Synthesis of Novel Fluorinated -Conjugated Silicon-Containing Polymers: Polysilynes and Polysilanes

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SYNTHESIS OF NOVEL FLUORINATED σ-CONJUGATED SILICON-CONTAINING POLYMERS: POLYSILYNES AND POLYSILANES

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ABSTRACT

The synthesis of fluorinated polysilynes, a new class of silicon-silicon network materials, has been achieved by reductive coupling of fluorinated trichlorosilanes with molten sodium in a mixture of toluene and diglyme (4:1) as a new synthetic route. Homopolysilynes containing fluorinated organogroups were insoluble in organic solvents due to side reactions. To improve solubility, copolysilynes were synthesized by co-polymerization of fluorinated trichlorosilanes with cyclohexyltrichlorosilane. All spectroscopic data indicate that the structure of the resulting fluorinated copolysilynes is a rigid, irregular network of monoalkyl sp^3-hybridized silicon units which exhibit extensive Si—Si σ-delocalization. They are more thermally stable than unfluorinated polysilynes. Upon exposure to deep-UV radiation in air, they undergo photooxidative crosslinking to give insoluble glass-like materials. This photooxidation process is accompanied by a large decrease in refractive index from $n = 1.61$ to $n = 1.485$. These results suggest that their potential applications include photoresists and optical waveguides. In order to understand the mechanism of reductive coupling of fluorinated trichlorosilanes, fluorinated linear polysilanes were also prepared.

INTRODUCTION

The preparation of soluble polymers by the reductive coupling of trichlorosilanes has been previously reported [1, 2]. These materials were called "polysilynes" or "branched polysilanes." The formation of insoluble, crosslinked product might be expected from trifunctional organosilanes. Instead of linear, soluble polyalkylsilenes (...RSi=SiR...), ^{29}Si NMR revealed that a rigid, irregular network polymer with silicon atoms bound to three neighboring silicon atoms was formed. The structure of the resulting polymer (poly(alkylsilyne)) is thought to be sheets or cages of fused five- to six-membered rings. Polysilynes exhibit intense UV-visible absorption bands due to Si—Si σ-conjugation. Upon exposure to UV oxidation, these materials undergo a photooxidative bleaching involving the insertion of oxygen into Si—Si bonds which leads to the formation of insoluble glass-like polysiloxane materials. This photooxidation process is accompanied by a large decrease in refractive index. These results suggest that their potential applications are as photoresists and optical waveguides in optical interconnect systems [3]. Recently, technology based on optical communications has become very important for improving high-speed integrated systems since optical signal transmission may have advantages including high propagation speed, high space density, and excellent bandwidth when compared to electronic equivalents.

Polymeric waveguide materials must retain their environmental and thermal stability, low optical propagation loss, good transmission, and possess a low dielectric constant. Several polymers (e.g., PMMA [4], polyimides [5], or polyphenylene [6], have been extensively studied as polymeric waveguides. In the case of polyimides, when fluorocarbon groups are incorporated into polyimides, their optical properties and thermal stability are improved. For these reasons we prepared soluble fluorocarbon-containing polysilynes by reductive coupling of fluorinated trichlorosilanes with sodium in a mixture of toluene and diglyme (4:1). Homopolysilynes containing fluorinated organogroups were insoluble in organic solvents due to side reactions. To produce soluble products, copolysilynes were therefore synthesized by copolymerization of fluorinated trichlorosilanes with cyclohexyltrichlorosilane. In order to understand the mechanism of the reductive coupling of fluorinated trichlorosilanes, fluorinated linear polysilanes were also prepared.

In this paper we report the synthesis and characterization of fluorinated polysilynes aimed at demonstrating and evaluating these polymers for thin film waveguides.

EXPERIMENTAL

1. Materials

Methylphenyldichlorosilane, cyclohexyltrichlorosilane, and tetrachlorosilane (Petrarch Systems) were dried and distilled over CaH_2 prior to use. Fluorinated organic bromides (Aldrich) were dried and distilled over CaH_2. Grignard reagents were prepared by reaction of fluorinated organic bromides with magnesium which had been activated with a tiny amount of I_2 in tetrahydrofuran. Toluene and tetrahydrofuran were dried over CaH_2, distilled over CaH_2, and then distilled over a

Na-benzophenone mixture. Diglyme was dried and distilled over LiAlH$_4$ under reduced pressure. All materials were stored over drying agents or under inert gas prior to use. Other commercial compounds were used as received.

2. Preparation of p-Fluorophenyltrichlorosilane

p-Fluorophenyltrichlorosilane was prepared by the reaction of tetrachlorosilane with p-fluorophenylmagnesium bromide in THF. A 500-mL three-necked, round-bottomed flask equipped with a magnetic stirrer was placed in an ice-water bath. This flask was fitted with a reflux condenser and a pressure-equalizing addition funnel. A known amount of tetrachlorosilane (21.0 g; 0.125 g-mol) and 80 mL THF were added to the flask under argon gas. A known amount of p-fluorophenylmagnesium bromide (100.0 mL of 1.0 M in THF) was placed in the addition funnel and added to the flask at 0°C over 50 min. After completing the addition, the mixture was heated to room temperature. After stirring the reaction mixture overnight, THF was removed by simple distillation under nitrogen gas, and 90 mL hexane was added to the reaction mixture to precipitate the salt of MgBrCl. The mixture was filtered using a filtering aid (Celite) under vacuum and nitrogen gas to remove the salt. The product of p-fluorophenyltrichlorosilane was distilled under reduced pressure [yield: 35%; bp, 80–81.5°C (1.2 mmHg)]. ^{1}H NMR (300 MHz, CDCl$_3$) δ8.0–7.5 ppm (multiplet, 4H); ^{19}F NMR (376 MHz, CDCl$_3$) δ − 97.90 ppm.

