great shrinkage in the patterned films during thermal cyclization. Therefore, fully imidized photosensitive polyimides are highly desired to overcome these problems.

In this text, an aromatic diamine 4,6-diaminoresocinol hydrochloric (DAR) was chosen to copolymerize with 4, 4'-oxydianiline (ODA) and 4,4'-oxydiphthalic anhydride (ODPA) to get hydroxyl-polyimide (PI-OH), which can be used as the positive PSPIs in the presence of diazonaphthoquinone (DNQ) as photoreactive compound because the phenol group makes PI-OH dissolved in alkali solution. The acrylate group can be introduced into the PI-OH chain through acylation of phenol group to get PI-A, which can be used as a novel negative PSPIs.

2. Experimental Part

Materials

1,2-Naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC-5) and 4,6-diaminoresocinol

dihydrochloric (DAR) (Synthesized in our lab according to references [18,19]), 4, 4'-oxydianiline (ODA), 4,4'-oxydiphthalic anhydride (OPDA) (From Shanghai Research Institute of Synthetic Resins), 2-mercaptobenzazole (MBO), γ -valerolactone (from Acros), methyl acryloyl chloride (Shanghai Zhixing Chemical Company). 25% tetramethylammonium hydroxide (TMAH) aqueous solution (From Guoyao Chemical Reagent Company). Hexaarylbiimidazole (HABI) (From Shanghai Jitong Company) .Other chemicals are of analytical grade except as noted.

Synthesis of hydroxyl polyimide (PI-OH)

DAR (2.13g 9 mmol), ODA (0.6g 3 mmol) and triethylamine(TEA, 2.08g, 20 mmol) were added to 25 ml N-methyl-2- pyrrolidone (NMP) and 8 ml toluene solution. After the mixture was completely dissolved, ODPA (3.72 g, 12 mmol), γ -valerolactone (0.2g, 2 mmol) and pyridine(0.16g, 2 mmol) were added to the solution. Then the mixture was stirred under N_2 at 180°C for 5 hours. After cooling to the room temperature, 20 ml NMP was added to the mixture, which was precipitated in methanol/water (V/V=1/1). The polymer (PI-OH) was collected by filtration and dried in vacuo 80°C.

$M_n=8.6 \times 10^4$ (determined by GPC using DMF as eluent). 1H NMR ($[-d_6]$ DMSO, 400 MHz): $\delta=6.63-8.08$ (19H, aromatic), 10.15 (3H, OH). FT-IR (KBr cm^{-1}): 3 100-3500(O-H), 1778, 1721, 1376 (imide ring). T_g (DSC in N_2 , 10°C/min): 350°C; T_d (TGA in N_2 , 15°C/min): 425°C.

Synthesis of acrylated photosensitive polyimide (PI-A)

An excess amount (2.01g 20 mmol) of methyl acryloyl chloride was dissolved in 10 ml NMP, then added dropwise to a solution of PI-OH (2.0g) and TEA (2.02g 20mmol) in 20 ml NMP solution over 1h at 0°C. The mixture was warmed to room temperature and stirred for 12 h. Then the mixture was filtered to remove triethyl ammonium chloride and poured into methanol. The precipitate was collected by filtration and dried in dried in vacuo 40°C.

1H NMR ($[-d_6]$ DMSO, 400 MHz): $\delta=6.53-8.08$ (19H, aromatic), 5.99-5.95 (6H, $CH_2=C$), 1.83 (9H, CH_3); FT-IR (KBr):1778, 1376 (imide ring), 1720-1730(imide ring and $\overset{O}{\parallel}C-$), 2950 (C-H), 1626 cm^{-1} (C=C). T_g (DSC in N_2 , 10°C/min): 250 °C; T_d (TGA in N_2 , 15°C/min): 350°C.

Analysis

Molecular weights were determined by gel permeation chromatography (GPC) on a PerkinElmer Series 200 apparatus on the basis of linear polystyrene (PS) standards. DMF was used as eluent.

