

Synthesis and Characterization of σ - π Conjugated Poly(methylphenyldiethynylsilane-co-methyltetraphenylphenylsilane)

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ABSTRACT: Diacetylenemethylphenylsilane (**1**) and dichloromethyltetraphenylphenylsilane (**2**) were synthesized by the reactions of ethynylmagnesium bromide with dichloromethylphenylsilane and dichloromethylvinylsilane with tetraphenylcyclopentadienone, respectively. The copolymers of **1** and **2** were obtained by sodium condensation reaction. They were characterized by FTIR, ¹H- and ¹³C-NMR, and both UV and fluorescence spectroscopy. The

molecular weights of polymers were determined by GPC relative to polystyrene standards. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 806–810, 2003

Key words: polysilanes; σ - π conjugated silane copolymer; synthesis; electroluminescent properties; gel permeation chromatography (GPC)

INTRODUCTION

Since Burroughes first discovered the electroluminescence properties of poly(4-phenylene vinylene) (PPV) in 1990,¹ many different conjugated polymers emitting light in various portions of the visible spectrum have been reported, such as PPV derivatives,^{2–4} poly(*p*-phenylene) derivatives,^{5,6} and polythiophenes.⁷ Recently, in addition to these well-known π -conjugated polymers, a new class of σ - π conjugated polymers with Si—Si bonds and π -electron systems, such as thienylene⁸ and anthrylene⁹ in the polymer backbone, have been attracting considerable interest with respect to their electroluminescence properties, and have been used in the manufacture of light-emitting diodes (LEDs). Ishikawa et al.¹⁰ demonstrated that organosilicon polymers, characterized by a regular alternating arrangement of a disilanylene unit and π -electron system, are photoactive and show conducting properties when the polymers are doped by exposure to antimony pentafluoride vapor. In a previous study,¹¹ we reported the preparation and characterization of various polysilanes containing tetraphenylphenyl groups in the side chains and studied the formation of charge-transfer complexes of these polysilanes with electron acceptors [e.g., tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), antimony pentaflu-

oride (SbCl₅), I₂] and their conducting properties. We found that the conductivity of these complexes was $8.0 \times 10^2 \Omega \text{ cm}^{-1}$ and the maximum UV-absorption wavelength was at $\lambda = 725.8 \text{ nm}$, which suggested that tetraphenylphenyl group is a large π -conjugated system and the π -electrons easily cause the σ -electrons in the Si—Si bond to delocalize. However, as far as we know, there are no studies of σ - π conjugated polymers with condensed rings in the side chain. It can be predicted that these polymers would have good anti-oxidative stability and conducting properties, and could be used as light-emitting materials for the manufacture of LEDs. We report here the synthesis and characterization of a σ - π conjugated copolymer containing the tetraphenylphenyl group in the side chain.