Similarly, 3,5-bis(trifluoromethyl)phenyltrichlorosilane and 4-(trifluoromethyl)phenylmethyldichlorosilane were prepared by the reaction of tetrachlorosilane with 3,5-bis(trifluoromethyl)phenylmagnesium bromide and by the reaction of methyltrichlorosilane with 4-(trifluoromethyl)phenylmagnesium bromide in THF, respectively. The product, 3,5-bis(trifluoromethyl)phenyltrichlorosilane, was distilled under reduced pressure [yield, 25%; bp, 95–97°C (0.25 mmHg)]. ^{1}H NMR (300 MHz, CDCl$_3$) δ8.0–7.5 ppm (multiplet, 3H); ^{19}F NMR (376 MHz, CDCl$_3$) δ − 56.48 ppm. 4-(Trifluoromethyl)phenylmethyldichlorosilane was distilled under reduced pressure [yield, 27%; bp, 70–72°C (1.6 mmHg)]. ^{1}H NMR (300 MHz, CDCl$_3$) δ8.0–7.5 ppm (multiplet, 4H), 1.06 (singlet, 3H); ^{19}F NMR (376 MHz, CDCl$_3$) δ − 56.53 ppm.

3. Synthesis of Fluorinated Polysilynes

A 500-mL three-necked, round-bottomed flask was fitted with a reflux condenser and a pressure-equalizing additional funnel. All systems were thoroughly flame-dried under nitrogen gas. Known amounts of sodium (0.03 mol) were added in a flask, filled with 80 mL toluene, and purged with dry nitrogen. The flask was heated to around 110°C to activate the sodium particle. A solution of trichlorosilane or mixed trichlorosilanes (0.013 mol) in 20 mL diglyme was added dropwise to the reaction flask in a controlled manner (4 drops/min) under an inert gas within 25 min. The reaction mixture was stirred overnight; it turned from grey to dark purple. After the required time, the samples were quenched with 10 mL ethanol and then washed several times with 75 mL water. The organic phase was later added to a large excess (250 mL) of ethanol, leading to the precipitation of the polymer. The polymer was dried and the yield was determined gravimetrically.

Molecular weights and polydispersities were determined by GPC based on polystyrene standards. The polymers were characterized by IR, UV, ^{1}H NMR, ^{19}F NMR, and elemental analysis. The copolymer compositions were measured by ^{1}H NMR. The filtrate remaining after the evaporation of solvents was analyzed by GC/MS, GPC, ^{1}H NMR, and ^{19}F NMR.

4.   Synthesis of Fluorinated Polysilanes

A 500-mL three-necked, round-bottomed flask with a magnetic stirrer was fitted with a reflux condenser and a pressure-equalizing addition funnel. This apparatus was thoroughly dried with a flame. Known amounts of sodium (0.06 mol) were placed in a flask which was filled with 60 mL toluene and purged with dry nitrogen. The monomer solutions in 10 mL toluene were added to the reaction flask in a controlled manner (4 drops/min) under nitrogen gas. The reaction mixture was stirred overnight and turned from grey to dark purple. The reaction was quenched with ethanol after the required time, and the reaction medium was washed with water three times. The organic phase was later added to a large excess of ethanol and the polymer was precipitated. The polymer was dried, and the yield was determined gravimetrically. Molecular weights and polydispersities were determined by GPC based on polystyrene standards. The polymers were identified by UV, IR, ^{1}H NMR, ^{19}F NMR, and elemental analysis. The copolymer compositions were measured by ^{1}H NMR. The filtrate remaining after the evaporation of the organic solvents was analyzed by GC/MS, GPC, and ^{1}H NMR.

5.   Spectroscopic Analysis

NMR spectra were recorded at room temperature in CDCl$_3$ solutions with a IBM 300 MHz NR-300 instrument or a Varian XL-400 NMR Spectrometer. ^{19}F NMR chemical shifts were determined by using external standards such as fluorobenzene (-106.2 ppm) in CDCl$_3$ solutions. Electronic spectra were measured over the range 190–820 nm on either a Hewlett-Packard 8452 UV-diode array spectrometer or an IBM 9430 UV-Visible spectrophotometer in films or in CH$_2$Cl$_2$ solutions. Infrared spectra were recorded on a Nicolet 5-DX FTIR instrument. Thermal stability of polymers was analyzed by TGA using a Mettler TG 50 Thermobalance with a Mettler TC 10A TA Processor. The GPC analysis was carried out in THF solution using a Waters GPC with three μ-Styragel columns (linear, 500 Å, and 1000 Å) in series, a model 510 pump, a model 410 refractive index detector, and a model 450 UV detector. The molecular weights and polydispersities reported are based on polystyrene standards.

RESULTS AND DISCUSSION

1.   Synthesis of Fluorinated Polysilanes

In a conventional synthesis of polysilanes [7–9], diorganodichlorosilanes are treated with sodium metal in a hydrocarbon solvent (usually toluene) at temperatures above 100°C. This process is called thermal polymerization. Homopolymers

and copolymers, which can include a wide variety of aryl and alkyl groups, can be prepared by the reductive coupling reaction of dichlorosilanes with Na. Thermal polymerization leads to the formation of polymodal products which contain a high molecular weight polymer, a low molecular weight polymer, and cyclic compounds. The number-average molecular weight (M_n) of the high molecular weight component is above 100,000 and the number-average molecular weight range (M_n) of the low molecular weight fraction is from 1000 to 6000. Cyclic oligomers (4-, 5-, and 6-membered rings) are also often formed.

