

Main-Chain Photosensitive Polyimides Using Alkaline Aqueous Solution as Developer

Hou Haoqing, Yang Zhenghua, Ding Mengxian*

(Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China)

Abstract

In order to develop photosensitive polyimide developed to image in alkaline aqueous solution, a photosensitive diamine and relevant polymer containing conjugated double bond in main chain were synthesized. The photosensitive characteristic and thermal stability of the polymers were investigated. These polymers possessed good thermal stability and sensibility to UV irradiation and could be used to form PSPI resist using alkaline aqueous solution as developer.

Key words: Main-chain photosensitive, photosensitive polyimide, alkaline aqueous solution, development

Introduction

Photosensitive polyimides (PSPI) are a class of high performance polymers which are widely used in microelectronics devices as interlayer insulation, passivation, and buffer coating materials because of PI's high thermal stability and excellent electric properties^[1]. In the past decade years, PSPIs have been studied and developed in world-wide research groups^[2-8]. And three kinds of negative-tone PSPIs (ester-type, ion-type and imide-type) have been commercially available since 1980's. But, these PSPIs must be developed to image in organic solvent. Largely using organic solvent is disadvantageous to reducing cost of production and harmful to our environment. Therefore, it is necessary to develop a type of PSPI using alkaline aqueous solution as developer.

In recent, we synthesized a photosensitive diamine with which we obtained series of main chain photosensitive polyamic acids. The latter can be formed PSPIs using alkaline aqueous solution as developers and thermally converted to the imide structures easily. In this paper we would like to introduce the synthesis and properties of the PSPI.

Experimental

Materials: 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-thioetherdiphthalic dianhydride (TDPA) and 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA) were prepared from 4-chlorophthalic anhydride in our laboratory^[9-11]; 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), m-nitrobenzaldehyde (mNBA), cyclohexanone and other reagents were available commercially. Dianhydrides and mNBA were purified by recrystallization or vacuum distillation prior to use. N,N'-dimethyl acetamide (DMAc) was distilled over P₂O₅ under vacuum.

Monomer Synthesis

2,6-Bis(3-nitrophenylmethyl)cyclohexanone (2,6-BNPC)

mNBA 16.62g (0.11mol) and cyclohexanone 4.90ml (0.05mol) were dissolved into 120ml mixing solution of ethanol and tetrahydrofuran (7:5v/v). To the mixture was added dropwise 12.00ml 20%wt. NaOH aqueous solution at room temperature under stirring for 30min. The reaction was completed at 45-50°C in 3h. After cooled for 2h, the yellow crystalline product was collected by filtration and recrystallized from nitromethane to give bright yellow crystals; m.p.: 191-192.5°C. The yield was 88%. FTIR (KBr): 1529.5, 1346.2 (s, -NO₂), 1662.2 (m, C=O), 1609 (m, C=C) cm⁻¹. ¹H-NMR (DMSO-d₆): δ (ppm) = 1.88 (m,

CH₂-); 3.06(t, 2*-CH₂-); 7.86(d, 2*H-C=); 7.80(t, 2*Ar-H); 8.12(d, 2*Ar_H); 8.35(d, 2*Ar-H); 8.45(s, 2*Ar-H).

Anal. Calcd for C₂₀H₁₆N₂O₂(364.35): C,65.93%; H,4.43%; N, 7.68%. Found: C, 65.89%; H,4.35%; N, 7.65%

2,6-Bis(3-aminophenylmethenyl)cyclohexanone(2,6-BAPC)

The dinitro compound 2,6-BNPC 9.11g(0.025mol), 2.0gNH₄Cl and 0.8g p-phenylenediol, 200ml ethanol into a 500ml three-necked flask, into which 14.58g(0.26mol) active Fe powder was gradually added over a period of 30min at 78-80°C under stirring and N₂ atmosphere. After that, the reaction was continued to keep refluxing for another 2.5h. The mixture was cooled at 0-5°C for 5h, and filtered. The filtered liquid was poured into 2000ml water. The precipitate was collected by filtration and recrystallized from chloroform to give yellow powder crystals. The yield was 52%. The FTIR(KBr): 1654(m,C=O), 1593.7(s, C=C), 1248.2(s, C-N)cm⁻¹. ¹H-NMR(DMSO-d₆): δ(ppm)=1.82(m,-CH₂-); 3.00(t, 2*-CH₂-); 5.32(s, 2*-NH₂); 6.72(d, 2*Ar-H); 6.79(d, 2*Ar-H); 6.85(s, 2*Ar-H); 7.20(t, 2*Ar-H); &.58(s, 2*=C-H).

