

Synthesis and Characterization of Silicon-Containing Poly(amide-amide)s

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ABSTRACT: A modified new aromatic diacid, bis[(4-carboxyphenyl) 4-benzamide] dimethylsilane (**IV**) with preformed amide linkages and a silicon moiety was synthesized and characterized by IR, NMR, mass spectroscopy, and a physical constant. Novel poly(amide-amide)s were synthesized from **IV** and aromatic diamines by Yamazaki's direct polyamidation method in *N*-methyl pyrrolidinone. The polymers were obtained in excellent yields and showed reduced viscosities in the range of 0.42–6.15 dL/g. They were readily soluble in aprotic polar solvents. These poly(amide-amide)s showed glass-transition temperatures of 303–378°C as measured by DSC and showed no weight loss below 377°C in a nitrogen atmosphere. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1610–1617, 2001

Key words: bis[(4-carboxyphenyl) 4-benzamide] dimethylsilane; aromatic diamines; silicon-containing poly(amide-amide)s; solubility and thermal properties

INTRODUCTION

Aromatic polyamides have been investigated for their high performance properties such as their high mechanical strength and high thermal stability. They have also been developed for their commercial applications as engineering plastic materials¹ (e.g., Nomex and Kevlar, a commercial product of Dupont). Recently we reported the synthesis and characterization of aromatic poly(amide-amide)s having a phenylated thiophene moiety² in the polymer backbone from preformed diamide-containing aromatic diamine, thermally stable cardo polyesters from new phthalide-containing bisphenols,³ or silicon-containing diacid

chloride⁴ and poly(phenylquinoxaline)s.⁵ A number of sulfone ether polyamides,⁶ aromatic–aliphatic polyamides,⁷ silicon-containing⁸ phenylated polyamides,⁹ and other thermally stable polymers^{10–12} with improved solubility have been investigated in our laboratory. Their good solubility in common organic solvents for good processability while retaining their high thermal stability make their usage significant. These polymers are expected to have a wide range of applications such as coatings, bulk films, adhesives, and membranes.

In continuation of this research effort on high performance materials, the synthesis of polyamides containing silicon and the preformed diamide linkage groups in the aromatic polymer backbone was performed to obtain poly(amide-amide)s. These aromatic poly(amide-amide)s by direct polyamidation using Yamazaki's phosphorylation technique, with special interest in improved processability by introducing silicon in the rigid rod molecular structure, are reported here. Incorporation of silicon and preformed amide

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groups into the polymer structure is expected to alter certain important characteristics of these polymers, such as the chemical resistance, thermooxidative stability, gas permeability, optical transparency, and moisture uptake.

EXPERIMENTAL

Materials

Triphenyl phosphite (TPP, Merck), dichlorodimethyl silane (Aldrich), and methanol (s.d. fine, Mumbai, India) were used as received. The *p*-bromotoluene (Merck), pyridine (s.d. fine), *p*-aminobenzoic acid (PABA), *m*-aminobenzoic acid (MABA) (s.d. fine), *p*-phenylenediamine (*p*-PDA), *m*-PDA, benzidine (Bz), oxydianiline (ODA), diamino diphenyl methane (MDA), diamino diphenyl sulfone (SDA), and 1,5-naphthalene diamine (NDA) were purified before use following standard procedures. The polymerization solvents *N,N*-dimethyl acetamide (DMAc) and *N*-methyl pyrrolidinone (NMP) were distilled under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Monomer Synthesis

Bis[(4-carboxyphenyl) 4-benzamide] dimethyl silane (**IV**) was synthesized in the four steps that follow.