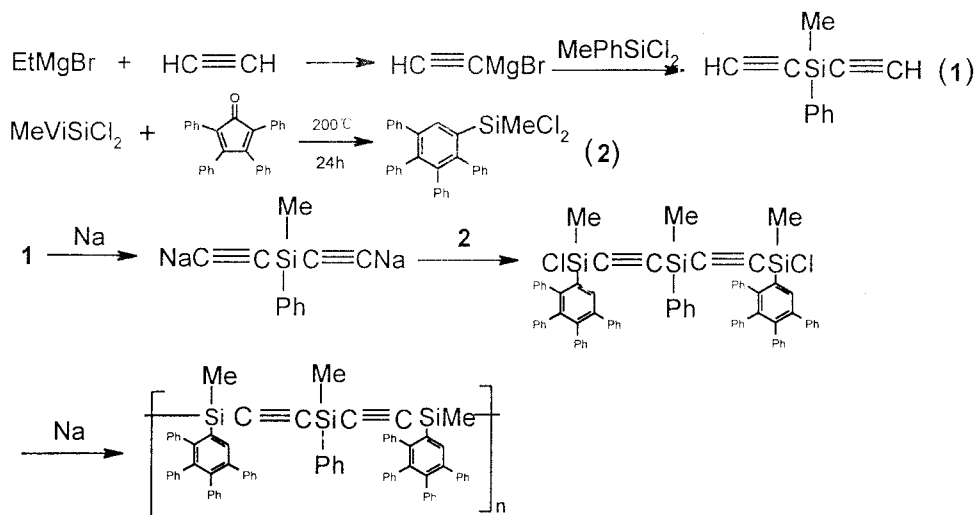
EXPERIMENTAL

Materials

All reactions, unless otherwise noted, were carried out under an atmosphere of dry nitrogen. Solvents toluene and THF were dried over sodium/benzophenone and distilled just before use. Ethylbromide was dried over CaCl₂ and distilled just before use. All glassware and magnesium turnings were thoroughly dried in an oven at 110–120°C and cooled under vacuum to room temperature. Acetylene was purified immediately before use by being passed successively through a dry ice/acetone trap, concentrated sulfuric acid, a potassium hydroxide column, and finally a column of activated alumina. Tetraphenylcyclopentadienone was prepared according to the literature.¹²

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Scheme 1 Three-step synthetic route to copolymer.

Measurement

FTIR spectra were recorded on a Nicolet FTIR 5DX spectrometer (Nicolet Instruments, Madison, WI). ^{13}C - and ^1H -NMR spectra were obtained on a 300-MHz JEOL FX-300Q instrument (JEOL, Tokyo, Japan). Ultraviolet (UV) spectra were measured with a Shimadzu UV-2510 UV spectrophotometer (Shimadzu, Kyoto, Japan). Photoluminescence spectra were recorded with an Edinburgh FLS920 spectrofluorometer (Edinburgh, UK). Molecular weights of copolymers were determined with Waters GPC apparatus (Waters Chromatography Division/Millipore, Milford, MA) relative to polystyrene standards.

Synthesis of diacetylenemethylphenylsilane (1)

Ethynylmagnesium bromide was prepared from the reaction of 0.5 mol of ethylmagnesium bromide (prepared from 0.5 mol ethylbromide and 0.5 mol Mg turnings in 350 mL dry THF) and dry acetylene in 500 mL of THF in a 1-L three-neck flask. To this was added 28.5 g (0.15 mol) dichloromethylphenylsilane through a dropping funnel over a period of 1 h. The resulting solution was allowed to stand at room temperature overnight, after which it was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether three times. The organic layer and the extracts were combined and washed with water. After the solvent was evaporated,

the residue was distilled under reduced pressure to give a colorless liquid 20 g [Yield: 80%; b.p. 120–122°C (30 mmHg)].

^1H -NMR (CDCl_3), δ = 0.66 (s, 3H, CH_3 -Si), 2.64 (s, 2H, $\text{C}\equiv\text{CH}$), 7.42–7.83 (m, 5H, phenyl ring protons). ^{13}C -NMR (CDCl_3), δ = 3.47 (CH_3 -Si), 89.5, 97.3 ($\text{C}\equiv\text{C}$), 127.8, 128.6, 132.5, 134.7 (phenyl ring carbons). IR: $\nu_{\text{C}\equiv\text{C}}$ 2039.8 cm^{-1} , $\nu_{\text{C}\equiv\text{H}}$ 3272.0 cm^{-1} .

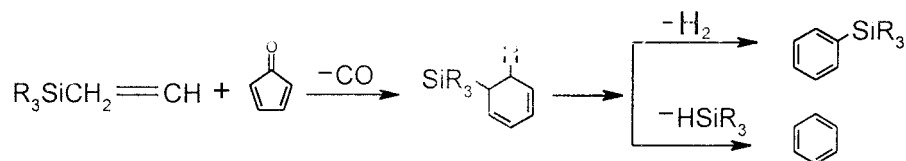
Synthesis of dichloromethyltetraphenylphenylsilane (2)

Dichloromethylvinylsilane [8.4 g (0.06 mol)] and tetraphenylcyclopentadienone [15.0 g (0.04 mol)] were sealed in an evacuated glass tube and heated in a hydrogenation bomb at 200°C for 24 h. After the tube was cooled and opened, the volatile silicone compounds were evaporated; 17.4 g of a light yellow solid were obtained (Yield: 90%).

