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Synthesis of New Functional Silicon-Based Condensation Polymers

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SYNTHESIS OF NEW FUNCTIONAL SILICON-BASED CONDENSATION POLYMERS

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ABSTRACT

A new class of photosensitive aromatic polymers containing disilane units was successfully synthesized from new disilane-based monomers such as 1,2-bis(diethylamino)tetramethyldisilane and 1,2-bis(*p*-aminophenyl)tetramethyldisilane. The disilane-containing aramids and polyimides had glass transition temperatures above 190°C, and all the polymers were thermally stable up to 300°C in air. The polymers were photosensitive; their molecular weight decreased rapidly upon ultraviolet light irradiation. The photosensitive polymers, especially the soluble polyimides having diphenyl sulfone units, were potential candidates for positive working photoresist materials. New highly branched polysiloxane starburst polymers were synthesized by a siloxane synthetic reaction starting from tris[(phenyldimethylsiloxy)dimethylsiloxy]methylsilane and bis[(phenyldimethylsiloxy)methylsiloxy]dimethylsilanol as the initial core (G0-Ph) and the building block, respectively. Thus, the first generation polymer G1-Ph, second generation polymer G2-Ph, and third generation polymer G3-Ph had 6, 12, and 24 phenylsilyl groups in their exterior layers. The formation of the siloxane-based starburst polymers were confirmed by means of ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy. These polysiloxane starburst polymers were suggested to have spherical structure. Some functionalized starburst polymers were further synthesized by the introduction of functional groups in their exterior layers. New silica-polyimide hybrid materials were prepared by the sol-gel process through the hydrolysis-condensation reactions of tetraethoxysilane in the presence of the polyamic acid (polyimide precursor) in dimethylacetamide, followed by heating at 270°C. The hybrid system having silica content up to 70 wt% had good quality films. The spherical silica particles were dispersed homogeneously in the polyimide matrix. With increasing silica content, the glass transition temperature and decomposition temperature, as well as the modulus of the hybrid films, increased, while the coefficient of thermal expansion decreased.

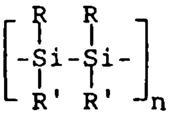
INTRODUCTION

Silicon is the element most like carbon in its atomic structure, but it has some differences in size, electronegativity etc. Significantly, the silicon–silicon bond is weaker than the carbon–carbon bond, whereas the silicon–oxygen bond is stronger than the carbon–oxygen bond. Silicon-oxygen-containing polymers, polysiloxanes, have been known for many years [1]. Another important aspect of the silicon bond is its σ-π conjugation, and the polysilanes have been increasingly important because of their unusual electronic properties [1]. Additional progress has been made in utilizing the silica sol-gel process to prepare silica-polymer hybrid materials [1].

We recently investigated specific silicon chemistry and functional silicon-based condensation polymers. This article covers three topics: 1) the synthesis of new disilane-containing condensation polymers, 2) the synthesis of new siloxane-based starburst polymers, and 3) the preparation of new silica–polyimide hybrid materials by the sol-gel process.

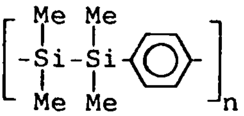
SYNTHESIS OF NEW DISILANE-CONTAINING CONDENSATION POLYMERS

Much interest has been shown recently in polysilanes (I) [2–4] and polydisilanylenephenylenes (II) [5, 6] as a new class of functional polymers with potential applications as photosensitive materials, photo and charge-conducting materials, and materials with interesting nonlinear optical properties.



$$\left[-\overset{R}{\underset{R'}{\mathrm{Si}}}-\overset{R}{\underset{R'}{\mathrm{Si}}}-\right]_n$$

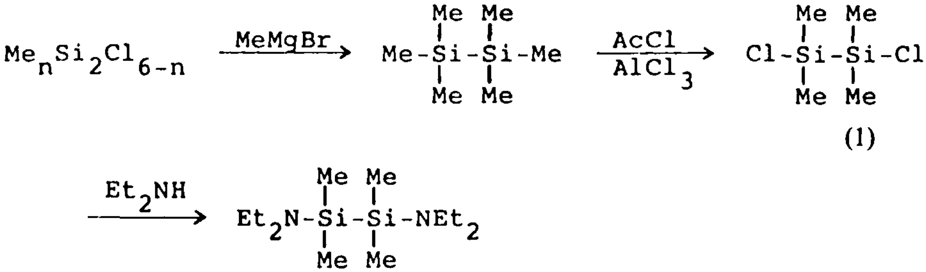
I



$$\left[-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\overset{Me}{\underset{Me}{\mathrm{Si}}}-C_6H_4-\right]_n$$

II

Our attention has focused on the synthesis of photosensitive disilane-containing condensation polymers having high thermal stability. We first synthesized a new disilane-containing condensation monomer, 1,2-bis(diethylamino)tetramethyldisilane, starting from chloromethylsilanes (Eq. 1) [7].

