Synthesis and Characterization of Photosensitive Copolysiloxaneimides

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ABSTRACT: Photosensitive copolysiloxaneimides were prepared by adding a photosensitive monomer such as hydroxyethylacrylate (HEA) to copolyisoimides, which were synthesized by the copolycondensation of pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride with oxydianiline, and bis(p-aminophenoxy)dimethylsiloxane. The forming process of isoimide rings caused by the reaction of polyamic acid with dicyclohexylcarbodiimide and the disappearance process of isoimide rings caused by the reaction of copolyisoimide with HEA were monitored *in situ* by infrared approach. A series of photosensitive copolysiloxaneimides films were prepared, and the desired structure–properties relationships about inherent viscosities, thermal expansion coefficient, thermal stability and glass transition temperature, dielectric constants, moisture absorption, and photosensitivity were also discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1463–1468, 1997

Key words: photosensitive polyimide; copolysiloxaneimide; polyisoimide; copolycondensation

INTRODUCTION

Polyimides have played an important role in the electronics industry because they retain their excellent physical properties (dielectric, mechanical, and thermal) at high temperatures, up to 450–500°C.[1] But the patterning of nonphotosensitive polyimides is very complicated. To reduce the number of patterning steps, considerable effort has been made to develop photopatternable polyimides.[2–5] Of particular interest are photosensitive polyamic acid esters pioneered by Ahne and colleagues.[6] It has been found that these esters have several disadvantages; specifically, the molecular weight control of the polymers is difficult and the reaction process introduces chloride ions.

Our group[7–8] has reported two photosensitive polyimide precursors by Ahne and colleagues' method. In this work, we introduced an improved process for the synthesis of photosensitive siloxane-containing copolyimide precursors. A series of photosensitive copolysiloxaneimides films were prepared and the desired structure–properties relationships are discussed in this article.

EXPERIMENTAL

Reactants

Monomers pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic dianhydride (BTDA), and oxydianiline (ODA) were obtained from Shanghai Chemical Reagent Co. Comonomer bis(p-aminophenoxy)dimethylsiloxane (APDS) was prepared in our own laboratory.[8] Hydroxyethylacrylate (HEA) and all other solvents were obtained from Tianjin Chemical Reagent Co. and purified by distillation before use.

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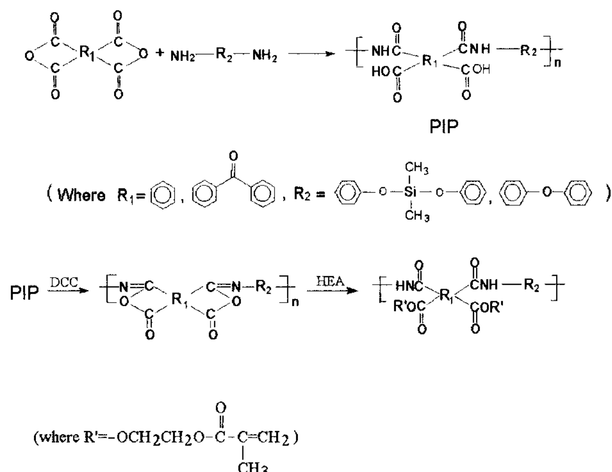


Figure 1 A schematic representation of PSCOPI precursor.[9–11]

Synthesis of Photosensitive Copolysiloxaneimide (PSCOPI) Precursor

BTDA, 3.542 g (0.011 mol), and PMDA, 2.398 g (0.011 mol), were dissolved in 27 mL *N*-methyl-2-pyrrolidone (NMP) with stirring. APDS, 0.548 g (0.002 mol), in NMP was added at room temperature for 3 h, then a solution of ODA, 3.6 g (0.020 mol), in NMP was added at the same temperature by overnight stirring, giving a polyamic acid solution. Dicyclohexylcarbodiimide (DCC), 9.064 g (0.044 mol), was added to the polyamic acid solution with stirring for 1 h, giving a polyisoimide solution, and then HEA, 5.8 g (0.05 mol), was added dropwise to this stirred solution at 50°C for 10 h. The mixture was filtered to remove byproducts and the filter liquid was precipitated into deionized water with stirring. The product was washed with deionized water repeatedly until there was no solvent in the product, then dried at room temperature under vacuum.

The schematic of the synthesis is given in Figure 1. Five copolyimide precursors were prepared with different contents of APDS, as shown in Table I.

