

# Synthesis and characterization of copolyimides from bis(3, 4-dicarboxyphenyl)dimethylsilane dianhydride

Lin Baoping<sup>1</sup> Qian Ying<sup>1</sup> Pan Ying<sup>1</sup> Yuan Chunwei<sup>2</sup>

<sup>1</sup>Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

<sup>2</sup>Key Laboratory of Molecular and Bio-molecular Electronics of Ministry of Education, Southeast University, Nanjing 210096, China)

**Abstract:** The silicon-containing poly(amic acid)s were synthesized from bis(3, 4-dicarboxyphenyl)dimethylsilane dianhydride (SIDA), pyromellitic dianhydride (PMDA) and 4, 4'-oxydianiline (4, 4'-ODA) in N, N-dimethylacetamide (DMAc). The poly(amic acid) films were obtained by solution-cast method from DMAc solutions and thermally converted into transparent, flexible and tough polyimide films. The wide-angle X-ray diffraction diagrams revealed that all the polyimides possessed amorphous character, and the regulation of those polyimides were decreased with the increase of the molar ratio of SIDA to PMDA. Differential scanning calorimeter measurements showed that the introduction of SIDA to polyimide backbone would make glass transition temperature shift to lower temperature. Thermogravimetric analyses indicated that the silicon-containing polyimides lowered decomposition temperature as compared with PMDA/4, 4'-ODA polyimides. However, UV-visible transmission and reflection spectra showed that the optical transparency of silicon-containing polyimide thin films was superior to that of PMDA/4, 4'-ODA polyimide thin films.

**Key words:** bis(3, 4-dicarboxyphenyl)dimethylsilane dianhydride; polyimide; synthesis

Aromatic polyimides possess marked thermal stability, and excellent mechanical, electrical and solvent resistance properties. Therefore, they have been used in such applications as automobile and aircraft parts and packaging in printed electronic circuitry. The conventional polyimide synthesized from pyromellitic dianhydride (PMDA) and 4, 4'-oxydianiline (4, 4'-ODA) shows an excellent combination of thermal and mechanical properties as judged by high elongations to break. In addition, these properties can be retained up to 400 °C. However, PMDA/4, 4'-ODA polyimides exhibit brownish color due to the existence of large conjugated structure and/or strong charge transfer complex. When a polyimide is applied in optical devices, its optical transparency is of vital importance<sup>[1]</sup>.

Introduction of a bulky central moiety such as dimethylsilylene into the backbone of a polyimide can improve the properties of the polyimides in optical transparency, oxidative resistance, solubility, softening point, adhesion, permeability and permselectivity<sup>[2-9]</sup>. Polyimides prepared from aromatic diamines and bis(3, 4-dicarboxyphenyl)dimethylsilane dianhydride (SIDA) are heat resistant, with their 5% weight loss in

air occurring within 430 to 470 °C<sup>[3]</sup>; polyimide from SIDA and 4, 4'-ODA has lowered glass transition temperature as compared with PMDA/4, 4'-ODA polyimide. And the color of polyimides can be reduced by the application of silicon-containing monomer that has the tendency of reducing formation of a charge transfer complex and destroys conjugated structure.

In this article, we use a SIDA to partially replace the conventional PMDA, in an attempt to improve the properties of rigid PMDA/4, 4'-ODA polyimide through copolymerization. The effects of SIDA on the basic thermal and optical properties of copolyimides are described.

## 1 Experimental

### 1.1 Materials

PMDA was purified by sublimation before use. 4, 4'-ODA was purified by recrystallization from tetrahydrofuran. N, N-dimethylacetamide (DMAc) was purified by distillation under ambient pressure from P<sub>2</sub>O<sub>5</sub> prior to use. The remaining chemical reagents (all from Shanghai Chemical Reagents Company) were used without additional purification.

### 1.2 Synthesis of SIDA

SIDA was synthesized according to the method of previous works<sup>[10]</sup>. 4-Bromo-1, 2-dimethylbenzene (74

Received 2003-12-23.

