

Autophotosensitive Negative Polyimide

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ABSTRACT: A novel autophotosensitive polyimide (APSPI) was synthesized through introducing benzophenone (BP) moiety into the backbone chain and acrylate group into side chain of PI. The BP moiety can generate active radicals, which can initiate acrylate group to form crosslinked network. The study of photosensitive pro-

perties revealed its good photolithographic properties, with a resolution about 12 μm and a sensitivity of 330 mJ/cm^2 . © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3057–3062, 2009

Key words: autophotosensitive; negative; polyimide

INTRODUCTION

As one of the most important high-performance polymer materials with exceptional thermal stability and mechanical and electrical properties, polyimides (PIs) have been widely applied in the aerospace, electrical, and microelectronics industries.^{1–5} Because their applications allow more simplified and safer processing steps required for obtaining a desired pattern, photosensitive polyimides (PSPIs) have recently received much attention and played very important roles in the field of semiconductor manufacturing as protection and insulation layers.^{6–12} In most of the PSPI systems, low-molecular-weight molecule such as photoinitiators must be sensitive to UV light for fabrication of pattern.^{3,5} In fact, only a part of photoinitiators can be used in the illumination process, resulting in a large amount of photoinitiator residues. These small molecules lead to the decrease in thermal, mechanical, and electrical properties of photoresistant films, resulting in the limited application of PIs in some aspects.^{13,14} Therefore, autophotosensitive polyimides (APSPI) are highly desired to overcome this problem.

In the last decades, several types of APSPI, especially based on the benzophenone-containing polyimide (BP-PI), have been developed. Reiser and Yamashita^{15–17} reported that BP can abstract the hydrogen from alkyl group to generate radicals

under UV light, which can form crosslinked network by coupling according to Scheme 1. However, the photosensitivity of these APSPIs is low (about 1000 mJ/cm^2) because of the low crosslinked efficiency of coupling reaction of radicals.

Here, APSPI of high photosensitivity was synthesized by introducing acrylate groups into BP-PI. The unit of BP and alkyl-substituted benzene ring can be seen as Type-II photoinitiator systems to generate radicals under UV light, which can initiate polymerization of acrylate group to form crosslinked network. Compared with coupling reaction, the chain propagation of radicals is more efficient to form network, leading to higher photosensitivity. The APSPI photoresistant film shows a photosensitivity of 330 mJ/cm^2 .

EXPERIMENTAL PART

Materials

2,2'-Bis(3,5-dimethyl-4-aminophenyl)propane (BAPP) was purchased from Ken Seika Corp. 3,3',4,4'-Benzophenone dianhydride (BTDA) and 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (BAPAF) were purchased from TCI. Methyl acryloyl chloride was purchased from Shanghai Zhixing Chemical Company. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Aldrich. *N*-Methyl pyrrolidone (NMP) was dehydrated, by refluxing with calcium hydroxide, and redistilled. Pyridine and toluene were used as received.

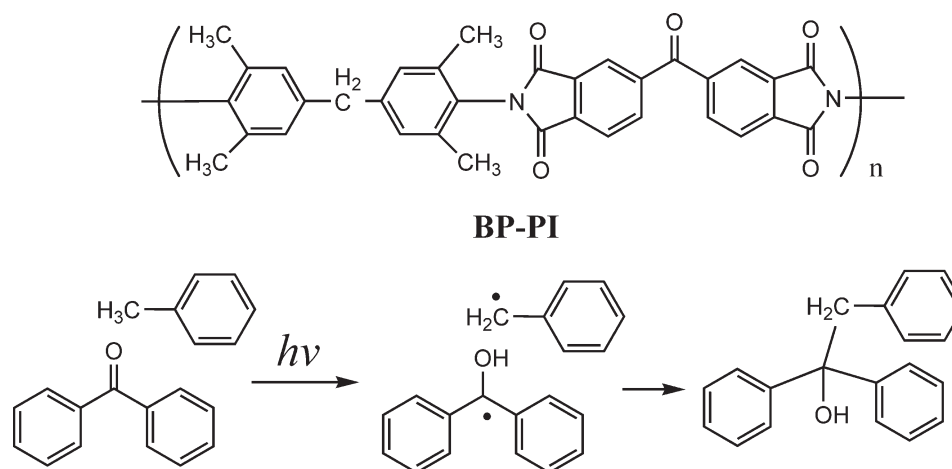
Polymer synthesis

PIs were prepared by a direct one-pot polycondensation of dianhydride with diamine in the presence of pyridine as catalyst. A typical example for the

