

Synthesis, Characterization, and Properties of Photosensitive Silicon-Containing Copolyimides

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Synopsis

Copolyimides with siloxane moieties in the main chain were synthesized by solution polycondensation of 1,3-bis(3-aminopropyl) tetramethyldisiloxane (APMS), oxydianiline (ODA) with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) in *N*-methyl-2-pyrrolidone (NMP). The adhesion properties between copolyimides and silicon wafer were improved significantly with incorporation of siloxane moiety into polymer chain.

Photosensitive copolyimide precursor was obtained by further reaction of silicon-containing copolyamic acid with 2-isocyanatoethyl methacrylate (IEM). The insoluble fraction of photosensitive copolyimide precursor reached 90% after 10 min of irradiation with UV light. In comparison, the thermal imidization of irradiated photosensitive copolyimide precursor was more difficult than that of silicon-containing copolyamic acid. A longer heating time or higher imidization temperature was required.

INTRODUCTION

The use of polyimide as the polymer for planar metallization in very large-scale integration (VLSI) is well known because of its super thermal and dielectric properties. However, used as the interlayer dielectric film, the adhesion between polyimide and silicon wafer is not always satisfactory. To enhance the bonding strength between polymer and silicon wafer, the surface of silicon wafer was sometimes treated with an adhesion promoter,¹⁻³ for example, 3-aminopropyltriethoxy silane (APS). Although improvement of adhesion strength was observed, APS nevertheless caused thermal instability in a high temperature surrounding.⁴ Another approach to solve the adhesion problem is to incorporate siloxane moiety into the main chain of polyimide. Silicon-containing polyimides⁵⁻¹⁰ have been investigated extensively with respect to the improvements of processability, thermo-oxidative stability, mechanical properties, and gas permeability. However, only limited examples were found in the literature for the purpose of adhesion improvements.¹¹⁻¹²

For photolithographic applications, the use of photo-cross-linkable polyimide would reduce the processing steps markedly.¹³ The first photosensitive polyimide was prepared by Kerwin and Goldrick¹⁴ in 1971. Since then, a number of photosensitive polyimides have been reported and appeared mainly in patents.¹⁵⁻²⁴ Most recently, a new positive type photosensitive polyimide was syn-

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thesized by Kubota and coworkers.²⁵ Their photosensitive polyimide precursor contained *o*-nitrobenzyl ether and was soluble in alkaline solution. No swelling phenomenon was observed after being developed.

In this article, silicon-containing polyimide was prepared by the condensation reaction of 1,3-bis(3-aminopropyl) tetramethyl disiloxane (APMS), oxydianiline (ODA) with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) in *N*-methyl-2-pyrrolidone (NMP). Then photosensitive functional groups were incorporated through the reaction between the —NCO group of 2-isocyanatoethyl methacrylate (IEM) and the —COOH group of silicon-containing polyamic acid to yield a photosensitive silicon-containing copolyimide. In addition to synthesis details and characterizations, adhesion properties and UV-curing behavior were reported.

EXPERIMENTAL

Reactants

Monomers BTDA and ODA were purified by sublimation before use. APMS (Silar) was distilled under reduced pressure in the presence of a small amount of metal sodium. NMP was distilled before being stored in 4 Å molecular sieves. The structural formulae of monomers are shown in Figure 1.

Preparation and Characterization of Silicon-Containing Copolyimides

Homopolyamic acids were obtained by the reaction of ODA and BTBA in NMP at 15–20°C for 10 h. Constant stirring was maintained during the reaction. The molar ratios of ODA/BTDA were 1/1 and 0.97/1, respectively. Silicon-

