Preparation and Properties of New Disilane-Containing Polyamide and Polyimides from Diaminodisilanes and Bisphenol Compounds

Munirathina PADMANABAN, Masa-aki KAKIMOTO, and Yoshio IMAI*

*Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan*

(Received November 13, 1989)

ABSTRACT: Two new diaminodisilanes, 1,2-bis(diethylamino)tetramethyldisilane and 1,2-bis(anilino)tetramethyldisilane were synthesized from 1,2-dichlorotetramethyldisilane and the respective amines. These disilane-containing monomers were reacted with bisphenols containing amide and imide groups, giving disilane-containing polyamide and polyimides which had rather low inherent viscosity around 0.1 dl g^{-1} . The polymers were characterized by UV, IR, and elemental analysis. All the polymers were soluble in *N,N*-dimethylacetamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, and some of them were also soluble in tetrahydrofuran. The polymers had glass transition temperatures between 105–120°C and were thermally stable up to 300°C in both air and nitrogen atmospheres. A decrease in the molecular weight was observed upon exposure to UV light indicating the photosensitivity of the disilane-containing polymers.

KEY WORDS Disilane-Containing Polymers / Polyamide / Polyimides / Solubility / Thermal Stability / Photosensitivity /

Recently, we have reported the synthesis and properties of new photosensitive polyamides¹ and polyimides^{2,3} from a disilane-containing diamine, bis(*p*-aminophenyl)tetramethyldisilane, and various aromatic diacid chlorides and aromatic tetracarboxylic dianhydrides, respectively. These polyamides and polyimides were found to undergo a decrease in inherent viscosity upon exposure to UV light, indicating the silicon-silicon bond scission, and were thermally stable up to 350°C with glass transition temperatures (T_g) around 220°C. These photosensitive polymers may be promising candidates for thermally stable positive working photoresist materials.

In our further efforts to obtain new thermally stable photosensitive polymers containing disilane unit, we were successful in synthesizing a new series of polymers, poly(oxyaryleneoxydisilane)s, from the bulk polymerization of 1,2-bis(diethylamino)tetramethyldisilane and

various bisphenols.⁴ The poly(oxyaryleneoxydisilane)s were thermally stable up to 300°C, but their glass transition temperatures varied from –65° to 135°C, highly depending on the arylene moiety of the bisphenol component. For example, the polymer possessing rigid and bulky fluorene group was white solid with a T_g of 135°C, and the polymer with *m*-phenylene unit was a viscous liquid with a T_g of –65°C. If these novel photosensitive polymers are to be considered for application as photoresist materials, it is desirable to increase the T_g . One easy approach would be to react bisphenols containing amide and imide moieties with above mentioned diaminodisilane. This paper deals with one such attempt in obtaining disilane-containing polymers **IIIa–c** by the reaction of diaminodisilanes (**Ia** and **b**) and bisphenols containing amide (**IIa**) and imide (**IIb** and **c**) groups (eq 1). For comparison, the properties of poly(oxyaryleneoxydisilane) **III d**

* To whom all correspondence should be addressed.

obtained previously⁴ by the reaction of **Ia** and 2,6-dihydroxynaphthalene **IIc** is also included

EXPERIMENTAL

Materials

1,2-Dichlorotetramethyldisilane was synthesised starting from hexamethyldisilane according to the reported procedure.¹ Diethylamine, triethylamine, and aniline were dried with calcium hydride and distilled before use. *m*-Aminophenol was recrystallized from water. Isophthaloyl chloride was distilled under reduced pressure. Pyromellitic dianhydride (PMDA), 4,4'-sulfonyldipthalic dianhydride (DSDA) were purified by sublimation. Solvents such as *m*-cresol, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), chloroform, toluene, and benzene were distilled before use.

