

Comparative Study of Silicon-Containing Polyimides from Different Oxydianilines

Bao-Ping Lin,¹ Ying Pan,¹ Ying Qian,¹ Chun-Wei Yuan²

¹Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China

²Key Laboratory of Molecular and Biomolecular Electronics of Ministry of Education, Nanjing 210096, China

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ABSTRACT: Silicon-containing polyimides were synthesized by solution polycondensation of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride with 3,4-oxydianiline and 4,4'-oxydianiline, respectively. All the poly(amic acid) films could be obtained by solution-casting from *N,N*-dimethylacetamide solutions and thermally converted into transparent and tough polyimide films. The physical properties of thin films of those polyimides were compared by DSC, TGA, UV-visible spectroscopy, and dynamic mechanical analysis. The polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 3,4-oxydianiline exhibited superior energy-damping characteristic, mechanical properties, and optical transparency, whereas that from

bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 4,4'-oxydianiline possessed higher glass-transition temperature and thermal stability. Because of the unsymmetric structure of the polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 3,4-oxydianiline, its increasing rate of linear coefficient of thermal expansion with temperature was quicker than that of the polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 4,4'-oxydianiline. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2363–2367, 2004

Key words: polyimides; synthesis; films; polycondensation; oxydianilines

INTRODUCTION

Polyimides prepared from aromatic monomers are widely used in the microelectronic industry, the manufacture of automobile parts and aircraft parts, and as gas-separation films because of their excellent high-temperature thermal stability, and mechanical, electrical, and solvent-resistance properties.^{1–4} With the increasing use of polyimides for gas-separation and microelectronic applications, permeability of polyimides and adhesive ability between substrates and polyimides have become of increasing importance. Introduction of a bulky central moiety, such as dimethylsilylene, into the backbone of a polyimide can promote significant increases in permeability, permselectivity, and adhesive ability.^{5–11} More recently, silicon-containing aromatic polymers have attracted much scientific technological interest because of their potential applications for the production of optoelectronic materials, resulting from the ability of silicon, when placed among aromatic neighbors, to give a σ - π conjugation and thus support the transport of electrons along the macromolecular chain.^{12,13}

Johnston and Jewell¹⁴ prepared silicon-containing polyimides from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SIDA) and 4,4'-oxydianiline (4,4'-ODA), and discussed their mechanical properties and thermal stability. They found that silicon-containing polyimides had inferior tensile properties, glass-transition temperatures, and thermal stability compared to those of nonsilicon-containing polyimides. Koton et al.¹⁵ investigated thermal properties and solubility of polyimides prepared from SIDA and aromatic diamines. The results showed that SIDA-containing polyimides were heat resistant and storage stable.

The polyimide from oxyalkylene-containing diamine had a lowered softening point, and that from phenoxy-containing diamine could dissolve in some organic solvents. Buhn¹⁶ performed a comparative study of silicon-containing polyimides from different diaminodiphenylmethanes. The polyimides from 4,4'-diaminodiphenylmethane had higher glass-transition temperature than those containing 3,3'-diaminodiphenylmethane. All polyimides showed an initial weight gain during thermal gravimetric analysis, attributed to oxidation of methylene groups to carbonyl. Kumar and Crupta¹⁷ synthesized a silicon-containing polyimide film based on keto-ether-containing aromatic diamine and SIDA. The polyimide film possessed higher optical transparency than that of conventional polyimides. Hamciuc et al.¹⁸ synthesized a series of silicon-containing

Correspondence to: B.-P. Lin (lbp@seu.edu.cn).

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phenylquinoxaline-imide polymers and investigated their properties.

Among silicon-containing polyimides, little is known about polyimide obtained from SIDA and 3,4-oxydianiline (3,4-ODA). In this article, silicon-containing polyimides were prepared by SIDA reacting with 4,4'-ODA and 3,4-ODA, respectively. The effect of the structures of polyimides on the thermal properties, dynamic mechanical properties, and optical properties was investigated.