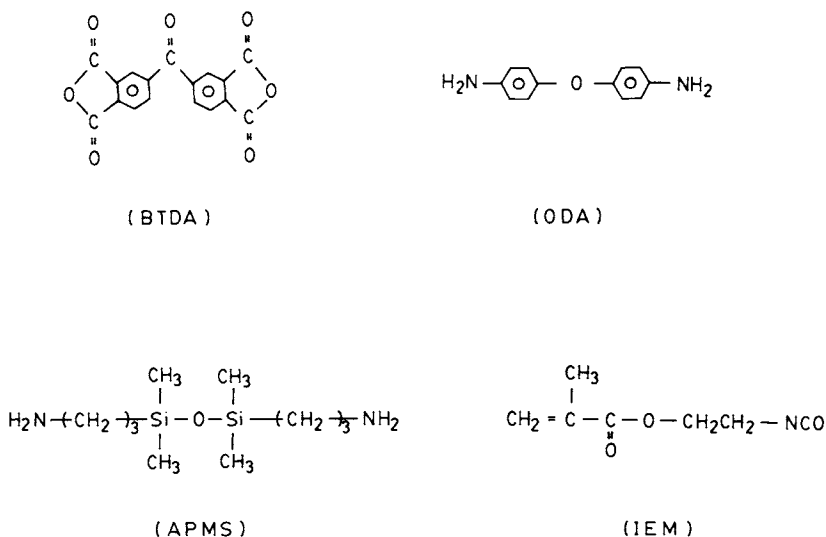


Fig. 1. Structural formula and codes of chemicals used in this study.

containing copolyamic acids were prepared similarly except that ODA was replaced by the mixture of ODA and APMS. The molar ratios of ODA/APMS varied from 9/1 to 6/4 while equivalent amount of dianhydride (BTDA) was used.

The obtained homopolyamic or copolyamic acid solution was cast on a glass plate at 80°C in vacuum. Then the cast film was imidized at 200°C for 1 h, 300°C for 1 h, and 350°C for 30 min in N₂. The same cure conditions were adapted for peel strength test.

The inherent viscosities of polymers were determined at 30°C in NMP (0.5 g/dL) with an Ubbelode type viscometer. T_g was measured with a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of 20°C/min in N₂. TGA data were obtained by employing a Perkin-Elmer TGS-2 Thermogravimetric Analyzer at a heating rate of 20°C/min in N₂. Tensile strength was determined according to ASTM D412 with an elongational rate of 2 mm/min. The average film thickness was 0.4 mm. The peel test was performed by employing the apparatus shown in Figure 2. The substrate can be either silicon wafer or silicon oxide wafer. The silicon oxide wafer was obtained simply by thermal oxidation of the silicon wafer at 1100°C for 1 h. For comparison purposes, the adhesion strength between polymer and wafer treated with APS, an adhesion promoter, was also measured. The treatment was done by dipping the wafer in a 1% solution of APS in ethanol for 3 min, then rinsing the wafer with water and drying it at 100°C for 20 min. The solution of APS in ethanol was used directly after preparation to avoid hydrolysis.

In this series, two homopolyimides and four silicon-containing copolyimides were prepared. Their code names, compositions, and inherent viscosities are listed in Table I.

Synthesis of IEM

IEM was synthesized according to the method of Lieser.²⁶ The synthesis scheme is shown in Figure 3. The final product was distilled and the distillate

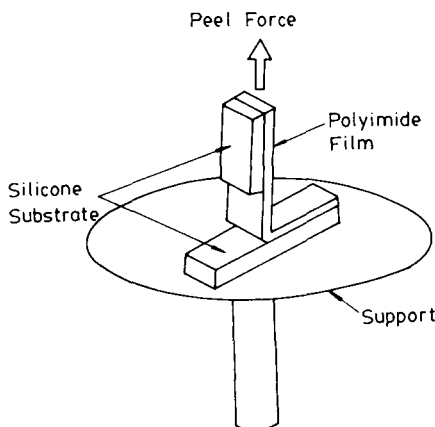


Fig. 2. Device for peel test.

TABLE I
Compositions and Inherent Viscosities of Copolyamic Acids

Polymer code	Reactant quantities (mol ratio)			Inherent viscosity (g/dL)
	BTDA	ODA	APMS	
P-1	1	1	0	1.25
P-2	1	0.97	0	1.12
P ₉ S ₁	1	0.9	0.1	0.958
P ₈ S ₂	1	0.8	0.2	0.804
P ₇ S ₃	1	0.7	0.3	0.784
P ₆ S ₄	1	0.6	0.4	0.701

collected at 74–76°C/3 mm Hg only. The structure of IEM was confirmed both by IR and NMR spectra as shown in Figure 4.

