

Photoimageable Polyimides Dervied from α, α –bis (4-amino-3, 5-dimethylphenyl phenylmethane and Aromatic Dianhydride

¹ Zhao Ning

**1, First Author and Corresponding Author* Shenzhen Polytechnic College, Shenzhen, China,

E-mail: zhaoning2@yeah.net

Abstract: Soluble and inherent photoimageable polyimides with improved photo-patterning features were prepared from α, α -bis (4-amino-3,5-dimethylphenyl)phenylmethane (BADP) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The polyimides possess good combined chemical and physical properties, of which thermal stability with initial thermal decomposition temperature of 525°C and high glass transition temperature of 318°C were observed. Homogeneous polyimide solution in common organic solvents with as high as 20 wt % of solid content could be prepared, which is stable for storing of >3 months. The polyimide has high electric insulating properties and low dielectric constant and dissipation factor. Fine patterns could be processed by directly exposing the polyimide coating upon UV i-line, followed by developing with an organic developer.

Keywords: *Polyimides, BADP, BTDA*

1. Introduction

Photosensitive polyimides, due to the excellent combined physical and chemical features and easy processing characteristics, have been extensively employed in advanced microelectronics packaging as interlayer dielectrics in multilayer structure and MCM-D, passivation layers and α -particle barriers on chip, stress relief buffer coatings in high-density electronic packaging, etc [1-5]. Photosensitive polyimides (PSPI) are usually negative photoimaged mode, which are formulated from poly(amic acid)s (PAAs) which contain photosensitive cross-linking sites in polymer backbones introduced either by chemical bonding or by salt-like linking [6-8]. Their major drawbacks for the advanced microelectronics applications include the heavy dimensional shrinkage and the deteriorated mechanical properties of the thermally cured polyimide photopatterns caused by evolving a lot of organic volatiles derived from the photosensitive additives and solvents. Another kind of photosensitive polyimides, which are fully imidized and soluble photoimageable without addition of any photosensitizers and crosslinking agents, can be directly photoimaged on exposure with 365 nm (i-line) to produce less dimensional shrunken photopatterns [9-12]. Such polyimides are prepared by the polycondensation of ortho

multialkyl-substituted aromatic diamine and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). However, to our knowledge, these inherent photoimaged polyimides suffer the limited solubility in organic solvent and the moisture sensitive features, which hamper their widespread applications in advanced microelectronics manufacturing process.

Recently, many reports regarding with fully imidized polyimides with improved solubilities have been made which are prepared either by incorporating of flexible asymmetric substituents, or by introducing of bulky pendant groups into the rigid polymer backbone [10-16]. However, there are few papers regarding with the improvement in solubility of self photoimaged polyimides. A new phenyl-substituted aromatic diamine, α, α -bis(4-amino-3,5-dimethylphenyl)phenyl methane (BADP) has been synthesized in this laboratory, which was employed to polycondense with BTDA to afford a series of fully imidized polyimides. Photosensitive resins could be formulated with the fully imidized polyimides which are used to directly photo-image high quality patterns. The developed polyimide films, after final cured at relative low temperatures, exhibited great combined physical and chemical features, including high thermal stability, high mechanical properties, high electrical insulating and low

dielectric constant and dissipation factor, as well as low moisture uptakes.

2. Experimental

2.1. Materials

2,6-dimethylaniline and 3,3',4,4'-benzophenonetetracarboxylic dianhydride were purchased from Acros Organics Chemicals Co. and purified by recrystallization prior to use. Benzaldehyde, hydrochloric acid and iso-propyl alcohol were purchased from Beijing Chemical Reagents Co. and was used without further purification. TMDA was synthesized according to the literature [25]. Commercially available N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF) were purified by vacuum distillation prior to use.

2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer 782 Fourier transform spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out with a Perkin Elmer TGA-7 thermogravimetric analyzer in nitrogen at a heating rate of 20 °C/min. Inherent viscosities were measured in 0.5% solutions in NMP at 25 °C. Ultraviolet-visible (UV-Vis) spectra were recorded on a Hitachi U-3210 spectrophotometer.