Bis(4-tolyl) Dimethyl Silane (I)

Into a 1000-mL, three-necked round-bottom flask equipped with magnetic stirrer, a double walled reflux condenser with a calcium chloride guard tube, a dropping funnel, and a nitrogen gas inlet were placed 18.9 g of magnesium metal turnings, 40 g (37.6 mL, 0.6596 mol) of dichlorodimethyl silane, and 140 mL of dry diethyl ether. The reaction mixture was heated to its reflux temperature under a steady flow of nitrogen. A solution of 112.8 g (81.50 mL, 0.6596 mol) of *p*-bromotoluene in 160 mL of dry diethyl ether was added dropwise and the reaction was initiated by iodine. The reaction mixture was refluxed for an additional 2 h after which the ether was evaporated completely, and the mixture was kept at 180°C for 18 h and then poured into 200 mL of water. The aqueous layer was extracted 3 times with ether. The ether layer was combined; washed successively with water, 5% hydrochloric acid, 5% so-

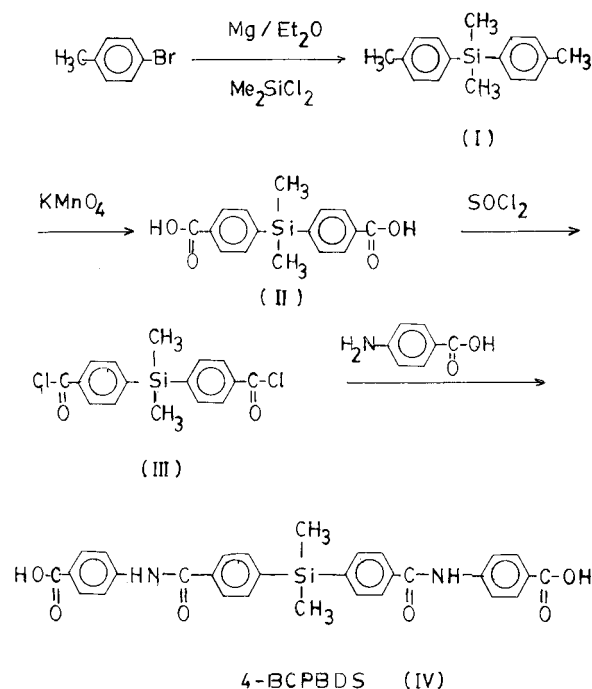
dium hydroxide solution, and water; and dried over magnesium sulfate. The ether was evaporated and residual **I** was distilled under a vacuum at 135°C/0.1 mmHg in a yield of 57 g (76.6%).

Bis(4-carboxyphenyl) Dimethyl Silane (II)

Into a 1000-mL round-bottom flask equipped with an oil bath, a reflux condenser, and a magnetic stirrer were placed 33 g (0.137 mol) of **I**, 184 mL of pyridine, and 70 mL of water and then 147 g of potassium permanganate was added in small lots at 60°C to keep the solution in reflux. The mixture was refluxed for an additional 2 h and then cooled to room temperature; the excess of potassium permanganate was destroyed by adding methanol. The manganese dioxide was removed by filtration and washed with sodium bicarbonate in the filter. The filtrate was treated with activated charcoal and acidified with hydrochloric acid. The precipitate was collected by filtration, dried, and recrystallized from aqueous alcohol to give a colorless solid (**II**). Yield: 23.0 g (55.75%); mp 291°C (lit. 287–290°C).

Bis[(4-chlorocarbonyl) phenyl] Dimethyl Silane (III)

Into a 250-mL round-bottom flask equipped with a magnetic stirrer, an oil bath, and a reflux con-



Scheme 1 The synthesis of the diamide-containing organosilicon diacid (**IV**).