Preparation and Characterization of Photosensitive Copolyimide Precursor

The acid value of silicon-containing copolyamic acid (P₉S₁) was first determined by titration with a 0.1 N NaOH solution. Then IEM reacted with P₉S₁ in NMP under stirring with equal molar ratio of NCO/COOH. The solid content

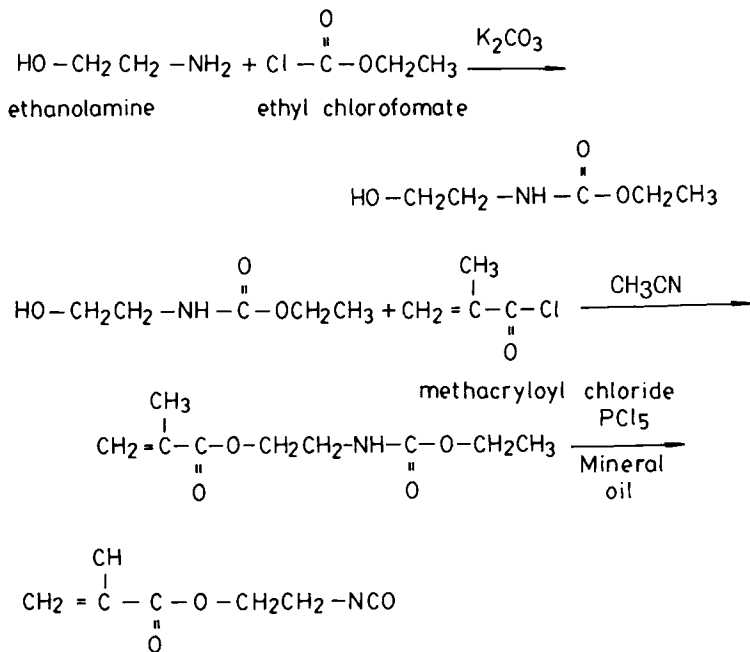


Fig. 3. Synthesis scheme for 2-isocyanatoethyl methacrylate (IEM).

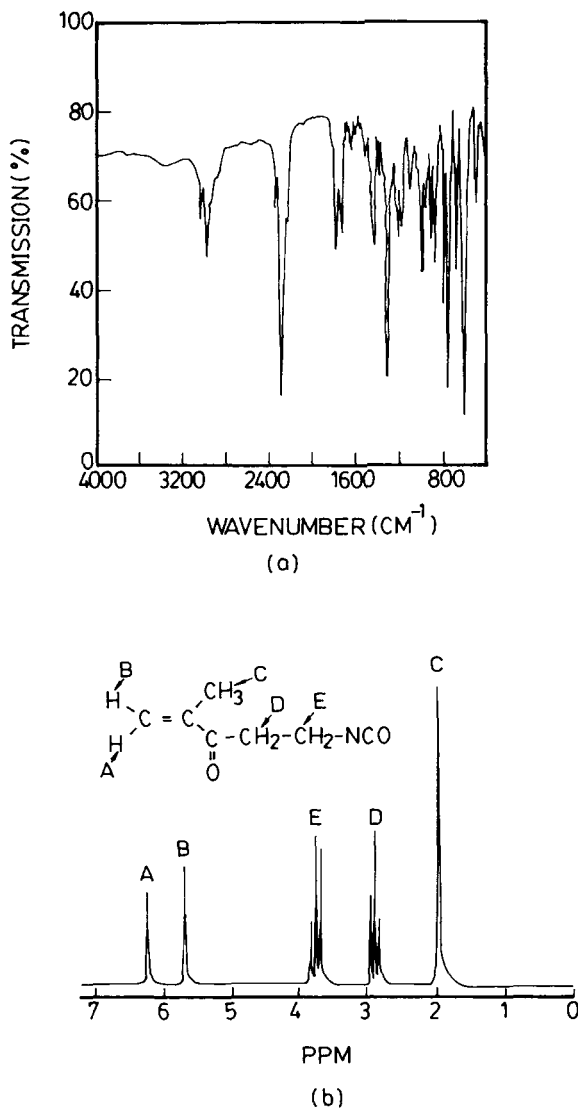


Fig. 4. Structural identification of 2-isocyanatoethyl methacrylate (IEM): (a) IR spectrum; (b) ¹H-NMR.