A new monomer, 4-(trifluoromethyl)phenylmethyldichlorosilane (M_1) was prepared by reaction of methyltrichlorosilane with 4-(trifluoromethyl)phenylmagnesium bromide in tetrahydrofuran at room temperature. The ^{19}F-NMR spectrum showed a peak at -56.53 ppm when compared to the chemical shift of fluorobenzene as an external standard. Fluorinated polysilanes were synthesized by homopolymerization of 4-(trifluoromethyl)phenylmethyldichlorosilane as well as by copolymerization with methylphenyldichlorosilane (M_2) in toluene at 110°C. The results are summarized in Table 1.

The fluorinated homopolysilane was formed with a yield of 38.5%. The homopolysilane was insoluble in organic solvents, in contrast to soluble poly(methylphenylsilane). IR data showed that the characteristic peak for the Si—H bonds, which could be formed from protonation of silyl anions with ethanol as the quenching solvent after polymerization [1b], appeared around 2121 cm^{-1}. The observed insolubility could be due to side reactions (see Scheme 1), since one usually expects that partially fluorinated polymers dissolve better than unfluorinated polymers in organic solvents.

TABLE 1. Results of Polymerization of 4-(Trifluoromethyl)phenylmethyldichlorosilane (M_1) and Methylphenyldichlorosilane (M_2) with Sodium in Toluene at 110°C[a]

M_1/M_2	1/0	1/6.4[b]	0/1[c]
Yield, %	38.5	17.0	42.0
M_{nH}[b] $\times 10^{-3}$	—	11.8	1.07
(M_w/M_n)		(6.98)	(1.81)
M_{nL}[d] $\times 10^{-3}$	—	—	3.3
(M_w/M_n)			(1.69)
Solubility	Insoluble	Soluble	Soluble
H/L[e]	—	1/0	1/1.43
λ_{max}, nm	—	323	340
$\epsilon_{max} \times 10^{-3}$ $M^{-1} \cdot cm^{-1}$	—	3.2	9.0

[a]$[M]_0 = 0.32$ mol/L, $[Na]_0/[Si\text{-}Cl]_0 = 0.98$, 20 h, toluene, reaction temperature $\simeq 110$°C.
[b]Copolymerization by simultaneous addition.
[c]Polymerization of methylphenyldichlorosilane under similar conditions.
[d]The ratio of high polymer (H) to low polymer (L).
[e]Polymerization of methylphenyldichlorosilane under similar conditions.
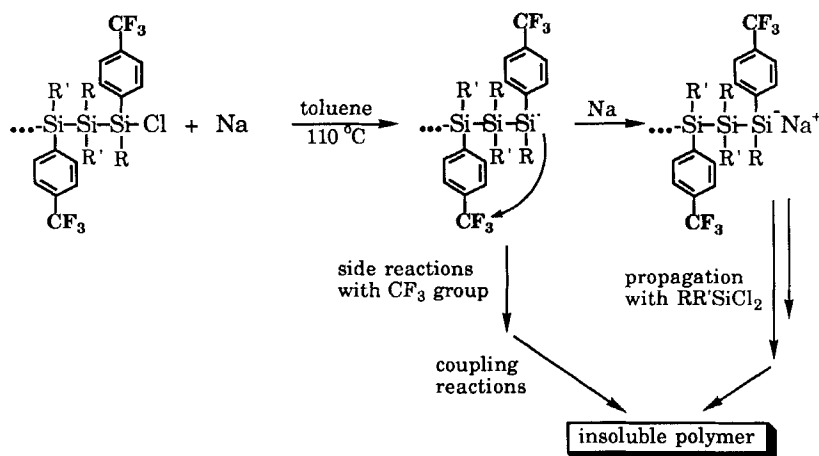
SCHEME 1.   Possible pathway for the reductive coupling of 4-(trifluoromethyl)phenylmethyldichlorosilane with molten sodium in toluene.

To understand the reductive coupling of 4-(trifluoromethyl)phenylmethyldichlorosilane and to improve the solubility of fluorinated polymer, copolymerization with methylphenyldichlorosilane was achieved under similar conditions. Copolymer was obtained with a yield of 17.0%. From GPC analysis, monomodal copolymer was formed with a number-average molecular weight (M_n) equal to 11,800 and a relatively high polydispersity $[(M_w/M_n) = 6.98]$. IR data on the compound showed that the characteristic absorbance of the Si—H bonds appeared around 2121 cm^{-1}. The ^{1}H-NMR spectrum showed the presence of methyl and aryl groups. ^{19}F-NMR data (Fig. 1) showed the presence of several peaks such as —CF$_3$ (−55.78 ppm), —CF$_2$— (−115 to −135 ppm), and =CF— (−150 to −175 ppm) groups [10]. In its UV spectrum the polymer absorbed at 323 nm (Fig. 2), in contrast to poly(methylphenylsilane). From thermogravimetric analysis (TGA) the final polymer was thermally stable up to 400°C (4% weight loss).

It has been previously observed that polymerization to form poly(silane) proceeds by an anionic chain growth process [11]. A chloro-terminated chain end can participate in a two-electron-transfer process with sodium. Silyl anions are formed via silyl radical species which are formed in the first-electron-transfer from sodium and considered as very short-lived intermediates [12]. The polymeric silyl anion can react with additional dichlorosilane.

