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Polymer 47 (2006) 2942–2945

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Polymer Communication

A novel negative photoinitiator-free photosensitive polyimide

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Received 15 January 2006; received in revised form 21 February 2006; accepted 5 March 2006

Abstract

A novel negative photoinitiator-free photosensitive polyimide (PFPS–PI) was synthesized through introducing the photosensitive 4,4-bis[(4-amino)thiophenyl] benzophenone (BATPB) into backbone chain and methyl acrylate group into side-chain of the polyimide, respectively. Photosensitive properties study revealed its good photolithographic properties, with a resolution about 5 μm and a sensitivity of 150 mJ/cm^2.

Keywords: Photoinitiator-free; Photosensitive; Polyimide

1. Introduction

Polyimides (PIs) are high-performance polymer materials with exceptional thermal stability and mechanical and electrical properties, which have been widely applied in the aerospace, electrical, and microelectronics industries [1–7]. Because their applications allow much simplified and safer processing steps required for obtaining a desired pattern, photosensitive polyimides (PSPIs) have recently gotten much attention and played very important roles in the field of semiconductor manufacturing as protection and insulation layers [8–16]. In the most of photosensitive polyimide systems, low-molecular weight molecule such as photoinitiators must be needed to sensitive to UV-light for pattern [3,5]. In fact, only a little part of photoinitiators can be used up in illumination process, resulting in a large amount of photoinitiator residues, which leads to decrease in thermal, mechanical and electrical properties of photoresist films [17,18]. Therefore, photoinitiator-free photosensitive polyimides are highly desired to overcome this problem.

In this text, a photosensitive aromatic diamine 4,4-bis[(4-amino)thiophenyl] benzophenone (BATPB) was chosen to copolymerize with 4,6-diaminoresocinol hydrochloric (DAR) and 4,4′-oxydiphthalic anhydride (ODPA) to get hydoxy–polyimide (PI–OH), which can be further acidylated by methyl acryloyl chloride to obtain negative photoinitiator-free photosensitive polyimide. The photoresist show a patterning resolution than 5 μm with low 365 nm-UV exposure dose 450 mJ/cm^2.

2. Experimental part

2.1. Materials

4,6-Diaminoresocinol dihydrochloric (DAR) and 4,4-bis[(4-amino)thiophenyl] benzophenone (BATPB) (synthesized in our lab according to references [19,20]), 4,4′-oxydiphthalic anhydride (OPDA) and γ-valerolactone (from Acros), methyl acryloyl chloride (Shanghai Zhixing Chemical Company). Other chemicals are of analytical grade except as noted.

2.2. Synthesis of hydroxyl polyimide (PI–OH)

DAR (2.13 g 0.9 mmol), BATPB (0.501 g 0.1 mmol) and triethylamine(TEA, 0.208 g, 2 mmol) were added to 25 ml methyl pyrrolidone (NMP) and 8 ml toluene solution. After the mixture was completely dissolved, ODPA (3.10 g, 1 mmol), γ-valerolactone (0.2 g, 2 mmol) and pyridine(0.16 g, 2 mmol) were added to the solution. Then the mixture was under N_2 at 180 °C for 5 h. 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.

$M_n = 7.7 \times 10^4$ (determined using DMF as eluent). Elemental analysis: Calcd C 64.6, H 2.6, N 6.4, S 1.3. Found C 64.7, H 2.5, N 6.3, S 1.4. ^{1}H NMR ([-d_6] DMSO, 400 MHz): $\delta = 6.63$–8.08 (5H, aromatic), 10.15 (1H, OH). FT-IR (KBr): 3 100–3500 (O–H), 1778, 1721, 1376 (imide