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Scheme 1 Crosslinked mechanism for benzophenone-containing polyimide.

synthesis of APSPI is described as follows. BAPP (0.002 mol), BAPAF (0.002 mol), and pyridine (1 mL) were added to 20 mL of NMP and 7 mL of toluene solution. After the mixture was completely dissolved, BTDA (0.004 mol) was added to the solution. After stirring under N_2 for 1 h, the mixture was heated at 180°C for 2 h. Then, 7 mL toluene was added to the solution, which reacted for another 2 h. After cooling to room temperature, the resulting mixture was poured into 2-propanol, and then the precipitate (PI-OH) was collected by filtration and dried under vacuum at 80°C with a 89% yield. FTIR (KBr, cm^{-1}): 3100–3500 (O–H), 1780, 1725, 1372 (imide ring). 1H -NMR (DMSO- d_6 , 400 MHz): $\delta = 10.25$ (2H, O–H), $\delta = 7.02$ –8.25 (22 H, aromatic), 3.92 (2H, CH_2), 2.0 (12H, CH_3).

The obtained PI-OH (1.0 g) was dissolved in 20 mL NMP, and then 5 mL triethylamine (TEA) was added. An excess amount (5 mL) of methyl acryloyl chloride was added dropwise to the mixture over 2 h at 0°C. The mixture was warmed to room temperature and stirred for 5 h. Then, the mixture was filtered to remove triethyl ammonium chloride and poured into 2-propanol. The polymer (APSPI) was collected by filtration and dried under vacuum at 80°C with a 85% yield. FTIR (KBr, cm^{-1}): 1780, 1725, 1372 (imide ring), 1640 cm^{-1} (C=C). 1H -NMR (DMSO- d_6 , 400 MHz): $\delta = 7.02$ –8.25 (22 H, aromatic), 5.99–6.12 (4H, $CH_2=C$), 3.92 (2H, CH_2), 2.0 (12H, CH_3), 1.83 (6H, CH_3).

We also synthesized BP-PI through the reaction of BTDA and BAPP. BAPP (0.004 mol) and pyridine (1 mL) were added to 20 mL NMP and 7 mL toluene solution. After the mixture was completely dissolved, BTDA (0.004 mol) was added to the solution. After stirring under N_2 for 1 h, the mixture was heated at 180°C for 2 h. Then 7 mL toluene was added to the solution, which reacted for another 2 h.