1H NMR spectra were recorded on a Mercury Plus 400Hz spectrometer with DMSO- d_6 as solvent.

FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer.

UV-vis spectra were recorded by Perkin-Elmer Lambda 20 UV-vis spectrophotometer. PI was coated on the quartz slide.

Differential scanning calorimetric (DSC) analysis was conducted on a Pyris 1 DSC.

Themogravimetric analysis (TGA) was recorded on PerkinElmer TGA-7.

The polyimide patterning images were obtained with JSM-7410F scanning electron

microscope.

Determination of the photosensitivity

The positive PSPI was formulated by PI-OH as a matrix resins and DNQ compound, PC5 (Scheme 2), as a photosensitive agent (20 wt% for PI-OH) dissolved in N,N-dimethyl acetamide (DMAc) at a solid content of 10 wt%. The films were prepared via spin coating on clean silicon substrates and prebaked at 80 °C for 30 min. The thickness of films was about 2 μm. The photoresist films were exposed to a 250 W high-pressure mercury lamp with a UV dose of 1.5 mW/cm². The films were then developed in aqueous tetramethylammonium hydroxide (TMAH 2 wt%) and rinsed with water. After the development, the films were dried at 80 °C for 2 h. The weights of the remaining films were plotted against the log of the exposure dose. The sensitivity and contrast of the photoresists were determined from the plots.

The negative PSPI was formulated by PI-A and photoinitiator systems containing HABI and MBO dissolved in DMAc at a solid content of 5 wt%. The processes for preparing the films and exposure are the same to positive PSPI. The films were developed in a mixture of DMAc/2-propanol (v/v=5/1) for 3 min and rinsed with 2-propanol. After the development, the films were dried at 80 °C for 2 h. The weights of the remaining films were plotted against the log of the exposure dose. The sensitivity and contrast of the photoresists were determined from the plots.

Preparation of polyimide patterns

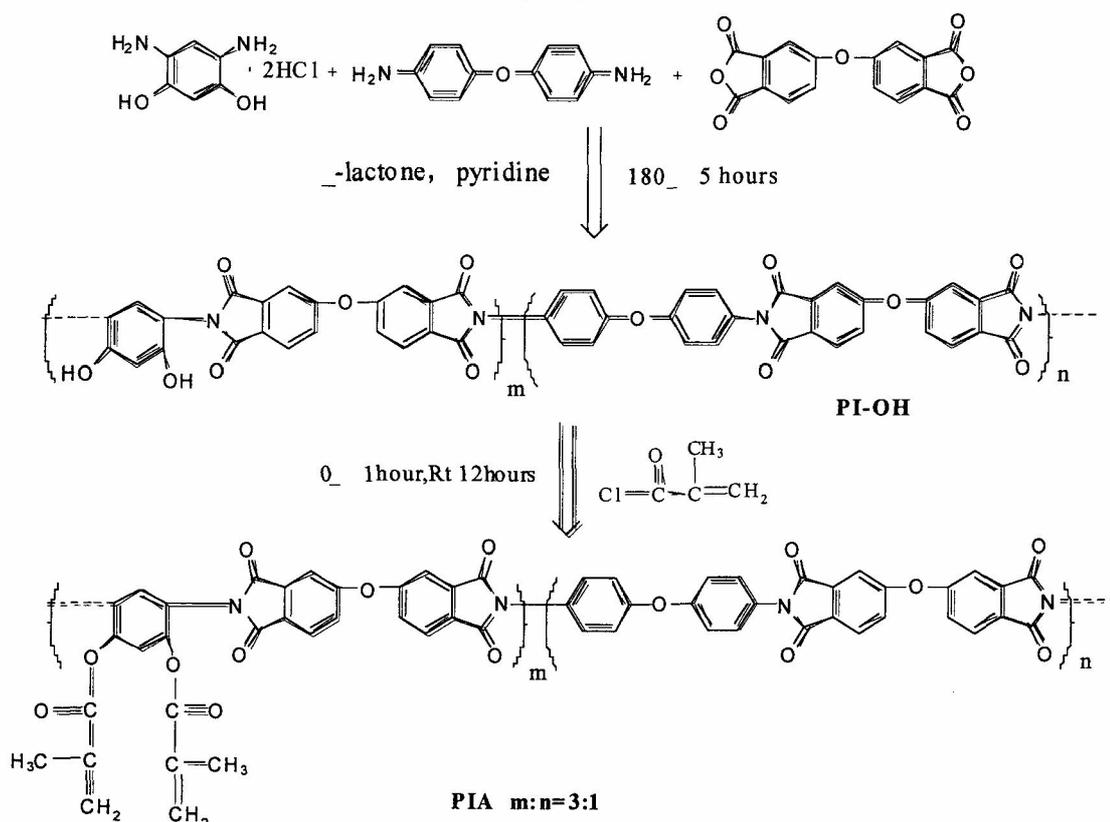
The polymer solutions were coated and prebaked with procedure described for photosensitivity study. The films were exposed in the contact mode with a mask using a 250 W high-pressure mercury lamp with a UV intensity of 1.5 mW/cm². The exposure doses for the positive and the negative films are 270 mJ/cm² and 450 mJ/cm², respectively. The positive PSPI films were then developed in aqueous tetramethylammonium hydroxide (TMAH 2 wt%) and rinsed with water. The negative PSPI films were then developed in a mixture of DMAc/2-propanol (v/v=5/1) for 3 min and rinsed with 2-propanol. After development, the patterns of positive and negative PSPI were dried for 2 h at 200 °C and 80 °C, respectively, and evaluated with microscope and SEM.