PSCOPI Film Preparation

PSCOPI precursors solution in NMP (10% concentration by weight) was coated on the glass plate and soft-baked at 70°C for 10 h in air. The soft-baked samples were then thermally imidized in a Heraeus oven with a nitrogen flow by a step-cure process: 150°C/1 h, 200°C/30 min, 250°C/30 min, 300°C/30 min, and 350°C/30 min. The heating rate for each step was 2°C/min and cooling rate was 1°C/min. The thickness of cured films was 20 to 40 μm.

Measurements

Infrared (IR) and ultraviolet (UV) spectra were recorded on a Nicolet 170SX and Shimadzu UV-3000 spectra photometer, respectively. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed at a heating rate of 5°C/min with a Perkin–Elmer DSC-7 and TGS-2, respectively. A thermomechanical analyzer (TMA) was used to measure the thermal expansion coefficient (TEC) of the PSCOPI films at heating rate of 5°C/min, and average TEC between room temperature and 250°C was calculated.

Dielectric constant of the PSCOPI films was determined on a dielectric constant detector AG-4311LCR at room temperature at 1 KHz.

The peel adhesion test was performed by the circle-cut method. In this method, according to the status of peeling off, the adhesion between film and substrate is assessed qualitatively on the 1 to 7 grade. A higher grade indicates a larger peeling area. In other words, the higher the grade, the worse the adhesion.

RESULTS AND DISCUSSION

IR Spectroscopy

The forming process of isoimide rings caused by the reaction of polyamic acid with DCC can be monitored by the IR method.

The procedure is as follows: Samples were taken from the reaction mixture of polyamic acid and DCC in NMP medium at certain interval times of reaction, and the samples sandwiched

Table I Code Names of PSCOPI Precursors and the Molar Ratio of ODA and APDS

Polymer Code	PSCOPI-1	PSCOPI-2	PSCOPI-3	PSCOPI-4	PSCOPI-5
BTDA : PMDA	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
ODA : APDS	100 : 0	95 : 5	90 : 10	85 : 15	80 : 20

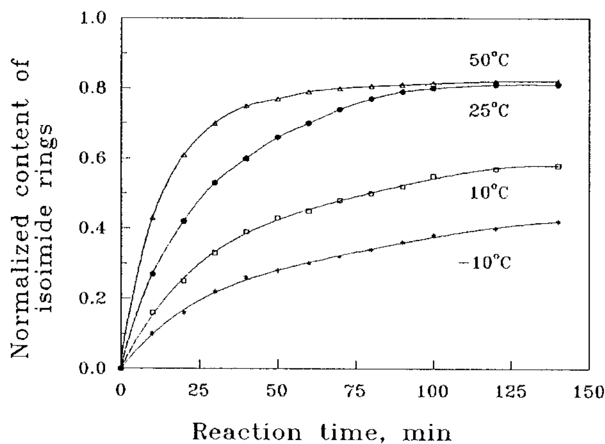


Figure 2 The normalized content of isoimide rings changes with reaction time (in minutes).

between two NaCl plates. IR spectra series were obtained at each interval time.

The extent of reaction at any time can be related to the ratio of the area of the isoimide peak at 1805 cm^{-1} to its initial area. To eliminate error due to sample slippage, etc., the isoimide peak can be normalized by dividing its area by that of reference peak 1500 cm^{-1}, which is due to C=C benzene skeletal vibration absorption.

Therefore

$$A_{\text{isoimide}}(t) = \frac{A_{1805}(t)}{A_{1500}(t)} \cdot \frac{A_{1500}(0)}{A_{1805}(0)}$$

where $A_{1805}(t)$ and $A_{1805}(0)$ are the absorbance at 1805 cm^{-1} at time t and zero, respectively; $A_{1500}(t)$ and $A_{1500}(0)$ are the absorbance at 1500 cm^{-1} at time t and zero, respectively; and $A_{\text{isoimide}}(t)$ is the fraction of isoimide at time t.