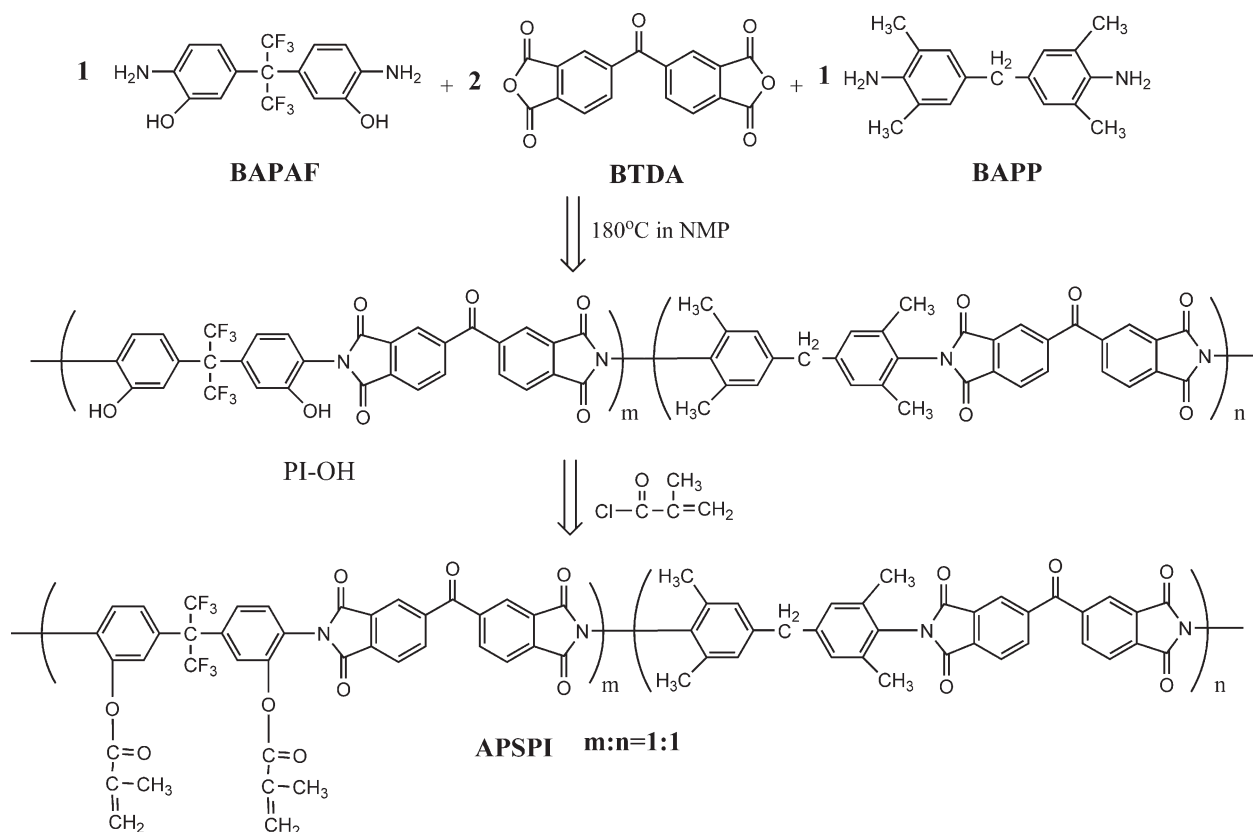
After cooling to room temperature, the resulting mixture was poured into 2-propanol, and then the precipitate (BP-PI) was collected by filtration and dried under vacuum at 80°C with a 82% yield. FTIR (KBr, cm^{-1}): 1780, 1725, 1370 (imide ring). 1H -NMR (DMSO- d_6 , 400 MHz): $\delta = 7.16$ –8.37 (6H, aromatic), 3.92 (2H, CH_2), 2.05 (12H, CH_3).

Analysis

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

1H -NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer with DMSO- d_6 as solvent. FTIR 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 at a scanning speed of 20°C/min. Thermogravimetric analysis (TGA) was recorded on PerkinElmer TGA-7 at a scanning speed of 20°C/min. The PI patterning images were obtained with FEI SIRION 200 scanning electron microscope (SEM).

ESR experiments were carried out with a Bruker EMX EPR spectrometer at 9.5 GHz with a modulation frequency of 200 kHz with DMPO as radical capturing agent. The PSPI was dissolved in chloroform. 0.5 mL of each sample was transformed into a quartz ESR tube and then purged with nitrogen to get rid of oxygen. A high-pressure mercury lamp with a cutoff filter (365 nm) was used for the irradiation on the polymer solution before ESR analysis.



Scheme 2 Synthesis of autophotosensitive polyimide (APSPI).

Determination of the photosensitivity

APSPI was dissolved in chloroform with a solid content of 10 wt %. The films were prepared via spin coating on clean silicon substrates and pre-baked at 80°C for 2 h. The thickness of films was about 2 μm. The photoresistant films were exposed to a 250-W high-pressure xenon lamp with a UV dose of 0.5 mW/cm². The films were then developed in a mixture of chloroform/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.

Preparation of polyimide patterns

The polymer solutions were coated and prebaked with the procedure described for photosensitivity study. The films were exposed in the contact mode with a mask for 20 min to a 250-W high-pressure xenon lamp with a UV dose of 0.5 mW/cm². The films were then developed in a mixture of chloroform/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.