Anal. Calcd for C₂₀H₂₀N₂O(304.38): C, 78.92%; H, 6.62%, N,9.20%. Found: C, 78.8%; H, 6.50%; N, 8.99%.

Polymerization

The typical example of polymerization is as follows. To a stirred solution of 3.0438g(0.01mol)2,6-BAPC in 40ml DMAc was 4.0232g(0.01mol)HQPDA gradually added under nitrogen atmosphere. The reaction mixture was stirred at 25-30°C for 10h after the complete addition of the dianhydride. The viscous solution was carefully poured into 300ml methanol to offer a yellow fibrous solid. The precipitate was collected by filtration, washed thoroughly with methanol and deionic water, and dried at 40°C under vacuum for 24h. The product PSPAA-I weighed 6.86g(yield 97%) and had inherent viscosity 0.61dL/g(30°C,at a concentration of 0.5g/dL, DMAc). FTIR(film): 3259(N-H, O-H), 1716.9,1662.6(C=O, carbonyl, amide, ketone), 1549.1(N-H, amide), 1594.2(C=C, conjugated double bond)cm⁻¹.

The other PSPAAs were obtained by the similar procedure, and their component and the inherent viscosities were listed in tab.1 .

Tab. 1 The inherent viscosity and component of PSPAAs

	PSPAA-I	PSPAA-II	PSPAA-III	PSPAA-IV
[η](dL/g)	0.61	0.51	0.49	0.65
Component	HQDPA/BAPC	BPDA/BAPC	TDPA/BAPC	BTDA/BAPC

Photolithography

Film Formation

Respectively, 2wt.%(based on polymer) sensitizer Mitchler's ketone or 6wt.% photocrosslinking reagent[2,6-Bis(4-azidophenylmethenyl)methylcyclohexanone(BAMC)] was added to a 20wt.% solution of PSPAA in a mixing solution of N-methyl-2-pyrrolidone (NMP), ethoxyethanol and xylene (2:2:1). The viscous solution was then coated on silicon wafers by means of a spincoater at a speed of 3000rpm to form a photosensitive layer; the wafers were prebaked at 85°C for 20min, and the layer thickness was determined with α-step-200 device (US,Tencor).