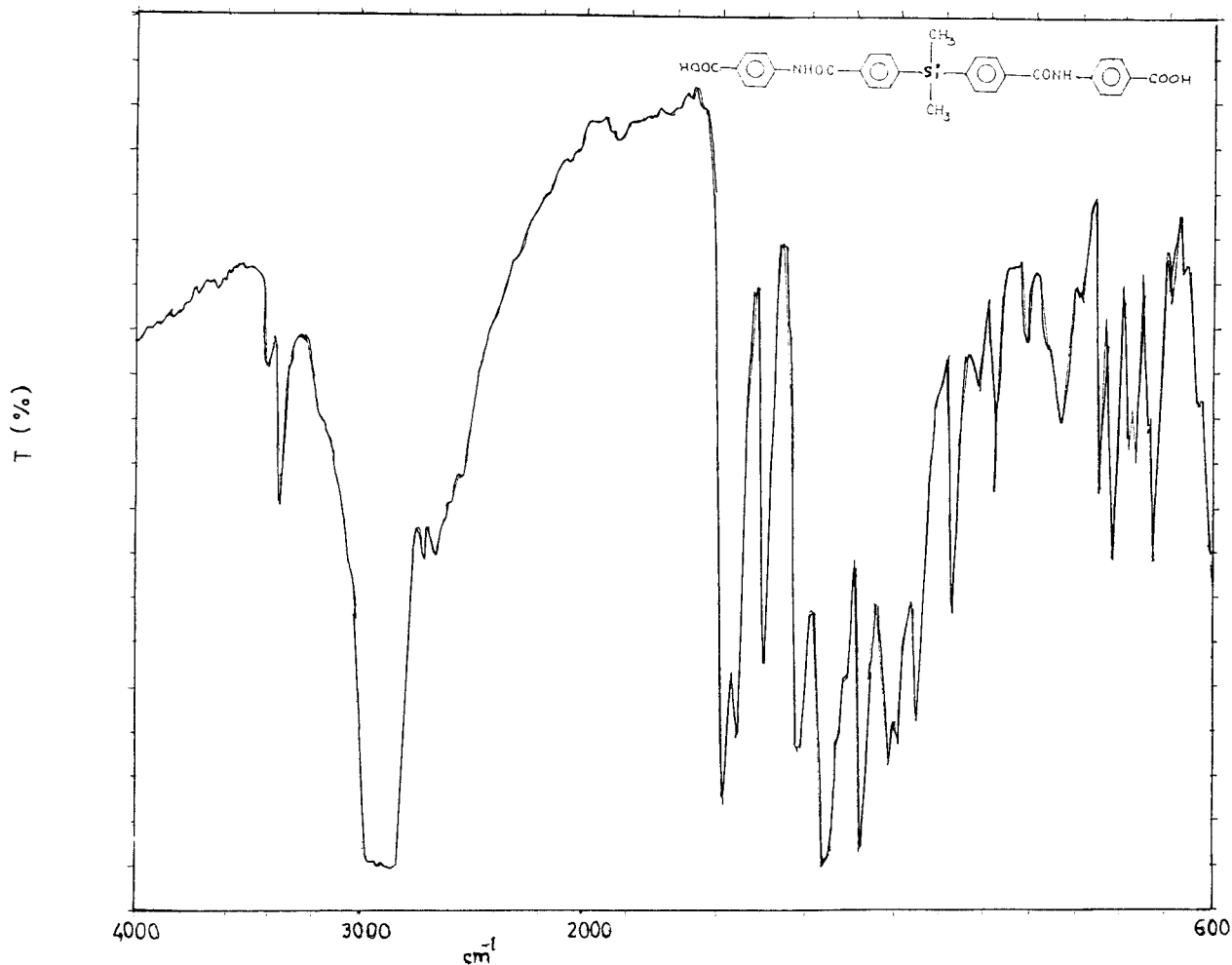


Figure 1 The IR spectrum (NUJOL) of IV.

denser with a calcium chloride guard tube were placed 15 g (0.0625 mol) of **II** and 100 mL of thionyl chloride and the mixture was refluxed for 4 h. Excess thionyl chloride was removed by distillation and traces of thionyl chloride were removed azeotropically by distillation with dry benzene. The residue was recrystallized from dry petroleum ether to yield white crystalline **III**. Yield: 13.98 g (64.4%); mp 71°C (lit. 69–71°C).

Bis[(4-carboxyphenyl) 4-benzamide] Dimethyl Silane (IV)

A three-necked round-bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet connected to a three-way stopcock, which was connected to nitrogen gas line and a vacuum pump, was flame dried under a vacuum and refilled with nitrogen.