RESULTS AND DISCUSSION

Polymer synthesis

The APSPI was synthesized through introducing acrylate groups into side chain of BP-PI according to Scheme 2. PI-containing benzophenone and hydroxyl group (PI-OH) was prepared through polycondensation of BTDA, BAPAF, and BAPP. Through acrylating of hydroxyl group in PI-OH, we could introduce methyl acrylate group easily into PI side chain to obtain APSPI. PI-OH and APSPI were characterized by FTIR, ¹H-NMR, and GPC. The signals related to

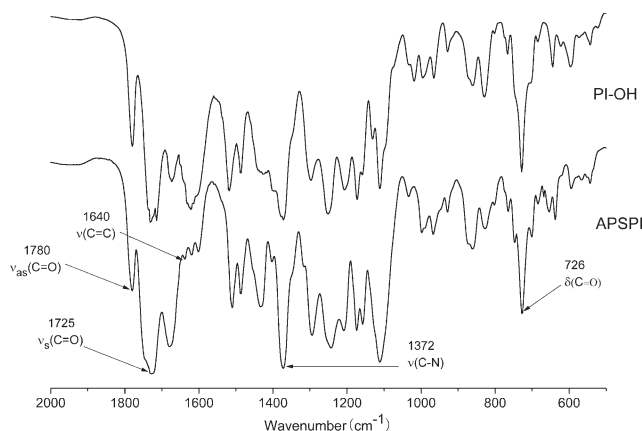


Figure 1 FTIR spectrum of PI-OH and APSPI.

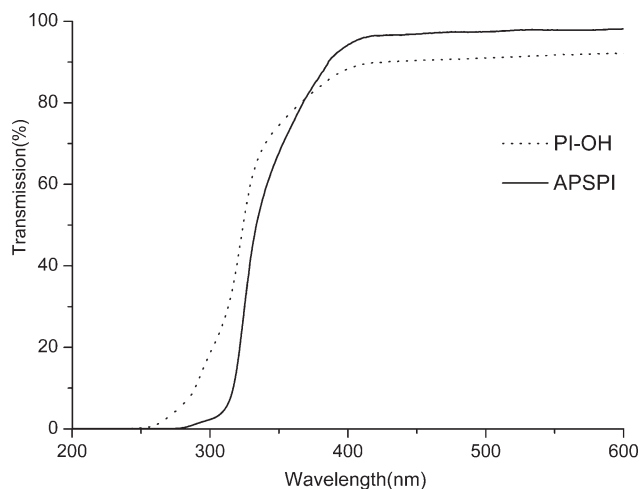


Figure 2 UV-vis transmission spectrum of PI-OH and APSPI.

the imide ring at 1780, 1725, and 1372 cm^{-1} in FTIR spectrum (Fig. 1) indicated the success of PI synthesis. Compared with PI-OH, the appearance of signal at 1640 cm^{-1} related to C=C shows that methyl acrylate group was successfully introduced into PI. This can be further confirmed by the disappearance of OH signal at 10.25 ppm and appearance of C=C signal at 5.99–6.12 ppm in $^1\text{H-NMR}$ spectra (see $^1\text{H-NMR}$ data in the “Experiment” section). The component of PI-OH was determined by $^1\text{H-NMR}$ (hydroxyl/methyl group), which showed $m : n$ is about 1 : 1, similar to the ratio of reaction material (BAPAF/BAPP). The molecular weight (M_w) of PI-OH and APSPI was determined by GPC as 3.4×10^4 and 4.6×10^4 , respectively. In comparison with PI-OH, the higher molecular weight of APSPI might be ascribed to the introduction of acrylate, which is in good agreement with FTIR and $^1\text{H-NMR}$ results.

