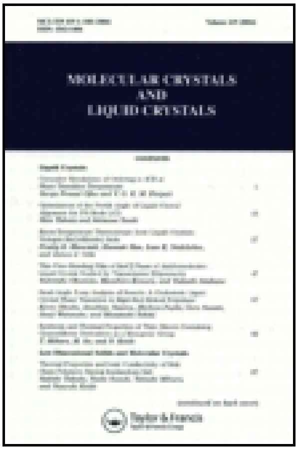

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Novel Fluorinated [sgrave]-Conjugated Polysilynes For Optical Waveguides

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NOVEL FLUORINATED σ-CONJUGATED POLYSILYNES FOR OPTICAL WAVEGUIDES

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Abstract Fluorinated polysilynes were prepared by the reductive coupling of 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 copolymerization of fluorinated trichlorosilanes with cyclohexyltrichlorosilane. All spectroscopic data indicate that the structure of the resulting polysilynes is a rigid, irregular network of monosubsituted sp^3-hybrid silicon atoms that have three neighboring silicon atoms. They exhibit extensive Si-Si σ-delocalization. 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 are as optical waveguides in optical interconnect systems.

INTRODUCTION

Recently, optical communication 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 good 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 such as PMMA, polyimides, or polyphenylene have been extensively studied as polymeric waveguides.[1-3] 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 the reductive coupling of fluorinated trichlorosilanes with sodium in a mixture of toluene and diglyme (4 : 1) as a new synthetic route. These materials were called "polysilynes" or "branched polysilanes".[4,5] The structure of the resulting polymers is thought to be sheets or cages of fused four to six membered rings. Polysilynes exhibit intense UV-visible absorption bands due to Si-Si σ-conjugation. Upon exposure to deep-UV radiation in air, they undergo photooxidative crosslinking to give insoluble glass-like materials.[6] 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 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

Tetrachlorosilane (Huls) and fluorinated organic bromides (Aldrich) were dried and distilled over CaH_2 prior to use. Grinard reagents were prepared by the reaction of fluorinated organic bromides with magnesium which had been activated with a tiny amount of I_2 in tetrahydrofuran (THF). Toluene and THF were dried over CaH_2, and distilled over CaH_2, and then redistilled 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. Synthesis of Fluorinated Polysilynes

p-Fluorophenyltrichlorosilane and 3,5-bis(trifluoromethyl)phenyltrichlorosilane were prepared by the reaction of tetrachlorosilane with p-fluorophenylmagnesium bromide and 3,5-bis(trifluoromethyl)phenymagnesium bromide in THF, respectively, as described in Reference 7. Polymerization of p-Fluorophenyltrichlorosilane and 3,5-bis (trifluoromethyl)phenyltrichlorosilane was carried out by the reductive coupling of fluorinated trichlorosilanes with molten sodium in a mixture of toluene and diglyme (4:1) as follows: 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 amount 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 controller 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, and ^{19}F NMR. The copolymer compositions were measured by ^{1}H NMR.

3. 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 an external standard 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 spectrometer in films or in CH_2Cl_2 solutions. Infrared spectra were recorded on a Nicolet 5-DX FT-IR 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 1000Å) in series, a model 510 pump, a model 410 refractive index detector, and a model 450 UV detector. Molecular weights and polydispersities were determined by GPC, relative to polystyrene standards.

RESULTS AND DISCUSSION

Polysilynes were previously prapared by ultrasound-mediated reductive coupling of trichlorosilanes with Na-K alloy or sodium in toluene.[4,5] They usually have low moelcular weight ($M_n \approx 2{,}000$) 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 trichlorosilanes 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.[8] The reductive coupling reaction of trichlorosilane to form polysilyne proceeds by an anionic chain growth process.[9] 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 to chloro-terminated silane and considered as very short-lived intermediates. The polymeric anion can react with additional chlorosilane.