EXPERIMENTAL

Materials

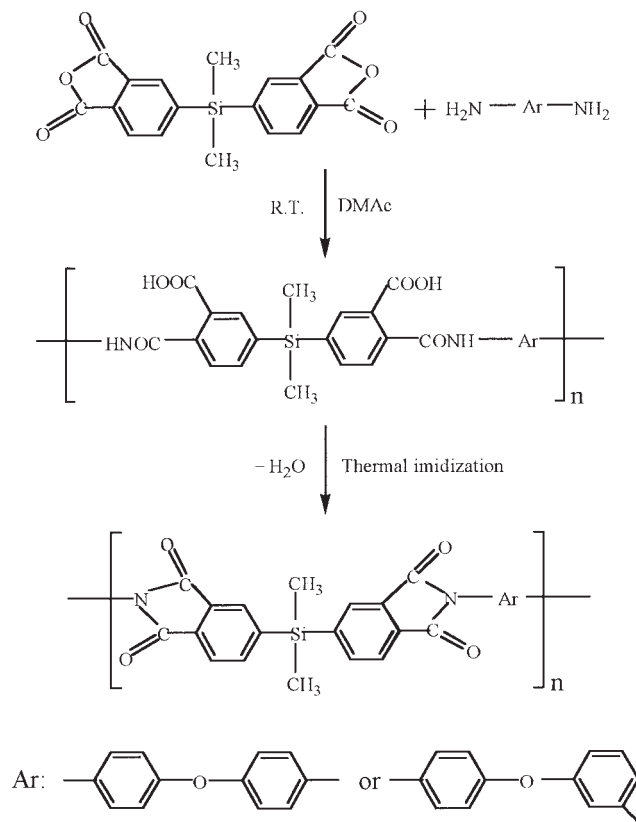
Monomer bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SIDA) was synthesized according to the method reported in the literature.¹⁹ 4,4'-Oxydianiline was purchased from Shanghai Chemical Reagent Co. and purified by recrystallization from tetrahydrofuran (THF). 3,4-Oxydianiline was obtained from Shanghai Chemical Reagent Research Institute and purified by recrystallization from THF. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under ambient pressure from P₂O₅ before use. All other chemical reagents were used without additional purification.

Preparation of polyimides

The polyimides were synthesized by mixing an equivalence of relevant SIDA and ODA (4,4'-ODA or 3,4-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 Scheme 1.

Measurements

The structures of polyimides were confirmed by FTIR (Nicolet Magna IR650; Nicolet Analytical Instruments, Madison, WI). Transmission and reflection UV-visible spectra of polyimide films were measured on a Shimadzu UV2200 UV-visible spectrophotometer (Shimadzu, Kyoto, Japan) in the transmittance mode and the reflection mode, respectively. Glass-transition temperature was measured on a TA Instruments Q10 differential scanning calorimeter (DSC; TA Instruments, New Castle, DE), under a nitrogen purge, at a heating rate of 10°C/min. The thermal stabilities of polyimides were characterized by thermogravimetric



Scheme 1 Synthesis scheme of polyimides.

analysis (TGA). 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. Dynamic mechanical analysis was performed on a Mark V dynamic mechanical thermal analyzer (DMTA; Rheometric Scientific, Piscataway, NJ). The run conditions were conducted at a frequency of 1 Hz and a heating rate of 3°C/min from -140 to 300°C in air. The mean values of the linear coefficient of thermal expansion (CTE) were obtained from measurements on a Rheometric Scientific Mark V at a heating rate of 3°C/min, from room temperature to 200°C.

RESULTS AND DISCUSSION

The polyimide synthesized from SIDA and 4,4'-ODA was designated PI-1; that from SIDA and 3,4-ODA was designated PI-2.