**Foundation item:** The Science Foundation of Southeast University (No. 9207041140).

**Biography:** Lin Baoping (1958—), male, associate professor, lbp@seu.edu.cn.

g, 0.2 mol) and dichlorodimethylsilane (25.8 g, 0.1 mol) in toluene were added to a stirred suspension of metal sodium (22 g, 0.94 mol) in anhydrous toluene (100 mL) dropwisely at ambient temperature under nitrogen. After dripping out, the solution was refluxed for 1 h. Then NaCl and NaBr in the solution were removed by filtration and toluene was removed *in vacuo*. Distillation afforded 38 g (70.9%) of bis(3, 4-dimethylphenyl) dimethylsilane (BDMS), which solidified on cooling, recrystallized from ethanol, mp 57 to 59 °C. FTIR (cm<sup>-1</sup>, KBr): 3 057(Ph-H); 1 254, 804 (Si-CH<sub>3</sub>); 1 448, 1 101(Si-Ph). <sup>1</sup>HNMR (CDCl<sub>3</sub>), δ: 7.15 to 7.33 (6H, m, aryl CH), 2.30 (12H, s, aryl CH<sub>3</sub>), 0.55 (6H, s, silyl CH<sub>3</sub>).

Solid KMnO<sub>4</sub> (109 g, 0.69 mol) was added portionwise to a refluxing solution of BDMS (15.3 g, 0.04 mol) in pyridine (230 mL) and water (63 mL). The solution was then refluxed for 1 h before adding methanol (10 mL) to destroy any unreacted permanganate. After suction filtration of MnO<sub>2</sub> followed by washing with hot water, pyridine was distilled off under ambient pressure. Acidification with 3 mol HCl to pH 1 gave 14 g of crude bis(3, 4-dicarboxyphenyl)dimethylsilane (BDCS).

Crude BDCS (14 g) was refluxed for 2 h with 50 mL of acetic anhydride. The solvents were boiled off by vacuum distillation and the leftover was recrystal-

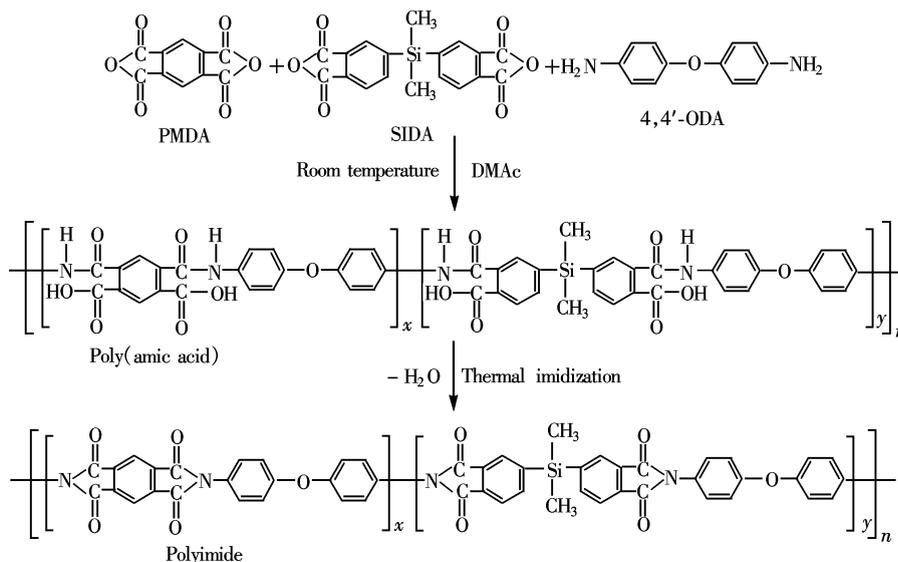
lized from benzene-hexane-chloroform to afford 7.0 g (55%) of SIDA, mp 181 to 183 °C. FTIR (cm<sup>-1</sup>, KBr): 1 855, 1 770 (—CO—), 1 279, 1 246, 814 (Si-CH<sub>3</sub>), 1 481, 1 119(Si-Ph); <sup>1</sup>HNMR (CDCl<sub>3</sub>), δ: 8.05 to 8.15 (6H, m, aryl CH), 0.80 (6H, s, silyl CH<sub>3</sub>).