of this solution was 20% by weight and 0.3% triethylene diamine was added as the catalyst. The reaction was operated under room temperature and the —NCO characteristic peak was monitored constantly with IR to ensure the completion of the reaction. After the reaction was completed, 5% (based on the weight of silicon-containing copolyamic acid) of photosensitizer (Micher's ketone) was added and stirred until it was fully dissolved. The solution was then cast on a quartz plate and dried. A 80-W mercury lamp was used as the UV light source for photoreaction. The distance from the lamp to the sample was 15 cm. The cast film was irradiated at room temperature and immediately

immersed in NMP. The insoluble fraction was dried under vacuum and measured by weighing the residual polymer.

RESULTS AND DISCUSSION

Characterization of Silicon-Containing Copolyimides

Figure 5 shows the changes of inherent viscosities during synthesis of the polyamic acid. The initial inherent viscosity was taken at the time when the addition of BTDA was completed. The inherent viscosity increased steadily with reaction time and leveled off at approximately 5 h. To ensure that the highest molecular weight was obtained, a reaction time of 10 h was chosen for all reactions. Table I lists the compositions and inherent viscosities of silicon-containing copolyamic acids. Having the highest inherent viscosities, samples P-1 and P-2 were homopolymer. Again, reaction under stoichiometric conditions gave the highest molecular weight. Incorporation of siloxane moiety in the polyamic acid would reduce the inherent viscosity and was proportional to the content of siloxane moiety. This reduction in inherent viscosity should not be thought of as decrease in molecular weight. Because all silicon-containing copolyamic acids were synthesized under stoichiometric conditions, highest molecular weight was expected. Besides, the inherent viscosity-molecular weight relationship could not be applied since the composition of each silicon-containing copolyamic acid was different. Rather, the cause for the reduction in inherent viscosity of silicon-containing copolyamic acid was attributed to the

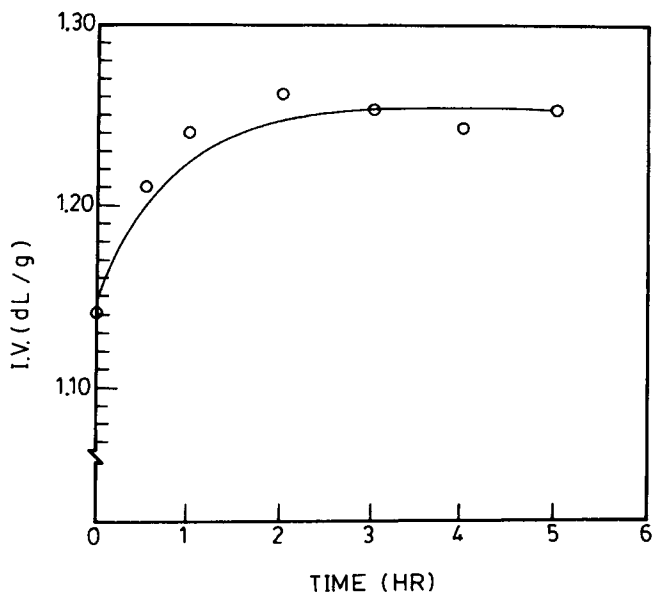


Fig. 5. Inherent viscosity vs. reaction time for homopolyamic acid (P-1). BTDA/ODA molar ratio = 1/1.

flexibilities of Si—O and Si—C bondings. This phenomenon is advantageous in processing.

Table II lists the tensile strengths and T_g of the silicon-containing copolyimide series. Both tensile strength and T_g decreased with increasing siloxane moiety content.