Monomer Synthesis

Synthesis of 1,2-bis(diethylamino)tetramethyldisilane (Ia). This compound was prepared by the reaction of 1,2-dichlorotetramethyldisilane with diethylamine in benzene. In a typical reaction, 83.67 g (1.14 mol) of diethylamine was placed in a dry three-necked flask fitted with a reflux condenser, a dropping funnel, a mechanical stirrer, and a nitrogen gas inlet along with 600 ml of dry benzene. The mixture was cooled to 0°C using an ice bath and to this

cold mixture was added a solution of 48.76 g (0.26 mol) of 1,2-dichlorotetramethyldisilane in 100 ml of benzene taken in the dropping funnel, dropwise over a period of 1 h. A white crystalline precipitate began to form almost immediately after the start of the addition of the dichlorosilane. After complete addition, the reaction mixture was stirred at room temperature for 12 h, and then at 100°C for 2 h. The white semi-solid reaction mixture thus obtained was filtered to remove the solid diethylamine hydrochloride salt under nitrogen flow. The solvent was distilled out from the filtrate and the crude product was purified by vacuum distillation at 110°C/11 Torr. The yield after two repeated distillations was 57.6 g (85%). The IR spectrum (neat) showed absorptions at 2925 and 1251 cm⁻¹ (Si-CH₃) and 520 cm⁻¹ (Si-Si). The ¹H NMR spectrum measured in CCl₄ gave signals at 0.2 ppm (s, 12H), 1.1 ppm (q, 12), and at 2.8 ppm (t, 8H). The UV absorption spectrum in THF showed an absorption maximum (λ_{max}) at 220 nm with a molar absorption coefficient (ε_{max}) of 3.13 × 10³. *Anal.* Calcd for C₁₂H₃₂N₂Si₂: C, 55.31%, H, 12.38%; N, 10.75%. Found: C, 55.09%, H, 12.08%, N, 10.59%.

Synthesis of 1,2-bis(anilino)tetramethyldisilane (Ib). To a solution of 9.31 g (0.1 mol) of aniline and 11.13 g (0.11 mol) of triethylamine in 150 ml of dry benzene was added a solution of 9.36 g (0.05 mol) of 1,2-dichlorotetramethyldisilane in 50 ml of benzene at 0°C dropwise over a period of 1 h. After complete addition, the reaction mixture was stirred at room temperature for 10 h, and then at 100°C for 2 h. The semi-solid reaction mixture thus obtained was filtered to remove the solid triethylamine hydrochloride salt under nitrogen flow. The solvent was distilled off from the filtrate, and the crude product was purified by vacuum distillation at 130°C/0.1 Torr. The yield after one distillation was 12 g (80%). The IR spectrum (neat) showed absorptions at 3384 cm⁻¹ (N-H), 1251 cm⁻¹ (Si-CH₃), and 520 cm⁻¹ (Si-Si). The ¹H NMR spectrum gave

signals at 0.43 ppm (s, 12H), 3.27 (s, 2H), and 6.73 (m, 10H). The UV absorption spectrum in THF showed two absorptions with maxima (λ_{max}) at 212 nm and 254 nm with molar absorptivity (ϵ_{max}) values of 1×10^4 and 1.95×10^4 , respectively. *Anal.* Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{Si}_2$: C, 63.94%, H, 8.05%, N, 9.32%. Found: C, 63.12%, H, 8.29%, N, 9.34%.

Synthesis of N,N'-bis(m-hydroxyphenyl)isophthalamide (IIa). In a 300 ml three-necked flask were placed 26.19 g (0.24 mol) of *m*-aminophenol and 150 ml of DMAc under nitrogen. To this was added 24.36 g (0.12 mol) of isophthaloyl chloride all at once after cooling the solution to 0°C. The solution was stirred at 6 h during which time the temperature had risen to room temperature. The reaction mixture was poured into 2 l of distilled water and filtered. The filtrate was washed several times with water, and dried under vacuum at 100°C. The yield was 35.5 g (85%). The compound was recrystallized from a water-ethanol mixture (1 : 1 by volume), giving white particle like crystals; mp 265°C (by DTA) (lit.⁵ mp 260–261°C). The IR spectrum (KBr pellet) exhibited absorptions at 3346 and 3308 cm^{-1} (O–H and N–H), and 1660 cm^{-1} (C=O). *Anal.* Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_2$: C, 68.95%; H, 4.63%, N, 8.04%; Found: C, 68.87%; H, 4.63%; N, 7.91%.