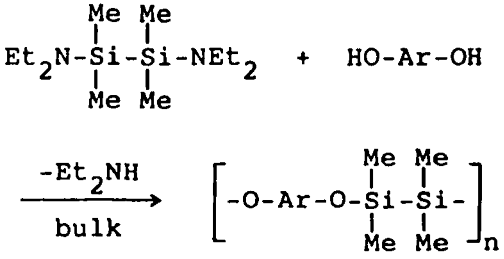


$$Me_nSi_2Cl_{6-n} \xrightarrow{MeMgBr} Me-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\overset{Me}{\underset{Me}{\mathrm{Si}}}-Me \xrightarrow[AlCl_3]{AcCl} Cl-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\overset{Me}{\underset{Me}{\mathrm{Si}}}-Cl \qquad (1)$$

$$\xrightarrow{Et_2NH} Et_2N-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\overset{Me}{\underset{Me}{\mathrm{Si}}}-NEt_2$$

The key intermediate compound, 1,2-dichlorotetramethyldisilane, was prepared by the reaction of a mixture of chloromethyldisilanes with methylmagnesium bromide, followed by chlorination with acetyl chloride. The reaction of the dichlorodisilane compound with diethylamine afforded bis(diethylamino)tetramethyldisilane monomer.

A new class of poly(oxyaryleneoxydisilanylene)s (III) was synthesized by the melt polycondensation of bis(diethylamino)tetramethyldisilane with various bisphenols (Eq. 2) [7].



$$Et_2N-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\overset{Me}{\underset{Me}{\mathrm{Si}}}-NEt_2 + HO-Ar-OH$$

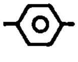
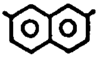
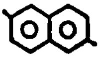
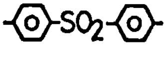
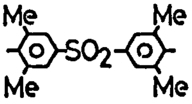
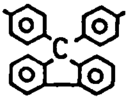
$$\xrightarrow[bulk]{-Et_2NH} \left[-O-Ar-O-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\overset{Me}{\underset{Me}{\mathrm{Si}}}-\right]_n \qquad (2)$$

III

The polymerization was carried out by successive heating to 260°C under a slow stream of nitrogen. The results of the polymerization and the thermal behavior data of the polymers are summarized in Table 1.

The physical appearance at room temperature of the disilane-containing polymers ranged from viscous liquids to hard glassy solids. The inherent viscosities of the polymers were between 0.1 and 0.6 dL/g. These polymers had a wide range of glass transition temperatures ranging from −65 to 135°C, and were thermally stable up to 300°C in air.

TABLE 1. Synthesis and Thermal Properties of Poly(oxyaryleneoxydisilanylene)s

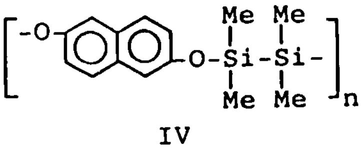
Ar	η_{inh},[a] dL/g	T_g,[b] °C	T_i,[c] °C	T_{10},[c] °C
	0.11	−65	320	430
	0.22	−45	340	445
	0.33	−5	355	520
	0.59	1	350	475
	0.12	71	350	445
	0.10	110	305	385
	0.18	135	375	405

[a] Measured in toluene, $C = 0.5$ g/dL, at 30°C.

[b] Determined by DSC, heating rate = 10°C/min.

[c] T_i: initial decomposition temperature. T_{10}: temperature at 10% weight loss. Determined by TG in air, heating rate = 10°C/min.

To study the photoreactivity of the disilane-containing polymers, ultraviolet light irradiation was carried out in toluene solution with cooling by using a high pressure mercury lamp. A typical example is shown for Polymer IV (Fig. 1).



IV

The inherent viscosity decreased rapidly with incremental irradiation time, especially in the initial stage of irradiation. This can be explained by chain scission of the silicon–silicon bond present in the polymer backbone upon ultraviolet light irradiation. This result demonstrates the photodegradability of this type of disilane-containing polymers.

Thus, poly(oxyaryleneoxydisilanylene)s (III) were photodegradable; however, their glass transition temperatures were too low for practical use [7].

Our next target was to synthesize disilane-containing aromatic polymers having both photosensitivity and higher glass transition temperatures. To achieve this goal, we synthesized a new disilane-containing

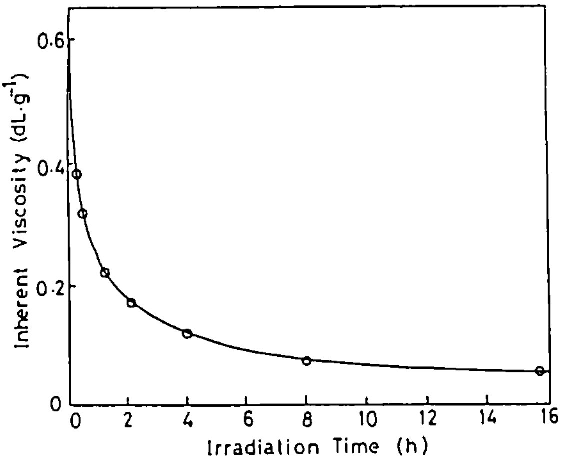
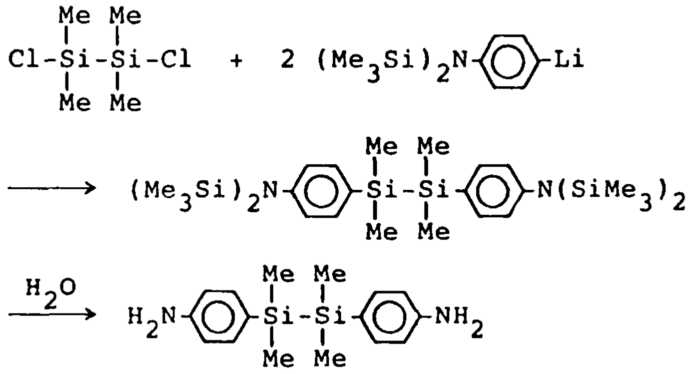