Two fluorinated monomers were prepared by reaction of tetrachlorosilane with 3,5-bis(trifluoromethyl)phenylmagesium bromide and tetrachlorosilane with p-fluorophenylmagnesium bromide in THF at room temperature. The fluorinated monomers were analyzed by ^{1}H NMR and ^{19}F NMR. The ^{19}F NMR spectrum showed at -56.48 ppm for 3,5-bis(trifluoromethyl)phenyltrichlorosilane and at -97.90 ppm for p-fluorophenyltrichlorosilane compared with the chemical shift of p-fluorobenzene as an external standard.[10]

The results of polymerization of 3,5-bis(trifluoromethyl)phenyltrichlorosilane (M_1) and cyclohexyltrichlorosilane (M_3) with sodium in a mixture of toluene and diglyme (4:1) are summarized in Table 1. 3,5-Bis(trifluoromethyl)phenyltrichlorosilane reacts with sodium in a mixture of toluene and diglyme (4:1) very easily. After 20 hours, fluorinated homopolysilyne was formed with a yield of higher than 90.0 %. The homopolysilyne was insoluble in any organic solvent, due to side reactions between silyl radicals and -CF_3 groups. Fluorinated trichlorosilane can be copolymerized with cyclohexyltrichlorosilane to generate fluorinated copolysilynes.

Only the copolysilynes with a high content of cyclohexytrichlorosilane (> 90.0 %) are soluble. A soluble copolysilyne I containing 10.0 % of 3,5-bis(trifluoromethyl)

TABLE 1. Results of polymerization of 3,5-bis(trifluoromethyl)phenyltrichlorosilane (M_1) and cyclohexyltrichlorosilane (M_3) with sodium in a mixture of toluene and diglyme (4:1)[a]

M_1/M_3[b]	1/0	1/4	1/19	0/1
Yield, %	> 90.00	90.0	24.0	17.0
m_1/m_3[c]	-	-	1/10	0/1
M_n[d] x 10^{-3}	-	-	5.2	2.0
M_w/M_n	-	-	10.0	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 comonmer;

[c] Copolymer composition was determined by ^1H NMR;

[d] Molecular weight based on polystyrene standards;

[e] Weight ratio of soluble fraction to insoluble fraction: 3/1

phenyltrichlorosilane unit was analyzed by GPC, IR, ^1H 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 = 2,000). IR data showed the absence of Si-O-Si bonds. ^1H NMR data showed the presence of aryl and cyclohexyl groups. The copolymer was more enriched (10/1) 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 fluoroarylgroup. The latter peak might be due to side reaction between silyl radicals and 3,5-bis(trifluoromethyl)phenyl groups.[7] A side reaction is consistent with the formation of insoluble homopolysilyne as well as the formation of a very broad molecular weight distribution (M_w/M_n = 10.0). The involvement of sily anions in the side reaction could be eliminated since Grignard reagents containing 3,5-bis (trifluoromethyl)phenyl groups were formed quantitatively in polar solvents. Silyl radicals, which are additionally stabilized by electron-withdrawing 3,5-bis (trifluoromethyl)phenyl groups, can be present as a longer-lived intermediate to give more opportunity for chain transfer reaction between silyl radicals 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.[4,5]

The results of polymerization of p-fluorophenyltrichlorosilane (M_2) and cyclohexyltrichlorosilane (M_3) with sodium in a mixture of toluene and diglyme (4:1) are summarized in Table 2. p-Fluorophenyltrichlorosilane reacts with sodium in a mixture of toluene and diglyme (4:1). After 20 hours, an insoluble polymer was formed in high yield (90.0 %). The monomer was copolymerized with cyclohexyltrichlorosilane to generate fluorinated copolysilynes.

The yield of polymer increased by copolymerization from 17 to 90 %, compared with the yield of poly(cyclohexylsilyne). 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, ^{1}H 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 cyclohexyltrichlorosilane had a higher molecular weight than that of homopoly(cyclohexylsilyne) (M_n= 2000). IR data showed the absence of Si-O-Si bonds (see Fig. 1).