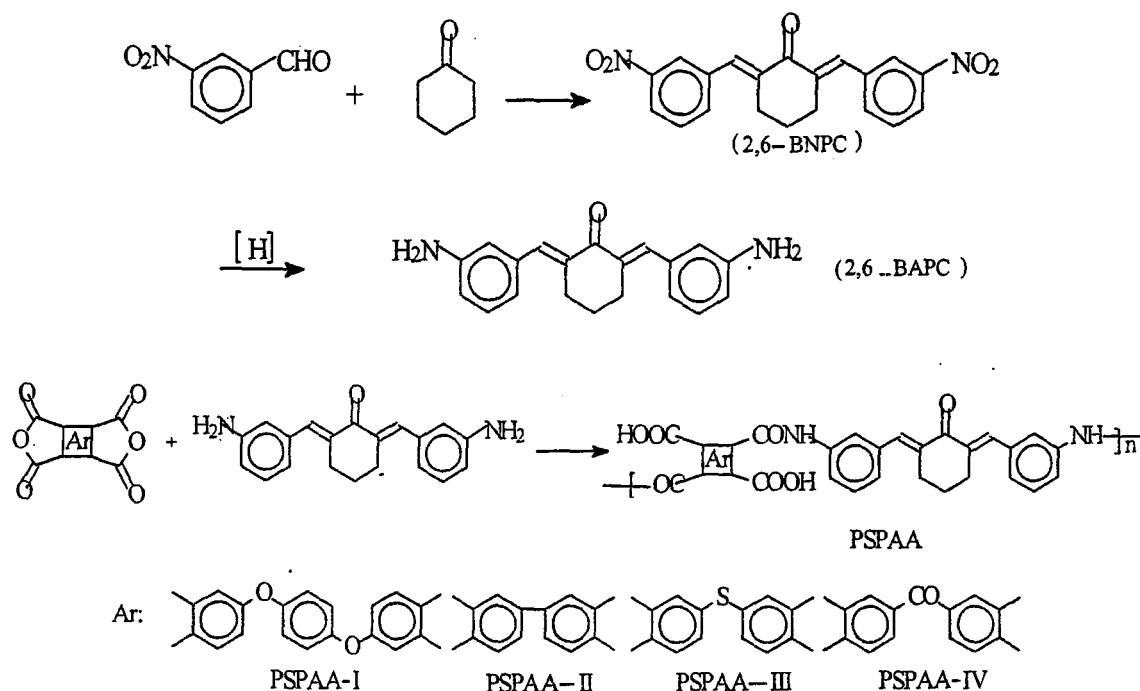


Fig. 1 Scheme for synthesis route of photosensitive diamine and polyamic acid

Photosensitivity and Imaging

The wafers with 2-3 μm thickness of PSPI film was exposed at 365 nm wavelength (the band width of the filter was 365 \pm 10nm) to a 200w high pressure mercury lamp, developed with a mixed aqueous solution of 1.5wt.% tetramethylammonium hydroxide and 10wt.% ethoxyethanol at 25 $^\circ\text{C}$ for 30s, then rinsed with deionic water. The remained film thickness of exposed area was detected with α -step-200. The characteristic curve was obtained by a ratio of remained film thickness to that of the origin against exposure energy.

A wafer with PSPI film out of PSPAA-I was exposed on the JKG-1 photolithographic machine (Shanghai Optic instrument plant) through a mask for 450mJ/cm², then developed and rinsed. After postbaked at 250 $^\circ\text{C}$ for 1h, the wafer with micro-patterns was photographed with JEOL JXA-840 SEM (Fig. 2).

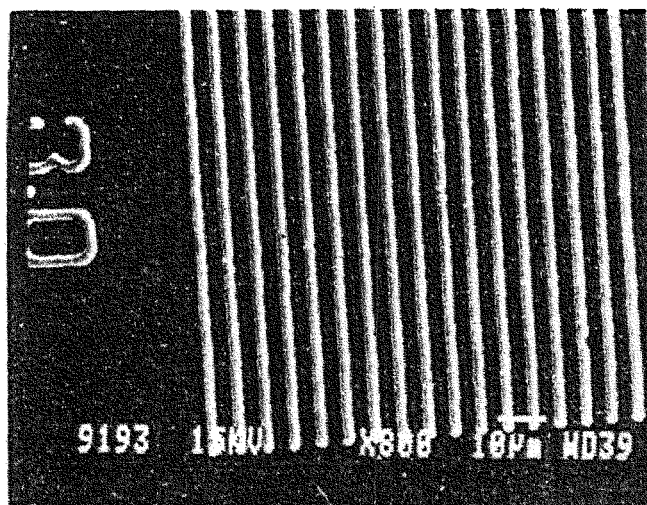


Fig.2 SME photography for the micro-patterns of PSPI based onPSPAA-I

Measurement

High-resolution NMR spectra were recorded with a Varian Unity-400 spectrometer. The chemical shifts were referenced to internal tetramethylsilane(TMS). FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Viscosity measurements were carried out by using an Ostward Viscometer at 30 $^\circ\text{C}$. The

exposure doses were determined with UV-A Model irradiance Meter of Photoelectric Instrument Factory of Beijing Normal University. Thermogravimetric(TG) imidization studies were performed on a Perkin-Elmer TGS-2 Thermogravimetric Analyzer at heating rate of 10°C/min under nitrogen. DSC experiments were carried out on a Perkin-Elmer DSC-7 system at heating rate of 20°C/min under nitrogen.