2.3. Photopatterning

Exposures were performed on a KG-706 mask-aligner in hard contact mode and spectral output at 436, 405 and 365 nm (g + h + I, broad band). A combination of a high resolution mask for CD-analysis together with a multi-density mask was used. Spectral sensitivities were determined using Oriel Hg-line interference filters. Photosensitivities, referred to the 400 nm probe of the OAI light sensitivity meter for broad band exposure, were obtained after optimization of developer and processing conditions according to standard methods. Layer thickness was controlled to $\pm 10\%$ for thin layers (1.0 μm) and 5% for thicker layers (5-10 μm).

2.4. α,α -Bis(4-amino-3,5-dimethylphenyl)phenylmethane

(BADP) 2,6-dimethylaniline (48.47g, 0.4 mol) was heated at 130 °C in nitrogen. To which benzaldehyde (143.0 g, 0.18mol) dissolved in 3.3 ml (12 N) of hydrochloric acid was added dropwise over a period of 1.5 hrs. The reaction mixture was continually refluxed at ca.120-124 °C for another 13 hrs. After cooled to room temperature, 7.92g of 20% aqueous solution of sodium hydroxide was added to yield a suspension which was then poured into excess of ethanol to afford pale blue precipitate. The solid was filtered, washed thoroughly with distilled water, and dried at

60 °C overnight. The product was purified by recrystallization in ethanol to afford pale crystal (54.2g, 90.3%). mp 182 °C (DSC in air) FT-IR(KBr, cm^{-1}): 3434, 3021, 2966, 2854, 1624, 1445. ^1H NMR (CDCl_3 , δ ppm): 7.091-7.245(m, 5H), 6.68(s, 4H), 5.26(s, 1H), 2.11(s, 12H). Ms (FAB intensity(%)) 330 (22, M⁺); Elemental analysis: Calcd. for $\text{C}_{23}\text{H}_{26}\text{N}_2$ C, 83.63%; H, 7.87%; N, 8.48%. Found: C, 83.68%; H, 7.84%; N, 8.46%.

2.5. Polymer Synthesis

In a typical experiment, BADP(3.3047g 1.00 mmol) was dissolved in 18ml of NMP. To which BTDA(3.2552g, 1.02 mmol) were added stepwise, and then 8 ml of NMP was added. The mixture was stirred in nitrogen at room temperature for 18 hrs to yield a viscous poly(amic acid) (PAA) solution with 20% solid content. The PAA solution was chemically converted into polyimide by the addition of 10 ml of an acetic anhydride/pyridine (5/4 v/v) mixture, followed by stirring at 60 °C for 4 hrs. The homogeneous polyimide solution was pouring into excess of methanol to produce a solid polymer, which was collected and washed with methanol thoroughly, and dried at 80 °C in vacuum (PSPI-2). FT-IR (KBr, cm^{-1}): 1779, 1725, 1485, 1371, 1206, 977, 839. Elemental analysis: C, 78.23%; H, 7.98%; N, 3.58%; Found: C, 78.18%; H, 8.01%; N, 3.62%. ^1H NMR (CDCl_3 , δ ppm): 8.12-8.28(m, 6H), 7.35-7.17(m, 5H), 6.68(s, 4H), 5.26(s, 1H), 2.11(s, 12H).

PSPI-1, PSPI-3 and PSPI-4 were synthesized in the similar procedure with PSPI-2 except for the molar ratio of BTDA/BADP, in which the BTDA/BADP molar ratio is 1.04/1.0 for PSPI-1, 1.00/1.00 for PSPI-3 and 0.98/1.00 for PSPI-4.

BTDA-TMDA polyimide was prepared in the similar procedure with PSPI except that TMDA was used instead of BADP as the aromatic diamine monomer.