In the case of the reductive coupling of 4-(trifluoromethyl)phenylmethyldichlorosilane, analytical data and high polydispersity indicate that Si—Si bonds are interrupted by other molecules and the final product is not a regular polysilane. This observation may be due to side reactions either by silyl anions or by silyl radicals. The involvement of silyl anions may be eliminated since Grignard agents containing 4-(trifluoromethyl)phenyl groups were formed quantitatively in the monomer synthesis step [13]. The side reactions could alternatively be caused by the involvement of chain transfer reactions between the silyl radical species (formed in the first-electron-transfer reaction from sodium to chloro-terminated chains) and trifluoromethyl (CF$_3$) groups, as shown in Scheme 1. Silyl radicals can be stabilized
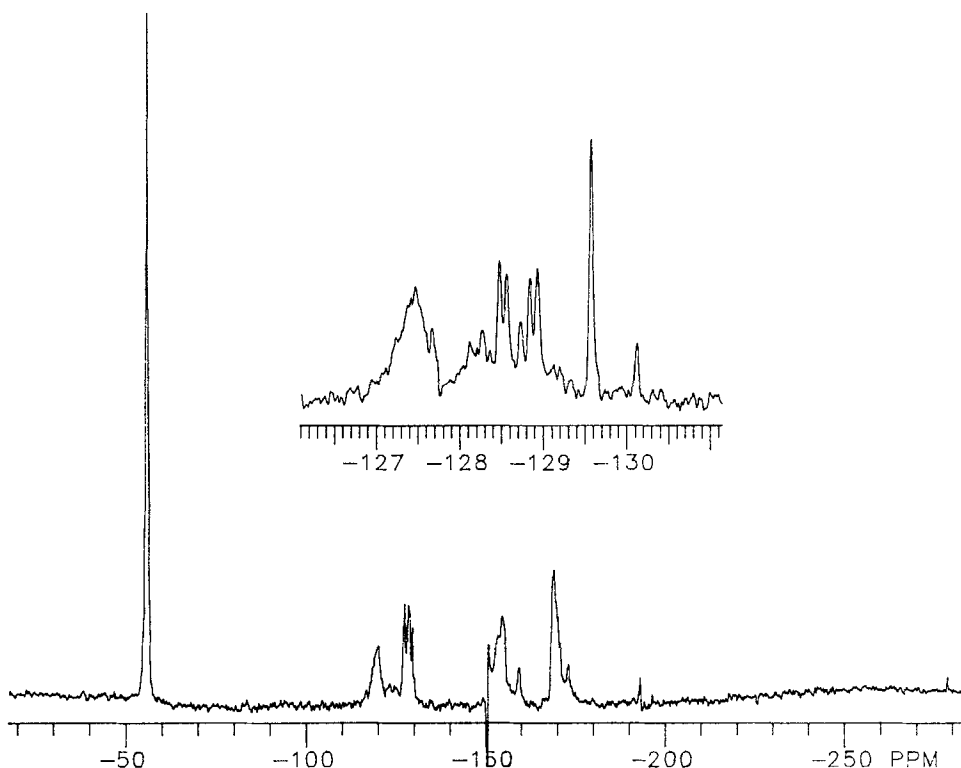
FIG. 1. ^{19}F-NMR spectrum of the final product formed by copolymerization of 4-(trifluoromethyl)phenylmethyldichlorosilane and methylphenyldichlorosilane with sodium in toluene at 110°C.

by electron-withdrawing CF_3 groups. This stabilization might allow the silyl radical to be present as a longer-lived intermediate and to give more opportunity for chain transfer reactions between silyl radical species and trifluoromethyl groups to occur. Chain transfer reactions could produce polymeric species terminated with fluorine atoms and $-CF_2\cdot$ which may couple together or couple with silyl radicals to generate polymeric molecules containing CF_2 groups. The chemical shift of CF_2 groups appeared to lie in the range of -115 to -135 ppm for ^{19}F NMR. Similarly, the side reactions between silyl radicals and CF_2 groups might occur to yield the CF groups which appeared in the range of -150 to -170 ppm in ^{19}F NMR. Therefore, after the first-electron-transfer reaction there is a competition between side reactions and the second-electron-transfer reaction followed by the propagation reaction with monomer. In the case of homopolymerization of 4-(trifluoromethyl)phenylmethyl-dichlorosilane, side reactions are favored to yield crosslinked, insoluble polymer. In the case of copolymerization with methylphenyldichlorosilane, side reactions are still favored, but the crosslinking density is reduced by copolymerization with a high fraction of methylphenyldichlorosilane to yield soluble, fluorinated copolysilanes (see Table 1).
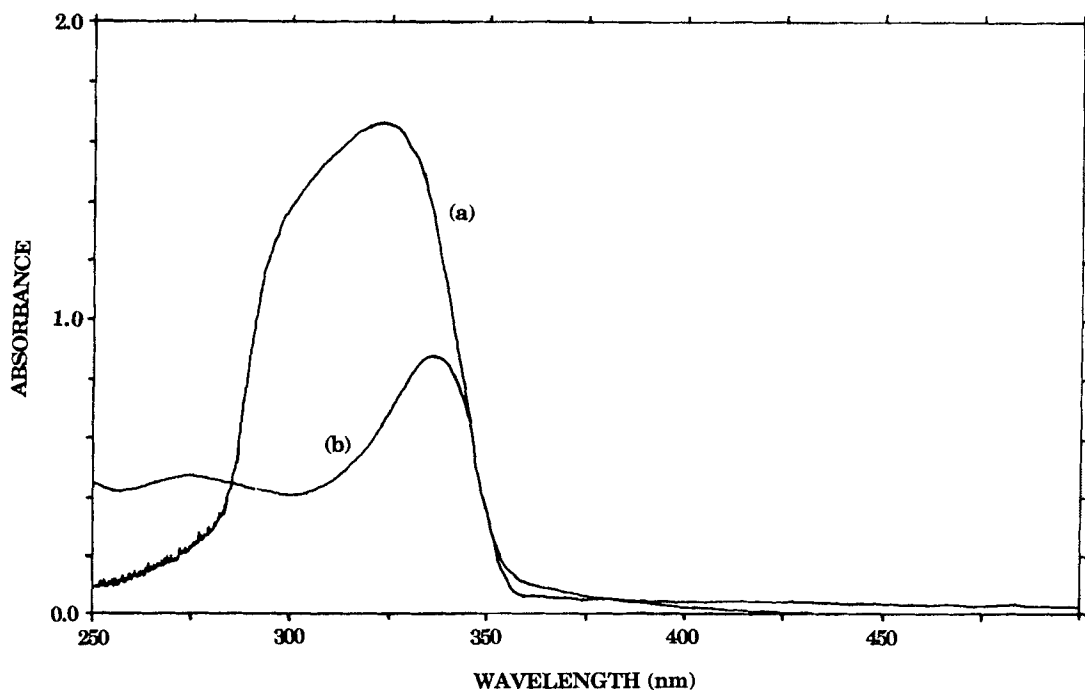
FIG. 2.   UV spectra of the final product (a) formed by copolymerization of 4-(trifluoro-methyl)phenylmethyldichlorosilane and methylphenyldichlorosilane with sodium in toluene at 110°C and (b) poly(methylphenylsilane).