### 1.3 Preparation of polyimide films

Tab.1 lists the components of polyimides prepared with varying molar ratios of SIDA and PMDA. Polyimides were synthesized by mixing an equivalence of relevant dianhydride and 4, 4'-ODA at room temperature in DMAc solutions, reacting for 24 h. After reaction, the solutions were clarified and coated on glass substrates. When the coats were gently baked at 50 °C *in vacuo* for 6 h, with most of the solvent withdrawn, gel films were formed. To evacuate the DMAc remaining in the films, polyamic acid gel films were continuously treated at 150 °C *in vacuo* for 10 h. Finally, the imidization of polyamic acid thin films was performed in steps for 1 h at 200 °C and 2 h at 280 °C. **The preparation process is described in Fig.1.**

**Tab.1** Components of polyimides under different molar ratios %

Sample code	PMDA	SIDA	4, 4'-ODA
PI-1	100	0	100
PI-2	75	25	100
PI-3	50	50	100



**Fig.1** Preparation of copolyimides

### 1.4 Measurements

The structures of BDMS and SIDA were confirmed by Fourier transform infrared (FTIR, Nicolet Magna IR750) and nuclear magnetic resonance (NMR,

Bruker AC-300, 300 MHz) spectroscopy. The structures of the polyimide films were characterized by ATR-FTIR (Nicolet Magna IR650).

X-ray diffraction (XRD) measurement was carried out via a Shimadzu XD-3A diffractometer with Cu-K $\alpha$

radiation.

UV-visible transmission and reflection spectra of polyimide films were measured on a Shimadzu UV2200 UV-visible spectrophotometer in the transmittance mode and the reflection mode, respectively.

Differential scanning calorimeter (DSC) measurement was conducted on a TA Instruments Q10, under a nitrogen purge, at a heating rate of 10 °C/min. The thermal stabilities of polyimides were characterized by thermogravimetric analysis (TGA). The TGA spectra were recorded on a TA Instruments SDT Q600, under a nitrogen purge or an air purge. The scanning rate was 20 °C/min.

## 2 Results and Discussions

The ATR-FTIR spectrum of PI-3 film is shown in Fig.2. The characteristic absorption at 1710  $\text{cm}^{-1}$  and 1775  $\text{cm}^{-1}$  of C=O stretching in imide groups was observed. The absorption of C—N stretching at 1370  $\text{cm}^{-1}$  and C—N bending at 721  $\text{cm}^{-1}$ , respectively, in imide groups was also observed. The characteristic Si—Ph absorption appeared at 1409  $\text{cm}^{-1}$  and 1059  $\text{cm}^{-1}$  as well as 675  $\text{cm}^{-1}$ . The absorption at 1231  $\text{cm}^{-1}$  was based on the aromatic ether —O— in polyimide. The observation of these absorption bands clearly indicated the existence of imide groups and silicon groups, and confirmed the successful synthesis of polyimide.

The regularity of polyimide films was proved by XRD measurement. In this test, three kinds of polyimide films exhibited no obvious sharp diffraction peaks of crystalline, but only wide diffraction peaks of the amorphous structure, as shown in Fig.3. With the

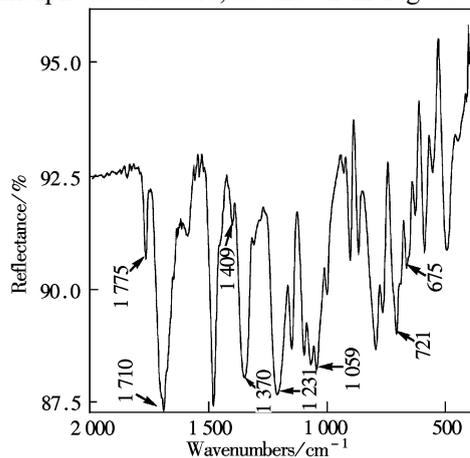


Fig.2 ATR-FTIR spectrum of PI-3 film

increase of the molar ratio of SIDA in the polyimides, diffraction peaks became blunt, which revealed that the structure regularity of copolyimides was lower. The results also implied that reactivity of bis(3, 4-dicarboxyphenyl) dimethylsilane dianhydride was different from that of pyromellitic dianhydride.