The flame drying under the vacuum and refilling with nitrogen was repeated 3 times. The flask was charged with 4.878 g (0.0356 mol) of PABA and 45 mL of NMP under a flow of nitrogen. Then the flask was deaerated again by alternately evacuating and filling it with nitrogen. The reaction mixture was stirred at room temperature for 30 min and cooled to 0°C, and 4 g (0.0018 mol) of **III** was added at once. The reaction mixture was stirred for 15 min at 0°C and 30 min at room temperature and then poured into a stirred mixture of ice and water. The precipitate was filtered on a Buchner funnel and washed with plenty of water and then with hot methanol. Product **IV** was finally dried under a vacuum at 80°C for 10 h. Yield: 5.4 g (83%); mp: 334°C. IR: 3410 (OH); 3290 (NH); 1690 (>C=O); 1640, 1550 (amide **I** and **II**); 840 cm⁻¹ (Si—CH₃). Mass: *m/e* 538 (M⁺), 402, 137.

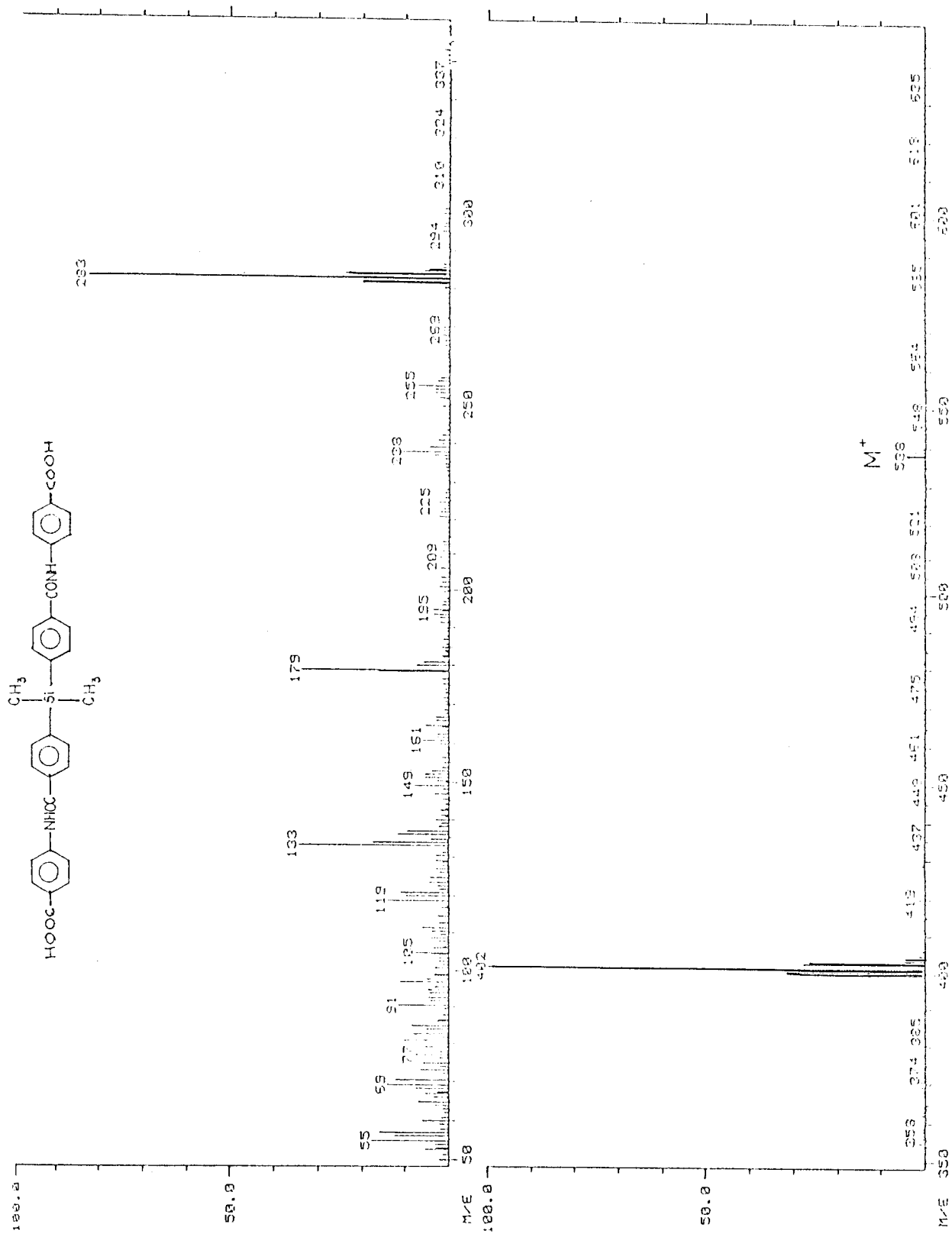
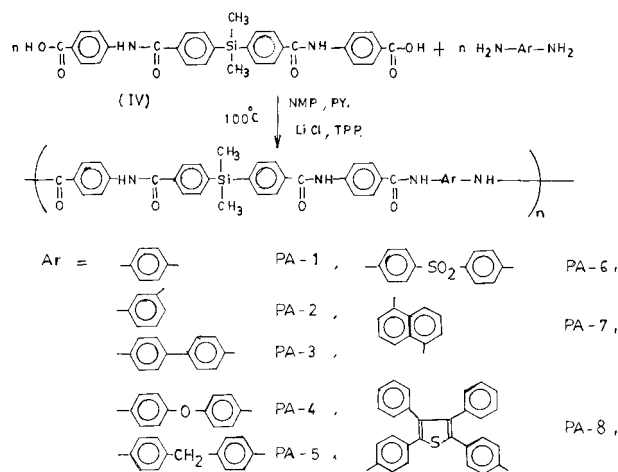