3. Results and Discussion

3.1. Monomer

Diamine BADP was synthesized in a one-step process (Scheme 1), in which 1 mole of benzaldehyde was coupled with 2 mole of 2,6-dimethylaniline in the presence of hydrochloric acid to afford the diamine.HCl salt. The pure compound was released by addition of aqueous sodium hydroxide solution and purified by recrystallization in anhydrous ethyl alcohol. The chemical structure of BADP was confirmed by elemental analysis, IR, ^1H NMR, ^{13}C NMR and mass spectrum. The elemental analysis values are in good agreement with the calculated ones; The molecular weight determined by mass spectrum is 330.0, which is the same value with the calculated one. The purity is >98% and impurities determined by atom absorption spectrum are Na^+ 2.0 ppm; K^+ 0.9 ppm; Mg^{++} 1.3ppm; Ca^{++} 1.3ppm; Fe^{++} 0.6ppm

3.2. Polyimide Synthesis

Polyimides were synthesized from the condensation of BADP with BTDA through a two-step pathway (Scheme 2). Poly (amic acid) solution (20% of solid content) in NMP was first prepared at room temperature, which was chemically imidized in the presence of acetic anhydride/pyridine mixture to produce polyimide. The polymers were isolated and purified by precipitation of the polyimide solution in excess of ethyl alcohol, and washed

thoroughly with methanol. The molar ratios of dianhydride to diamine (BTDA/BADP) were changed in order to produce polyimides with different molecular weights (Table 1). Thus, a series of polyimides with different inherent viscosities in the range of 0.148-0.412 were obtained when the BTDA/BADP molar ratios changed from 0.98:1.00 to 1.04:1.00. The polyimide with the maximum inherent viscosity (0.32) was obtained at BTDA/BADP mole ratio of 1.02:1.00.

Table 1 Inherent viscosities of polyimides prepared with different BTDA/BADP molar ratios

	<i>PSPI-1</i>	<i>PSPI-2</i>	<i>PSPI-3</i>	<i>PSPI-4</i>
BTDA/BADP molar ratio	1.04:1	1.02:1	1:1	0.98:1
Inherent viscosity(dL/g)	0.268	0.4122	0.344	0.148

The yellowish polymers have elemental analysis values being exactly the same as expected (Table1). Figure 1 depicts the FT-IR spectrum of PSPI-2 polyimide. The characteristic absorptions for the asymmetric and symmetric C=O stretching vibrations of imide groups are observed. And the absorption at 1383 cm^{-1} is assigned to the C-N stretching vibration of imide structure. Figure 2 shows the ^1H NMR spectrum of the polyimide, in which the assignments of protons are in good agreement with the expected chemical structure.

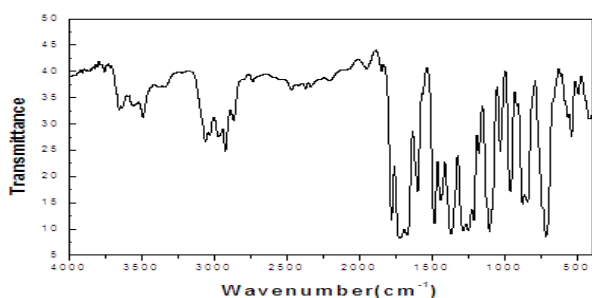


Figure 1. FT-IR spectrum of PSPI-2 polyimide

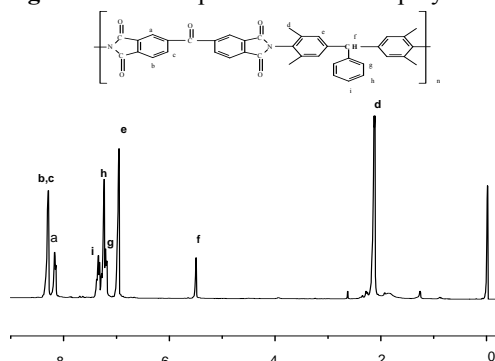


Figure 2. ^1H NMR(CDCl₃, 300MHz) spectrum of PSPI-2 polyimide

Figure 3 shows UV-visible spectrum of the polyimide. The sample film with 0.25 mm thick was prepared by spun coating polyimide solution on quartz surface, followed by thermally curing at $120\text{ }^\circ\text{C}$ for 0.5 hrs in an oven. It can be seen that the maximum absorption appeared at 330 nm and

there is relative strong absorption at 355 nm(i-line). The absorption cut-off wavelength is located at 425 nm, which is lower than the g-line (436 nm) absorption.