3 Results and discussions

3.1 Synthesis of photosensitive polyimide PI-OH and PI-A, and their properties

The photosensitive polyimides PI-OH and PI-A were synthesized according to Scheme 1. In the presence of catalyst γ -valerolactone and pyridine, the positive PSPI PI-OH were prepared by polycondensation of ODPA, ODA and DAR. The methyl acrylate group can be further introduced into the side-chain of PI-OH to obtain the negative PSPI PI-A by acrylation of hydroxyl group in PI-OH. The molecular weight (M_n) and polydispersity (M_w/M_n) of PI-OH were 8.6×10^4 and 2.2, respectively, determined by GPC. The structure of PI-OH and PI-A was fully characterized by FT-IR (Fig. 1) and ¹H NMR (Fig. 2). FT-IR study showed the characteristic absorption of imide ring at 1778, 1721 and 1376 cm⁻¹. The signal for hydroxyl group appeared in both ¹H NMR (10.14 ppm) and FT-IR (3100-3500 cm⁻¹) spectra. These indicate the success for synthesis of PI-OH. The component of PI-OH was determined by ¹H

NMR (hydroxyl/aromatic ring), which showed m:n is about 3:1, almost same to the ratio of reaction feed (DAR/ODA). Through acrylation of hydroxyl group in PI-OH, methyl acrylate group can be easily introduced into the side-chain to obtain PI-A. Compared with PI-OH, FT-IR and ^1H NMR of PI-A showed signals related to methylacrylate groups and no characteristic signal of hydroxyl group, which indicated the successful introduction of methylacrylate groups and almost complete acrylation of the hydroxyl groups in PI-OH.