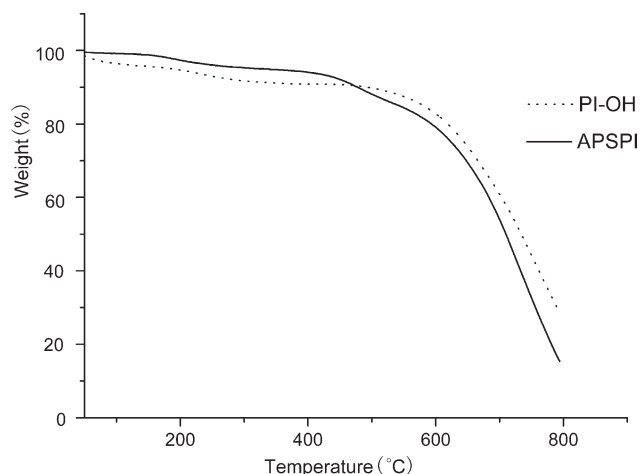
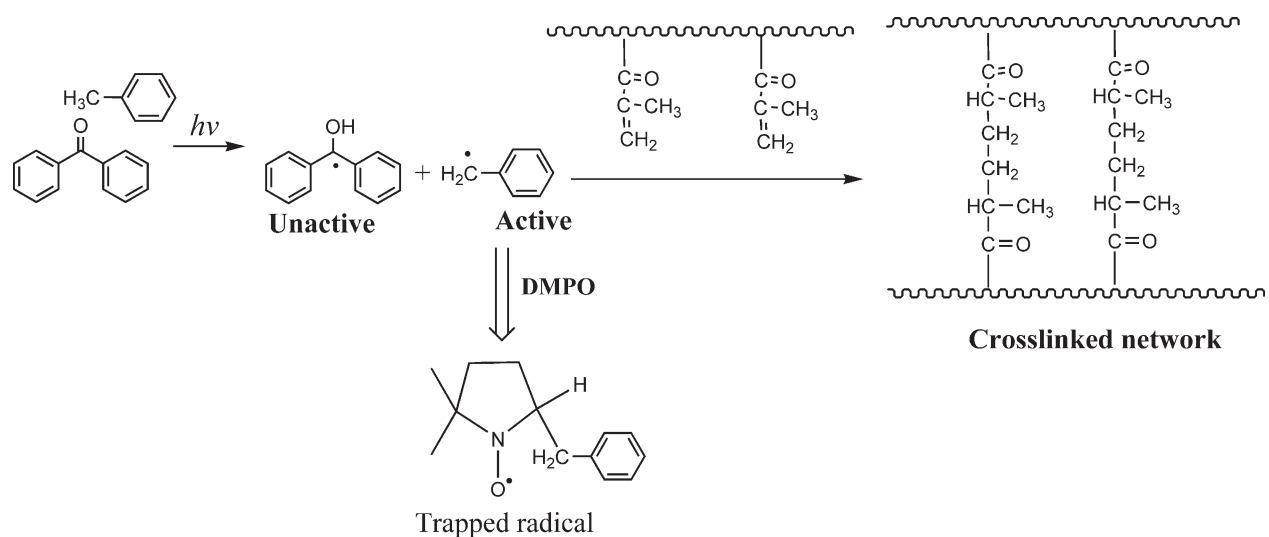


Figure 3 TGA curves of PI-OH and APSPI.

To investigate the properties of APSPI, we synthesized BP-PI through reaction of BTDA and BAPP as reference. The molecular weight (M_w) of BP-PI is about 8.8×10^4 , with polydispersity of 2.2.

Polymer properties

Figure 2 shows the UV-vis spectra of PI-OH and APSPI. Films of about 2- μm thickness were prepared by the spin coating of polymer solution on quartz slide. Both PI-OH and APSPI had a cutoff wavelength below 400 nm. The TGA curves for PI-OH and APSPI are shown in Figure 3. The decomposition temperature for PI-OH is about 420°C. In comparison with PI-OH, two decomposition temperatures were observed in the TGA curve for APSPI. The first at 350°C was attributed to the heat decomposition of methylacrylate groups in the side chain. The amount of weight loss in the first degradation



Scheme 3 Mechanism for radical generation of APSPI to form crosslinked network.

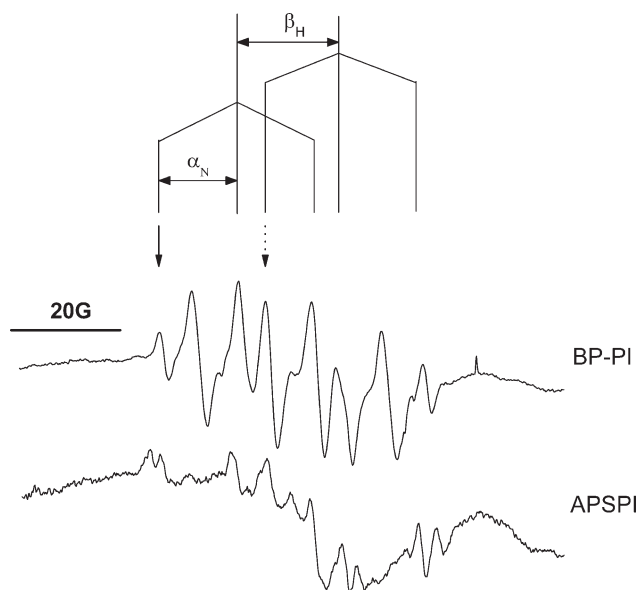


Figure 4 ESR spectrum of BP-PI and APSPi.