IR spectra of polyimides

The ATR-FTIR spectra of polyimides are shown in Figure 1. The characteristic absorption at 1713 and 1775 cm⁻¹ of C=O stretching in imide groups was observed. The absorption of C-N stretching at 1360 cm⁻¹ and C-N bending at 729 cm⁻¹, respectively, in imide groups was also observed. The characteristic

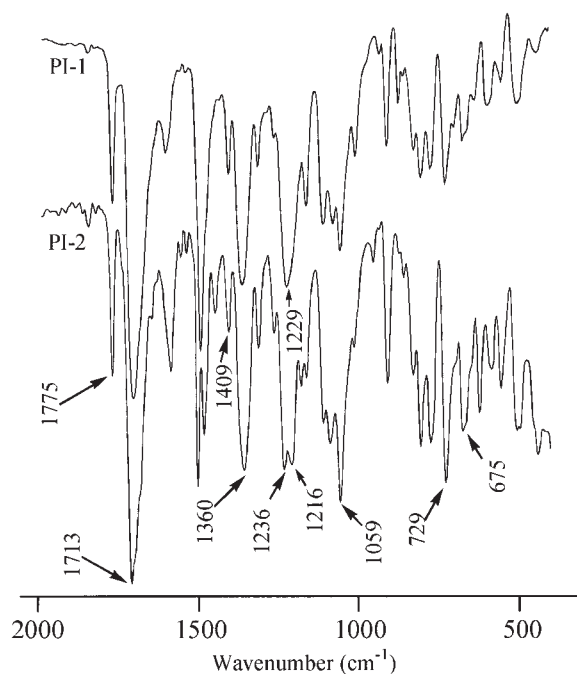


Figure 1 ATR-FTIR spectra of polyimide films.

Si-Ph absorption appeared at 1409 and 1059 cm^{-1} as well as at 675 cm^{-1} . The absorption at 1229 cm^{-1} was based on the aromatic ether $-\text{O}-$ in PI-1. However, the absorption of the aromatic ether $-\text{O}-$ in PI-2 became separated into twin peaks, at 1236 and 1216 cm^{-1} . The observation of these absorption bands clearly indi-

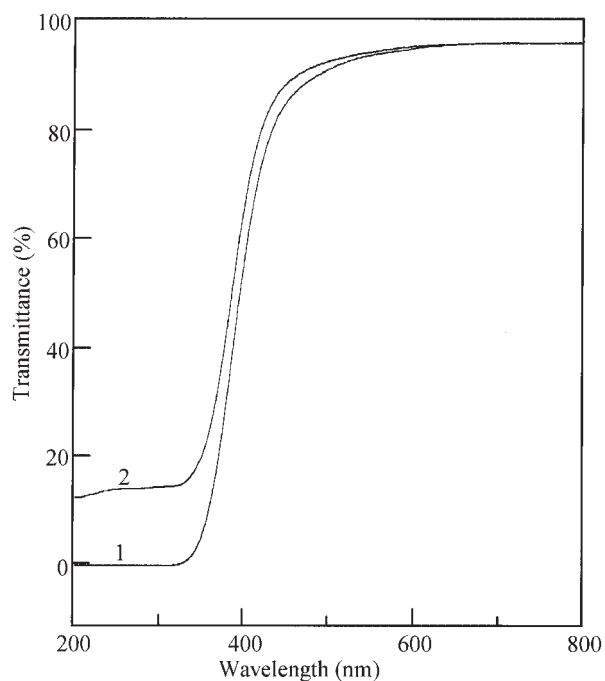


Figure 2 UV-vis transmittance spectra of polyimide films. (1) PI-1; (2) PI-2.

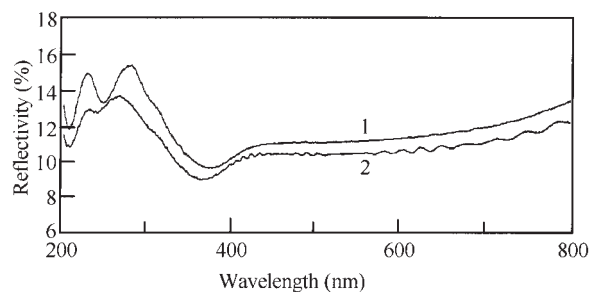


Figure 3 UV-vis reflection spectra of polyimide films. (1) PI-1; (2) PI-2.

cated the existence of imide groups and silicon groups, and confirmed the successful synthesis of polyimides and the difference of chemical structure between PI-1 and PI-2.