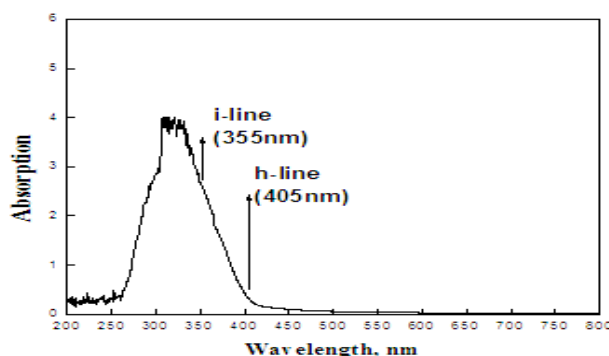


Figure 3. UV-visible spectrum of PSPI-2 polyimide film

3.3. Polymer Solubility

Polymer solubility was qualitatively determined by dissolving 1.50g of solid polymers in 8.5g of organic solvent which was then mechanically stirred in nitrogen for 24 hrs at room temperature (Table 2). The polyimide derived from BTDA and BADP could be easily dissolved both in strong aprotic solvents, such as NMP, DMF, DMAc and in common organic solvents such as m-cresol, γ -butyrolactone and chloroform. In comparison, the polyimide derived from BTDA and TMDA was partly soluble in m-cresol and chloroform although it could be dissolved in the strong aprotic solvents. Hence, low boiling point organic solvents such as cyclopentane, chloroform could be employed to dissolve PSPI-2 to afford homogeneous polymer solution, which could process coatings or thin films at relatively low curing temperature. For instance, PSPI-2 in 1,2-dichloroethane (mp $83.5\text{ }^\circ\text{C}$) could be thermally processed to produce thin polyimide coating at $90\text{--}110\text{ }^\circ\text{C}$, lower than the polymer in NMP solution (thermal curing at $200\text{--}210\text{ }^\circ\text{C}$).

Table 2. Polyimide solubility in different organic solvents

<i>Solvent</i>	<i>PSPI-2</i>	<i>BTDA-TMDA</i>
NMP	++	++
DMF	++	++
m-Cresol	++	+
CDCl ₃	++	+
1,2-dichloroethane	++	+
cyclopentane	++	++
γ -butyrolactone	++	+
iso-propyl alcohol	-	-
Toluene	+	-

a) Solubility was determined by mixing 1.5g of polymer with 8.5g of solvent, followed by stirring for 24 hrs. ++) The solid polymer was completely dissolved in the solvent to afford a homogeneous solution at room temperature; +) The solid polymer could be dissolved with heating at 80 °C; -) The solid polymer could not be dissolved or only swollen in the solvent.

b) NMP: 1-methyl-2-pyrrolidone; DMF: N,N-dimethylformamide; THF: tetrahydrofuran

PSPI-2 polyimide showed different solubility in different organic solvents. The complete dissolution time for PSPI-2 in different solvents depends on the solvent quality (Fig. 4). When solid polymer powder was mixed with the solvent, the complete dissolution time, defined as the time for the solid being disappeared completely, decreased in the following order: THF > γ -BL > DMF > NMP > CHCl₃ (Fig.4). For instance, the polyimide can completely dissolve in CHCl₃ to afford a homogeneous solution in 35 minutes, compared with 14 hrs in THF and 12 hrs in NMP. Meanwhile, PSPI-2 polyimide showed greatly improved solubility compared with the corresponding BTDA-TMDA polyimide. For instance, PSPI-2 polyimide will dissolve in chloroform within 15 minutes, compared with BTDA-TMDA for 14 hrs. This improvement in solubility could be probably attributed to the combined effects of the pendant phenyl groups and the methyl groups in the polymer backbone. Due to the good solubility in low boiling point solvent, polyimide coatings or thin films could be processed at relatively low temperature (180-200 °C) by completely removing the trace of solvent in the fully imidized polyimide solution.

