

Synthesis and Properties of Organosoluble Polysiloxaneimides Derived from 5,5'-exo-(1,1,3,3,5,5-hexamethyl-trisiloxane-1,5-diyl)bisbicyclo[2,2,1]heptene-2,3-endo-dicarboxylic Dianhydride and Various Aromatic Diamines

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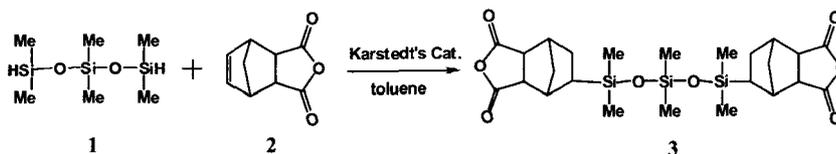
Introduction

Polyimides (PIs), a well-known class of high performance polymers, are used in various high-tech applications owing to their excellent combined physical and chemical properties.¹⁻⁶ Recently, low dielectric constant PIs with good processability have been desired in microelectronics fields in order to meet the requirements of high-density interconnection.^{1,4-7} However, their application is somewhat limited due to difficulties such as insolubility in conventional solvents and extremely high glass transition temperature or high melting temperature. Therefore, considerable effort has been made to minimize the disadvantages and to design polyimides with the desired properties.⁸⁻¹⁰ One method to improve the solubility and other desired properties of PIs is by structural modification, such as incorporation of siloxane flexible units into the polyimide backbone. Siloxane materials render a number of useful properties such as low temperature flexibility, high thermal stability, hydrophobicity, oxidative resistance, biocompatibility, high adhesiveness, low dielectric constants, and significant gas permeability. Thus the incorporation of siloxane groups into the aromatic polymer chains yielded soluble products having remarkable thermal stability and good film-forming ability.⁹⁻¹² Thus, we prepared new polyimides containing main chain siloxane groups to investigate processing and material properties.

Experimental Section

Synthesis of 5,5'-exo-(1,1,3,3,5,5-hexamethyl-trisiloxane-1,5-diyl)bisbicyclo[2,2,1]heptene-2,3-endo-dicarboxylic anhydride (3)

To a 20-mL two-necked, round-bottomed flask equipped with a magnetic stirrer were placed the 1,1,3,3,5,5-hexamethyl-trisiloxane(1) (5.0 g, 24 mmol), *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride (2) (10.0 g, 60 mmol) and toluene (40 mL) under an argon stream. The reaction was catalyzed by 0.2 mol % of Karstedt's catalyst (Pt(dvs)) and heated at 75 °C for 24 h. The product was purified in a 92 % (11.9 g) yield by recrystallization from hexane. mp 133.4-133.9 °C. MALDI-TOF MS = 560.6 (M+Na⁺, Calcd. value of 536.7). IR (KBr): ν = 1849, 1785 (anhydride C=O), 1260 (Si-CH₃), 1084 (Si-O-Si) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): 3.40 (4H, s), 2.85 (2H, s), 2.77 (2H, s), 1.71 - 1.55 (8H, m), 0.66 (2H, t, *J* = 8.7 Hz), 0.07 (6H, s), 0.04 (6H, s), 0.02 (6H, s) ppm. ¹³C -NMR (75

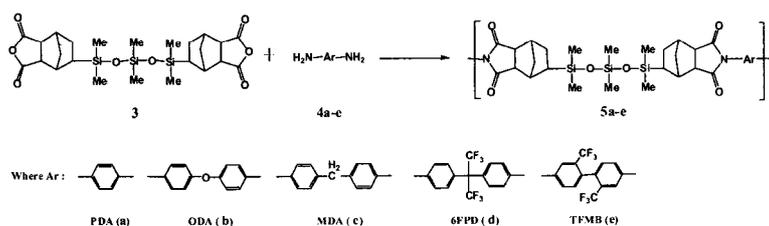


MHz, CDCl₃): 173.3, 172.9, 53.7, 50.5, 42.6, 42.2, 41.4, 27.7, 26.7, 2.4, -0.1 ppm. ²⁹Si-NMR (60 MHz, CDCl₃): 5.81, -19.5 ppm. Anal. Calcd. for C₂₄H₃₆O₈Si₃ (%): C, 53.70; H, 6.76. Found: C, 53.86; H, 6.68.