Optical transparency

UV-vis transmission spectra are shown in Figure 2. The optical transparency of the thin film of PI-2 polyimide was superior to that of PI-1 polyimide thin film. The transmittance of PI-2 polyimide film at 500 and 400 nm was 94 and 66% , respectively. However, the PI-1 polyimide film exhibited only the transmittance of 92 and 56% at 500 and 400 nm , respectively. UV-vis reflection spectra of polyimides, as shown in Figure 3, also proved that the maximum absorption wavelength of polyimide from SIDA and 3,4-ODA shifted to a lower wavelength. This was caused by the distortion of the conjugation and the reduction of charge transfer complex in the PI-2 polyimide. Therefore, by adjusting the regularity of the main chain in polyimides, the optical absorption in the visible and near-UV range could be effectively reduced.

Glass-transition temperatures and viscoelastic properties

The glass-transition temperatures (T_g s) and viscoelastic properties of polyimides are tabulated in Table I. The glass-transition temperatures of polyimides were determined by means of DSC measurement. T_g s values of polyimides were clearly observed and ranged

TABLE I
 T_g and Viscoelastic Properties of Polyimides

Sample code	T_g^a ($^{\circ}\text{C}$)	T_g^b (α)		β^b	
		($^{\circ}\text{C}$)	$\tan \delta$	($^{\circ}\text{C}$)	$\tan \delta$
PI-1	256	251	1.134	88	0.054
PI-2	228	226	1.546	60	0.062

^a From the second heating trace of DSC measurements conducted at a heating rate of $10^{\circ}\text{C min}^{-1}$.

^b DMTA, data collected at $3^{\circ}\text{C min}^{-1}$ in air and 1 Hz .

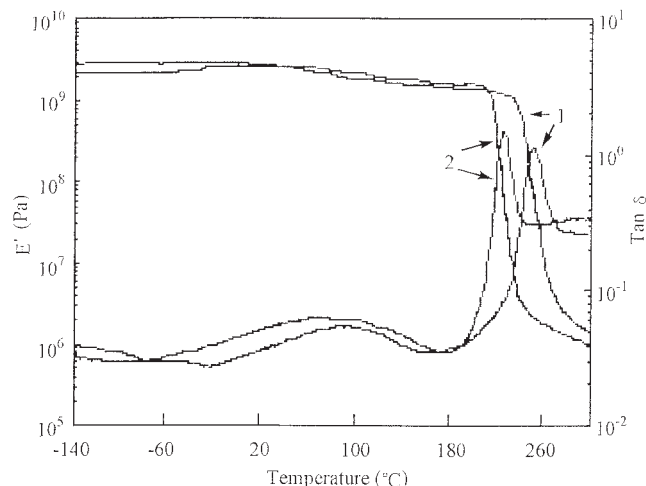


Figure 4 Dynamic viscoelastic spectra of polyimide films. (1) PI-1; (2) PI-2.

from 228 to 256°C. T_g of polyimide obtained from SIDA and 4,4'-ODA was higher than that of polyimide from SIDA and 3,4-ODA. The region of glass transition of the PI-2 polyimide also was wider than that of PI-1. This was attributed to the difference of regularity between PI-1 and PI-2 polyimides. In addition, no melting endothermal peak was observed from DSC traces. This also verified the amorphous nature of those polyimides.

Viscoelastic analysis of polyimide films is shown in Figure 4. The films of PI-1 and PI-2 polyimides exhibited the typical behaviors of linear thermoplastic polyimides in losing their storage modulus above the softening point. The magnitude of the storage modulus of PI-1 and PI-2 polyimides was consistent with that of conventional polyimides below the softening point. T_g values of polyimides measured by DMTA were slightly lower than those determined by DSC. The magnitude of $\tan \delta$ at T_g is a measure of the energy-damping characteristic of a material and is related with the impact strength of a material.^{20,21} The impact strength increases with the addition of $\tan \delta$ value at T_g . The value of $\tan \delta$ at T_g for PI-2 polyimide was about 1.546; however, that for PI-1 polyimide was only about 1.134. The results indicated that the energy-damping characteristic and mechanical properties of PI-2 polyimide were superior.