Figure 2 The mass spectrum of 4-BCPBDS (IV).



Scheme 2 The synthesis of poly(amide-amide)s (PA) from **IV**.

Polymerization

Synthesis of Polyamide (PA-4)

Into a three-necked round-bottom flask equipped with a magnetic stirrer, a reflux condenser with a calcium chloride guard tube, and a nitrogen gas inlet were placed 2 mL of NMP containing 4 wt % lithium chloride, 0.5 mL of pyridine, 0.62 g (0.005 mol) of TPP, 0.538 g (0.001 mol) of **IV**, and 0.200 g (0.001 mol) ODA. The compounds were mixed well with stirring. The temperature was slowly raised to 100°C over a period of 1 h. The stirring was continued at 100°C for 3 h. After cooling, the highly viscous solution was poured into 50 mL of methanol; the precipitated polymer was filtered, washed with methanol, and then air dried. The polymer was purified by dissolving it in DMAc and reprecipitating it in methanol, which removed the TPP and lithium chloride entrapped in the polymer bulk. The polymer was filtered, washed with methanol, and dried under a vacuum at 100°C for 8 h. Yield: 0.686 g (97.7%); viscosity (η_{sp}/c): 2.65 dL/g (in DMAc). The IR spectrum (film) of poly(amide-amide) PA-4 exhibited absorptions at 3410, 3290, 1690, 1640–1550, and 840 cm^{-1} .

All other polyamides (PA-1 to PA-3, PA-5 to PA-8) were similarly synthesized.

Measurements

Mass spectra were recorded on an IIMS-30 double beam mass spectrometer. Viscosity measurements were made with a 0.5% (w/v) solution of polymer in DMAc at 30°C using a suspended-type

Ubbelohde viscometer. The solubility of the polyamides was determined at a 3% concentration in the mentioned solvent. IR spectra were recorded on a Perkin–Elmer 883 IR spectrophotometer as a KBr pellet or polymer film. DSC and TGA were performed on a Rigaku Thermoflux TG-8110 at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Monomer Synthesis

The organosilicon acid chloride (**IV**) was prepared as described in the literature (Scheme 1). In the first step the synthesis involved Grignard's reaction of *p*-bromotoluene with dichlorodimethyl silane. The reaction was carried out in dry ether. The resulting compound **I** was isolated and purified by vacuum distillation. Purified **I** was subjected to potassium permanganate (KMnO_4) oxidation in a water–pyridine mixture to yield an organosilicon diacid (**II**) that was subsequently converted to the corresponding acid chloride (**III**), which was purified by recrystallization from dry hexane. From **III** a new organosilicon diacid (**IV**) containing preformed diamide linkages was synthesized in 83% yield by reacting it with PABA in NMP at low temperature. The formation of **IV** was confirmed by IR and mass spectroscopy.