Scheme 1 Process for synthesis of polyimide

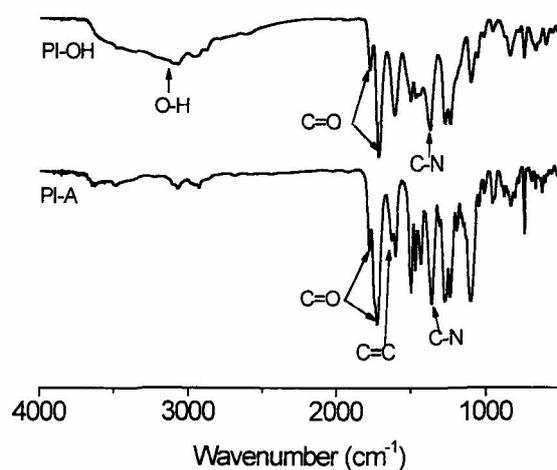


Figure 1. FT-IR spectra of PI-OH and PI-A

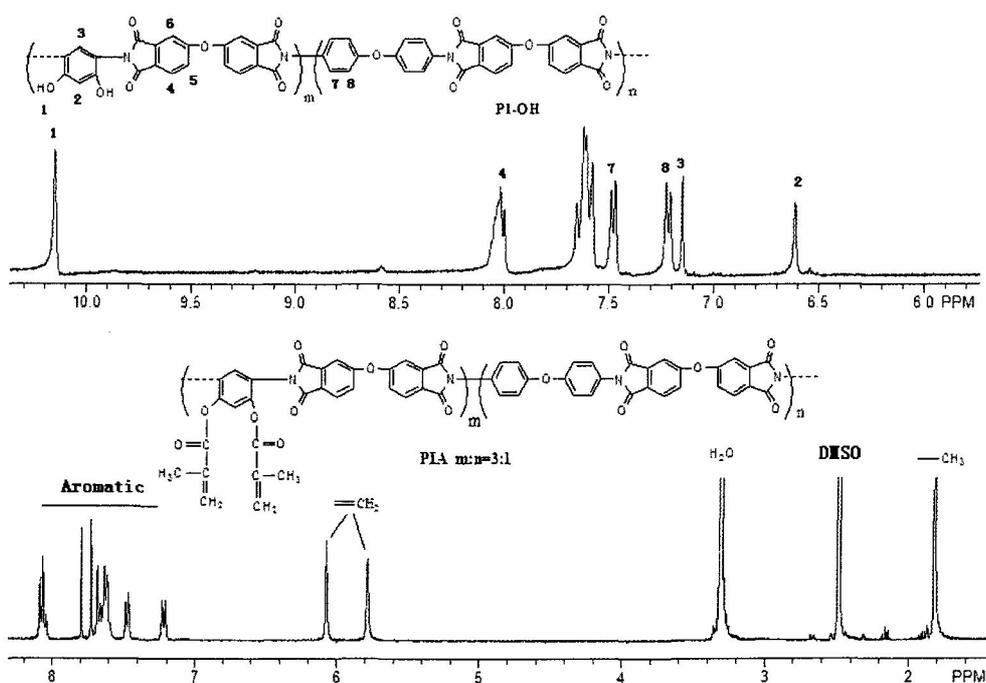


Figure 2. ^1H NMR spectra of PI-OH and PI-A

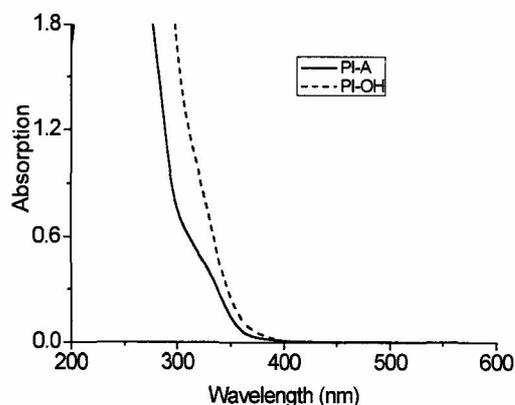


Figure 3. UV-Vis absorption spectra of PI-OH and PI-A

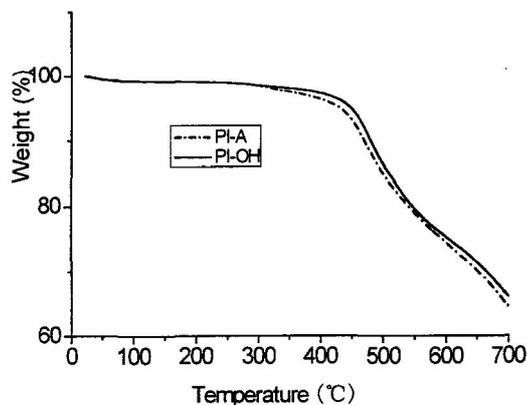


Figure 4. TGA curves of PI-OH and PI-A

Fig. 3 shows the UV-vis spectra of PI-OH and PI-A. Films of about $2\ \mu\text{m}$ thick were used and prepared by the spin coating of polymer solution on quartz slide. Both PI-OH and PI-A had a cutoff wavelength below 400nm. Compared with PI-OH, the UV-vis absorption of PI-A is shorter, which may be caused by introduction of methylacrylate groups through acrylation of hydroxyl groups in PI-OH. The larger methylacrylate