

# Preparation and Characterization of Negative Photosensitive Polysiloxaneimide

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## SYNOPSIS

A photosensitive polysiloxaneimide precursor was synthesized from oxydianiline, bis(*p*-aminophenoxy)dimethylsilane, and a diacid chloride. This diacid chloride was prepared by the reaction of thionyl chloride with a diacid, which resulted from the reaction of pyromellitic dianhydride with hydroxyethylacrylate in *N*-methylpyrrolidone (NMP). The adhesion properties between polyimide and substrates such as SiO<sub>2</sub> wafer were improved with introduction of siloxane moiety into the polyimide chain. The dielectric constant decreased with increasing siloxane moiety content. The photocrosslinking reaction results show that an 88–90% gel fraction was reached under the irradiation of a high-pressure mercury lamp.

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## INTRODUCTION

Photosensitive polyimides have been playing an important role in the electronic industry as multilayer circuit insulation of integrated circuit, passivation layers, planarization, and alpha particle barriers and the like, due to their outstanding properties, such as thermal stability, low dielectric constant, and good mechanical properties at high temperature.<sup>1–4</sup> However, the flexibility and the adhesion between polyimide and substrate such as silicon wafer are not always satisfactory. An approach to increase the flexibility and to enhance the bonding strength between polymer and substrate is to introduce a siloxane-containing moiety into the main chain of a polyimide.

Recently, some examples were found in the literature and patents for such purposes.<sup>5–13</sup> The patterning of nonphotosensitive polysiloxaneimide films can be carried out by using a photoresist pattern as the etching mask. After removal of the photoresist, the polysiloxaneimide precursor is cured to obtain the final imidized pattern. This process is

complicated, and when a photosensitive polysiloxaneimide is employed, the pattern generation procedures can be simplified.

In this work, a photosensitive siloxane-containing polyimide was prepared. To introduce siloxane groups into the polymer chain, bis(*p*-aminophenoxy)dimethylsilane (APDS) was synthesized as a comonomer. This study deals with the synthesis and characterization of photosensitive polysiloxaneimide.

## EXPERIMENTAL

### Reactants

Monomer pyromellitic dianhydride (PMDA) and oxydianiline (ODA) were obtained from Shanghai Chemical Reagent Co. and purified by sublimation before use. *p*-Aminophenol (PAP) was purified by recrystallization from deionized water. Dimethyldichlorosilane, diethylamine, thionyl chloride, hydroxyethylacrylate (HEA), *N*-methylpyrrolidone (NMP), and all the solvents were obtained from Tianjin Chemical Reagent Co. and purified by distillation before use.

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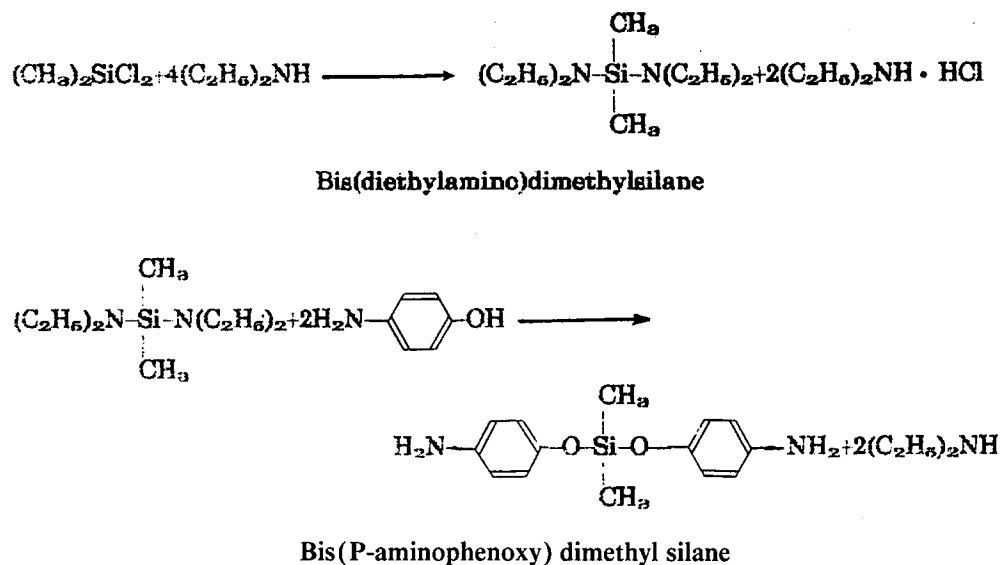


Figure 1 Synthesis scheme for bis(*p*-aminophenoxy)dimethylsilane (APDS).