Synthesis of N,N'-bis(m-hydroxyphenyl)pyromellitimide (IIb). In a 500 ml three-necked flask fitted with a nitrogen gas inlet, reflux condenser, and Dien-Stark apparatus were placed 21.81 g (0.1 mol) of pyromellitic dianhydride, 21.83 g (0.2 mol) of *m*-aminophenol, and 250 ml of *m*-cresol under nitrogen atmosphere. The mixture was stirred at room temperature for 3 h and then heated to 220°C and maintained at that temperature for 3 h. Initially the reaction mixture was heterogeneous but after a reaction time of about 15 min a homogeneous solution was obtained. The water formed was removed azeotropically, and the remaining *m*-cresol was distilled out under

reduced pressure. The reaction mixture was poured into 2 l of hexane, and the yellow powder was filtered. The product was washed with hexane, and dried. The yield was 40 g (94%). Recrystallization from a toluene–DMAc (4 : 1 by volume) mixture afforded yellow color particles; the compound degraded before melting and no clear melting temperature could be observed by DTA. The IR spectrum showed absorptions at 3370 cm^{-1} (O–H), and 1780, and 1720 cm^{-1} (C=O, imide). *Anal.* Calcd for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{N}_2$: C, 65.99%; H, 3.02%, N, 6.99%; Found: C, 65.96%, H, 2.92%; N, 6.89%.

Synthesis of N,N'-bis(m-hydroxyphenyl)-4,4'-sulfonyldipthalimide IIc. This compound was prepared similar to the method described for **IIb** with an yield of 85%. The compound was used without further purification. No clear melting temperature could be observed by DTA. The IR spectrum of the yellow color compound showed absorptions at 3375 cm^{-1} (O–H), 1780 and 1720 cm^{-1} (C=O, imide) and 1330 cm^{-1} (O=S=O). *Anal.* Calcd for $(\text{C}_{28}\text{H}_{16}\text{O}_8\text{N}_2\text{S}_1)$: C, 62.22%; H, 2.98%; N, 5.18%; S, 5.93%; Found: C, 61.79%, H, 3.18%, N, 5.18%; S, 5.09%.

Polymerization

A typical example is given for polymer **IIIb** and the other polymers were prepared in a similar manner.

Synthesis of polymer IIIb from Ib and IIb. In a 50 ml three-necked flask fitted with nitrogen gas inlet and reflux condenser were placed 0.800 g (2 mmol) of **IIb** and 0.600 g (2 mmol) of **Ib**. To this was added 5 ml of DMAc. The mixture, which was heterogeneous at the beginning, turned homogeneous upon heating to 150°C. After a reaction time of 12 h, the mixture was poured into 500 ml of water and filtered. The polymer was washed with water, and dried. The yield was 1.15 g (88%). The IR spectrum exhibited absorptions at 1780 and 1720 cm^{-1} (C=O, imide), and 1250 cm^{-1} (Si–O).

UV Light Irradiation

0.1 g of the sample dissolved in 20 ml of THF was placed in an UV cell. UV light irradiation was carried out using a Toshiba 400 W high pressure mercury lamp at a distance of 10 cm. The solution temperature was maintained at room temperature by water circulation. After UV light irradiation a portion of the solution was diluted for GPC measurements.

Measurements

IR spectra and UV spectra were recorded on a JASCO FT/IR-5000 fourier transform spectrophotometer and a Hitachi U-3400 spectrophotometer, respectively. ^1H NMR spectra were obtained on a JEOL-PMX 60 NMR spectrometer. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-40M and TG-40M, respectively. Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weight were obtained by means of GPC on the basis of a polystyrene calibration on a JASCO HPLC BIP-I apparatus (column, Shodex GPC KF-802.5 designed for measurement of molecular weights of the order 10^3 ; eluent, THF).