groups in side-chain of PI-A might lead to looser packing between imide rings, resulting in a lower charge-transfer effect and a lower cutoff wavelength. This also indicates the introduction of methylacrylate groups into the PI-OH chain. The TGA curves for PI-OH and PI-A are shown in Fig.4. The decomposition temperature for PI-OH and PI-A is about 400°C and 300°C , respectively. In comparison with PI-OH, the lower

decomposition temperature for PI-A may be attributed to the heat decomposition of methacrylate groups.

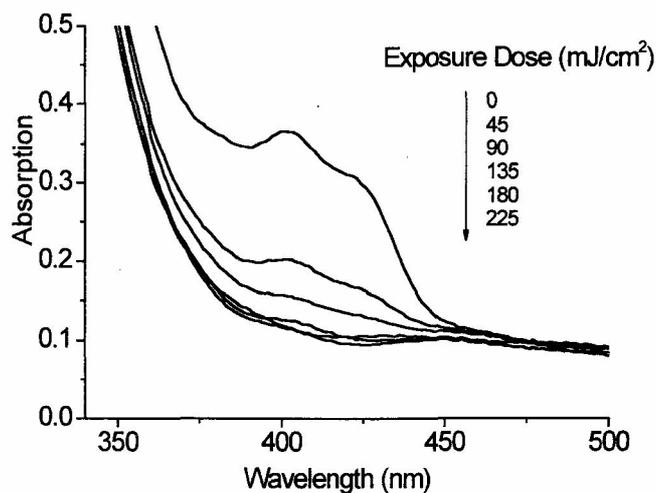


Figure 5. Changes of UV-vis spectra of the negative photoresist film consisting of PI-OH and PC5 (20 wt% for PI-OH)

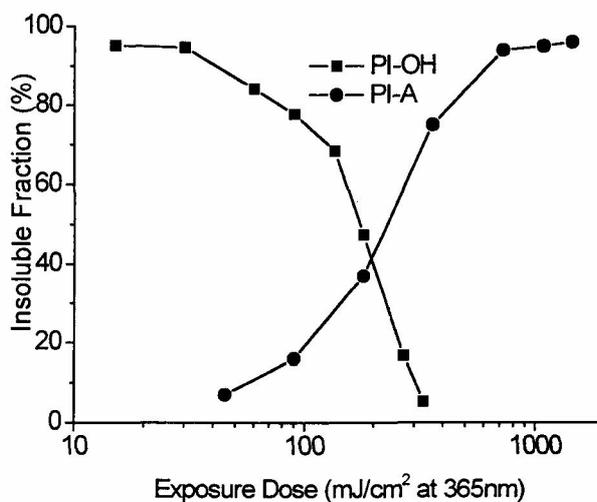


Figure 6. Characteristic UV-exposure curves for the positive PSPI PI-OH and the negative PSPI PI-A