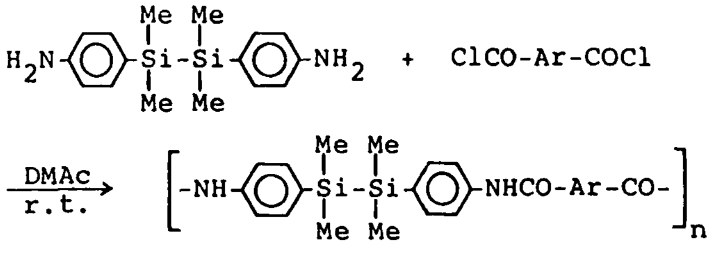
FIG. 1. Effect of UV light irradiation on inherent viscosity of disilane-containing Polymer IV.

diamine monomer, 1,2-bis(*p*-aminophenyl)tetramethyldisilane, for the preparation of aramids and polyimides. This diamine monomer was obtained by the reaction of 1,2-dichlorotetramethyldisilane with trimethylsilyl-protected *p*-aminophenyl lithium, followed by hydrolysis (Eq. 3) [8].



(3)

New disilane-containing aramids (V) were synthesized by the low temperature solution polycondensation of bis(*p*-aminophenyl)tetramethyldisilane with various aromatic dicarboxylic acid chlorides in *N*-methyl-2-pyrrolidone (NMP) (Eq. 4) [8]. The results of synthesis of the aramids and their thermal properties are summarized in Table 2.

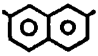
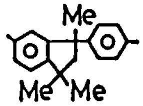


(4)

V

The disilane-based aramids (V) had moderate inherent viscosities between 0.3 and 0.7 dL/g. These polymers were soluble on heating in polar solvents such as NMP, dimethylformamide (DMF), and *m*-cresol. The

TABLE 2. Synthesis and Thermal Properties of Disilane-Containing Aramids

Ar	η_{inh},[a] dL/g	T_g,[b] °C	T_i,[c] °C	T_{10},[c] °C
	0.70	238	390	410
	0.27	194	390	410
	0.31	255	385	410
	0.42	–	400	420
	0.35	–	400	425

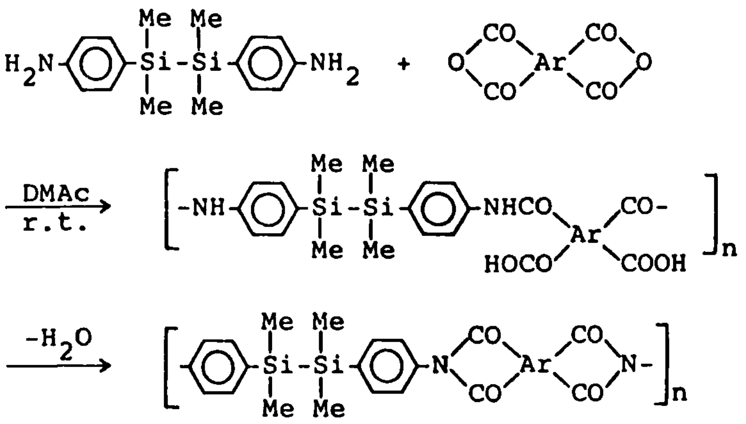
[a] Measured in NMP, C = 0.5 g/dL, at 30°C.

[b] Determined by DSC, heating rate = 10°C/min.

[c] T_i: initial decomposition temperature. T_{10}: temperature of 10% weight loss. Determined by TG in air, heating rate = 10°C/min.

aramids had glass transition temperatures above 190°C, and they did not decompose up to 380°C in air. The disilane-containing aramids were also found to be photosensitive, and the inherent viscosity decreased markedly upon ultraviolet light irradiation [8].

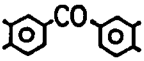
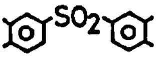
Next, the disilane-containing polyimides (VI) were synthesized by the ring-opening polyaddition of bis(*p*-aminophenyl)tetramethyldisilane to various tetracarboxylic dianhydrides in dimethylacetamide (DMAc) at room temperature, giving the corresponding polyamic acids, which were subjected to chemical imidization with a mixture of acetic anhydride and pyridine (Eq. 5) [9]. Table 3 summarizes the results of the synthesis of the polymers and their thermal properties.



(5)

VI

TABLE 3. Synthesis and Thermal Properties of Disilane-Containing Polyimides

Ar	η_{inh},[a] dL/g	T_g,[b] °C	T_i,[c] °C	T_{10},[c] °C
	0.85	–	410	505
	0.69	255	450	540
	0.63	235	420	515
	0.82	240	390	465

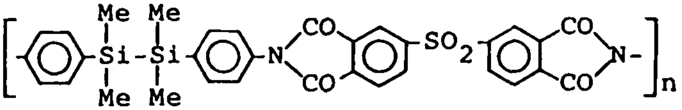
[a] Polyamic acid. Measured in DMAc, $C = 0.5$ g/dL, at 30°C.

[b] Determined by DSC, heating rate = 10°C/min.

[c] T_i: initial decomposition temperature. T_{10}: temperature of 10% weight loss. Determined by TG in air, heating rate = 10°C/min.

The polyamic acids had inherent viscosities between 0.6 and 0.8 dL/g. The polyimides had glass transition temperatures above 230°C, and they were thermally stable up to 390°C in air. All the polyamic acids showed a drastic decrease in inherent viscosity upon ultraviolet light irradiation [9].