2.   Synthesis of Fluorinated Polysilynes

Polysilynes have been previously prepared by ultrasound-mediated reductive coupling of trichlorosilanes with Na-K alloy [1] or sodium [2] in toluene. Polysilynes usually have low molecular weight ($M_n \approx$ 2000) based on polystyrene standards and moderate molecular weight distribution (M_w/M_n). The use of ultrasound limits large scale-up of the reaction. Therefore, to solve this problem, we prepared soluble fluorocarbon-containing polysilynes by reductive coupling of fluorinated trichloro-silanes with molten sodium in a mixture of toluene and diglyme (4:1) (as a new synthetic route). It has been reported that the addition of polar solvents such as diglyme or crown-ethers, which are known to effectively interact with sodium or potassium cations, accelerates the reductive coupling reaction of dichlorosilane with sodium [11].

Two fluorinated monomers were prepared by reaction of tetrachlorosilane with 3,5-bis(trifluoromethyl)phenylmagnesium bromide and tetrachlorosilane with p-fluorophenylmagnesium bromide in tetrahydrofuran at room temperature (Scheme 2). The fluorinated monomers were analyzed by ^{1}H NMR and ^{19}F NMR. The ^{19}F-NMR spectrum showed a peak at −56.48 ppm for 3,5-bis(trifluoromethyl)-phenyltrichlorosilane and at −97.90 ppm for p-fluorophenyltrichlorosilane compared with the chemical shift of fluorobenzene as an external standard.
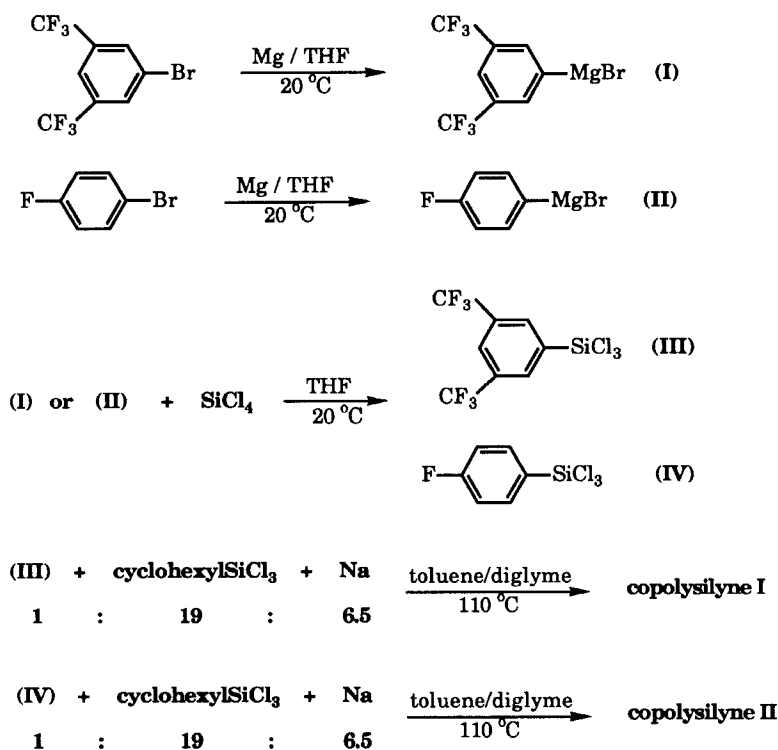
SCHEME 2.   Synthesis and polymerization of fluorinated trichlorosilanes.

The results of copolymerization of 3,5-bis(trifluoromethyl)phenyltrichlor-osilane (M_3) and cyclohexyltrichlorosilane (M_4) with sodium in a mixture of toluene and diglyme (4:1) are summarized in Table 2. 3,5-Bis(trifluoromethyl)-phenyltrichlorosilane reacts with sodium in a mixture of toluene and diglyme (4:1) very easily. After 20 h, fluorinated homopolysilyne was formed with a yield of higher than 90.0%. The homopolysilyne was insoluble in any organic solvent, similar to the formation of insoluble poly(4-(trifluoromethyl)phenylmethylsilane). IR data showed that the characteristic peak of Si—H bonds appeared at 2135 cm^{-1}. This peak might be due to side reactions between silyl radicals and —CF$_3$ groups (see Scheme 1). Fluorinated trichlorosilane can be copolymerized with cyclohexyltrichlorosilane to generate fluorinated copolysilynes.