### Synthesis of Bis(*p*-aminophenoxy)dimethylsilane (APDS)

The synthesis scheme is shown in Figure 1. The final product was recrystallized from benzene-petroleum ether as amber crystals.<sup>14</sup> The melting point (mp) was 62.5°C determined by DSC. The structure of APDS was confirmed both by elemental analysis and IR.

ANAL: Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Si: C, 61.28%, H, 6.61%; N, 10.21%.

Found: C, 61.21%; H, 6.68%; N, 10.41%.

The IR spectrum (KBr pellet) of APDS exhibited absorptions around 3200 cm<sup>-1</sup> (N-H), at 1255 cm<sup>-1</sup> (Si-CH<sub>3</sub>), and at 1010 cm<sup>-1</sup> (Si-O-Si).

### Preparation of Photosensitive Siloxane-containing Polyimide Precursor

To examine the characteristic changes of photosensitive resins with different contents of the siloxane group, five kinds of photosensitive resins were prepared in which the comonomer APDS was intro-

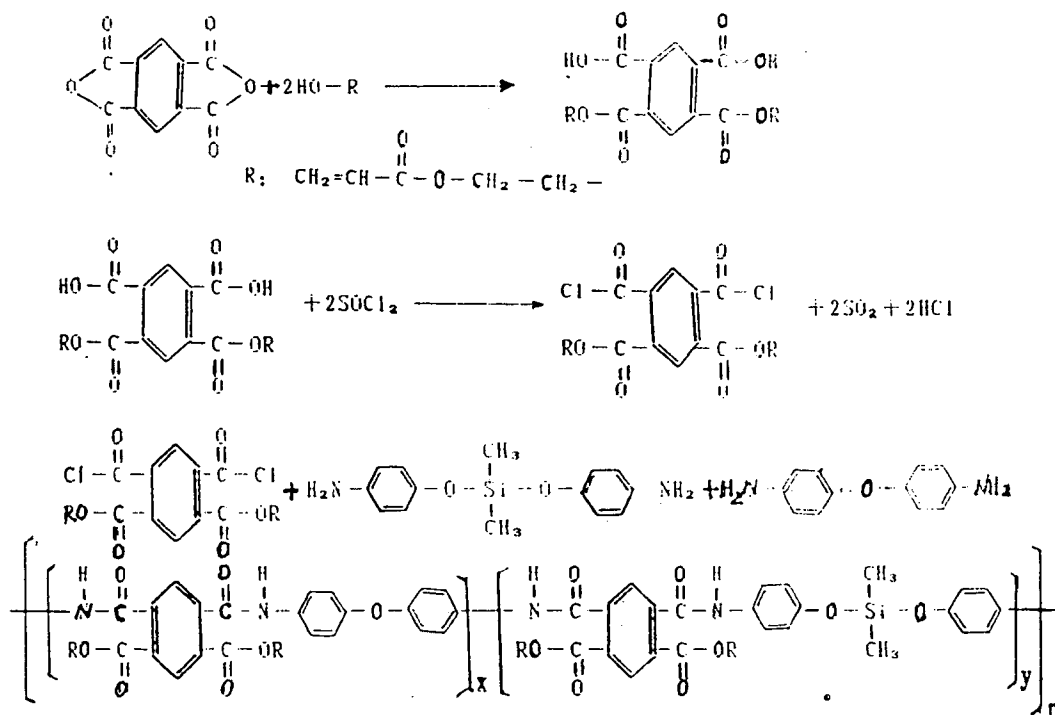
duced, according to various molar ratios of ODA and APDS, as shown in Table I.