RESULTS AND DISCUSSION

Polymer Synthesis

The UV absorption spectra of diaminodisilanes **Ia** and **Ib** gave absorptions at (λ_{max}) 220 nm and 212 nm, respectively, which were assigned to the presence of disilane unit.⁴ The molar absorptivity value (ϵ_{max}) of **Ia** was 0.31×10^4 and that of **Ib** was 1×10^4 . The red shift in λ_{max} and higher ϵ_{max} value for **Ib** compared to **Ia** may be due to the presence of aniline substituent. Further, **Ib** showed another absorption maximum at 254 nm with a ϵ_{max} value of 1.95×10^4 due to the aniline substituent.

First, **Ia** was reacted with **IIa** giving polymer **IIIa** under different reaction conditions to identify optimum reaction parameters (Table

Table I. Synthesis of polymer **IIIa** from **Ia** and **IIa** under various reaction conditions

Reaction conditions ^a			Polymer	
Solvent	Temperature	Time	Yield	η_{inh}^b
	°C	h	%	dl g ⁻¹
DMAc	150	12	80	0.08
DMSO	150	12	78	0.08
Bulk	25–240	12	95	0.11

^a Polymerization was carried out with 2 mmol of each monomer in 5 ml of the solvent, and in case of bulk 5 mmol of each monomer was used.

^b Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

I). Mixing of **Ia** and **IIa** at room temperature and a gradual increase of temperature to 240°C over a period of 2 h gave a homogeneous reaction mixture and the polymer thus obtained after a reaction time of 10 h had an inherent viscosity of 0.11 dl g⁻¹ (Table I). Our earlier studies on the reaction of **Ia** with various bisphenols in bulk also yielded polymers with higher inherent viscosity compared to the solution polycondensation.⁴ The bulk reaction of **Ia** with **IIb** proceeded heterogeneously and was incomplete due to the high melting temperature of **IIb**. Hence the polycondensation was carried out in DMAc solution, and the results are summarized in Table II. The polymers had inherent viscosity around 0.1 dl g⁻¹. Polymer **IIIa** and **c** had weight-average molecular ($\bar{M}_w$) weights of 1.12×10^4 and 1.09×10^4 and number-average molecular ($\bar{M}_n$) weights of 4.0×10^3 and 5.0×10^3 , respectively.

The structures of the polymers were confirmed by means of IR spectroscopy and elemental analysis. The IR spectra of **IIIa** showed absorptions at 3310 cm⁻¹ (N–H), 1660 cm⁻¹ (C=O), and 1250 cm⁻¹ (Si–O). The IR spectra of **IIIb** and **c** showed absorptions at 1780 cm⁻¹ and 1720 cm⁻¹ (C=O, imide) and 1250 cm⁻¹ (Si–O). The elemental analysis

Table II. Synthesis of polymers **III** from **I** and **II**^a

Monomers		Polymer					
I	II	Code	Yield	η_{inh}^b	Elemental analysis ^c		
			%	dl g ⁻¹	C (%)	H (%)	N (%)
Ia	IIa	IIIa	85	0.08	63.28 (62.30)	5.16 (5.67)	6.30 (6.06)
Ia	IIb	IIIb	88	0.13	66.82 (65.51)	3.17 (3.78)	4.14 (4.78)
Ia	IIc	IIIc^d	80	0.10	58.23 (58.69)	4.01 (4.00)	4.06 (4.28)
Ia	IIc	IIIc^e	95	0.59	61.34 (61.26)	6.81 (6.61)	—
Ib	IIa	IIIa	92	0.11			
Ib	IIb	IIIb	88	0.11			
Ib	IIc	IIIc	90	0.10			

^a Polymerizations were carried out by taking 2 mmol of each monomer in 5 ml of DMAc at 150°C for 12 h.^b Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.^c The values in the parantheses were the calculated values.^d Polymerization was carried out in *m*-cresol at 220°C.^e Polymerization was carried out in bulk at 130–260°C.**Table III.** Qualitative solubility of polymers **III**^a

Polymer	Solvent					
	DMAc	DMSO	NMP	THF	CHCl ₃	Toluene
IIIa	++	++	++	++	—	—
IIIb	++ ^b	+	+	—	—	—
IIIc	++	++	++	++	—	—
IIIc	++	++	++	++	++	++

^a ++, soluble at room temperature; +, soluble on heating; —, insoluble.^b Turbid at room temperature, but clear solution on heating.

values were in good agreement to the calculated values (Table II).