It is notable that the diphenyl sulfone-based polyimide (VII) was readily soluble in polar solvents such as DMF, DMAc, and pyridine at room temperature [10].



VII

This polymer had an inherent viscosity of 0.8 dL/g, and it gave a transparent, yellow-colored, and flexible film by solution casting. The polyimide had a glass transition temperature of 240°C. The disilane-containing polyimide also showed photodegradability. As shown in Fig. 2, ultraviolet light irradiation of the polyimide showed a rapid decrease in inherent viscosity with irradiation time [10].

In summary, a new class of disilane-containing aramids and polyimides had high glass transition temperatures above 190°C and were thermally stable up to 300°C in air. These polymers were photodegradable upon ultraviolet light irradiation. Therefore, these photosensitive polymers, especially polyimides, can be accepted as potential candidates for high-temperature and positive-working photoresist materials.

SYNTHESIS OF NEW SILOXANE-BASED STARBURST POLYMERS

Starburst polymers are highly branched dendritic polymers. They are constructed from an initial core upon which concentric branched layers are built by a geometric process [11]. Starburst polymers allow precision control of their molecular size and the disposition of desired functionalities.

Tomalia and coworkers extensively studied the synthesis and properties of polyamide-amine-type starburst polymers. They synthesized starburst dendritic polymers by starting from ammonia as the initial core,

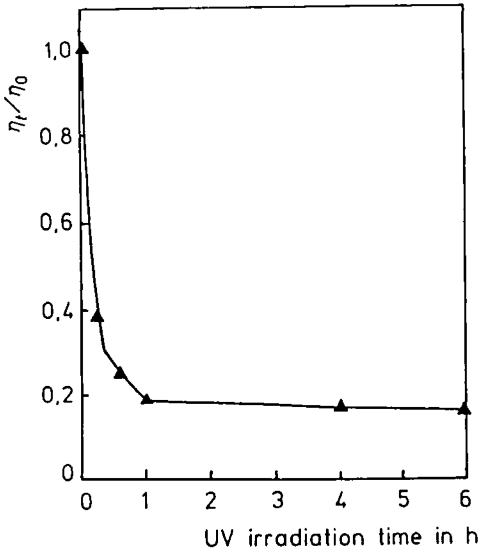


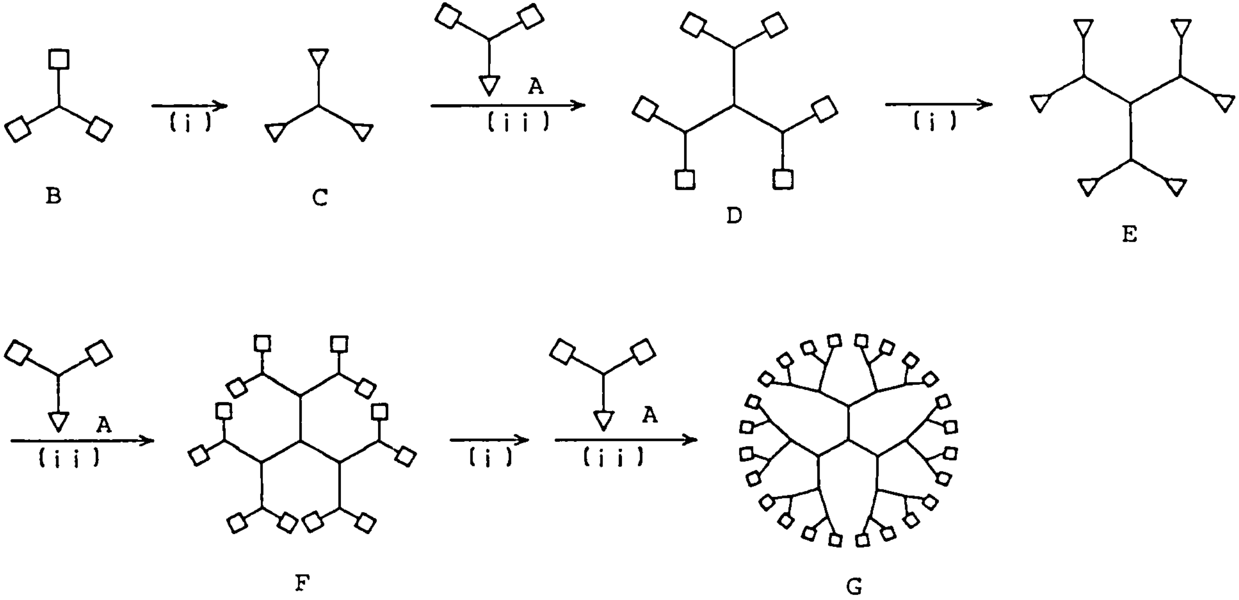
FIG. 2. Relative inherent viscosity η_t/η_0 versus UV light irradiation time for disilane-containing Polyimide VII.

followed by Michael addition of methyl acrylate to the core, and then amidation with ethylenediamine to yield the first generation compound. By repeating these addition-condensation reactions, starburst polymers up to the tenth generation were synthesized [11].

Starburst polymers can also be synthesized by a combination of condensation and protection-deprotection reactions, as shown in Scheme 1.