Thermal Stability of Silicon-Containing Copolyimides

Figures 6 and 7 show the thermogravimetric curves of homopolyimides and silicon-containing copolyimides, respectively. The summarized results are recorded in Table III. Of all the samples, P-2 had the lowest initial decomposition temperature (372°C). Because the ends of the P-2 chain were mostly anhydrides due to the excess amounts of BTDA during synthesis, it was more susceptible to thermal degradation. The initial decomposition temperature of silicon-containing copolyimide decreased with increasing siloxane moiety content. The first derivative curves of silicon-containing copolyimides show two maximum rate of decomposition temperatures (T_{max}). The lower one was subjected to the rapid decomposition of APMS while the higher one was due to the degradation of ODA. From the data of weight loss at 800°C, samples with more siloxane moiety content had less polymer residues. Our thermal stability studies concluded that the less the siloxane moiety content in copolyimide the better the thermal properties. Indeed, balanced thermal and adhesive properties of silicon-containing copolyimide can only be achieved with minimum siloxane moiety inclusion.

Adhesion Properties of Silicon-Containing Copolyimides

The peel strengths between two homopolyimides (P-1 and P-2), one silicon-containing copolyimide (P_9S_1), and substrates are listed in Table IV. Substrates were Si and SiO₂ wafers. For comparison purpose, peel strengths of substrate treated with adhesion promoter (APS) were also measured. It was found that P-2 had a better adhesion property than P-1, owing to its anhydride ends, while SiO₂ wafer was the better substrate because it had more hydroxyl groups on its surface. It was also found that adhesion promoter, APS, served its function very well. For the sample of silicon-containing copolyimide (P_9S_1), the adhesion strengths between it and substrates were so strong that they could not be peeled

TABLE II
Tensile Strengths and T_g of Copolyimides

Polymer code	Tensile strength (kg/mm ²)	T_g (°C)
P-1	13.9	279
P-2	11.7	268
P_9S_1	11.6	240
P_8S_2	6.84	218
P_7S_3	4.16	184
P_6S_4	2.08	158

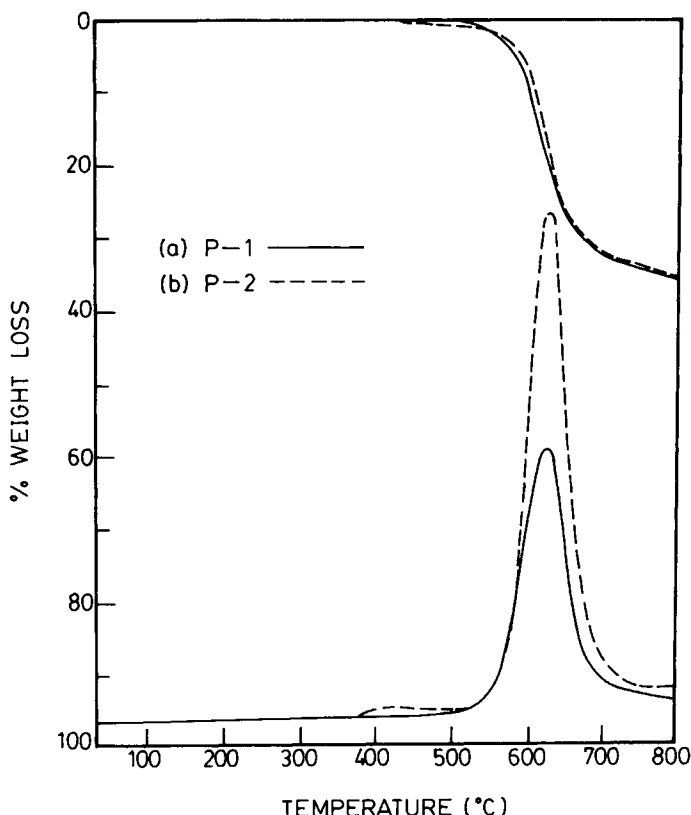


Fig. 6. Thermogravimetric curves of homopolyimides: (a) P-1; (b) P-2. Heating rate = 20°C/min.

apart. It was also interesting to note that sample P₉S₁ was the silicon-containing copolyimide with the least siloxane moiety content. In other words, significant improvement of adhesion strength could be obtained with only minimum incorporation siloxane moiety into the polymer chain.