The IR spectrum of **IV** (Fig. 1) shows the absorption bands at 3410 (OH stretch), 1690 (C=O stretch) for the carboxyl group, 3290 (NH stretch), 1640 (amide **I**), and 1550 cm^{-1} (amide **II**), indi-

Table I Synthesis of Poly(amide-amide)s from **IV**

No.	Polymer Code	Aromatic Diamine	Yield (%)	η_{sp}/c (dL/g)
1	PA-1	<i>p</i> -PDA	97	1.79
2	PA-2	<i>m</i> -PDA	98	2.57
3	PA-3	Bz	98	6.15
4	PA-4	ODA	97	2.65
5	PA-5	MDA	98	2.74
6	PA-6	SDA	98	0.83
7	PA-7	NDA	97	2.38
8	PA-8	TPTPDA	86	0.42

The polymerization was carried out with 1 mmol each of diamine and **IV**. The viscosity (η_{sp}/c) was measured at a concentration of 0.5 g/dL in DMAc at 30°C; TPTPDA, tetraphenylthiophenediamine.

Table II Solubility of Poly(amide-amide)s

Solvent	Polymer							
	PA-1	PA-2	PA-3	PA-4	PA-5	PA-6	PA-7	PA-8
Conc H ₂ SO ₄	++	++	++	++	++	++	++	++
DMAc	++	++	++	++	++	++	++	++
DMF	++	++	++	++	++	++	++	++
NMP	++	++	++	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++
Pyridine	-	++	-	++	++	++	-	++
<i>m</i> -Cresol	-	-	++	++	++	++	++	++
Formic acid	-	-	-	-	-	-	-	-
Trichloroethylene	-	-	-	-	-	-	-	-
Dichloromethane	-	-	-	-	-	-	-	-
EtOH	-	-	-	-	-	-	-	-

(++) soluble at room temperature; (-) insoluble.

cating formation of amide linkages. The absorption at 840 cm⁻¹ was for Si—CH₃.

The mass spectrum of **IV** (Fig. 2) was consistent with the proposed structure with the molecular ion peak at 538 and peaks at 137 and 402 assignable to generation of NH-Ph-COOH fragments. NMR spectra (¹H and ¹³C) could not be recorded because **IV** was sparingly soluble in CDCl₃ or DMSO-*d*₆.

Polymer Synthesis

Aromatic poly(amide-amide)s were synthesized by condensing **IV** with various aromatic diamines by the direct polycondensation technique (Scheme 2) using Yamazaki's phosphorylation method. TPP was used as the condensing agent wherein the mixture of NMP and pyridine containing lithium chloride was the solvent.

The viscosities and yields of the synthesized poly(amide-amide)s are summarized in Table I. All of these poly(amide-amide)s, except PA-8, were pale yellow to white fibrous material and were obtained in almost quantitative yield. Tough, flexible, transparent films of the polymers could be cast from a 5 to 10% solution of polymers in DMAc.

The poly(amide-amide)s exhibited reduced viscosities in the range of 0.42–6.15 dL/g, which indicated formation of high molecular weight polymers. These may be attributed to the activation of the carboxyl group that was due to the electron withdrawing effect of the diamide group in **IV**.

Polymer Characterization

The formation of poly(amide-amide)s was confirmed by the IR spectra. Thus, the IR spectra of

poly(amide-amide) films exhibited characteristic absorption bands at 3310, 1667, and 1590 cm⁻¹. The absence of bands at 3440 and 3350 cm⁻¹ indicated that the acid and amine groups of **IV** and aromatic diamines, respectively, reacted to yield high molecular weight polyamides.