TABLE 2. Results of polymerization of p-fluorophenyltrichlorosilane (M_2) and cyclohexyltrichlorosilane (M_3) with sodium in a mixture of toluene and diglyme (4:1)[a]

M_2/M_3[b]	1/0	1/4	1/19	0/1
Yield, %	90.00	60.0	40.0	17.0
m_2/m_3[c]	-	-	1/14	0/1
M_n[d] x 10^{-3}	-	-	3.52	2.0
M_w/M_n	-	-	1.93	2.1
Solubility	Insoluble	Insoluble	Soluble	Soluble

[a] $[M]_o$ = 0.95 mol/L; $[Na]_o/[Si\text{-}Cl]_o$ = 0.97; reaction time = 20 h; reaction temperature ≈ 110 °C; [b] Mole ratio of comonmer; [c] Copolymer composition was determined by ^{1}H NMR; [d] Molecular weight based on polystyrene standards;

^{1}H NMR data showed the presence of aryl and cyclohexyl groups. The copolymer was more enriched (1/14) in p-fluorophenyltrichlorosilane than the starting comonomer mixture (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 coupling reactions between silyl radicals and fluorophenyl groups. The involvement of sily anions in the side reaction could be eliminated for the same reason mentioned above, that is, Grignard reagents containing fluorophenyl groups were formed quantitatively in polar solvents. 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 coupling reaction between silyl radicals 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.

Fluorinated copolysilynes exhibited a broad and intense absorption band edge tailing

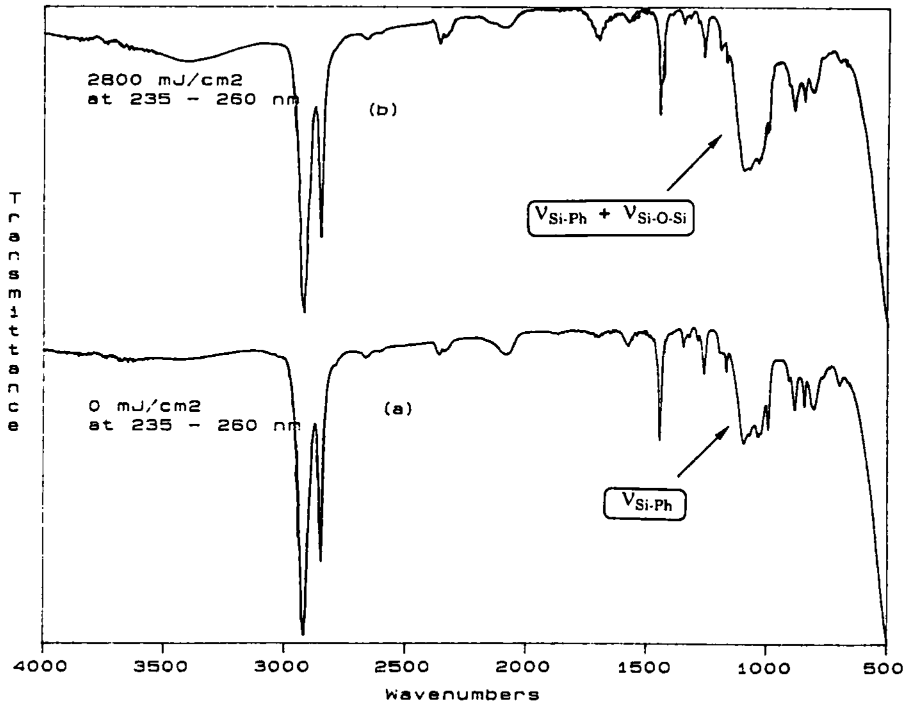


Fig. 1. IR spectra changes on exposure of copolysilyne II to deep-UV irradiation in the presence of air: (a) before exposur and (b) after 7-min irradiation.