Only the copolysilynes with a high content of cyclohexyltrichlorosilane (>90.0%) are soluble. A soluble copolysilyne I containing 10.0% of 3,5-bis(trifluoromethyl)phenyltrichlorosilane was analyzed by GPC, IR, ^{1}H NMR, ^{19}F NMR, and UV. From GPC analysis, the M_n of the copolysilyne was about 5200 with a very high polydispersity (M_w/M_n) of 10.0. The copolysilyne of 3,5-bis(trifluoromethyl)phenyltrichlorosilane with cyclohexyltrichlorosilane had a higher molecular weight than that of homopoly(cyclohexylsilyne) (M_n = 2000). IR data showed the absence of Si—O—Si bonds, while photooxidation in air led to the formation of intense Si—O—Si bonds as shown in Fig. 3. ^{1}H-NMR data showed the presence of aryl and cyclohexyl groups. The copolymer was more enriched

TABLE 2.   Results of Polymerization of 3,5-Bis(trifluoromethyl)-
phenyltrichlorosilane (M_3) and Cyclohexyltrichlorosilane (M_4) with Sodium in a
Mixture of Toluene and Diglyme (4:1)[a]

M_3/M_4[b]	1/0	1/4	1/19	0/1
Yield, %	>90.00	90.0	24.0	17.0
m_1/m_2[c]	—	—	1/10	0/1
M_n[d] $\times 10^{-3}$	—	—	5.2	2.0
M_w/M_n	—	—	10.0	2.1
Solubility	Insoluble	Insoluble	Partially soluble[e]	Soluble

[a]$[M]_0 = 0.95$ mol/L; $[Na]_0/[Si\text{-}Cl]_0 = 0.97$; reaction time $= 20$ h; reaction temper-
ature $\approx 110°C$.
[b]Mole ratio of comonomer.
[c]Copolymer composition was determined by ^1H NMR.
[d]Molecular weights based on polystyrene standards.
[e]Weight ratio of soluble fraction to insoluble fraction: 3/1.

(1/10) in 3,5-bis(trifluoromethyl)phenyltrichlorosilane than the starting comonomer
(1/19). ^{19}F-NMR data showed two peaks. One peak appeared around -55.85 ppm
for CF_3 groups in the 3,5-bis(trifluoromethyl)phenyl group, and the other peak
showed up in the range of -110 to -140 ppm for a CF_2 group in an unknown
fluoroaryl group [10]. The latter peak might be due to side reactions between silyl
radicals and 3,5-bis(trifluoromethyl)phenyl groups (see Scheme 1). A side reaction
is consistent with the formation of insoluble homopolysilyne as well as the forma-
tion of a very broad molecular weight distribution ($M_w/M_n = 10.0$) by GPC in the
case of the soluble polymer.

The results of the polymerization of p-fluorophenyltrichlorosilane (M_5) and
cyclohexyltrichlorosilane (M_4) with sodium in a mixture of toluene and diglyme
(4:1) are summarized in Table 3. p-Fluorophenyltrichlorosilane reacts readily with
sodium in a mixture of toluene and diglyme (4:1). After 20 h, an insoluble polymer
was formed in high yield (90.0%). The monomer could be copolymerized with
cyclohexyltrichlorosilane to generate a fluorinated copolysilyne. The yield of poly-
mer increased by copolymerization from 17 to 90%. Only copolysilyne with a high
content of cyclohexyltrichlorosilane (>90.0%) was soluble. A soluble copolysilyne
II containing 7.5% p-fluorophenyl comonomer was analyzed by GPC, IR, ^1H
NMR, ^{19}F NMR, and UV. From GPC analysis, the number-average molecular
weight (M_n) of the copolysilyne was about 3500 and the polydispersity (M_w/M_n) was
1.93. Copolysilyne II made from p-fluorophenyltrichlorosilane with cyclohexyl-
trichlorosilane had a higher molecular weight than that of homopoly(cyclohexylsi-
lyne) ($M_n = 2000$). IR data showed the absence of Si—O—Si bonds, while photoox-
idation in air led to the formation of these Si—O—Si bonds (see Fig. 3). ^1H-NMR
data showed the presence of aryl and cyclohexyl groups. The copolymer was more
enriched (1/14) in p-fluorophenyltrichlorosilane than the starting comonomer mix-
ture (1/19). ^{19}F-NMR data showed two peaks around -102.92 ppm for the CF
group in the p-fluorophenyl group and around -129.62 ppm for the CF group in
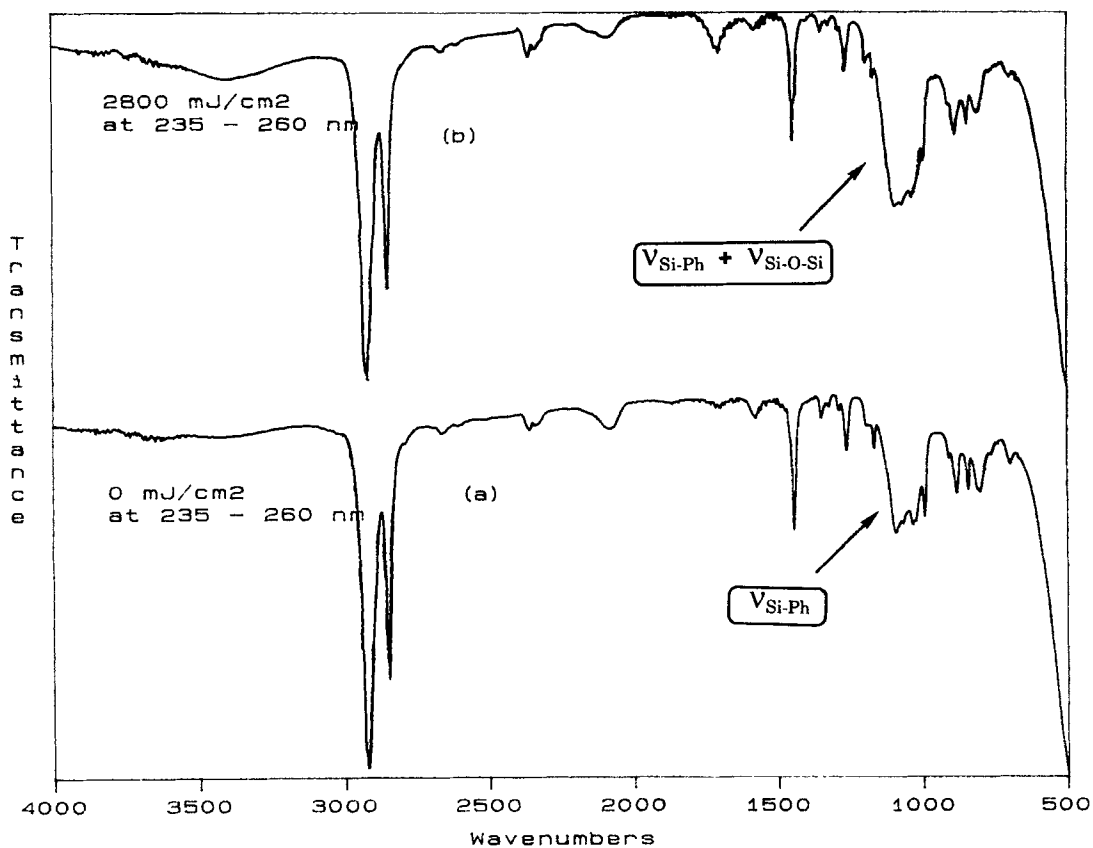an unknown fluoroaryl group [10]. The latter peak might be due to side reactions