### Synthesis Method

PMDA, 10.90 g (0.05 mol), was dissolved in 50 mL NMP at 50°C with stirring, HEA, 11.60 g (0.10 mol), was added dropwise, and the solution was stirred at 50°C for 7–8 h. Then, the solution was cooled to -10°C and SOCl<sub>2</sub>, 10.81 g (0.1 mol), was added dropwise. The reaction mixture was stirred for 3 h at -8 to -10°C. A solution of comonomer APDS 0.0025 mol in NMP, was added and stirring was continued at 0°C for 1 h; then, a solution of ODA 0.0475 mol in NMP was added at the same temperature, triethylamine, 0.1 mol, was added in one portion, and the reaction mixture was stirred for 2 h at 0°C. After the polycondensation, the precursor was precipitated by pouring the solution into deionized water with stirring. The product was washed with deionized water repeatedly until there was no chloride ion in the product, then dried at room temperature under vacuum. The equations for preparing

Table I The Code Names of Photosensitive Resins and the Molar Ratio of ODA and APDS

	Polymer Code				
	PI-1	PI-2	PI-3	PI-4	PI-5
ODA : APDS (molar ratio)	100 : 0	95 : 5	90 : 10	85 : 15	80 : 20



**Figure 2** The equations for preparing photosensitive polysiloxaneimide precursors.

the photosensitive polysiloxaneimide precursor are shown in Figure 2.

### Measurements

IR spectra and UV spectra were recorded on a Shimadzu IR-400 and UV-3000 spectrophotometer, respectively. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were performed at a heating rate 5°C/min with a Shimadzu thermal analyzer DSC-40M and a Rigaku TG-DTA, respectively. The dielectric constant was determined on a dielectric constant detector AG-4311LCR at room temperature at 1 kHz. The peel adhesion test was performed by a circle-cut method. In this method, according to the status of peeling off, the adhesion between resin and substrate is assessed

qualitatively on the 1–7 grade. The higher the grade is, the larger the peeling area is. In other words, the higher the grade is, the worse the adhesion is.

## RESULTS AND DISCUSSION

### Inherent Viscosities

Photosensitive polysiloxaneimide precursors shown in Table II were prepared similarly except that the molar ratio of ODA/APDS varied from 19/1 to 4/1, while an equivalent amount of dianhydride (PMDA) was used. From Table II, it is clear that introduction of the siloxane moiety into the polymer main chain would reduce the inherent viscosity. The cause was attributed to the flexibility of the Si—O

**Table II** The Intrinsic Viscosities of Various Photosensitive Precursors

	Polymer Code				
	PI-1	PI-2	PI-3	PI-4	PI-5
Intrinsic viscosity (mL/g)	15.84	13.44	11.72	10.34	9.59

<sup>a</sup> Measured with DMF at a concentration of 0.5 g/dL at 30°C.

**Table III** The Adhesion of Various Polysiloxaneimides to Different Substrates

Substrates	Polysiloxaneimides				
	PI-1	PI-2	PI-3	PI-4	PI-5
Fe	2	2	1	1	1
Si	2	2	2	2	1
SiO <sub>2</sub>	2	1	1	1	1

\* The higher the grade shown, the worse the adhesion is.

bonds. Besides, owing to both polymer polarity and solubility decreasing with increasing siloxane moiety content, the inherent viscosities also decrease.

### Adhesion Properties

The adhesion strengths between one siloxane-free photosensitive homopolyimide (PI-1), four photosensitive siloxane-containing polyimides (PI-2, PI-3, PI-4, PI-5), and substrates are listed in Table III. The substrates were Fe, Si, and SiO<sub>2</sub> wafers. The adhesion increased with increasing siloxane moiety content. This trend is shown in Table III. Relatively small fractions of siloxane groups were found to increase the adhesion of polyimides to substrates. The cause was attributed to that the flexible siloxane reduces the rigidity of imidized polymer chains and plays a role to tightly connect the polymer to the

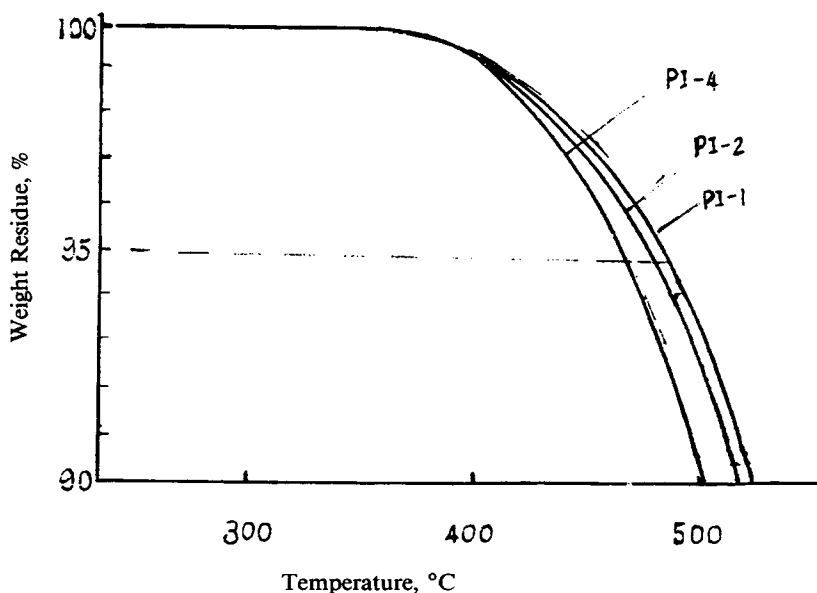
**Table IV** Thermogravimetric Results of PI-1, PI-2, and PI-4; Heating Rate 5°C/Min Under Air