Characterization of Photosensitive Silicon-Containing Copolyimide

By the reaction between the —COOH group in silicon-containing copolyamic acid and the —NCO group in IEM, a photosensitive silicon-containing copolyimide can be formed. In this experiment, sample P₉S₁ was chosen to be the silicon-containing copolyamic acid. The —COOH equivalent of P₉S₁ was titrated with 0.1 N NaOH solution and found to be 7.944×10^{-4} mol/g. It was reacted with stoichiometric amount of IEM in the presence of 0.3% triethylene diamine as the catalyst. The —NCO characteristic peak was monitored constantly with an IR spectrometer to ensure the completion of the reaction. The whole reaction time was 3 h. After adding photosensitizer, Michler's ketone, the photosensitive silicon-containing copolyimide precursor was cast on a quartz plate and dried. Then irradiation was performed using a mercury lamp. After

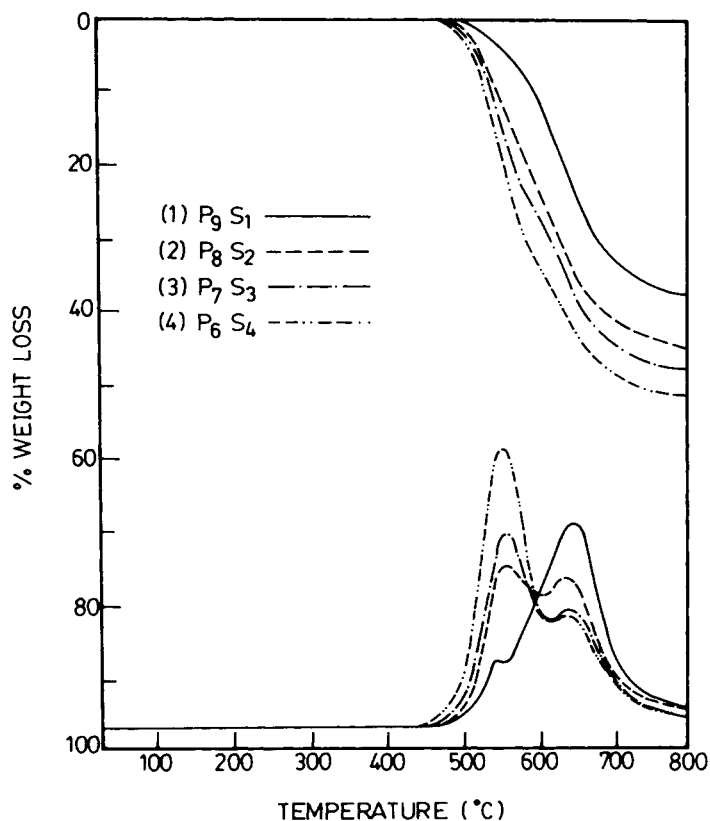


Fig. 7. Thermogravimetric curves of silicon-containing copolyimides. (1) P_9S_1 ; (2) P_8S_2 ; (3) P_7S_3 ; (4) P_6S_4 . Heating rate = $20^\circ\text{C}/\text{min}$.

development, the insoluble fraction of film was found to increase with increasing irradiation time, as shown in Figure 8. Over 90% insoluble fraction could be obtained at an irradiation time of 10 min. Figure 9 shows the simulated imidization processes of P_9S_1 with and without photosensitive functional group

TABLE III
TGA Characteristics of Copolyimides^a

Polymer code	T_0 ($^\circ\text{C}$)	T_{10} ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	Weight loss
P-1	472	598	627	36.3
P-2	372	604	(425), 625	36.3
P-3	468	592	540, 647	37.9
P_8S_2	463	542	558, 635	45.3
P_7S_3	455	535	555, 638	48.3
P_6S_4	445	527	552, 640	51.8

^a T_0 , initial decomposition temperature; T_{10} , 10% weight loss temperature; T_{max} , maximum rate of decomposition temperature.

TABLE IV
Peel Strengths of Homopolyimides and Copolyimide

Polyimide code	Peel strength (g/cm)	
	Without APS	With APS
P-1		
S ₁	50	245
S ₁ O ₂	65	430
P-2		
S ₁	—	No peel
S ₁ O ₂	—	No peel
P ₉ S ₁		
S ₁	No peel	—
S ₁ O ₂	No peel	—

(IEM). It showed that the imidization rate of P₉S₁ without IEM was much faster than that of P₉S₁ with IEM. The imidization reaction of P₉S₁ without IEM would be accomplished at approximately 300°C while that of P₉S₁ with IEM would be continued until serious decomposition occurred. In other words, the imidization process of P₉S₁ with IEM was much more difficult than that of P₉S₁ without IEM so that a longer time or higher temperature was required.