The solubility of the poly(amide-amide)s was checked in various organic solvents and the results are summarized in Table II. The polyamides were found to be soluble in aprotic polar solvents such as DMAc, DMF, and NMP. They also dissolved in DMSO and pyridine. These new silicon-containing polyamides exhibited better solubility than corresponding polyamides devoid of silicon in their backbone, for example, Kevlar and Nomex. The better solubility of the present poly(amide-amide)s may be attributed to the silicon moiety and additional amide groups, which contributes the significant effect of large polarity. The thermal properties of these polymers were evaluated in nitrogen by TGA and DSC. The TG curves of the poly(amide-amide)s are shown in Figure 3. Table III incorporates the thermal characteristics such as the glass-transition temperature (*T_g*), initial decomposition temperature (*T_i*), maximum decomposition temperature (*T_{max}*), and residual weight at 900°C. All the polymers showed an almost similar pattern of thermal degradation with the *T_g* in the range of 300–378°C, the *T_i* in the range of 377–408°C, and the *T_{max}* between 430 and 480°C, indicating high thermal stability.

CONCLUSIONS

A new organosilicon aromatic diacid containing a silicon moiety and preformed diamide linkages

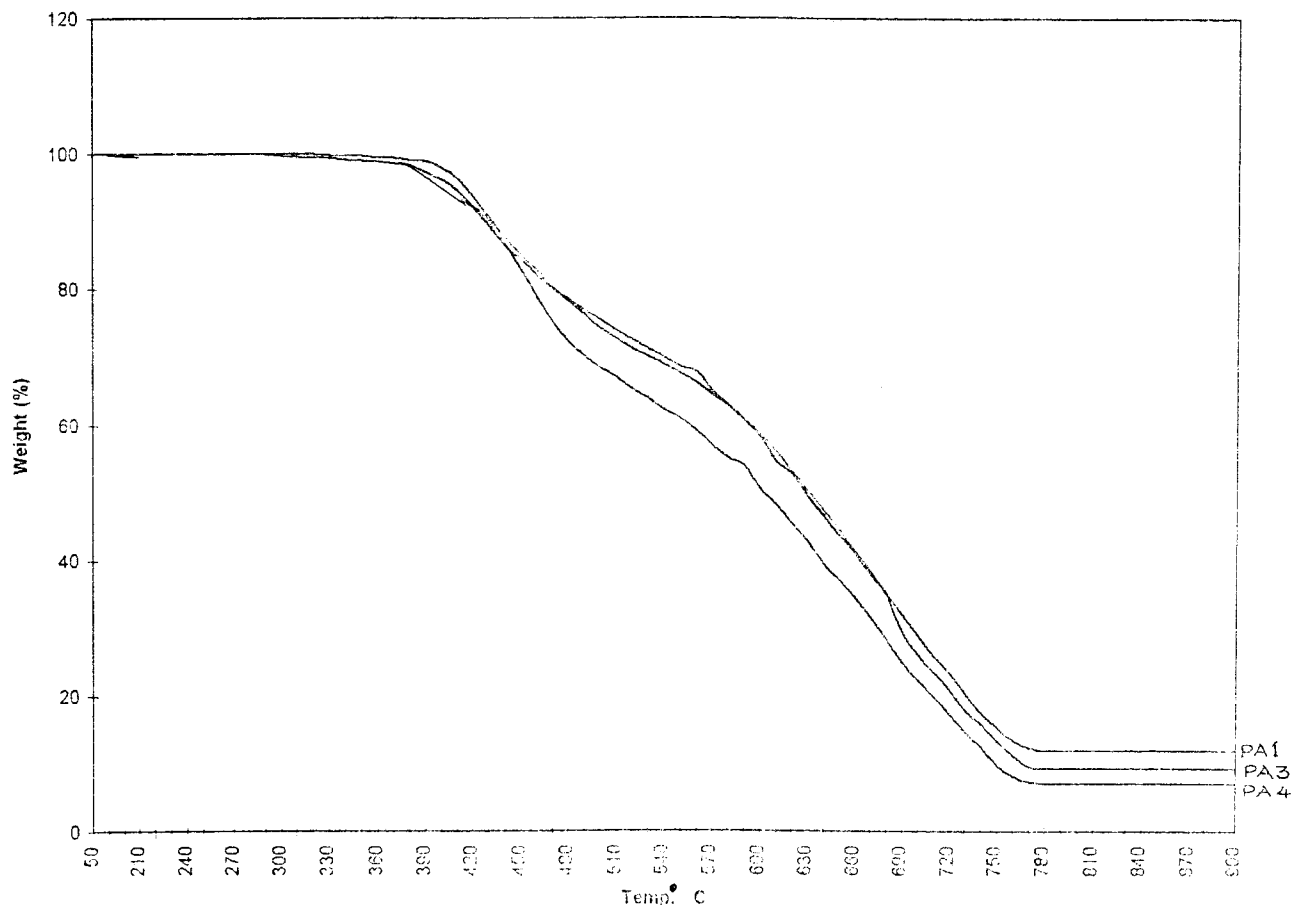


Figure 3 The TG curves of poly(amide-amide)s from **IV**.

(IV) was synthesized and characterized by spectral data. A series of eight silicon-containing ordered poly(amide-amide)s in high molecular weight form was prepared from **IV** and various aromatic diamines by Yamazaki's phosphorylation method. The resulting polymers had better

solubility in different amide-type polar aprotic solvents and excellent thermal stability with high glass-transition temperatures. These poly(amide-amide)s are expected to be used in applications where processable and high temperature materials are required.