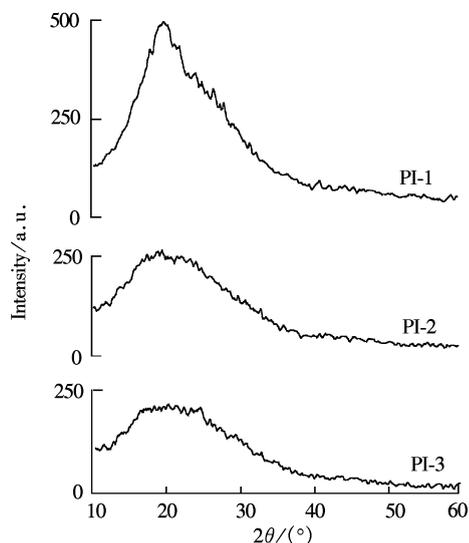


Fig.3 XRD of the polyimide films

The thermal properties of the polyimides are tabulated in Tab.2. The glass transition temperatures  $T_g$ 's of polyimides were determined by means of DSC measurement. It was known that polyimide obtained from PMDA and 4, 4'-ODA did not show clear inflection point of  $T_g$ . However, in the case of silicon-containing copolyimides, their  $T_g$ 's were clearly observed and ranged from 364 to 368 °C. In addition, no melting endothermal peak was observed from DSC traces. This also verified the amorphous nature of the polyimides.

Tab.2 Thermal properties of polyimides °C

Sample code	$T_g^*$	$T_{d5}^{**}$	
		In $\text{N}_2$	In air
PI-1	396	572	550
PI-2	364	542	491
PI-3	368	534	487

\* From the second heating trace of DSC measurements conducted at a heating rate of 10 °C/min;

\*\* Temperature at 5% weight loss ( $T_{d5}$ ) determined by TGA in nitrogen or in air at a heating rate of 20 °C/min.

The thermal stabilities of polyimides were characterized by TGA measurement. The temperatures at 5% weight loss of the polyimides are summarized in Tab.2. With the increase of the molar ratio of SIDA in polyimides, the temperatures at 5% weight loss of the polyimides were decreased whether in nitrogen or in air. PI-2 and PI-3 copolyimides exhibited relatively

lower temperature of thermal decomposition than PI-1, which was caused by the higher rigidity and thermal stability of the PMDA/4, 4'-ODA polyimide structure and by decomposition and oxidation of the silyl  $\text{CH}_3$  in PI-2 and PI-3 polyimide chain.

The UV-visible transmission spectra are shown in Fig. 4. The optical transparency of PI-2 and PI-3 copolyimides thin films was superior to that of PI-1

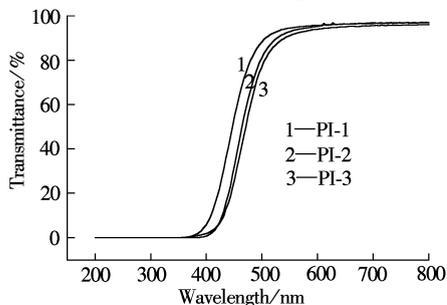


Fig. 4 UV-visible transmission spectra of the polyimide films

polyimide thin film. The transmittance of PI-3 polyimide film at 500 nm and 450 nm were 88% and 55%, respectively. However, the PI-1 polyimide film exhibited only the transmittance of 77% and 26% at 500 nm and 450 nm, respectively. This result supported the claim that the optical absorption in the visible and near UV range could be effectively reduced by the introduction of silicon atom other than that of highly electronegative fluorine atoms or the replacement of aromatic groups with nonaromatic groups. The UV-visible reflection spectra of polyimides, as shown in Fig. 5, also proved that the incorporation of silicon group to the polyimide backbones would lead to the “blue-shift” of the maximum absorption wavelength. Therefore, introduction of a bulky central moiety such as dimethylsilylene into the backbone of a polyimide could improve the optical transparency of the polyimide by the distortion of the conjugation or the reduction of charge transfer complex.

