

# Modification of Negative Auto-Photosensitive Polyimide

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**ABSTRACT:** This article describes the preparation of a kind of auto-photosensitive polyimide (PSPI) that contains organo-silicone moiety in its main chain. A group of novel auto-photosensitive polyimides were prepared based on the aromatic diamine monomers and 3,3',5,5'-benzophenontetracarboxylic dianhydride (BTDA) by the method of solution polycondensation at room temperature and imidized at a high temperature. The properties of PSPIs, such as ultraviolet (UV) absorption, electric and adhesion properties, and moisture absorption, were characterized by UV analysis, a dielectric constant detector, and so on. The relationship between the structure and properties of PSPIs is discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 943–947, 2000

**Key words:** auto-photosensitive polyimide; polysiloxaneimide; polycondensation

## INTRODUCTION

Over the past decade and a half, there has been substantial interest in photosensitive polyimides (PSPIs).<sup>1</sup> The photosensitive behavior allows the polyimides, which are widely used in electronics applications, to be patterned photolithographically. There is also a great interest in fully imidized soluble negative auto-photosensitive polyimides because of their unique properties, such as: less shrinking, good thermal and mechanical stability, good image resolution, and a simple photolithographic process.<sup>2–4</sup>

With the development of electronic technology, however, the disadvantages of the photoresist, of which PSPI is the main component, become more and more obvious. The moisture absorption of the photoresist poorly influences the electric property. The adhesion between the photoresist and

the substrate is fairly poor and requires rigorous conditions for the temperature, humidity, and the substrate surface.<sup>5–9</sup>

In order to modify these disadvantages, we introduced some siloxane structure into the main chain of the auto-photosensitive PSPI.

## EXPERIMENTAL

### Reactants

Monomer 3,3',5,5'-benzophenontetracarboxylic dianhydride (BTDA) was obtained from the Aldrich Chemical Co. (St. Louis, MO) and was purified by sublimation before use. Monomer 3,3',5,5'-tetraethyl-4,4'-diaminodiphenyl methane (monomer A) and bis(*p*-aminophenoxy)dimethylsilane (monomer B) were synthesized in our own laboratory. *m*-Cresol, hydroxyethylacrylate (HEA), *N*-methyl-2-pyrrolidone (NMP), toluene, and all other solvents were obtained from Tianjin Chemical Reagent Co. and were purified by distillation before use.

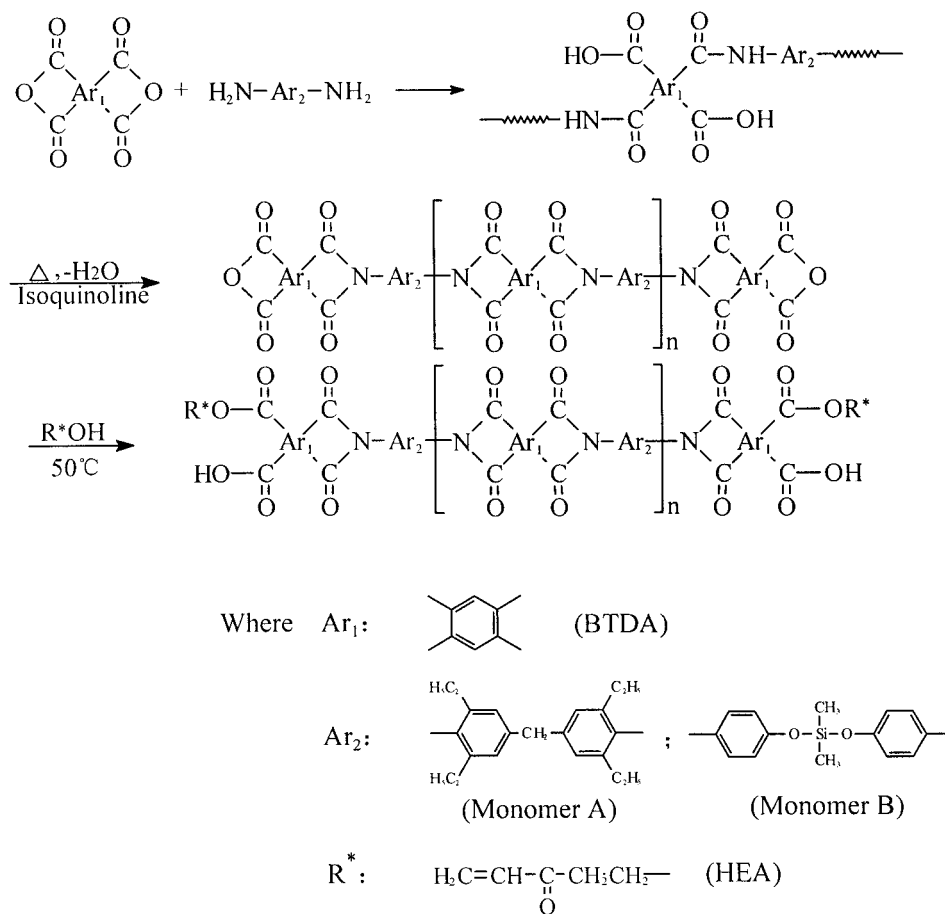
### Preparation of PSPIs

Monomer A (1.7698g, 0.0057 mol) and BTDA (1.9320g, 0.006 mol) were added to 30 mL of *m*-