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}).[11] UV data are consitent with a randomly constructed rigid network of monosubstituted sp^3-hybridized silicon units. These copolysilynes also photooxidized upon UV irradiation in air to form an insoluble polysiloxane network (see Fig. 1), in contrast to linear polysilanes which give cyclic oligomers and low molecular weight polymers on UV exposure. These 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. 2. 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, leading to the formation of an insoluble polysiloxane network.

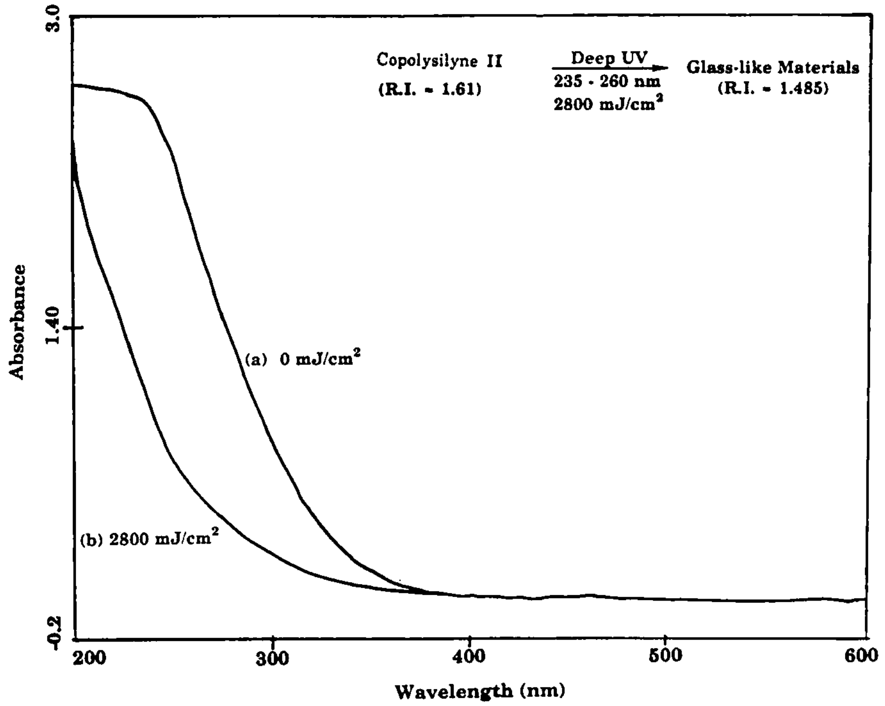
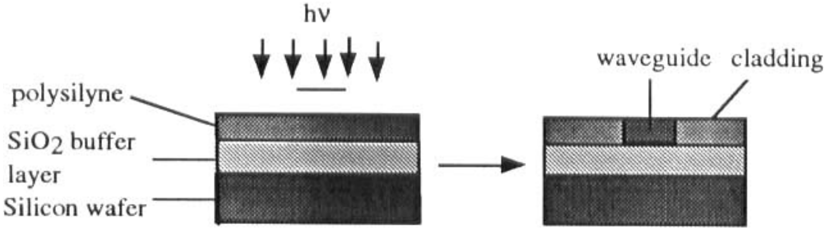


Fig. 2. UV spectral changes on exposure of copolysilyne II to deep-UV irradiation (λ= 235 - 260 nm) in the presence of air: (a) before exposure and (b) after 7-min UV irradiation.

The refractive index of 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 minute exposure to deep UV irradiation. The photooxidation results provide guidelines for determining the refractive indices of a waveguide through selection of patterning. After deep-UV exposure trough a photomask, as shown in Scheme 1, an exposed region with a lower refractive index behaves as a cladding material and an unexposed region with a higher refractive index behaves as a core waveguide material. From TGA analysis, the fluorinated copolysilyne I started to decompose at 280 °C, while poly(cylcohexylsilyne) began to decompose with the principal decomposition occurring at 260 °C.[7]



Scheme 1. Photolithographic fabrication of optical waveguides in polysilyne

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 phenyltrichlorosilane 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 refractive index, going from n= 1.61 to n= 1.485. The photooxidation studies suggest that their potential applications are as optical wavegides.

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