FIG. 3. IR spectra changes on exposure of copolysilyne **I** to UV radiation in the presence of air: (a) before exposure and (b) after 7-min irradiation.

TABLE 3. Results of Polymerization of *p*-Fluorophenyltrichlorosilane (M_5) and Cyclohexyltrichlorosilane (M_4) with Sodium in a Mixture of Toluene and Diglyme (4:1)[a]

M_5/M_4[b]	1/0	1/4	1/19	0/1
Yield, %	90.0	60.0	40.0	17.0
m_1/m_2[c]	—	—	1/14	0/1
M_n[d] $\times 10^{-3}$	—	—	3.52	2.0
M_w/M_n	—	—	1.93	2.1
Solubility	Insoluble	Insoluble	Soluble	Soluble

[a]$[M]_0 = 0.95$ mol/L; $[Na]_0/[Si\text{-}Cl]_0 = 0.97$; reaction time $= 20$ h; reaction temperature $= 110°C$.

[b]Mole ratio of comonomer.

[c]Copolymer composition was determined by ^{1}H NMR.

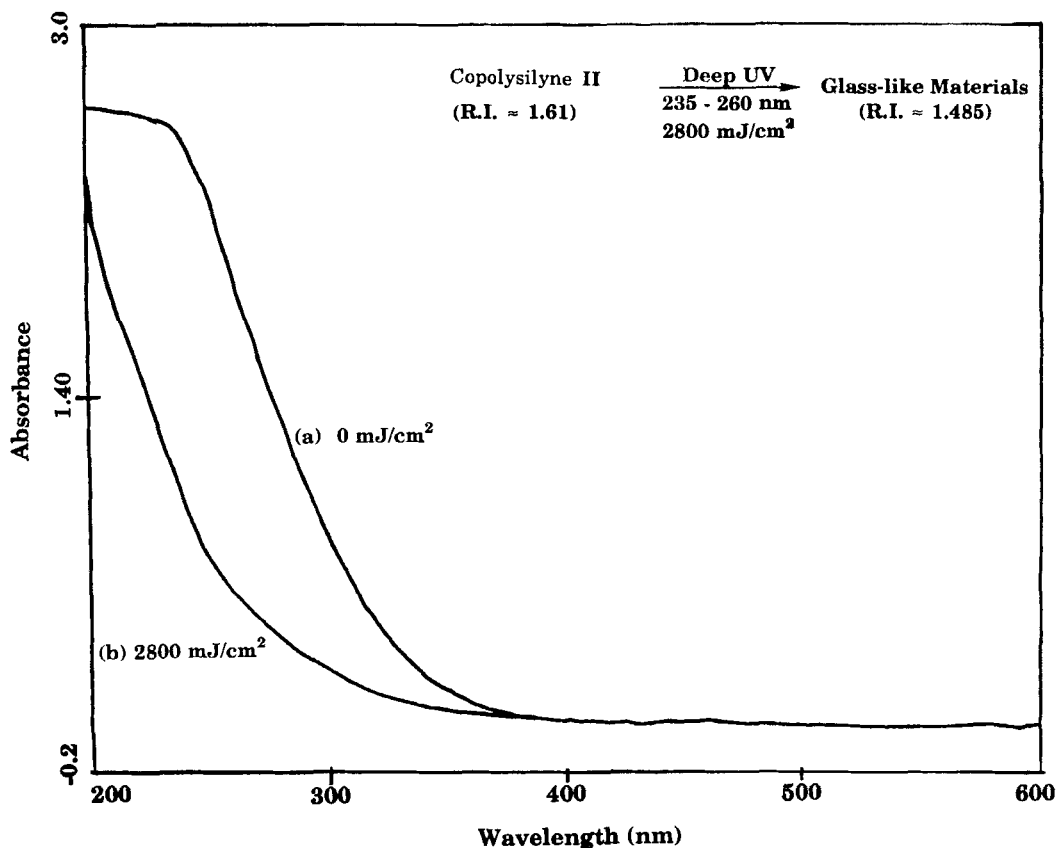[d]Molecular weight based on polystyrene standards.