Polymer Properties

While polymer **IIIc** was glassy rubber, polymers **IIIa–c** were hard, brown to yellow solid. The solubility behavior of the polymers is shown in Table III. Polymers **IIIa** and **c** were soluble in DMAc, DMSO, NMP, and THF at room temperature, whereas polymer **IIIb** was soluble in DMAc, DMSO, and NMP only on

Figure 1. DTA and TG curves of polyimide **IIIc** at a heating rate of 10°C min⁻¹.

heating. Polymers **IIIa–c** were insoluble in chloroform and toluene. Compared to polymer **IIIc** which was soluble in all the above mentioned solvents, the introduction of the amide and imide moieties decreased the solubility of the polymers.

The thermal behavior of the polymers was evaluated by DTA and TG. A typical example is shown in Figure 1, and the results are summarized in Table IV. Polymers **IIIa** and **c**

Table IV. Thermal behavior data of polymers **III**

Polymer	T_g^a	$T_i^{b/c}$		$T_{10}^{c/e}$		R_{800}^d
	°C	In air	In nitrogen	In air	In nitrogen	%
IIIa	120	330	300	429	427	55
IIIb	—	360	351	427	423	54
IIIc	106	343	302	455	439	54
IIId	1	352	353	473	444	43

^a Glass transition temperature determined by DTA at a heating rate of 10°C min⁻¹ in nitrogen.

^b Temperature of initial weight loss measured by TG at a heating rate of 10°C min⁻¹.

^c Temperature at 10% weight loss measured by TG at a heating rate of 10°C min⁻¹.

^d Residue at 800°C in nitrogen.

had glass transition temperatures (T_g) at 120 and 106°C, respectively. No glass transition temperature could be detected on DTA and DSC for **IIIb**. The above mentioned values may not be absolute, because the viscosity and hence the molecular weight values are low. It however shows that the polymers with higher T_g values could be obtained compared to the poly-(oxyaryleneoxydisilane)s. Yet, the values are less than those of aramids and polyimides, which are above 200°C and this may be due to the presence of flexible Si–O units.

The thermal stability of the polymers were studied in both air and nitrogen atmospheres. All the polymers were stable up to 300°C with their 10% weight loss being recorded above 420°C. The values were less than those of aramids and polyimides and almost comparable to that of **IIId**, indicating that the thermal break down occurs at the methyl or Si–O sites of the disilane units. The residue at 800°C under nitrogen atmosphere for polymers **IIIa–c** was above 50%.

The UV spectrum of polymer **IIIa** in THF solution showed an absorption at 216 nm ($\epsilon_{\max} = 5.4 \times 10^4$) with a shoulder peak at 276 nm. Similarly, **IIIc** also showed an absorption at 218 nm ($\epsilon_{\max} = 7.8 \times 10^4$) with a shoulder peak at 250 nm. Since polymer **IIIb**

was only soluble in hot DMAc, the UV spectra of the spin-coated film was measured, which gave an absorption peak at 220 nm with a shoulder at 256 nm. The peak around 220 nm was assigned to the disilane units, and the shoulder peaks to the substituted aromatic benzene rings. The photodegradability of the polymers were tested by measuring the molecular weight of polymer **IIIc** before and after UV irradiation in THF. The weight-average molecular ($\bar{M}_w$) decreased from the initial value of 1.09×10^4 to 1.7×10^3 after a irradiation time of 8 h indicating the scission of the disilane units present in the polymer backbone, similar to the other disilane containing polymer **IIId** as well as the aromatic polyamides and polyimides reported previously.^{1–3}

REFERENCES

1. M. Padmanaban, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A; Polym. Chem.*, **28**, 1569 (1990).
2. M. Padmanaban, M. Toriumi, M. Kakimoto, and Y. Imai, *Makromol. Chem. Rapid Commun.*, **11**, 15 (1990).
3. M. Padmanaban, M. Toriumi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A; Polym. Chem.*, accepted.
4. M. Padmanaban, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A; Polym. Chem.*, in press.
5. J. Preston, *J. Polym. Sci. A-1*, **8**, 3135 (1970).