	Polymer Code		
	PI-1	PI-2	PI-4
Initial decomposition temperature (°C)	325	324	324
Decomposition temperature at 95% weight residue (°C)	495	490	475

substrate. From Table III, it was also found that the SiO<sub>2</sub> wafer was a better substrate than were the others, due to more hydroxyl groups on its surface.

### Thermal Stability

Compared with siloxane-free polyimides, the thermal properties of polysiloxaneimides decreased somewhat because they have Si—CH<sub>3</sub> groups, which are susceptible to thermal degradation. The results are shown in Figure 3 and Table IV. The decomposition temperature at a weight residue of 95% decreased with increasing siloxane moiety content. It was found that the greater the siloxane moiety content in the main chain, the worse the thermal properties. This phenomenon was contrary to adhesion, and, so, balanced thermal and adhesive properties



**Figure 3** Thermogravimetric curves of PI-1, PI-2, and PI-4. Heating rate: 5°C/min, under air.

**Table V Dielectric Constants of Various Polyimides Under 1 kHz at Room Temperature**

	Polymer Code			
	PI-1	PI-2	PI-3	PI-5
Dielectric constant	3.34	3.20	3.05	3.04

of siloxane-containing polyimide would be achieved with a properly minimum siloxane moiety introduction.

### Dielectric Constants

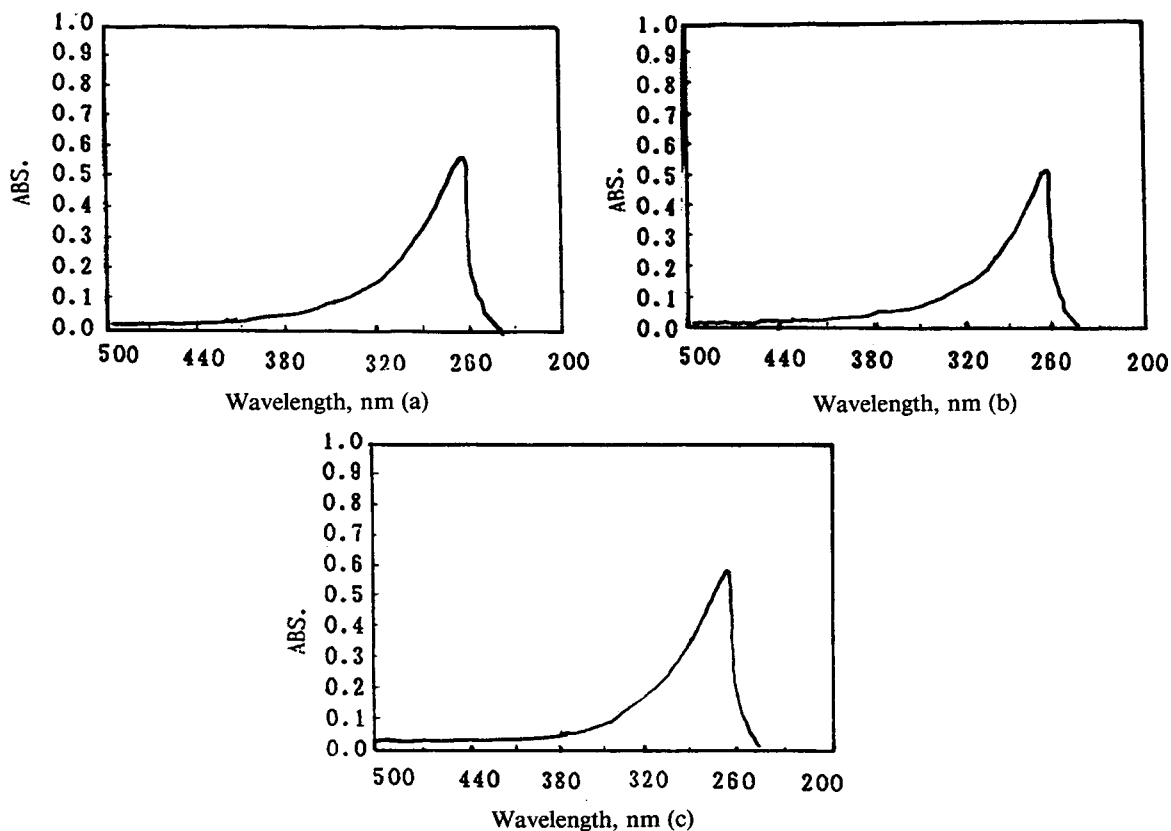
Compared with siloxane-free polyimide (PI-1), the dielectric constants of polysiloxaneimide are lower. The dielectric constant decreased with increasing siloxane moiety content. This trend is shown in Table V. The cause is attributed to a decrease of the polarity of polyimide when the siloxane groups are introduced.