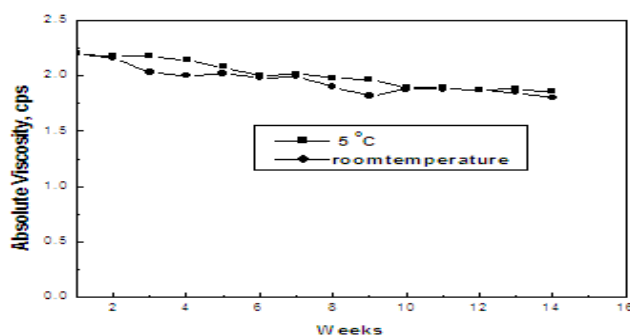


Figure 4. Dependence of the inherent viscosity of PSPI-2 polyimide on storing at room temperature and at 5 °C

The polyimide solutions are very stable in storing both at room temperature (25 °C) and in refrigerator (5 °C). Figure 5 depicts the changes of absolute viscosities with the storing time. It can be seen that the polyimide solution does not have apparent changes in absolute viscosities for storing longer than 14 weeks. No phase separation, precipitation or gel formation occurred during the tested storing period.

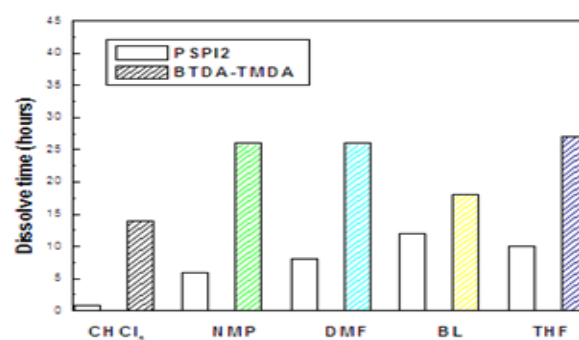


Figure 5. Comparison on the dissolution time of PSPI-2 and BTDA-TMDA polyimide with different solvents

3.4. Thermal and Physical Properties

Figure 6 depicts typical TGA curves of PSPI-2 polyimide, compared with BTDA-TMDA polyimide, in which a similar thermal decomposition behavior observed. The onset decomposition temperatures are measured at 532.2 °C for PSPI-2 polymer and 531.6 °C for BTDA-TMDA polymer. PSPI-2 polyimide shows the temperatures at 5% weight loss of 525 °C, 33 °C higher than that of BTDA-TMDA polymer (492 °C). Similarly, the temperature at 10% weight loss of PSPI-2 polyimide is 569 °C, 22 °C higher than that of BTDA-TMDA polymer (547 °C). Obviously, PSPI-2 polyimide showed improved thermal stability than BTDA-TMDA polyimide. It can be seen that there is no trace of weight loss detected for PSPI-2 before the scanning temperature reaches at 450 °C.

The glass transition temperature (T_g) of PSPI-2 is 318 °C determined by DSC (Fig. 7), compared with 311 °C for BTDA-TMDA. Figure 8 depicts the DMA curves of PSPI-2 polyimide, in which the glass transition temperature is measured at 296 °C, compared with 292 °C for BTDA-TMDA. The onset temperature for the storage modulus curve being declined swiftly is located at 275 °C, implying that the polyimide would possess strong mechanical strength at elevated temperature. Hence, the introduction of pendant phenyl groups in PSPI-2 polyimide backbone

ensure the polymer with an obvious improvements both in solubility and in thermal stability.