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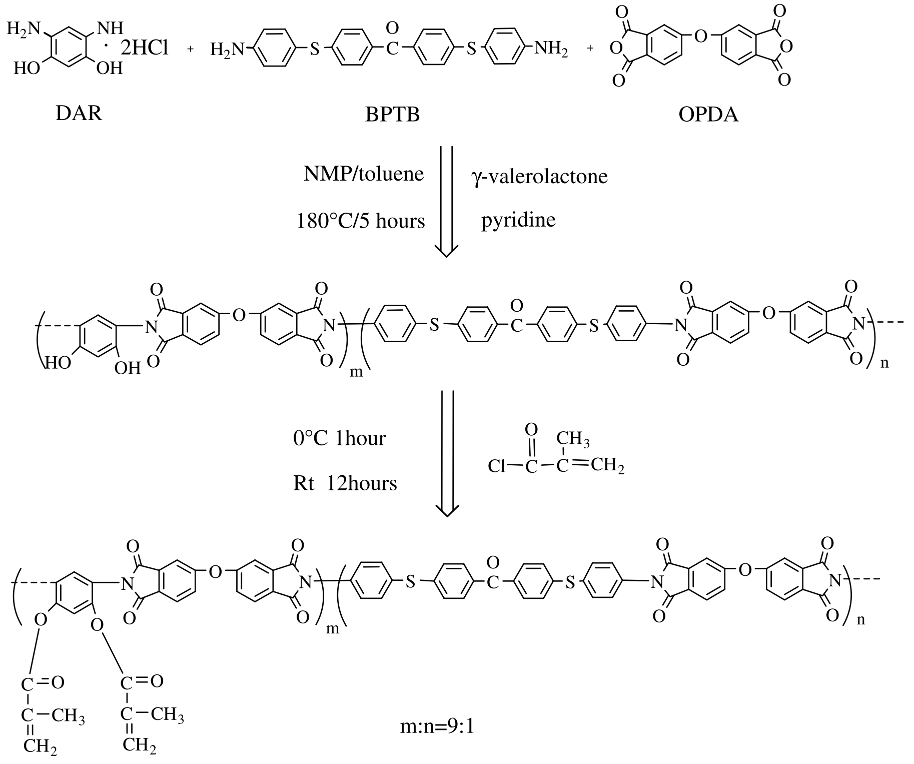
doi:10.1016/j.polymer.2006.03.022



Scheme 1.

ring), 1 652 cm^{-1}$\left(\mathrm{Ar-\overset{O}{\overset{\|}{C}}-Ar}\right)$. T_g (DSC in N_2, 20 °C/min): 285 °C; T_d (TGA in N_2, 20 °C/min): 400 °C.

2.3. Synthesis of photoinitiator-free photosensitive polyimide (PFPS–PI)

An excess amount (2.01 g 20 mmol) of methyl acryloyl chloride was dissolved in 10 ml NMP, then added dropwise to a solution of PI–OH (2.0 g) and TEA (2.02 g 20 mmol) in 20 ml NMP solution over 1 h 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.

^{1}H NMR ([-d_6] DMSO, 400 MHz): δ=6.63–8.08 (5H, aromatic), 5.99–5.95 (2H, CH_2=C), 1.83 (3H, CH_3); FT-IR (KBr):1778, 1376 (imide ring), 1720–1730 (imide ring and $\left(\mathrm{R-\overset{O}{\overset{\|}{C}}-}\right)$, 1 652$\left(\mathrm{Ar-\overset{O}{\overset{\|}{C}}-Ar}\right)$, 2950 (C–H), 1626 cm^{-1} (C=C). T_g (DSC in N_2, 20 °C/min): 235 °C; T_d (TGA in N_2, 20 °C/min): 300 °C.

2.4. Analysis

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

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

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

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

Elemental analysis was conducted on an Elementar Varioel apparatus.

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

Themogravimetric analysis (TGA) was recorded on Perkin–Elmer TGA-7.

The polyimide patterning images were obtained with Profile Measurement Microscope VF-7500 Series and FEI SIRION 200 scanning electron microscope.

2.5. Determination of the photosensitivity

The photosensitive PFPS–PI was dissolved in *N*,*N*-dimethyl acetamide (DMA) at a solid content of 10 wt%. The films were prepared via spin coating on clean silicon substrates and prebaked at 80 °C for 2 h. 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/cm^2. The films were then developed in a mixture of DMA/2-propanol (v/v=5/1) for 3 min and rinsed with 2-propanol. After 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.