Table III Thermal Analysis of Poly(amide-amide)s

No.	Polymer	T_i (°C)	T_{max} (°C)	Residual Mass at 900°C (%)	T_g (°C)
1	PA-1	408	450	12	338
2	PA-2	377	445	09	303
3	PA-3	400	460	07	320
4	PA-4	378	440	09	304
5	PA-5	393	460	09	300
6	PA-6	403	430	07	315
7	PA-7	385	480	04	378
8	PA-8	399	450	10	337

The thermogravimetric analysis was conducted at a heating rate of 10°C/min under nitrogen. T_i , the temperature at which the initial loss of mass was observed; T_{max} , the temperature of the maximum rate of decomposition from DTG; T_g , the glass-transition temperature determined by DSC at a heating rate of 10°C/min.

REFERENCES

1. Preston, J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, 2nd ed., p 381.
2. Basutkar, P. H.; Joshi, M. D.; Lonikar, S. V.; Maldar, N. N.; Idage, B. B. *J Appl Polym Sci* 1998, 68, 1523.
3. Vibhute, S. S.; Joshi, M. D.; Wadgaonkar, P. P.; Patil, A. S.; Maldar, N. N. *J Polym Sci Polym Chem Ed* 1997, 35, 3227.
4. Joshi, M. D.; Sarkar, A.; Yemul, O. S.; Wadgaonkar, P. P.; Lonikar, S. V.; Maldar, N. N. *J Appl Polym Sci* 1997, 64, 1329.
5. Joshi, M. D.; Lonikar, S. V.; Maldar, N. N.; Wadgaonkar, P. P. *J Macromol Sci Part A Pure Appl Chem* 1997, A34, 1077.
6. Jadhav, A. S.; Vernekar, S. P.; Maldar, N. N. *Polym Int* 1993, 32, 5.
7. Mahajan, S. S.; Sarwade, B. D.; Maldar, N. N. *Polym Bull* 1990, 24, 143.
8. Mohite, S. S.; Maldar, N. N.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1988, 26, 2777.
9. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem Ed* 1985, 23, 1797.
10. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem Ed* 1989, 23, 3771.
11. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem Ed* 1985, 23, 2077.
12. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem Ed* 1984, 22, 2189.