Result and Discussion

Syntheses of Monomer and Polymer

The condensation reaction between mNBA and cyclohexanone gave a good yield in mixing solution of tetrahydrofuran and ethanol in which the product dinitro compound is insoluble. But the reduction of the product is difficult because many reduction methods reported in literature are not suitable to the reduction of 2,6-BNPC which is a multifunctional molecule(containing nitro-, conjugated double band and carbonyl). Therefore, a method of Fe powder reduction in weak acid medium was used to reduce the dinitro compound(Fig. 1). The NH_4Cl is an activator in the reaction, and the p-phenylenediol is an inhibitor avoiding the thermopolymerization of the diamine product. The reaction gave 52% yield at reflux temperature(80°C), but would result a very low yield or even nothing when the reaction temperature was below 75°C. The m.p. of diamine product was not found because it was thermolability.

Generally, the condensation polymerization between the dianhydride and diamine easily takes place in an aprotic solvent such as DMAc(Fig. 1). But the molecular weight of condensation polymer greatly depends on the reaction activation of dianhydride or diamine. The reactions between 2,6-BAPC and several kinds of dianhydrides all gave lower molecular weight polymers because 2,6-BAPC is a low activation diamine which contains carbonyl.

Thermal Stability of Polymer

Fig. 3 showed the thermogravimetric behavior, under nitrogen, of the PSPAA-I,II,III,IV which were prebaked at 150°C/1h, 200°C/30min, 280°C/1h in air prior to thermogravimetric analyses. A 5wt.% weight loss in the temperature range 50-400°C and large weight loss at over 450°C were observed. This indicated that these polymer all possessed good thermal stability, although the main chains of these polymers all contained a part of non-aromatic structure. In differential scanning calorimetry (DSC) analysis (Fig. 4), there is no phase transition to be observed from 50-400°C for the prebaked PSPAA-I, which can be attributed to the crosslinking structure formed during the prebaking.

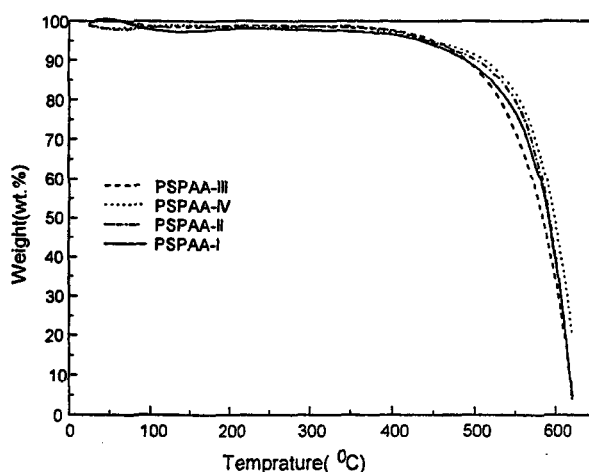


Fig. 3 TG curves of for the prebaked PSPAAs in nitrogen flow at $\Delta T=10/\text{min}$

Photosensitive Properties

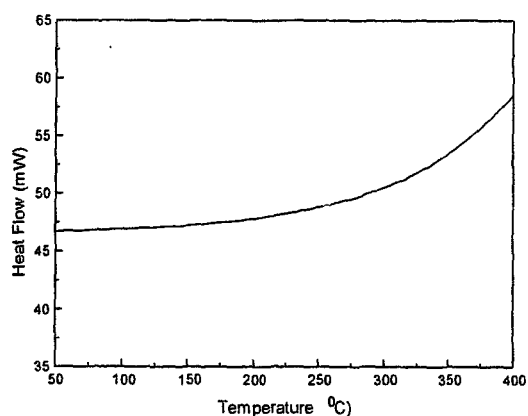


Fig. 4 DSC curve of the PSPAA-I prebaked at 280 °C/1h

showed the influence of additives to the sensitivity. The several kinds of PSPAAs almost had the same sensitivity, and the photocrosslinking reagent (BAMC) had a significant effect on the sensitivity because BAMC was a diazido compound which could form very reactive fragments, nitrenes, during the UV irradiation. The reactive nitrenes rapidly reacted with other compound, by insertion into a C-H bond or addition to double bond, to give rise to crosslinking structure^[12].