(10.4%) was in agreement with the acrylate content calculated by the $^1\text{H-NMR}$ integration values. The decomposition of APSPi main chain occurred at around 520°C .

To understand the mechanism of APSPi, spinning-trapping experiments with DMPO were performed to trap radicals formed upon irradiation (see Scheme 3). Figure 4 shows that ESR signals obtained had six-line spectrum, which is explained by a triplet with α -nitrogen and a further split into a doublet with a β -proton. The value of the magnetic parameter, factor- g , was 2.0050, thus indicating that the generated radicals had been released and trapped by DMPO. APSPi possessed the similar six-line ESR spectrum for BP-PI, indicating the same type of radicals generated in both systems. Compared with BP-PI, however, the intensity of radical

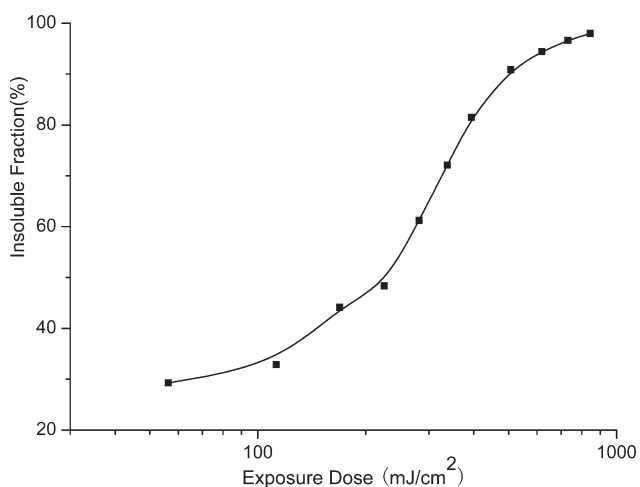


Figure 5 Characteristic UV-exposure curves for APSPi.

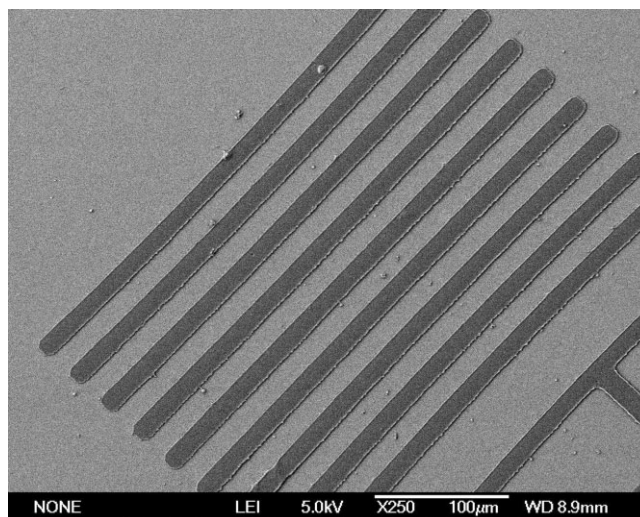


Figure 6 SEM photograph ($\times 250$) of photolithographic patterns for APSPi.

in APSPi is weaker, which maybe due to less content of alkyl group in APSPi.

Photolithography of APSPi

To determine the photolithographic properties of APSPi, thin films of about $2\ \mu\text{m}$ were prepared by spin coating. The photosensitivity was evaluated by the subsequent determination of the insoluble fraction as a function of exposure dose (Fig. 5). The exposure energy to obtain a 0.5-gel fraction ($D_g^{0.5}$) is about $330\ \text{mJ}/\text{cm}^2$. The patterning images of APSPi were obtained under a UV-exposure dose of $0.5\ \text{mW}/\text{cm}^2$ in a contact mode with a mask. Figure 6 shows the typical pattern of SEM micrographs of APSPi, from which we can know that APSPi shows good pattern with resolution of $12\ \mu\text{m}$. The aspect ratio of the film is about 0.17.

CONCLUSION

Through introducing benzophenone moiety into the backbone chain and acrylate group into the side chain of the PI, we successfully synthesized a novel APSPi. APSPi shows good photolithographic properties with a resolution of about $12\ \mu\text{m}$ and a sensitivity of $330\ \text{mJ}/\text{cm}^2$.

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