FIG. 4.   UV spectral changes on exposure of copolysilyne **II** to UV radiation in the presence of air: (a) before exposure and (b) after 7-min irradiation.

between silyl radical species and fluorophenyl groups (see Scheme 1). The involvement of silyl anions in the side reactions could be eliminated for the same reason mentioned above, that is, Grignard reagents containing fluorophenyl groups were formed quantitatively in polar solvents [13]. Silyl radicals, which are additionally stabilized by electron-withdrawing fluorophenyl groups, can be present as a longer-lived intermediate to give more opportunity for chain transfer reactions between silyl radical species and fluorophenyl groups. The intermolecular reaction between two polymeric chains may be more favored than the intramolecular reaction to yield insoluble polymer, since the structure of polysilyne is a rigid, irregular network polymer with silicon atoms bound to three neighboring silicon atoms [1, 2].

Fluorinated copolysilynes exhibited a broad and intense absorption band edge tailing into the visible, associated with an extension of Si—Si σ-conjugation, while linear polysilanes absorbed in the range of 300–350 nm (λ_{max}) (see Table 1). UV data are consistent with a randomly constructed rigid network of monoalkyl sp^3-hybridized silicon units [1, 3]. These copolysilynes also photooxidized upon UV irradiation in air to form an insoluble polysiloxane network (see Fig. 3), in contrast to linear polysilanes which give cyclic oligomers and lower molecular weight poly-
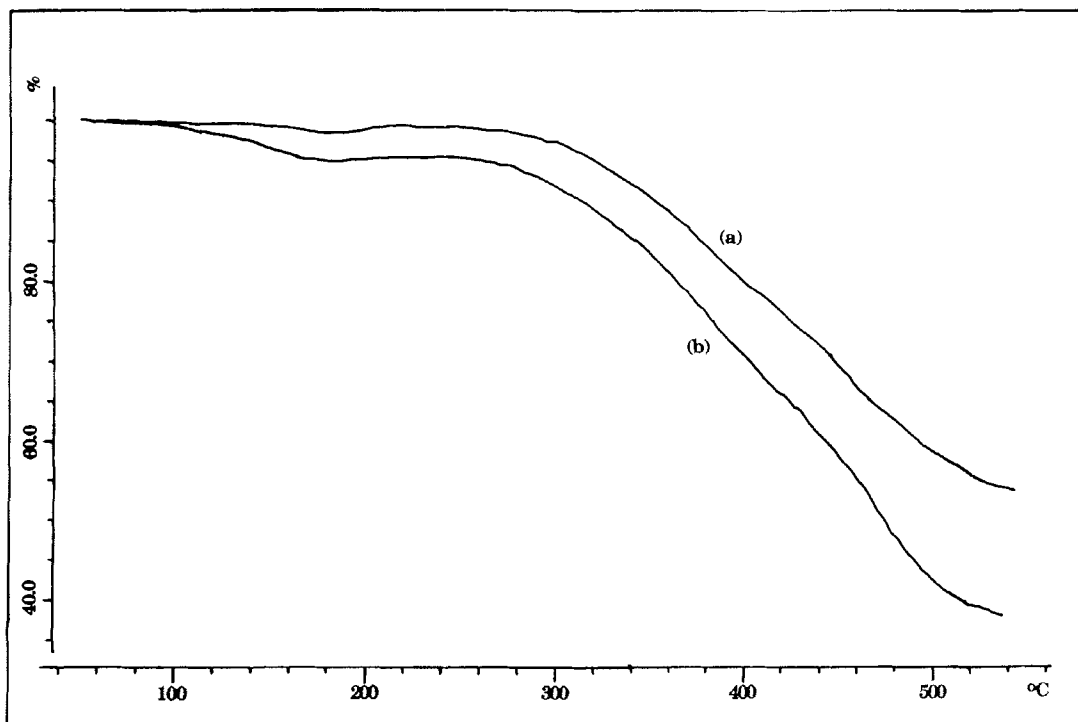
FIG. 5.   TGA traces of (a) copolysilyne I and (b) poly(cyclohexylsilyne).

mers on UV exposure [7, 8]. The response of a thin film of copolysilyne II to UV irradiation (λ = 235-260 nm) in air as a function of exposure time is shown in Fig. 4. Photooxidation proceeded with a large blue shift of the absorption band edge (photobleaching). Photobleaching is based on insertion of oxygen into the Si—Si bonds. The refractive index of exposed copolysilyne II was measured by ellipsometry. The results showed a large decrease in refractive index (n) from 1.61 for the unexposed copolysilyne II to a minimum refractive index (n) of 1.485 for the copolysilyne II after a 5-10 min exposure to deep UV irradiation.

From TGA analysis (Fig. 5), the fluorinated copolysilyne I started to decompose at 280°C, while poly(cyclohexylsilyne) began to decompose at 100°C with the principal decomposition occurring at 260°C. This can be ascribed to the dependence of thermal decomposition on the molecular weight, where the M_n of the fluorinated copolysilyne I was higher than the M_n of homopoly(cyclohexylsilyne). From GPC data, the M_n of homopoly(cyclohexylsilyne) is 2 × 10^3 g/mol, while the M_n of the fluorinated copolysilyne I is 5.2 × 10^3 g/mol. The homopoly(cyclohexylsilyne), it should be pointed out, did not contain a low molar mass volatile compound. The fluorinated copolysilyne I was more thermally stable (17% weight loss up to 400°C) than poly(cyclohexylsilyne) (25% weight loss up to 400°C). This observation agrees with the general phenomenon that fluorinated polymers tend to be more thermally stable materials than unfluorinated polymers.

CONCLUSION

Fluorinated copolysilynes can be prepared by the reductive coupling of fluorinated phenyl trichlorosilanes with cyclohexyltrichlorosilane using molten sodium in a mixture of toluene and diglyme (4:1). The resulting polymers are more thermally stable than unfluorinated polysilynes. Upon exposure to UV radiation, they undergo photooxidative crosslinking to produce insoluble glass-like materials. This photooxidation process is accompanied by a large decrease in their refractive index, going from $n = 1.61$ to $n = 1.485$.

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