Synthesis of polysiloxaneimides (PIs) 5

PIs **5b** is given as an example. The PI **5b** was prepared from solvent-catalyst combinations of *m*-cresol and isoquinoline (Method 1) or 1,2-dichlorobenzene and 2-hydroxypyridine (Method 2). Method 1: ODA (0.20 g, 1.0 mmol) and **3** (0.537 g, 1.0 mmol) were dissolved in 10.0 mL of *m*-cresol in a 50 mL three-necked round bottom flask. After the solution was stirred at room temperature for 30 min, isoquinoline (ca. 5 drops) was added and further stirring was conducted. The mixture was then heated at 180 °C for 6 h. The inherent viscosity of the resulting PI **5b** was 0.37 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. IR (KBr): $\nu = 1772, 1716$ (imide C=O), 1380 (C-N), 1264 (Si-Me), 1043 (Si-O-Si) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): 7.25-7.14 (8H, m), 3.25 (4H, br), 2.81 (4H, br), 1.76 -1.51(8H, m), 0.62 (2H, br), 0.07 (6H, br), 0.03 (6H, br), 0.01 (6H, br) ppm. ¹³C-NMR (75 MHz, CDCl₃): 178.4, 178.2, 157.4, 129.0, 128.1, 120.4, 52.0, 49.5, 42.2, 41.7, 40.7, 27.3, 26.4, 2.1, 0.0 ppm. ²⁹Si-NMR (60 MHz, CDCl₃): 5.89, -19.9 ppm. Method 2: ODA (0.20 g, 1.0 mmol) was dissolved in 4 mL 1,2-dichlorobenzene in a 25-mL three-necked. Then **3** (0.537 g, 1.0 mmol) and 2-hydroxypyridine(0.03 g, 3 wt%) were added, the system was equipped with an overhead mechanical stirrer and a Dean-Stark trap with condenser and nitrogen inlet. The mixture was warmed to 100 °C for 0.5 h to dissolve the monomers and catalyst then was maintained at 180 °C for 8h. The solution became noticeably more viscous and was then poured into methanol. The precipitate was filtered off, washed with water, and dried under vacuum at 180 °C. The inherent viscosity of the resulting PI **5b** was 0.58 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

PI **5a**, **5c**, **5d** and **5e** were prepared by Method 2 using diamines PDA, MDA, 6FPD and TFBD.



Results and Discussion

PIs **5** were identified by FT-IR and NMR spectroscopy. Figure 1-2 shows the ¹H, ¹³C-NMR spectra of monomer **3** and PI **5e**.

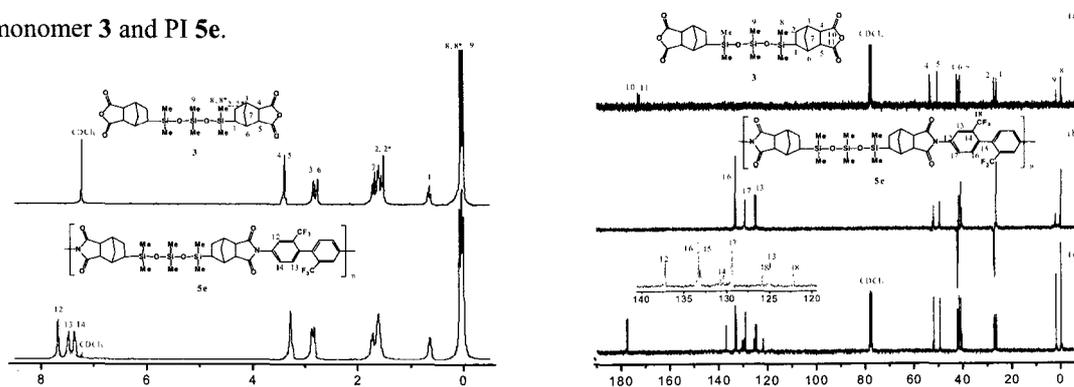


Figure 1. ¹H, ¹³C-NMR spectra of monomer **3** (a), PI **5e** (c) and ¹³C /DEPT90 (b) in CDCl₃.