### UV Absorption Spectrum

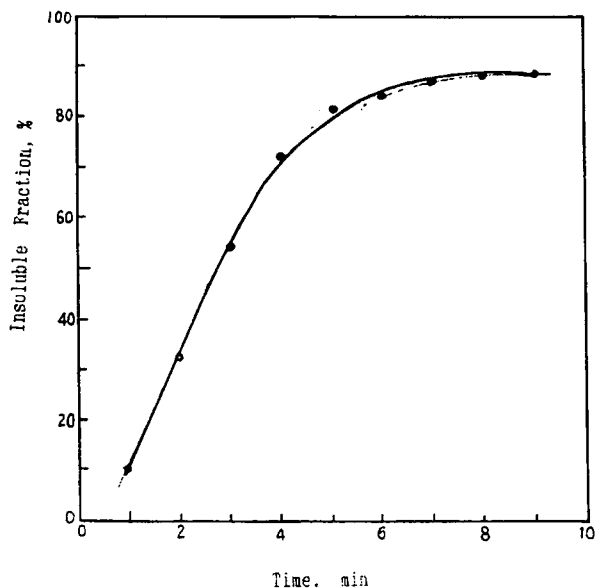
The introduction of the siloxane group and its content have no significant effect on the UV absorption of photosensitive polyimide precursors, as shown in Figure 4. The maximum UV absorptions of PI-1, PI-3, and PI-5 all are near 265 nm.

### Photocrosslinking Reaction

The photocrosslinking reaction was carried out by spin/coating the PI-3 precursor solution (which contains a suitable amount of Michler's ketone and bisazide) on a SiO<sub>2</sub> substrate and then drying it. Next, irradiation was performed using a high-pressure mercury lamp at room temperature.<sup>4</sup> The distance from the lamp (80 watt, the strongest emission strength is given as 365 and 435 nm) to the sample was 5 cm. After development in NMP, the insoluble fraction of the film can be determined by the weighing method. It was found that the insoluble fraction increased with increasing irradiation time, as shown in Figure 5. About 88–90% insoluble fraction could be obtained at an irradiation time of 9–10 min.



**Figure 4** UV absorption spectrum: (a) PI-1; (b) PI-3; (c) PI-5.



**Figure 5** Photocrosslinking reaction, insoluble fraction vs. irradiation time for PI-3.

## CONCLUSIONS

1. In this study, we synthesized a photosensitive polysiloxaneimide precursor. To introduce the siloxane moiety into polymer main chains, bis(*p*-aminophenoxy)dimethylsilane was prepared as a comonomer.
2. The inherent viscosity, thermal stability, and dielectric constant of siloxane-containing polyimides decreased with increasing siloxane moiety content.
3. A balance of thermal and adhesive properties can be achieved by adjusting siloxane moiety introduction.
4. The introduction of a siloxane group and its content have no significant effect on the UV absorption for PI-1, PI-3, and PI-5.

5. Photocrosslinking reaction results show that an 88–90% insoluble fraction was obtained under the irradiation of a mercury lamp.

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