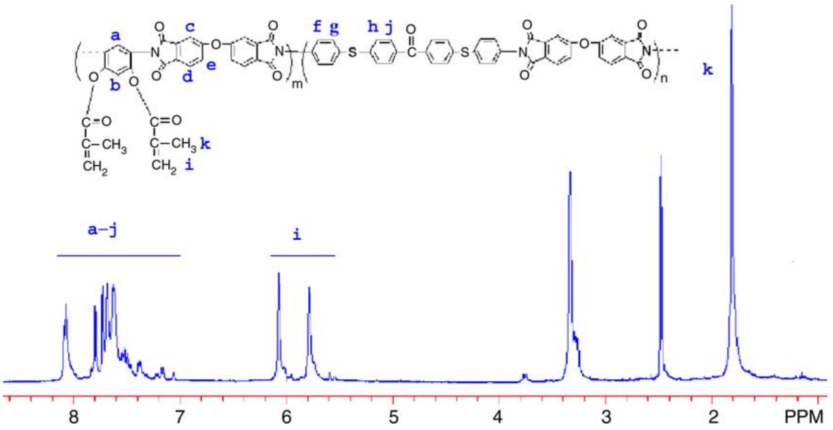


Fig. 1. ^{1}H NMR spectrum of PFPS–PI.

2.6. 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 for 3 min to a 250 W high-pressure mercury lamp with a UV dose of 1.5 mW/cm^2. The films were then developed in a mixture of DMA/2-propanol (v/v = 5/1) for 3 min and rinsed with 2-propanol. After development, the patterns were dried at 80 °C for 2 h and evaluated with SEM.

3. Results and discussions

The photosensitive polyimide was synthesized through two processes according to Scheme 1. The PI–OH was prepared through polycondensation in the presence of the catalyst systems of γ-valerolactone and pyridine. The molecular weight (M_n) and polydispersity (M_w/M_n) of PI–OH was determined by GPC as 7.7×10^4 and 2.1, respectively. The structure of polyimide was fully characterized by FT-IR, ^{1}H NMR (Fig. 1) and elemental analysis. 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 ^{1}H NMR (10.14 ppm) and FT-IR (3100–3500 cm^{-1}). These indicate the success for synthesis of PI–OH. The component of PI–OH was determined by elemental analysis result (sulfur content/nitro content) and ^{1}H NMR (hydroxyl/aromatic ring), which showed m:n is about 9:1, similar to the ratio of reaction material (DAR/BATPB). Through acrylation of hydroxyl group in PI–OH, methyl acrylate group can be easily introduced into polyimide side-chain to obtain photoinitiator-free photosensitive (PFPS–PI). FT-IR and ^{1}H NMR showed no characteristic signal of hydroxyl group, which indicated that the hydroxyl group was almost completely acrylated.

The UV–vis spectra of PI–OH and PFPS–PI are shown in Fig. 2(a), from which we can know that acrylation did not have obvious influence on the UV–vis absorption of polyimide. The films had a cutoff wavelength below 400 nm and a certain amount of absorption at 365 nm, which should be ascribed to C=O absorption of photosensitive BATPB. Because the high-pressure mercury lamp delivered a UV-light with the strongest emission at 365 nm, absorption at 365 nm can enhance the photosensitivity for photoresist film [21]. Upon the UV-light, BAPTB structure in the polyimide chain can photolysis to produce several kinds of radicals (Scheme 2), which can initiate polymerization of methyl acrylate group to form crosslinking system [22]. Similar to the other photoinitiator containing sulfur group such as phenylthiobenzophenone and keto-sulfoxide [22,23], BAPTB has the high photosensitivity, which is very important to photosensitivity of PFPS–PI. To determine the photolithographic properties of PFPS–PI, thin films about 2 μm thickness were prepared by spin coating on the silicon substrate. The photosensitivity was evaluated by the irradiation of the films with 365 nm UV-light and by the subsequent determination of the insoluble fraction