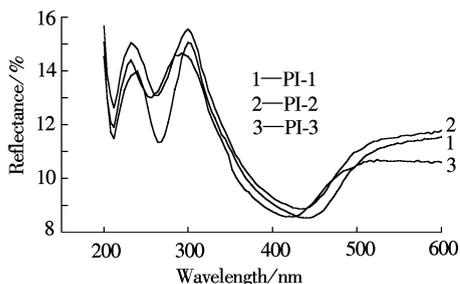


Fig. 5 UV-visible reflection spectra of the polyimide films

### 3 Conclusion

All the polyimides possessed amorphous character, and the regulation of those polyimides was decreased with the increase of the molar ratio of SIDA. Introduction of SIDA to polyimide backbone would make the glass transition temperature and the initial thermal decomposition temperatures shift to lower temperature. The optical transparency of SIDA-containing polyimide thin films was superior to those of PMDA/4, 4'-ODA polyimide thin films.

### References

- [1] Lu Q H, Yin J, Xu H J, et al. Preparation and properties of organo-soluble polyimides based on 4, 4'-diamino-3, 3-dimethyldiphenylmethane and conventional dianhydrides [J]. *J of Applied Polymer Science*, **1999**, *72*: 1229 - 1304.
- [2] Mittal K L. *Polyimides: synthesis, characterization, application* [M]. New York: Plenum Press, 1984. 51 - 56.
- [3] Koton M M, Zhukova T I, Florinskii F S, et al. Aromatic polyimides based on bis (3, 4-dicarboxyphenyl) dimethylsilane dianhydride [J]. *Vysokomol Soedin, Ser B*, **1980**, *22*(1): 43 - 45.
- [4] Stern S A, Vaidyanathan R, Pratt J R. Structure/permeability relationships of silicon-containing polyimides [J]. *J of Member Science*, **1990**, *49*(1): 1 - 14.
- [5] Chen P, Xu X, Wang D. Synthesis of silicon-containing aromatic diamines and thermal properties of corresponding polyimide siloxanes [J]. *Acta Polymerica Sinica*, 1994(6): 717 - 724. (in Chinese)
- [6] Zhou W, Lu F. Silicon-containing polyimides for gas separation [J]. *Polymer*, **1994**, *35*(3): 590 - 593.
- [7] Kumar D, Gupta A D. A new optically transparent silicon-containing polyimide film [J]. *Polymer Preprint (Am Chem Soc, Div Polym Chem)*, **1995**, *36*(5): 49 - 50.
- [8] Zhu P, Li Z, Feng W, et al. Preparation and characterization of negative photosensitive polysiloxaneimide [J]. *J of Applied Polymer Science*, **1995**, *55*(7): 1111 - 1116.
- [9] Li Y, Wang X, Ding M. Effects of molecular structure on the permeability and permselectivity of aromatic polyimides [J]. *J of Applied Polymer Science*, **1996**, *61*(5): 741 - 748.
- [10] Pan Y, Lin B P, Qian Y, et al. Synthesis of a silicon-containing aromatic dianhydride and its polyimide [J]. *J of Functional Polymers*, **2003**, *16*(2): 225 - 228. (in Chinese)

# 基于双-(3, 4-苯二甲酸酐)二甲基硅烷 共聚酰亚胺的合成及表征

林保平<sup>1</sup> 钱 鹰<sup>1</sup> 潘 英<sup>1</sup> 袁春伟<sup>2</sup>

(<sup>1</sup> 东南大学化学化工系, 南京 210096)

(<sup>2</sup> 东南大学分子与生物分子电子学教育部重点实验室, 南京 210096)

**摘要:** 由双-(3, 4-苯二甲酸酐)二甲基硅烷、均苯四甲酸酐和 4, 4'-二氨基二苯醚制备了含硅聚酰胺酸. 通过溶液浇铸方法制得聚酰胺酸薄膜, 经热处理将其转化为聚酰亚胺薄膜. X-衍射测量表明, 该类型聚酰亚胺具有非晶态结构, 且规整性随双-(3, 4-苯二甲酸酐)二甲基硅烷含量的增加而减少. 含硅共聚酰亚胺与传统均苯四甲酸酐/4, 4'-二氨基二苯醚聚酰亚胺相比, 呈现较低的玻璃化转变温度和分解温度, 但共聚酰亚胺中双-(3, 4-苯二甲酸酐)二甲基硅烷含量增加将导致薄膜的透光率增加.

**关键词:** 双-(3, 4-苯二甲酸酐)二甲基硅烷; 聚酰亚胺; 合成

**中图分类号:** TQ323.7