^1H -NMR (CDCl_3), δ = 0.15 (s, 3H, CH_3 -Si), 6.60–7.60 (m, 21H, Ar-H). ^{13}C -NMR (CDCl_3), δ = 6.5 (CH_3 -Si), 126.9–131.5 (Ar-C).

Copolymerization of 1 and 2

Into a 100-mL three-neck flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 1.04 g (45 mmol) of sodium and 30 mL of dry toluene. The contents of the flask were heated to reflux under nitrogen atmosphere and then stirred vigorously to



Scheme 2 Reaction of silicone compound containing vinyl group with cyclopentadiene in sealed tube at high temperature.

prepared the sodium dispersion. To this was added a solution of 1.7 g (10 mmol) **1** dissolved in 10 mL of dry toluene over a period of 1.0 h at 90–100°C. After the mixture was heated to reflux for 4 h and cooled to room temperature, a solution of 9.68 g (20 mmol) **2** dissolved in 20 mL of dry toluene was quickly added through a dropping funnel. The resulting mixture was stirred at room temperature for 8 h, and then refluxed for 30 h. The remaining sodium was decomposed with a 1 : 1 mixture of ethanol and acetic acid. The mixture was then hydrolyzed with water. The organic layer was separated, and the aqueous was extracted with toluene. The organic layer and extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated to give a solid polymer product, which was purified three times by reprecipitation from methanol/isopropyl alcohol to give 6.0 g (60% yield) of copolymer as a yellow solid.

RESULTS AND DISCUSSION

Synthesis of silane copolymer

The synthetic strategy, consisting of three steps, to obtain the desired polymer from simple starting materials is outlined in **Scheme 1**.

Reaction of silanes containing Si—X (X = F, Cl, Br, I) with Grignard agents RMgX (R = alkyl, alkenyl, aryl; X = F, Cl, Br, I) is one of the common methods to form a new Si—C bond and obtain new organosilicon compounds in the laboratory. Generally, ether, tetrahydrofuran (THF), and toluene can be used as solvents in the reactions. However, because of its low boiling point, ether easily vaporizes and would have to be replenished when acetylene gas would be successively introduced. Furthermore, it would take more time to finish the transfer from ethylmagnesium bromide to ethynylmagnesium bromide if ether were used as a solvent. Thus, we used THF as a solvent and obtained good experimental results. The key point of the first step is to control the amount of the acetylene gas; if it is not sufficient, diethynylmagnesium bromide will be formed and a low yield of the expected product will be obtained.

In the second step, literature reported that two competing reactions took place during the aromatization of the silicon compound containing a vinyl group with cyclopentadienone in the sealed tube (see **Scheme 2**).¹³

The ratios of two products were determined by reaction conditions and the properties of the groups bonded to the Si atom. Chen et al.¹⁴ reported the reactions of the silicon compound containing vinyl groups with tetraphenylphenylcyclopentadienone in α -chloronaphthalene as a solvent in an open system instead of in a sealed tube could give high yield of the expected product because H₂ could easily escape, and

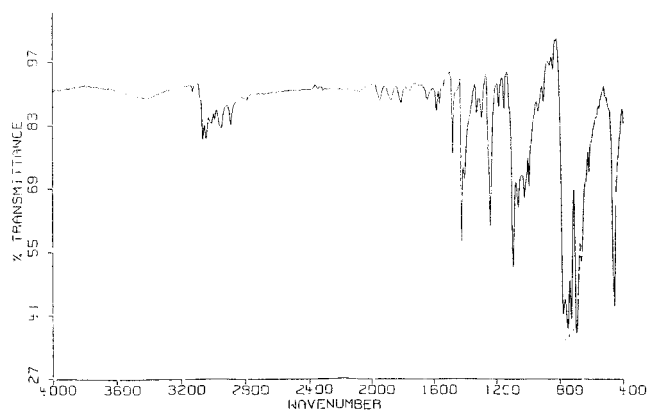


Figure 1 IR spectrum of copolymer.