First, Core B, having a protected group, is subjected to deprotection to yield Core C. The reaction starts from Core C having reactive group and building Block A having reactive group, yielding the first generation Compound D having a protected group. The deprotection of the first generation Compound D affords Compound E having reactive group. Higher generation dendritic polymers F and G are synthesized by repeating these reactions.

We aimed at the synthesis of new siloxane-based starburst polymers [12]. For the siloxane-forming reaction, we selected a silanol as the silicon nucleophile and a phenylsilane as the silicon electrophile, as shown in Scheme 2. The latter phenylsilane is a protected synthetic equivalent of bromosilane and silylamine. The reaction of a silanol with a silylamine yielded a siloxane compound almost quantitatively.

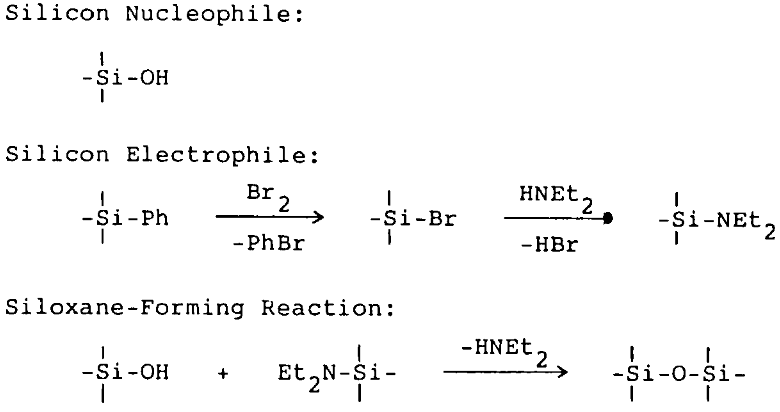


□ : Unreactive Group   △ , ▽ : Reactive Group

(i) : Conversion to Reactive Molecule

(i i) : Reaction with Building Block

SCHEME 1.



$$\equiv Si{-}OH$$

$$\equiv Si{-}Ph \xrightarrow[-PhBr]{Br_2} \equiv Si{-}Br \xrightarrow[-HBr]{HNEt_2} \equiv Si{-}NEt_2$$

$$\equiv Si{-}OH + Et_2N{-}Si\equiv \xrightarrow{-HNEt_2} \equiv Si{-}O{-}Si\equiv$$

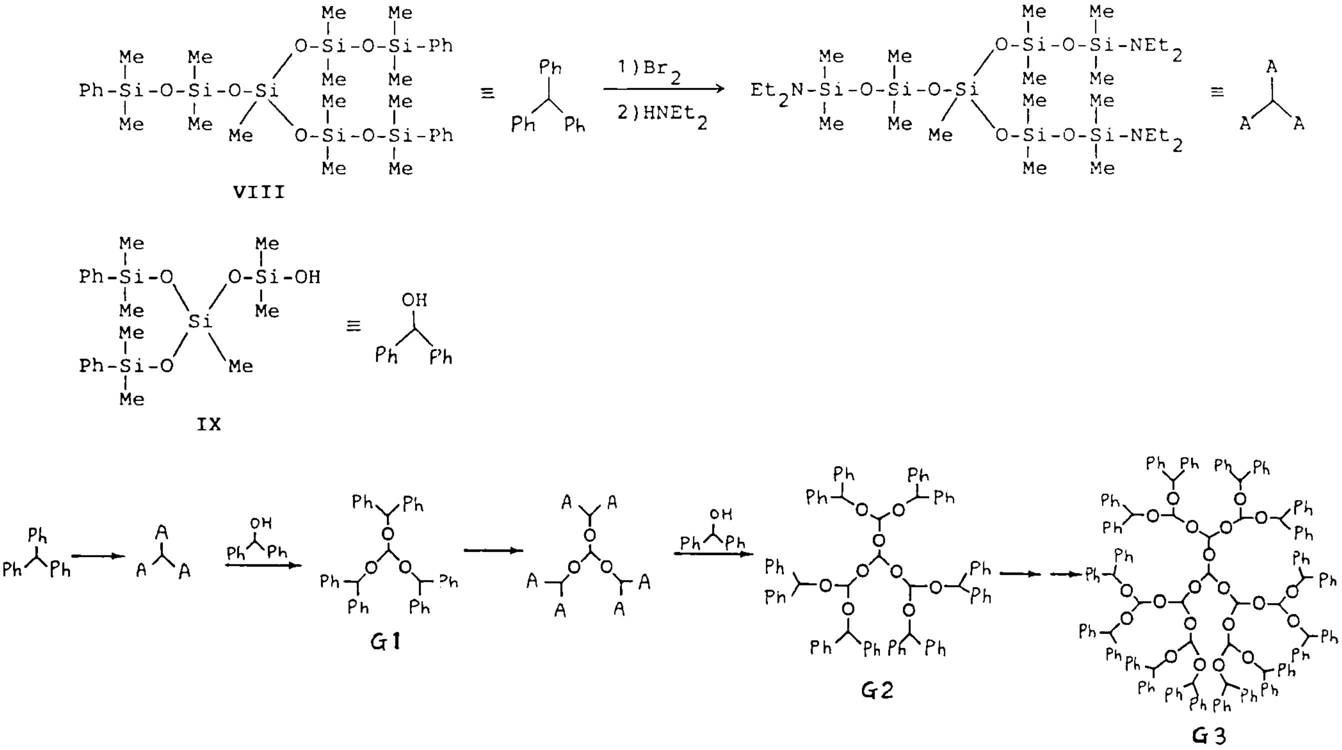
SCHEME 2.