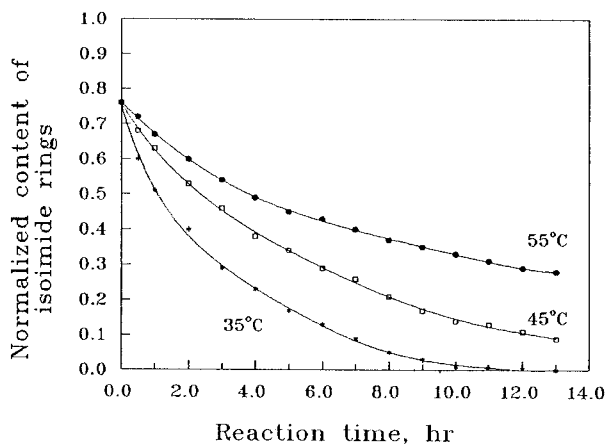
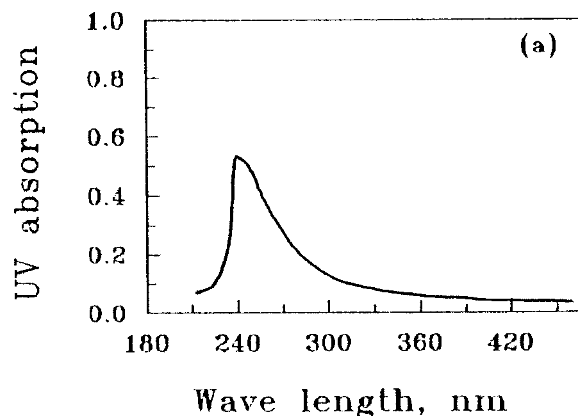
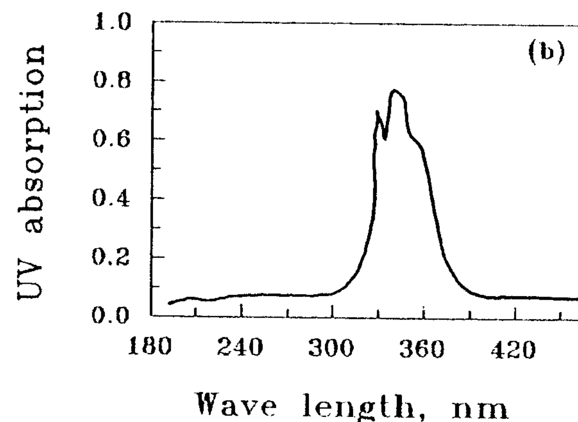


Figure 3 The normalized content of isoimide rings changes with reaction time (in hours).





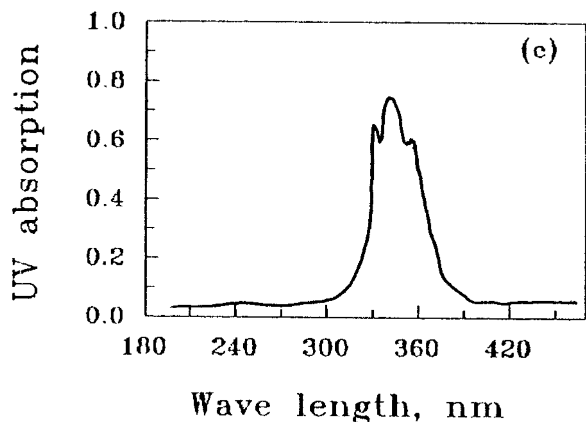


Figure 4 UV absorption spectrum: (a) PI; (b) PSCOPI-1; (c) PSCOPI-2 ~ 5.

Figure 2 shows that the normalized contents of isoimide rings changed with reaction time when the polyamic acid reacted with DCC in NMP medium at −10°C, 10°C, 25°C, and 50°C.

Table II Inherent Viscosities of PSCOPI

Polymer Code	PSCOPI-1	PSCOPI-2	PSCOPI-3	PSCOPI-4	PSCOPI-5
Inherent viscosities (mL/g)	41.79	37.34	34.68	31.34	26.79

Measured with NMP at concentration of 0.5 g/dL at 30°C.

Table III Thermal Expansion Coefficients of PSCOPI Films

Polymer Code	PSCOPI-1	PSCOPI-2	PSCOPI-3	PSCOPI-4	PSCOPI-5
TEC ($\times 10^5$ K^{-1})	3.7	3.9	4.24	4.63	4.80

Experimental results showed that the isoimide rings rise very sharply at the beginning of the reaction and then leveled off after 1 to 1.5 h.

According to similar method, the disappearing process of isoimide rings caused by the reaction of isoimide rings with HEA can also be monitored by the IR method. Figure 3 shows that the normalized content of isoimide rings changed with time when the isoimide rings were reacted with HEA in NMP medium at 35°C, 45°C, and 55°C. Experimental results showed that the isoimide rings fell quickly at the beginning of the reaction and then slowly after 8–10 h. The higher the reaction temperature, the faster the concentration of isoimide rings decreased.