Tab. 2 The influence of additives to the sensitivities of PSPAAs (mJ/cm²)

	PSPAA-I	PSPAA-II	PSPAA-III	PSPAA-IV
Control	450	470	490	465
Michler'sKetone	370	370	410	350
BAMC	140	180	200	150

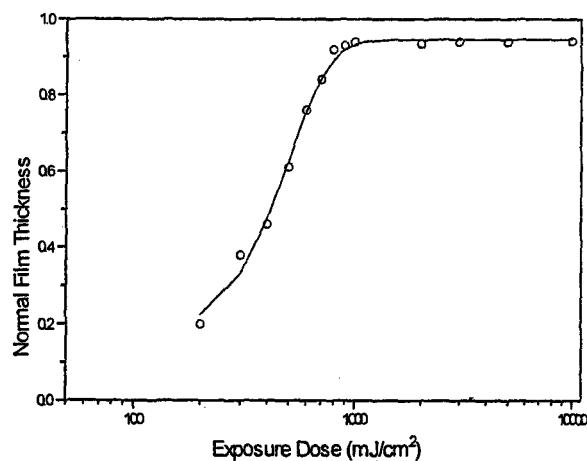


Fig. 5 Sensitivity curve for PSPI based on PSPAA-I

Reference

1. H. Haoqing, L. Yuesheng, D. Mengxian, J. of Functional Polymers, 9(2): 279 (1996).
2. J. M. Bureau and J. P. Droguet, in Polyimides: Applications of Polyimides as Photosensitive Materials (M.K. Ghosh and K.L. Mittal, eds.), 1996, pp. 743.
3. H. Neuhaus, Proc. Int. Conf. on Multichip Modules, Denver, 1993, CO: SPIE, pp. 51.
4. R. Rubner, W. Kleeberg and E. Kuhn, German Pat. 2437348 (1974).
5. H. J. Merrem, R. Klug and H. Härtner, Polyimides: Synth., Charact., Appl. [Proc. Tech. Conf.

PSPAA is the polyamic acid soluble in alkaline aqueous solution and possesses the conjugated double bond sensitive to violet light in the main chain. Therefore, it is suitable to being used as the film former of photoresist, which can be developed in alkaline aqueous solution. Fig. 5 represented the sensitivity curve for the PSPAA-I at 365nm and showed that the PSPAA-I had, without any additives, a sensitivity of about 450mJ/cm². Sensitizer and photocrosslinking reagent were effective to improving the sensitivity of PSPAA. Tab. 2

Conclusions

We have successfully synthesized a photosensitive diamine, with which we prepared a negative-tone main chain photosensitive polyamic acid (PSPAA). The PSPI based on these PSPAAs were found to be developed in alkaline aqueous solution after UV irradiation. And the PSPAA can conveniently be converted to PI that possesses a good thermal stability. Work is continuing to extend the limits of sensitivity and to optimize image dimensions.

- Polyimides], 1st, 1982(pub., 1984)2, pp.919.
- 6.T. Yamaoka and T. Omote, Polyfile 27(2): 14(1990).
- 7.G. C. Davis, ACS Symp. Ser., 242: 259 (1984).
- 8.H. Nishizawa, K. Sato, M. Kijima and H. Satou, Polym. Eng. Sci., 32(21): 1610 (1992).
- 9.M.T.Pottiger, D.L. Goff and W.J.Lautenberger, Proc., 38th Electronic Components Conference, 1988, pp.315.
- 10.L. Minnema and J.M. Vander Zande, Polym. Eng. Sci., 28(12):815 (1988).
- 11.D. Mengxian and Y. Zhenghua, CN90109003·4(1990).
- 12.G. A. Delzenne, Encycl. Polym. Sci. Technol., Suppl. 1, pp.401-443 (1976).

用碱性水溶液显影的主链型光敏聚酰亚胺

侯豪情 杨振华 丁孟贤*

(中国科学院长春应用化学研究所, 吉林, 长春, 130022)

为了发展在水溶液中显影的光敏聚酰亚胺 (PSPI) 光刻胶, 合成了一种光敏性二胺 [2, 6-双(3-氨基苯甲叉)环己酮] 及其相应的光敏聚酰胺酸 (PSPAA)。这些 PSPAA 可配制用碱性水溶液显影的 PSPI 光刻胶, 它们对 365nm 紫外线的感度大约为 $450\text{mJ}/\text{cm}^2$ 。某些增感剂或交联剂可用来改善这种光刻胶的感光性能。由这些 PSPI 光刻胶转变成的聚酰亚胺的热稳定性大于 400°C 。