We designed and used Silanol VIII as a building block and Phenylsilane IX as an initial core. Scheme 3 illustrates the general synthetic procedure for siloxane-based starburst polymers.

First, initial core G0-Ph having a formula molecular weight of 718 was treated with excess bromine in carbon tetrachloride to generate bromosilane G0-Br. Then G0-Br was converted to silylamine G0-NEt$_2$ by reaction with diethylamine. Next, silylamine G0-NEt$_2$ was reacted with building block Silanol VIII in carbon tetrachloride, yielding the first generation polymer G1-Ph having a formula molecular weight of 1792. This G1-Ph has six phenylsilyl groups in the exterior layer. The further generation polymers could be built up by repeating a series of reactions, that is, bromination, amination, and reaction with the building block. G0-Ph and G1-Ph were purified by vacuum distillation, and pure G2-Ph and G3-Ph were isolated by preparative gel permeation chromatography. Thus, the third generation polymer G3-Ph has a formula molecular weight of 8324 and 24 phenylsilyl groups in the exterior layer. Formation of the siloxane-based starburst polymers were confirmed by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy.

Figure 3 shows GPC curves of the starburst polymers, obtained by using polystyrene standards, and Table 4 summarizes the number-average molecular weights and molecular weight distributions.

The number-average molecular weights of G0-Ph and G1-Ph were in good agreement with the formula molecular weights, whereas the number-average molecular weights of G2-Ph and G3-Ph were far lower than the formula molecular weights. This is probably because the ex-



SCHEME 3.

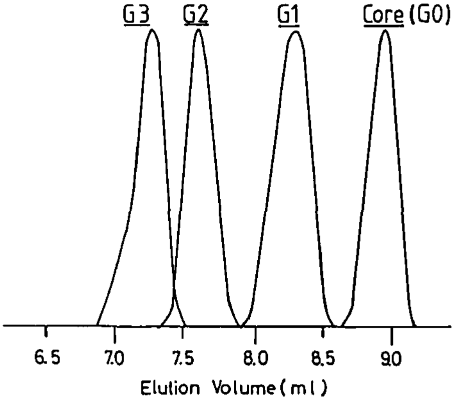


FIG. 3. GPC curves of siloxane-based starburst polymers (eluent: THF).

terior layers of G2-Ph and G3-Ph have densely packed dendritic structures. All the polymers had nearly monodispersed molecular weight distributions, suggesting that these siloxane-based starburst polymers had high purity.

The relationship between intrinsic viscosity $[\eta]$ measured in THF and molecular weight M is shown in Fig. 4.

The Mark-Houwink constants K and α were calculated to be 4.7×10^{-3} and 0.21, respectively, from

$$[\eta] = KM^{\alpha} \tag{6}$$

TABLE 4. Number-Average Molecular Weights and Molecular Weight Distributions of Siloxane-Based Starburst Polymers

Polymer	Formula molecular weight	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
G0 (core)	718	878	1.01
G1	1792	1613	1.06
G2	3940	2792	1.06
G3	8326	4819	1.14

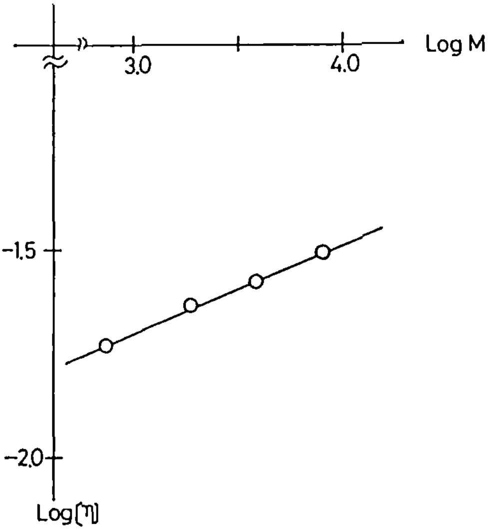
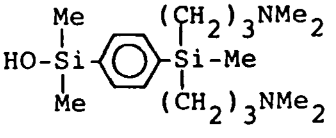


FIG. 4. Relationship between intrinsic viscosity and molecular weight for siloxane-based starburst polymers.

The α value of 0.21 suggests that these polymers have a spherical structure. The molecular weights of the polymers of all generations are proportional to their size based on the space-filling CPK model. Therefore, in the case of G3-Ph polymer, the diameter of the polymer sphere was calculated to be 2.3 nm.

We further synthesized some functionalized starburst polymers by the introduction of functional groups in their exterior layers. For example, the siloxane-based starburst polymer having 24 dimethylamino groups in the exterior layer was synthesized by the reaction of G2-NEt_2 with dimethylamine-containing Silanol X.

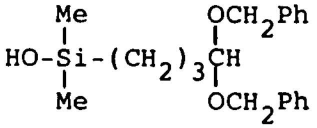


$$HO-Si(Me)_2-C_6H_4-Si(Me)[(CH_2)_3NMe_2]_2$$

X

The third generation polymer having dimethylamino groups was quite different in solubility from the above-mentioned starburst polymer G3-Ph having phenylsilyl groups, and it is readily soluble in dilute hydrochloric acid solution whereas polymer G3-Ph is soluble in THF, chloroform, and toluene.