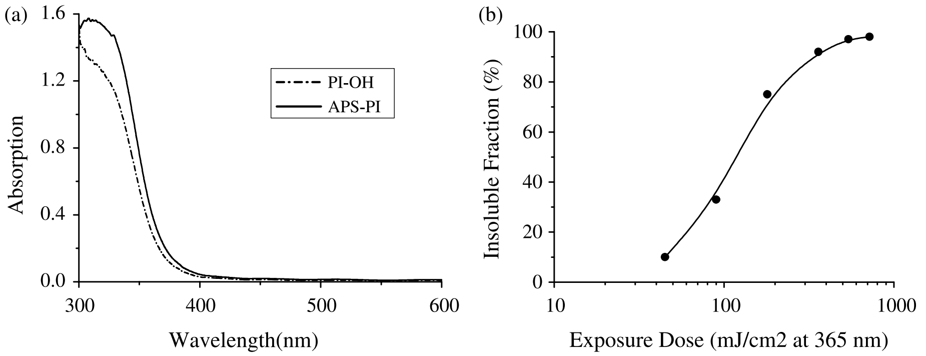
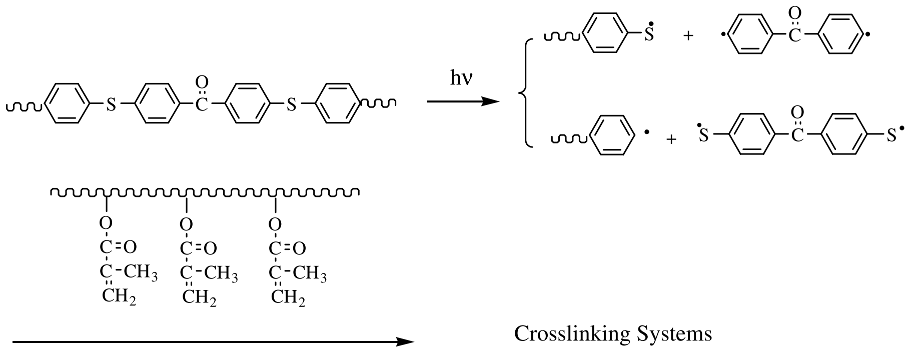
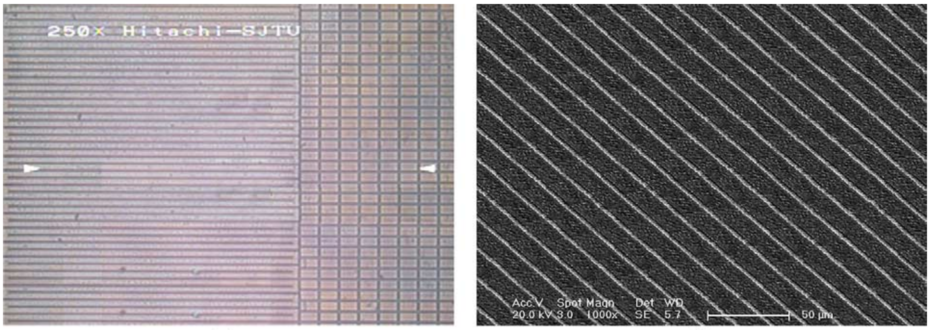


Fig. 2. (a) UV–vis absorption spectra of PI–OH and PFPS–PI; (b) characteristic UV-exposure curves for PFPS–PI.



Scheme 2.



(a) (b)

Fig. 3. Images of photolithographic patterns for PFPS–PI (a), optical photograph 250×; (b), SEM photograph 1000×.

after development as a function of exposure dose (Fig. 2(b)). The exposure energy to attain a 0.5 gel fraction ($D_g^{0.5}$) is about 150 mJ/cm^2, and showed high photosensitivity, which may be due to high photosensitivity of BATPB [20,22].

The patterning images of the PFPS–PI were obtained under a UV exposure dose of 450 mJ/cm^2 in a contact mode with a mask. Fig. 3 shows the typical pattern of the micrographs of PFPS–PI, from which we can know that the resolution is about 5 μm.

In conclusion, through introducing the photosensitive 4,4-bis[(4-amino)thiophenyl] benzophenone (BATPB) into backbone chain and methyl acrylate group into side-chain of the polyimide, we synthesized a novel negative photoinitiator-free photosensitive polyimide (PFPS–PI), which has its good photolithographic properties with a resolution about 5 μm and a sensitivity of 150 mJ/cm^2. Studies will be ongoing concerning the effect of BATPB amount in polyimide chain on the photosensitivity and the influence of acrylation reagent such as cinnamyl chloride and acryloyl chloride on the electrical and mechanical properties.

Acknowledgements

We thanks the Ministry of Science and Technology of China (NO: 2004AA33H010), Ministry of Education of China (Kuashiji Scholar Project) and the Science and Technology Commission of Shanghai Municipal Government for their financial support.

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