The beta relaxation β occurs below the T_g and is associated with local bond rotations and molecular segment motions along the polymer backbone, and the magnitude of this relaxation is proportional to the concentration of segments contributing to the relaxation. In general, these motions are considered to be primarily a function of the type of diamine in the polyimide, and their presence and magnitude have been ascribed to several material properties.²² In our experiments, PI-2 polyimide exhibited a higher $\tan \delta$

TABLE II
TGA Data Summary of Polyimides

Sample code	T_{d5}^a		Char yield ^b (%)
	In N ₂ (°C)	In air (°C)	
PI-1	531	519	11.86
PI-2	512	481	11.82

^a Temperature at 5% weight loss (T_{d5}) determined by TGA in nitrogen or in air at a heating rate of 20°C min⁻¹.

^b Char yield at 800°C in air.

value at the β -transition and a wider region of the β -transition. Hence, increasing of the number of PI-2 polyimide segments in motion was evident from the increase of $\tan \delta$ at the β -transition compared with that of PI-1 polyimide. PI-1 polyimide possessed a higher temperature at the β -transition than did PI-2 polyimide, which indicated that a higher energy barrier in PI-1 polyimide existed for molecular motions.

Thermal stability

The thermal stabilities of polyimides were characterized by TGA measurement. The temperatures at 5% weight loss (T_{d5}) of the polyimides are summarized in Table II. T_{d5} values of those polyimides reached 512–531 and 481–519°C in nitrogen and air atmosphere, respectively. This showed that heat resistance of polyimides prepared from SIDA and ODA were superior. PI-1 polyimide exhibited a slightly higher temperature of thermal decomposition compared with that of PI-2 polyimide, whether in nitrogen or in air atmosphere, which was attributed to the greater rigidity of the structure of the polyimide prepared from SIDA and 4,4'-ODA.

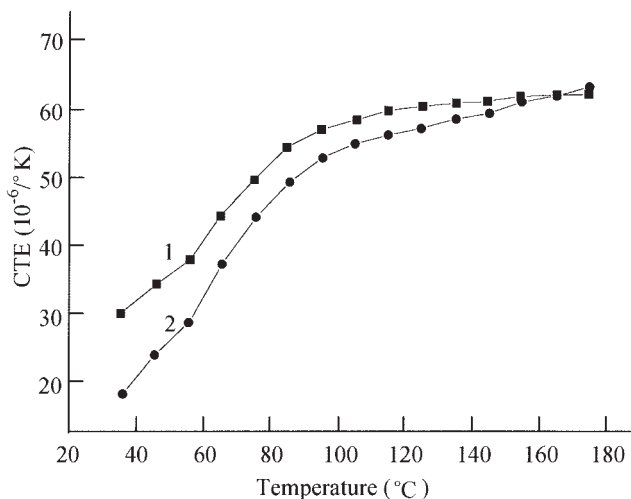


Figure 5 Variations in CTE values with temperature for films of PI-1 and PI-2 polyimides. (1) PI-1; (2) PI-2.

Coefficient of thermal expansion

The coefficient of thermal expansion (CTE) is an important parameter of a material. Figure 5 shows typical variations in CTE values with temperature for films of PI-1 and PI-2 polyimides. The CTE values were obtained from the second heating trace of DMTA measurements conducted at a heating rate of $3^{\circ}\text{C min}^{-1}$. The rate of increase of CTE with temperature for PI-1 and PI-2 polyimides was greater from room temperature to 90°C , but the rate of the increase of CTE with temperature decreased over the range $90\text{--}180^{\circ}\text{C}$. This was in concordance with β -relaxations revealed in the dynamic mechanical tests. Because of the unsymmetric structure of PI-2 polyimide, the increasing rate of CTE with temperature for PI-2 polyimide was quicker than that for PI-1 polyimide.

CONCLUSIONS

Silicon-containing polyimides were synthesized by solution polycondensation of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride with 4,4'-oxydianiline and 3,4-oxydianiline, respectively. All the polyimides possessed an amorphous character. Polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 4,4'-oxydianiline showed a higher glass-transition temperature and thermal stability. Polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 3,4-oxydianiline exhibited superior energy-damping characteristic, mechanical properties, and optical transparency. The increasing rate of linear CTE of polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 3,4-oxydianiline with temperature was quicker than that of polyimide from bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and 4,4'-oxydianiline.

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