Another example is the synthesis of the starburst polymer having 24 hydroxyl groups in the exterior layer by the reaction of G2-NEt$_2$ with Silanol XI having benzyloxy groups, followed by deprotection. This type of hydroxyl-containing starburst polymer is soluble in ethanol but insoluble in toluene.



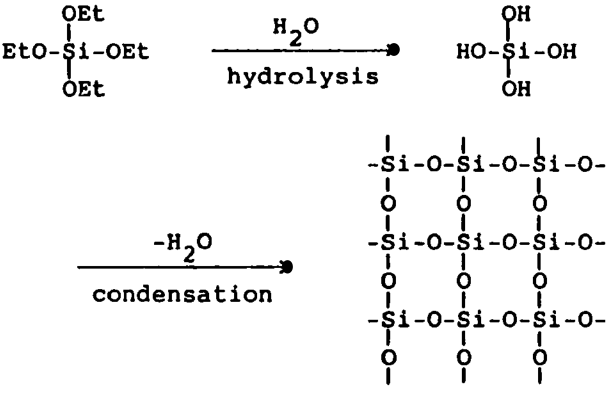
$$HO-\underset{Me}{\overset{Me}{Si}}-(CH_2)_3\underset{OCH_2Ph}{\overset{OCH_2Ph}{C}}H$$

XI

Thus, new siloxane-based starburst polymers were synthesized by a siloxane synthetic reaction starting from nucleophilic silanol and electrophilic phenylsilanes. One of the potential applications of the siloxane-based starburst polymers, and those having additional functional groups would be use as drug microcarriers that can be directly injected into the living body because of the harmless nature of polysiloxanes. After completion of our work, we learned of the recent synthesis of another type of siloxane-based starburst polymer [13].

PREPARATION OF NEW SILICA-POLYIMIDE HYBRID MATERIALS BY SOL-GEL PROCESS

Much attention has recently been devoted to the sol-gel process for the preparation of inorganic glass at relatively lower temperatures. For example, silica glass can be obtained readily from tetraethoxysilane by hydrolysis and subsequent condensation (Eq. 7).



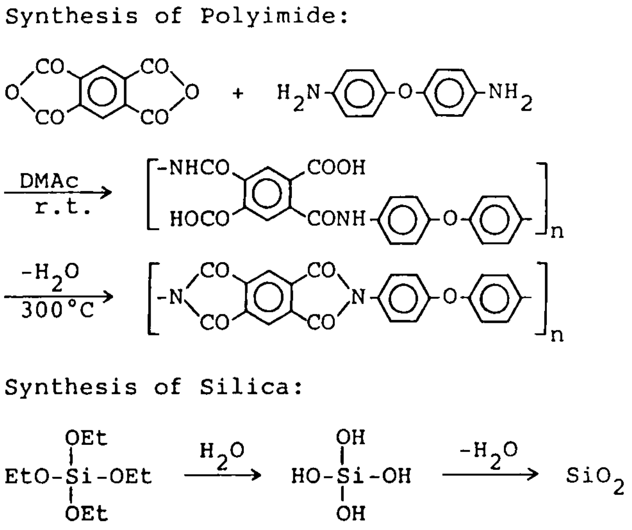
(7)

The sol-gel reactions have been applied further to the preparation of new silica-polymer hybrid materials that have some potential technological values [14]. These hybrid materials can be prepared either by the sol-gel reaction in the presence of polymers having reactive end groups or by reaction in the presence of nonreactive polymers.

We aimed at the preparation of new silica-polyimide hybrid materials to improve the thermal and mechanical properties of polyimides through the sol-gel process [15]. Polyimide was usually synthesized in two steps by the reaction of pyromellitic dianhydride with bis(*p*-aminophenyl) ether in DMAc, giving polyamic acid, followed by thermal imidization. Here, the sol-gel reaction of tetraethoxysilane was carried out in the presence of polyamic acid, a precursor of polyimide (Scheme 4).

Before preparation of the silica-polyimide hybrid material, hydrolytic stability of the polyamic acid in water containing DMAc solution was examined. Only a slight decrease in the inherent viscosity of the polyamic acid was observed in a dimethylacetamide solution containing 10 wt% water after stirring at room temperature for 24 h. Thus, the inherent viscosity was little affected by the presence of water, and this enabled us to prepare the hybrid material without difficulty.

The preparation of silica-polyimide hybrid film is as follows: To a



SCHEME 4.

solution of the polyamic acid in DMAc was added tetraethoxysilane and water, and the mixture was stirred at room temperature until the mixture became homogeneous. Then the solution containing polyamic acid and silica sol was cast on a glass plate and dried overnight at 60°C. The dried film was heated at 270°C for 3 h under nitrogen, affording the silica-polyimide hybrid film.

The progress of both silica formation and thermal imidization of the polyamic acid was followed by means of infrared spectroscopy. The infrared spectrum of the hybrid material was identical with that of an authentic silica-containing polyimide prepared from physical blending of the polyamic acid solution and colloidal silica. This clearly indicated the formation of silica from tetraethoxysilane and the polyimide from the polyamic acid by the sol-gel process. The formation of silica from tetraethoxysilane in the presence of the polyamic acid was further supported by the solid-state ^{29}Si-NMR spectrum of the silica-polyimide hybrid material.

Table 5 summarizes the results of the preparation of the silica-polyimide hybrid films.