3.2 Photolithography of the positive PSPI PI-OH

The PC5 was chosen as photoactive DNQ compound for PI-OH. Under the UV irradiation, the changes of the UV-vis spectra corresponding to PSPI films of PI-OH containing 20 wt% of PC5 are shown in Fig. 5. The intensity of characterized absorption band at 400nm decreased rapidly upon irradiation. This absorption band disappeared completely at 225 mJ/cm², which indicates that the positive PSPI systems consisting of PI-OH and PC5 would be expected work as photoresist. Fig.6 shows the sensitivity curves of PSPI film consisting of PI-OH and 20 wt%

of PC5. The thickness of film is about 2 μ m. Using 2% TMAH aqueous solution as the developer, the sensitivity (D^0) is about 225 mJ/cm².

The pattern images of positive PSPI PI-OH were obtained under a UV exposure dose of 225mJ/cm² in a contact mode with a mask. Fig. 7 shows the typical pattern of micrographs of positive PSPI PI-OH, from which we can know the resolution is about 4 μ m.

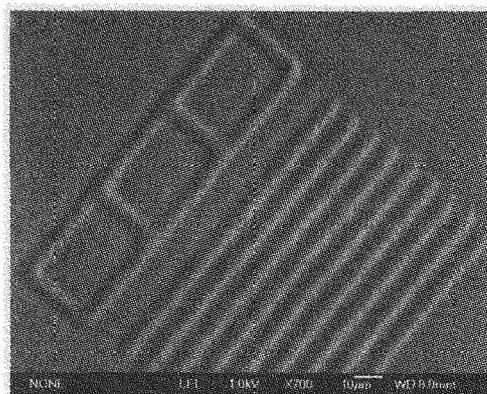


Figure 7. SEM image of photolithographic patterns for the positive PSPI PI-OH

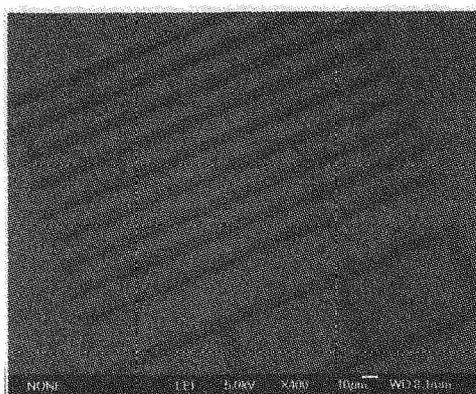


Figure 8. SEM image of photolithographic patterns for the negative PSPI PI-A

3.3 Photolithography of the negative PSPI PI-A

To determine the photolithographic properties of the negative PSPI PI-A, thin films of about 2 μ m were prepared by spin coating. The photosensitivity was evaluated by the subsequent determination of the insoluble fraction as a function of exposure dose (Fig. 6). The exposure energy to obtain a 0.5 gel fraction ($D_g^{0.5}$) is about 250 mJ/cm². The patterning images of the PFPS-PI were obtained under a UV exposure dose of 450 mJ/cm² in a contact mode with a mask. Figure 8 shows the typical pattern of the micrographs of PFPS-PI, from which we can know that the width of line is about 8 μ m.

Conclusions

Two kinds of photosensitive polyimides PI-OH and PI-A were synthesized by condensation of DAR, ODA and ODP, and by introducing methylacrylate groups into PI-OH chain. In the presence of PC5 (20wt% for PI-OH), the positive PSPI PI-OH shows a sensitivity (D^0) of 225 mJ/cm² and a resolution of about 3 μ m with development in 1% tetramethylammonium hydroxide (TMAH) aqueous solution. The negative PSPI PI-A shows good photolithographic properties, with a line width about 8 μ m and a sensitivity ($D^{0.5}$) of 250 mJ/cm².

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