UV Spectroscopy

Photosensitivity of photosensitive polyimide is very important in electronics industry applications. One of the main purposes of this study is to increase photosensitivity by introducing a benzophenone-containing polyimide system. In order to evaluate the photosensitivity of synthesized PSCOPI, its solution was spun onto quartz to create a thin film; its UV absorption spectrum was then measured. Figure 4(a) UV absorption spectrum corresponds to BTDA-free and siloxane-free photosensitive polyimide precursor (i.e., PMDA/ODA/HEA); Figure 4(b) UV absorption spectrum corresponds to PSCOPI-1; and Figure 4(c) UV absorption spectrum corresponds to PSCOPI-2–PSCOPI-5. Experimental results revealed that the introduction of siloxane moiety and its content in copolymers have no significant effect on UV absorption of the polymer, as shown in Figure 4(b,c).

However, the effect of introducing benzophenone moiety into the polymer main chain on UV absorption is significant by comparing Figure 4(a) and (b). It is clear from Figure 4(a,b) that the introduction of benzophenone moiety to the polymer backbone can increase the photosensitivity to *i*-line (365 nm) and *j*-line (334 nm). The cause was attributed to the inherently photosensitive C═O of BTDA.

Inherent Viscosities

Photosensitive copolysiloxaneimide precursors shown in Table II were prepared similarly, except that the molar ratio of ODA/APDS varied from 1 : 0 to 4 : 1 while the molar ratio of BTDA/PMDA was 1 : 1. It can be seen clearly from Table II that the inherent viscosity decreased with increasing APDS content in the polymer main chain. This result might be attributed to the flexibility of the Si—O bonds. On the other hand, because both the polymer polarity and solubility are decreased

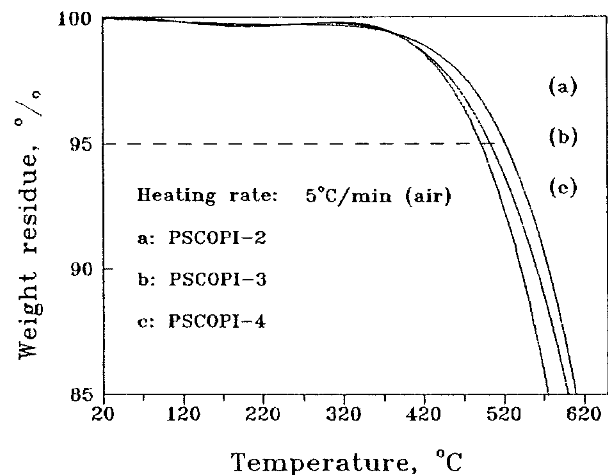


Figure 5 TGA curves for PSCOPI films.

Table IV Glass Transition Temperature (T_g)

Polymer Code	PSCOPI-1	PSCOPI-2	PSCOPI-3	PSCOPI-4	PSCOPI-5
T_g (°C)	268°C	252°C	240°C	238°C	235°C

Table V Dielectric Constant of PSCOPI Films Under 1 KHz at Room Temperature

Polymer Code	PI[a]	PSCOPI-1	PSCOPI-2	PSCOPI-3	PSCOPI-5
Dielectric constant (ϵ)	3.80	3.67	3.05	2.74	2.45

[a] Prepared from PMDA/ODA/HEA.

with increasing siloxane moiety content, the inherent viscosities also decreased.

Thermal Expansion Coefficient

PSCOPI films were run in the tensile mode on the TMA in order to determine the average TEC between 30 and 250°C. As shown in Table III, the TEC increased with increasing siloxane moiety content. It is estimated that the cause was that the siloxane is flexible.

Thermal Stability and T_g

Figure 5 shows the TGA curves for the PSCOPI films. The TGA results indicate that the decomposition temperature at weight residue 95% occurs at 430 to 550°C in air. Polyimides generally have good thermal stability. However, as shown in Figure 5, some reduction in the thermal stability of polymer was observed with increasing siloxane content because of the Si—CH_3 groups are susceptible to thermal degradation, so the greater the siloxane moiety content in the main chain, the worse the thermal stability of the PSCOPI. This is thought to be due to the introduction of flexible spacer units (O—Si—O) that are randomly distributed in the backbone of the polymer.