Hybrid films containing less than 8 wt% of silica were yellow and transparent, whereas films containing more than 10 wt% of silica were yellow and opaque. It is worth noting that the hybrid system could contain silica up to 70 wt% and still afford good quality films. Spherical silica particles with diameters around 5 μm dispersed homogeneously in the polyimide matrix were observed by a scanning electron microscope photograph of the fracture surface of the hybrid film containing 70 wt% silica. In contrast, in the case of the physical blend system obtained by solution blending of the polyamic acid and colloidal silica, the incorporation of silica over 10 wt% was very difficult and a good quality polyimide blend film could not be obtained.

Figure 5 shows the influence of silica content on the density of the resulting silica-polyimide hybrid films.

A linear relationship was obtained; that is, the density of the hybrid films increased linearly with increasing silica content. The density of the silica was estimated to be 1.62 g/cm^3 by extrapolating this straight line to 100 wt% silica content. This value is far lower than the 2.2 g/cm^3 of silica glass. This suggests that the silica-polyimide formed has a porous structure.

Thermogravimetry curves of the silica-polyimide hybrid materials in air revealed that the decomposition temperatures rose slightly with increasing silica content, while the weight residues at 800°C increased

TABLE 5. Preparation of Silica-Polyimide Hybrid Films[a]

TEOS, mL	Silica,[b] wt%	Remarks[c]
0	0	Tr
0.1	3	Tr
0.3	8	Tr
0.5	13	Op
1.0	22	Op
1.5	30	Op
3.0	46	Op
4.5	56	Op
6.0	63	Op
8.0	70	Op

[a] The reaction of tetraethoxysilane (TEOS) with water (1.0 mL) was carried out in the 10 wt% polyamic acid-DMAc solution (10 mL) at room temperature for 3-8 h, and finally at 270°C for 3 h under nitrogen.

[b] Silica in final product.

[c] Tr = transparent; Op = opaque.

markedly. The results of dynamic mechanical analysis of the silica-polyimide hybrid films showed that a gradual increase of the storage modulus E' was observed with increasing silica content. This is probably due to the incorporation effect of silica particles in the polyimide matrix. The glass transition temperatures of the hybrid films, obtained from the peak temperatures on the loss modulus curves, were around 400°C.

The hybrid films changed their properties from ductile to rather brittle, depending markedly on silica content, as shown in the stress-strain curves of the silica-polyimide hybrid films. In general, the tensile strength and elongation at break decreased with increasing silica content, while the tensile modulus increased slightly.

Figure 6 shows a plot of the coefficient of linear thermal expansion against the silica content of silica-polyimide hybrid films. A linear relationship was obtained, and the thermal expansion coefficient decreased with increasing silica content. The results could also be explained by the incorporation effect of silica particles in the polyimide matrix.

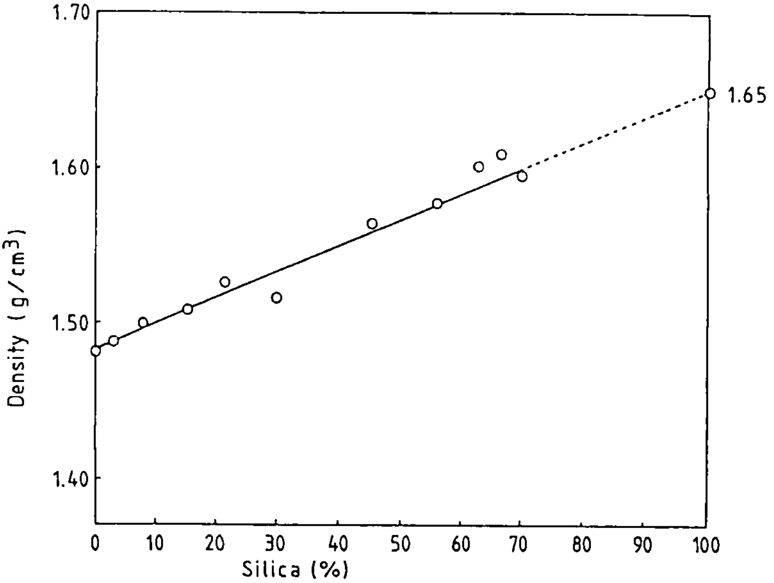


FIG. 5. Density of silica-polyimide hybrid films.

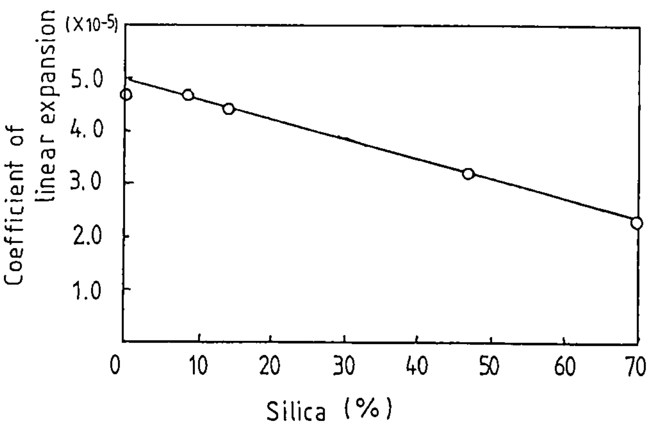


FIG. 6. Linear thermal expansion coefficient of silica-polyimide hybrid films.

Thus, the sol-gel process was found to be promising for improving the thermal properties of polyimides. This type of silica-polyimide hybrid materials as new high performance materials will find applications in microelectronics and other fields.

Further studies on the synthesis of silicon-based functional condensation polymers are now in progress.

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