CONCLUSIONS

In this research, two homopolyimides and four silicon-containing copolyimides were prepared by solution condensation in NMP. The tensile strengths,

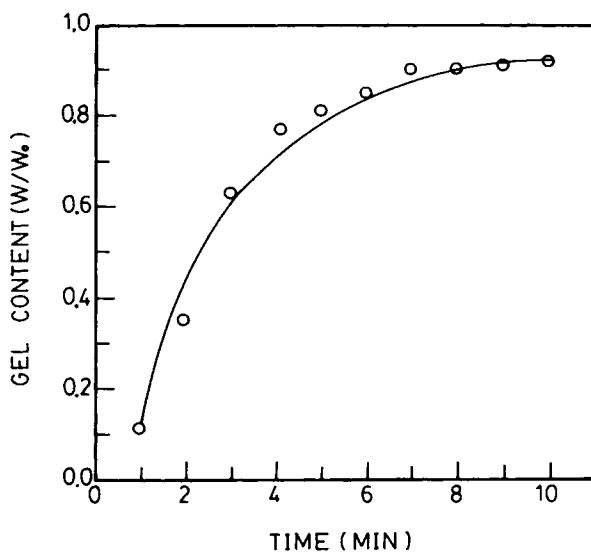


Fig. 8. Photo-cross-linking measurement of P₉S₁-IEM photosensitive silicon-containing copolyimide precursor.

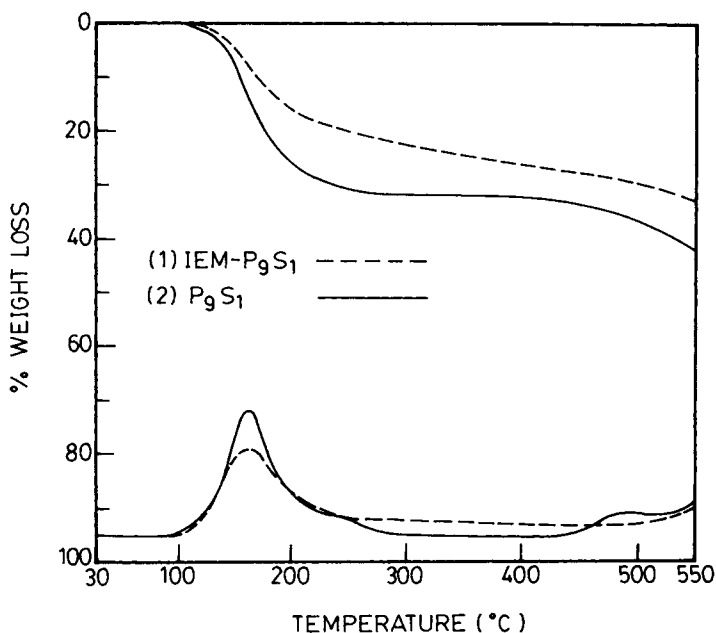


Fig. 9. Thermogravimetric curves for simulated imidization reaction: (1) P_9S_1 -IEM precursor; (2) P_9S_1 precursor. Heating rate = $20^\circ\text{C}/\text{min}$.

T_g , and thermal stability of silicon-containing copolyimides decreased with increasing siloxane moiety content. The first derivative curves of the thermogravimetric data revealed two maximum rate of decomposition temperatures that were closely related to the composition of the polymer. Copolyimides with siloxane moiety in the main chain exhibited excellent adhesion strength for the wafers. For the sample tested in this research (P_9S_1), a balance of thermal and adhesive properties could be achieved. The reaction between P_9S_1 copolyamic acid and IEM yielded a photosensitive copolyimide precursor. Under the irradiation of a mercury lamp, a 90% insoluble fraction was reached. The imidization reaction of P_9S_1 with IEM simulated with a TGA apparatus was much more difficult than that of P_9S_1 without IEM. A higher temperature or longer time for imidization was required.

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