Table IV gives the glass transition temperature (T_g) data of PSCOPI films measured on a DSC. The T_g of PSCOPI films decreased with increased content of siloxane moiety. This phenomenon was caused by two possible reasons. One is the change in molecular polarity. Since O—Si—O is a relatively weak-polar group, the interaction among the polar group of polymers would decrease with increasing the content of O—Si—O and the molecular chains would become more flexible. The other reason is the change in regularity of macromolecule. The PSCOPI precursor is a random copolymer composed of more than two monomers. The chain's arrangement is lost due to the poor regularity of molecule, which causes the increase of free volume fraction in the polymer.

Dielectric Constants

The dielectric constants (ε) were determined using a dielectric constant detector. The measured dielectric constant values of PSCOPI films are listed in Table V. It is observed that the dielectric constants reduced proportionally with the amount of siloxane content in PSCOPI films, which may be the result of the decrease in PSCOPI polarity when the siloxane groups were introduced.

Moisture Absorption

Figure 6 displays the moisture absorption for PSCOPI films, determined by monitoring capaci-

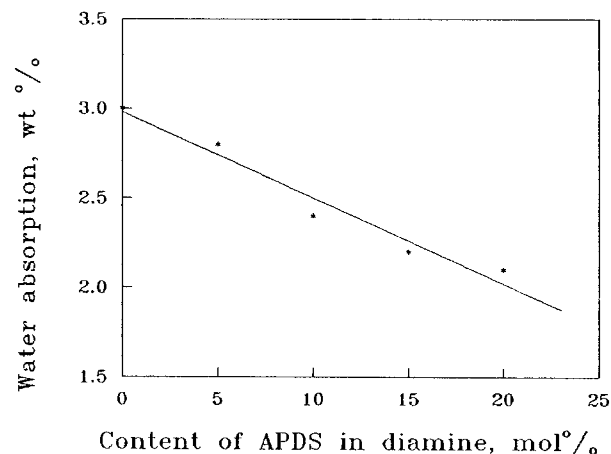


Figure 6 Moisture absorption of PSCOPI films.

Table VI Adhesion of Various PSCOPI Films to Different Substrates

Polymer Code	PSCOPI-1	PSCOPI-2	PSCOPI-3	PSCOPI-4	PSCOPI-5
Fe	2	2	1	1	1
Si	2	2	2	2	1
SiO_2	2	1	1	1	1

Higher grade indicates worse adhesion (i.e., 1 indicates better adhesion than 2).

tance change on exposure to a pre-set moisture room. The linear decrease of the moisture absorption appeared with increasing content of randomly incorporated O—Si—O moieties. The reduction in moisture absorption is thought to be due to the introduction of the O—Si—O units which reduce the polarity of PSCOPI so it decreases moisture absorption.

Adhesion Properties

The adhesion strengths between one siloxane-free PSCOPI, four siloxane-containing PSCOPI, and substrates are listed in Table VI. Substrates are Fe, Si, and SiO_2 wafers.

All samples were prepared by spin-coating on the substrate at 2000 rpm, followed by soft-baking in a Hearaeus oven by a step-cure process: 150°C/30 min, 200°C/30 min, 250°C/30 min, 300°C/30 min, and 350°C/30 min. The heating rate for each step is 2°C/min and the cooling rate is 1°C/min. The thickness of cured films is 20 to 40 μm.

Table VI indicates that the adhesion strength increases with increasing siloxane moiety content. Relatively small fractions of siloxane reduce the rigidity of imidized polymer chains and play an important role in tightly connecting the polymer to the substrate. From Table VI, it is also found that the SiO_2 is a better substrate than the others.

CONCLUSIONS

1. In the present study, photosensitive copolysiloxaneimide precursors were successfully prepared from corresponding polyamic acid using DCC as a dehydrating agent to produce polyisoimide. The photosensitive monomer HEA was then easily incorporated into the polymer chain.
2. The adequate conditions of synthesis PSCOPI were studied *in situ* by IR monitoring.
3. The introduction of BTDA has a significant effect on the UV absorption for PSCOPI-2, PSCOPI-3, PSCOPI-4, and PSCOPI-5, but the introduction of a siloxane group and its contents have no significant effect on UV absorption.
4. The thermal stability, dielectric constant, and moisture absorption of siloxane-containing PSCOPI decreased with increasing siloxane moiety content.

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