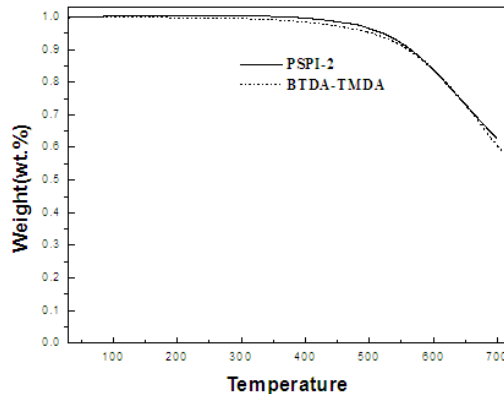


Figure 6. Typical TGA curves of polyimides derived from BTDA and BADP or TMDA

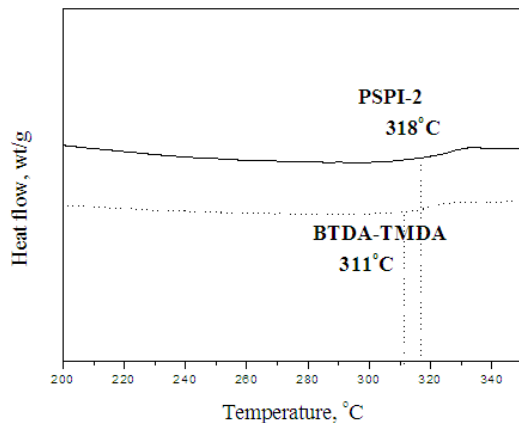


Figure 7. DSC curves of PSPI-2 and BTDA-TMDA polyimides

3.5. Electrical and Dielectric Properties

PSPI-2 polyimide exhibits lower dielectric constant (2.89 at 1MHz) than the common PMDA-ODA polyimide (3.40 at 1 M Hz), compared with BTDA-TMDA (2.98 at 1M Hz) (Table 3). The dissipation factor is at the order of $3-4 \times 10^{-4}$. The volume resistance is measured at $2.4 \times 10^{16} \Omega \cdot \text{cm}$ and surface resistance at $2.46 \times 10^{15} \Omega$. Meanwhile, PSPI-2 has a very low moisture uptake (0.24 wt. %), compared with BTDA-TMDA polyimide (0.54 wt%) and with commercial Probimide 400 (2.0%)[26]. The low moisture absorption could ensure the polymer possessing stable and constant electric insulating and dielectric performance.

Table 3 Electrical and dielectric properties of the polyimides (25 μm)

<i>Polyimide</i>	<i>BTDA-TMDA</i>	<i>PSPI-2</i>
Surface resistance, Ω	2.04×10^{15}	2.42×10^{15}
Volume resistance, $\Omega \cdot \text{cm}$	2.25×10^{16}	2.46×10^{16}
Dielectric constant (1MHz)	2.98	2.89
Dissipation factor	0.0035	0.0029
Dielectric strength (kV/mm)	100	120
Moisture uptake (%)	0.54	0.24

3.6. Patternability

PSPI-2 polyimide exhibit the UV-visible absorption peaked at 320 nm and there is strong absorption at 365 nm (i-line). Experimental results indicated that the material is primarily sensitive to the i-line exposure and compatible with exposure in the contact or proximity mode. Fine patterns could be processed by UV exposing the polymer coating on silicon wafer, followed by developing with an organic developer using γ -butyrolactone and DMF as main solvents (Fig. 9). The polymer coated silicon wafer was prepared by spun coating the polymer solution in NMP on silicon wafer, followed by thermal baking at 200 °C to completely remove the solvent. Figure 10 shows the AFM 3D micrograph of the pattern, in which a smooth surface both for the top and sidewall is obtained. Using contact or i-

line stepper exposures, aspect ratios of 1.0 are easily obtained for over 5 μm thick films, and 1.5 for 1-5 μm thick films. The photopatterns exhibit only 8-12 % of dimensional shrinkage upon final thermally curing (300-350 °C), implying that the geometrical distortions of the photopatterns are minimal. Figure 11 depicts the photosensitivity curve of PSPI-2, compared with BTDA-TMDA polyimide. It can be seen that similar photosensitive behaviors are observed. The photospeed for PSPI-2 is determined at $\sim 180 \text{ mJ/cm}$.