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**Figure 1** The equation for preparing PSPIs.

cresol at room temperature in a 100-mL four-necked flask, which was dry, purged with nitrogen, and fitted with a mechanical stirrer and a condenser. After awhile, isoquinoline (7 drops) and fresh, distilled toluene (33 mL) were added, and the solution was gradually heated. Water produced by imide was removed from the flask by azeotropic distillation with the toluene. After the reaction mixture was maintained at 180°C for 2 h, it was cooled to room temperature, and monomer B (0.0823g, 0.0003 mol) was added. After the solution was stirred for 2 h at room temperature, isoquinoline (1 drop) and fresh, distilled toluene (3 mL) were added to it. The mixture was heated to 180°C, stirred for 1.5 h, and then cooled to 50°C. HEA (0.08352g, 0.00072 mol) was added to it. The reaction mixture was maintained at 50°C for 2 h and then was cooled to room temperature. The solution was slowly poured into ethanol to precipitate a yellow solid, which was washed with ethanol and dried at room temperature under

vacuum. The inherent viscosity at a concentration of 0.5% in NMP at  $30 \pm 0.1^\circ\text{C}$  is  $42.5 \text{ mL g}^{-1}$ . The equations for preparing the PSPIs are shown in Figure 1.

### Measurements

The ultraviolet (UV) spectra were recorded on a UV-3000 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed at a heating rate  $5^\circ\text{C min}^{-1}$  with a Shimadzu thermal analyzer DSC-40M and a Rigaku TG-4311LCR at room temperature at 1 kHz. The adhesion strength on the substrates was determined by the anticorrosion time. In this method, according to the time of peeling off, the adhesion intensity between film and substrate was assessed qualitatively by time. The longer the time that the PSPI film adhered to the substrate, the stronger the adhesion.

**Table I The Inherent Viscosities of PSPIs with Different Molar Ratio of Monomer A-to-Monomer B in Diamine**

Polymer Code	Molar Ratio of Monomer A-to-Monomer B	Inherent Viscosities (mL g <sup>-1</sup> )
PPSI-1	0.90 : 0.10	19.0
PSPI-2	0.93 : 0.07	24.5
PSPI-3	0.95 : 0.05	30.8
PSPI-4	0.97 : 0.03	41.5

## RESULTS AND DISCUSSION

### Inherent Viscosities

The molecular weight of a polymer is of prime importance in its synthesis and application. Generally, the molecular weight of the photosensitive resin, which is used as the photoresist, should be about 10,000. If it is lower than 10,000, the resin is too inferior to be a film, and the film surface is not good. Conversely, if it is too large, some remains after development badly influence the photolithographic quality; so it is important to control the molecular weight of PSPI resins. By changing the molar ratio of dianhydride-to-diamine, we prepared some resins with different molecular weight and fixed the molar ratio as 1.03 : 1. In this work, we used inherent viscosities to indicate the molecular weight.

Table I shows the inherent viscosities of different PSPIs with different molar ratios of monomer A-to-monomer B in diamine. Table I shows that the inherent viscosities of polysiloxaneimide decrease with increasing monomer B. In other words, the introduction of siloxane groups into the polymer main chain reduce the inherent viscosities. The cause is attributed to the flexibility of the Si—O bonds. Also, both polymer polarity and solubility decrease with increasing siloxane moiety content, so the inherent viscosities decrease.

### Electric Properties

Used as the insulating layer of the electronic devices, the PSPI films must have excellent electric properties. In general, the PSPI films need a lower dielectric constant and a higher surface resistance and volume resistance. Table II shows the dielectric constant, the surface resistance, and the volume resistance of PSPI films with and without siloxane groups. It is clear that the electric properties of the siloxane-containing PSPIs

**Table II Electric Properties of the PSPIs**

Property	Polymer Code	
	PSPI <sup>a</sup>	PSPI-4
Dielectric constant	2.25	2.05
Surface resistivity (×10 <sup>14</sup> Ω)	6.0	6.5
Volume resistivity (×10 <sup>13</sup> Ω)	8.2	9.0

<sup>a</sup> Prepared by BTDA/monomer A, without monomer B.

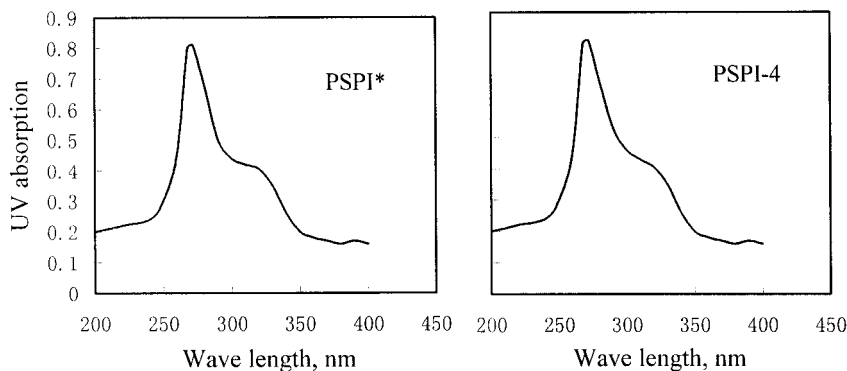
are better than those of the siloxane-free PSPIs. The cause is attributed to a decrease of the polarity of polyimide when the siloxane groups are introduced into the polymer main chain.