The thermal properties of the PIs **5** evaluated by DSC and TGA are listed in Table 1. The PIs have glass transition temperature between 138 and 251 °C in N₂. The T_g of the PIs are not extremely high so should facilitate easier processing, except for PI **5a** which does have a high glass transition temperature. The temperature at 5% weight loss (T_{d5}) ranged from 460 and 470 °C in air, similar to 460 and 470 °C in nitrogen (Figure 6). The 10% weight loss temperatures (T_{d10}) in air (470-480 °C) are also similar to those measured in nitrogen (470 - 480 °C). The results show that the thermal stability of these PIs are similar to other semiaromatic polyimides used in microelectronic applications.

Table 1. Summary of the properties of the PIs

PIs	T_g^a (°C)	T_{d5}^b (°C)		T_{d10}^c (°C)		Contact Angle (°)
		N ₂	Air	N ₂	Air	
5a	252	465	465	475	475	- ^d
5b	138	470	470	480	480	74
5c	139	465	465	480	480	72
5d	155	465	460	475	475	78
5e	151	460	460	470	470	79

^a From DSC on the second heating at a heating rate of 30 °C/min in nitrogen or air. ^b Temperature at which 5 % weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in nitrogen or air. ^c Temperature at which 10 % weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in nitrogen or air. ^d Insoluble at room temperature.

These PIs showed low water adsorption, especially PI **5b** at 0.3 % (Table 4). They were much lower than that of PI derived from pyromellitic dianhydride (PMDA)/ODA (4.8 %).¹³ The PIs **5a-e** have a higher contact that conventional polyimides against water as shown in Table 1. The lower water adsorption and higher contact angle due to the present of the hydrophobic nature of the siloxane segments in the polymer backbone.

Table 2. Mechanical properties, dielectric constant and water adsorption of PI **5b**, **5c**, **5e**

PI	Tensile Strength (MPa)	Elongation (%)	Initial modulus (GPa)	Dielectric constant	UV cutoff Wavelength (nm)	Water adsorption (%)
5b	52	7.9	0.56	2.73	288	0.4
5c	44	5.8	0.68	2.76	289	0.4
5e	48	6.1	0.60	2.65	269	0.3

These PIs could be cast into flexible, tough films from a DMAc solution. As shown in Table 2, the membranes had tensile strengths in the range of 44-52 MPa, tensile modulus in the range of 0.56-0.68 GPa, and elongations at break from 5.8-7.9 %. PI **5b** derived from ODA had the highest elongation of 7.9 %, which can be attributed to added flexibility from the ether linkage in the polymer backbone. As

listed in Table 2, the PIs **5** possess lower dielectric constants (2.65-2.76 at 1 MHz) than that of a typical semiaromatic polyimide (2.83).¹⁴ This might be attributed to the lower polarity of the silicon groups, which in turn reduces the dielectric constant of the films.¹⁵

Conclusions

A novel siloxane containing dianhydride was prepared by hydrosilylation reaction of trisiloxane having with Si-H group. A series of organosoluble semiaromatic siloxane containing polyimides (PI **5a-e**) from the dianhydride **3** with various aromatic diamines **4** were prepared by the one-step high-temperature polycondensation method. These PIs **5b-e** were readily soluble in organic solvents at room temperature. The PIs have glass transition temperatures between 138 and 251 °C in N₂, and the 5% weight loss temperatures ranged over 450 °C in air. The membranes have a good mechanical properties with elongation at break up to 7.9 % (**5b**). The flexible and hydrophobic siloxane moiety endows the PI films with dielectric constants below 2.8, and less than 0.5 % of water adsorption.

References and Notes

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