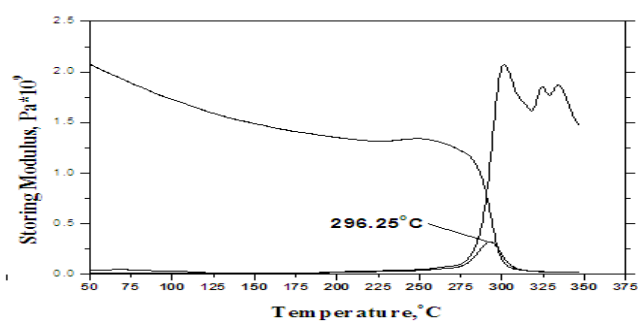


Figure 8. DMA curves of PSPI-2 polyimide

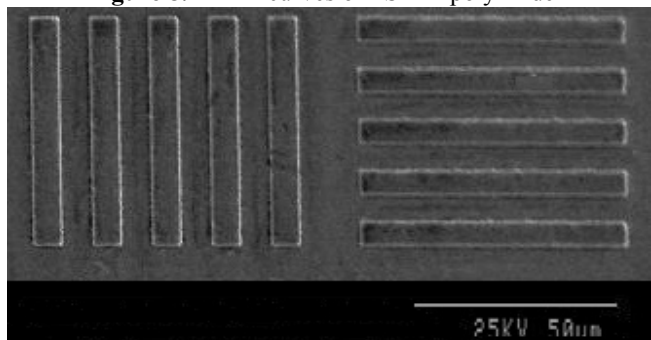


Figure 9. SEM of the pattern from the system containing BTDA-BADP polyimide

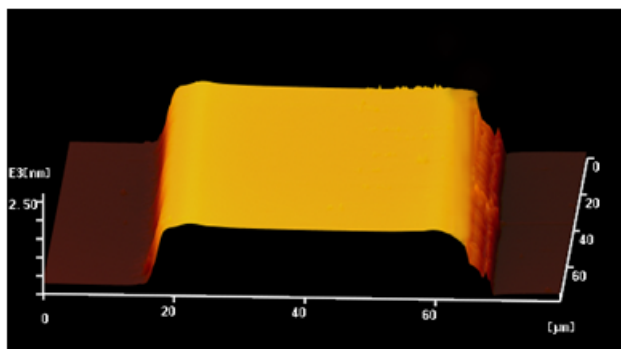


Figure 10. AFM 3D micrograph of the BTDA-BADP photopattern

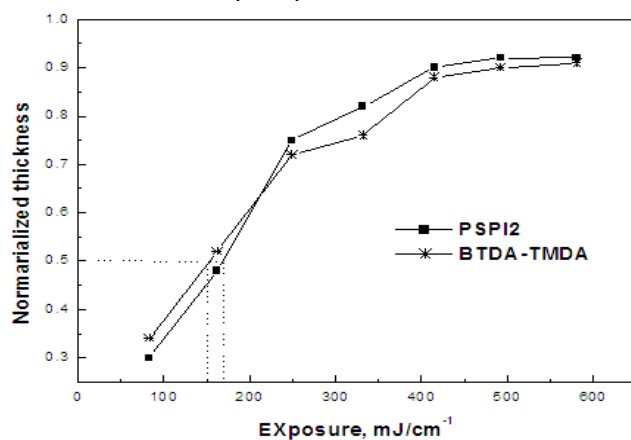


Figure 11. Characteristic curve of PSPI-2 polyimide

4. Conclusions

Soluble fully imidized polyimide with pendant phenyl groups in the polymer backbone was prepared, which exhibited great combined chemical and physical properties. The polyimide has an excellent thermal stability with initial thermal decomposition temperature of 525 °C and glass transition temperature of 318 °C. Homogeneous polyimide solution with as high as 20 wt % of solid content could be prepared, which is stable for storing of >3 months. The polyimide has high electric insulating properties and low dielectric constant and dissipation factor. Fine patterns could be processed by exposing the polyimide coating to UV i-line, followed by developing with organic developer. The aspect ratios are 1.0 for 5 μm thick coatings and 1.5 for 1-5 μm thick coatings. The photosensitive polyimide exhibit minimal dimensional shrinkage of 8-12% for the finally cured photopattern with photospeed of ~180 mJ/cm.