### Adhesion Properties

In the whole photolithographic process, high adhesion strength is required between the PSPI film and the substrate. Especially in the corrosion procedure, the SiO<sub>2</sub> wafer, which is used as the substrate, is corroded by hard etchant at 30°C. If the adhesion strength is not strong, the PSPI films will peel from the substrate before the wafer is corroded to the proper depth. We used the anticorrosion time to indicate the adhesion strength; the longer the time, the stronger the adhesion. The result is shown in Table III. We can draw a conclusion from Table III that the anticorrosion time of PSPI films with the siloxane moiety is longer than that of the PSPI films without it. This shows that the siloxane group can increase the adhesion strength. The cause is that the O—Si—O structure in the polymer main chain can change its conformation easily, which enhances the interactional strength between the SiO<sub>2</sub> mole-

**Table III The Anticorrosion Time of Various PSPIs**

Postbaking Time (°C; 30 min)	The Anticorrosion Time (s)	
	PSPI*	PSPI-4
160	90	120
180	110	140
200	140	160
220	150	170
240	180	200
260	200	210



**Figure 2** UV absorbance spectra of PSPIs.

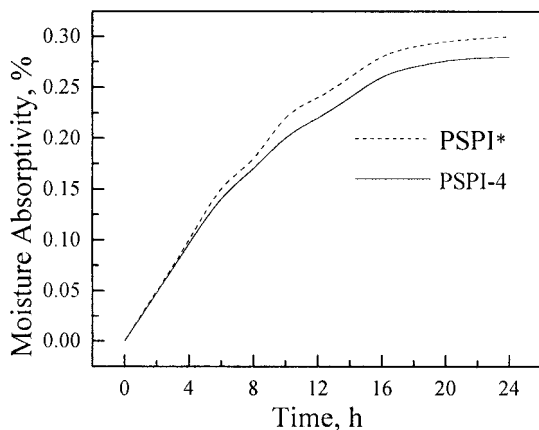
cules and the PSPI molecules. The etchant is composed of HF,  $\text{NH}_4\text{F}$ , and  $\text{H}_2\text{O}$  with the volume ratio of 3 : 6 : 9.

### UV Adsorption Spectra

In order to check the influence of the siloxane structure on the photosensitivity of the photoresist, the UV absorption spectra of PSPIs with and without siloxane groups were measured, as shown in Figure 2. The maximum UV absorption band of PSPI\* and PSPI-4 are the same at 280 nm. The introduction of the siloxane groups has no significant effect on the UV absorption of PSPIs.

### Moisture Absorptivity

The lower the moisture absorptivity of the PSPI film, the longer its useful lifetime is. Compared with siloxane-free polyimides (PSPI\*), the moisture absorptivity of polysiloxaneimide (PSPI-4) is lower, as shown in Figure 3.



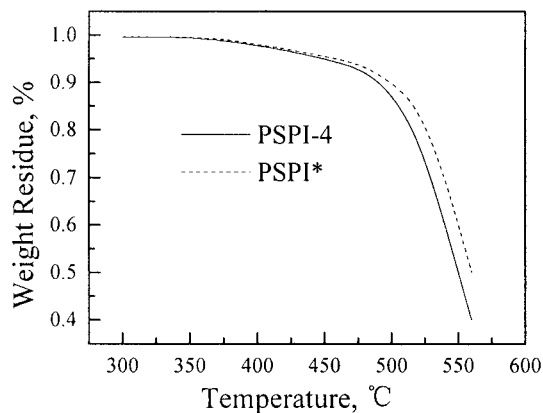
**Figure 3** The moisture absorptivity cures of PSPI\* and PSPI-4.

### Thermal Stability

Compared with siloxane-free polyimides, the thermal properties of polysiloxaneimide decreased somewhat because it has  $\text{Si}-\text{CH}_3$  groups, which are susceptible to thermal degradation. The results are shown in Figure 4. The decomposition temperature at a weight residue of 95% decreased with the introduction of siloxane moiety. This phenomenon is contrary to the adhesion results.

### CONCLUSION

In this study, we synthesized a photosensitive polysiloxaneimide. The molar ratios of dianhydride-to-diamine were fixed. The inherent viscosity, thermal stability, moisture absorptivity, and dielectric constant of siloxane-containing PSPIs decrease by the introduction of the siloxane group. The surface and volume resistance and adhesion are enhanced by the siloxane structure.



**Figure 4** Thermogravimetric curves of PSPI\* and PSPI-4. The heating rate is  $5^\circ\text{C}/\text{min}$ , under air.

The introduction of siloxane groups has no significant effect on the UV absorption.

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