5. Acknowledgements

I would like to express my gratitude to all those who helped me during the writing of this thesis. I gratefully acknowledge the help of my supervisor, Ms. Liu.LeHua, who has offered me valuable suggestions in the academic studies. In the preparation of the thesis, she has spent much time reading through each draft and provided me with inspiring advice. Without her patient instruction, insightful criticism and expert guidance, the completion of this thesis would not have been possible.

I also appreciate Liu Min colleagues, in English translation for help.

6. References

- [1] Hore K. In: Ito H, Tagawa S, Horie K, editors, "Polymeric Materials for Microelectronic Applications", Washington DC: American Chemical Society, Vol.163,pp.32-35,1994.
- [2] Licar J, Hughes LA, "editors. Handbook of Polymer Coating for Electronics", Noyes Data: Park Ridge, NJ, pp.30-62,1990.
- [3] Katritzky A R, Zhu D W, Schanze K S, "Synthesis of substituted poly(12vinylprene) s and investigation of their fluorescent properties", J Poly Sci : part A , pp.31:2187 ,1993.
- [4] Ree M , Chen KJ R , Czornyj G, "Effect of UV exposure and thermal history on properties of a preimidized photo-sensitive polyimide", Polym Eng Sci , Vol.32,No. 14,pp .924, 1992 .
- [5] Chiang W Y, Mei W P, "Synthesis and characterization of photosensitive polyimide from methylthiomethylsubstituted 4,4'-diaminodiphenylmethanes and 3,3',4,4'-benzophenonetetracarboxylic dianhydrid", J Poly Sci : part A , pp.31 :1195,1993.

- [6] [Feld WA, Ramalingam B, Harris FW, "Hydrogen Storage Based on Physisorption", J Polym Sci Polym Chem Ed , Vol.113.No.14.pp.4708:4717,2009.
- [7] Ghatge ND, Shinde BM, "Polyimides From Dianhydrides And Bis(Para-Aminophenyl) Alkane Diamines",Journal Of Polymer Science Part A-Polymer Chemistry, Vol.22, No.11, pp.3359-3365, 1984.
- [8] Rohde O, Smolka P , Falcigno P, "A novel auto2photosensitive polyimides with tailored properties", Poly EngSci , Vol.32,No. 21,pp .1623,1992.
- [9] W. J. Jackson Jr. H. F. Kuhfuss, "Comments on Liquid crystal polymers. I. Preparation and properties of p-hydroxybenzoic acid copolyesters", J. Polym. Sci. Polym. Chem. Ed.,Vol.34, No.15, pp.3029:3030 ,1996.
- [10] Kahen KB, "solution of the vector wave-equation using green-function techniques" ,Journal of Applied Physics ,Vol.71 .No.9, pp.4577-4582,1992 .
- [11] Katritzky,AR, "Advances in Heterocyclic Chemistry", Vol.99 ,pp.32-36,1993.
- [12]Komatsu T, Fujita K, Matusita K, "Resistometric and Mössbauer studies on structural relaxation in (Ni,Fe)75Si10B15 metallic glasses", J. Appl. Phys .No.5 .Vol.68 ,pp.68:72,1990.
- [13]Stoenciu A, Fedotova O, Korshak VV. "Investigation of the thermooxidative degradation of aromatic polycarbamides" Polymer Science U.S.S.R.VOL16,pp.82:85,1975.
- [14]HongYu Feng, JianPing Wang, HaiFang Dai, "The Study in Composition Analysis and Prediction of Wheat Seedling Using RBF Neural Network", IJACT: International Journal of Advancements in Computing Technology, Vol. 4, No. 22, pp. 436 ~ 443, 2012
- [15]ZHANG Li, ZHANG Chun Li, YAN Ping, KANG Lei, WEI Hai Liang, GUO Feng Qin, LI Ling, WANG Rong Fu, "Design, Preparation and Characterization of Cyclic RGD Dimer for Targeting Integrin $\alpha V\beta 3$ ", JCIT: Journal of Convergence Information Technology, Vol. 6, No. 12, pp. 442 - 450, 2011