cracking of the Si—Ar bond could be prevented at high temperatures. We attempted to get dichloromethyltetraphenylphenylsilane in this way. However, because of the low boiling point of dichloromethylvinylsilane, the expected products were not obtained after refluxing for a considerable time under nitrogen gas.

To obtain high contents of the —Si—Si—C≡C— unit in the Wurtz-type reductive condensation polymerization, the toluene solution of **2** should be added quickly to the system, and the resulting mixture should react at room temperature for several hours before refluxing. Because of the obvious space-hindering effect and electron-rich properties of the tetraphenylphenyl group, the polymerization reaction proceeded slowly. Thus, the polymerization reaction time should be sufficient to ensure completion of the reaction. The copolymer is solid and is soluble in common organic solvents. The molecular weight was determined to be 18,700 for the copolymer, relative to polystyrene standards; the polydispersity was 1.94.

Characterization of copolymer

The IR spectrum of the copolymer is shown in Figure 1. The C—H stretching vibrations of Si—CH₃ can be seen between 3000 and 2800 cm⁻¹. The aromatic ring vibrations and deformation vibrations of the side chains appear in the fingerprint region between 1600 and 1300 cm⁻¹. The peaks at 1597 and 1405 cm⁻¹ are attributed to the feature absorption of the tetraphenylphenyl group. The strong band at 1244 cm⁻¹ is attributed to CH₃ symmetric deformation vibration of the Si—CH₃ group. The plane-swing vibration of CH₃ and the stretching vibration of the Si—C bond of the Si—CH₃ group appeared at 781 and 729 cm⁻¹. It should be noted that there is a weak band at 3044 cm⁻¹ that is attributed to the C—H stretching vibration of the aromatic ring. A strong absorption corresponding to the stretching vibration of the Si—C bond and vibration of the aromatic ring of Si—Ar groups is

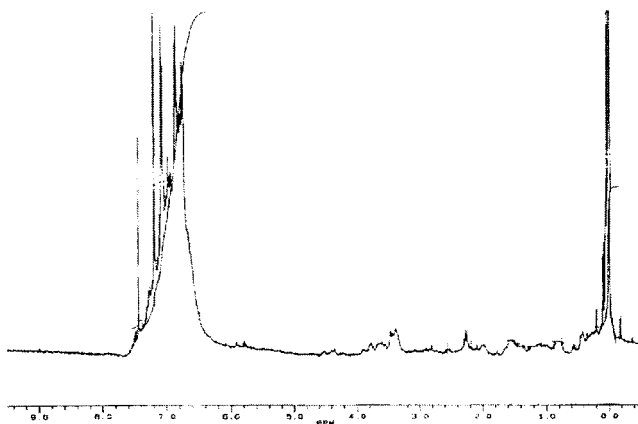


Figure 2 ^1H -NMR spectrum of copolymer.

observed at 1066 cm^{-1} . Because of the symmetric structure of the $\text{C}\equiv\text{C}$ group, no absorption of the $\text{C}\equiv\text{C}$ group was observed in the IR spectrum.

Further support for the structure is obtained by ^1H - and ^{13}C -NMR spectra, as shown in Figures 2 and 3, respectively.

In Figure 2, chemical shifts at 0.15 ppm are attributed to the absorption of protons of $\text{Si}-\text{CH}_3$, whereas chemical shifts at 6.4–7.6 ppm are assigned to the absorptions of protons of $\text{Ar}-\text{H}$. From Figure 3 we learn that the chemical shift at 1.0 ppm is attributed to the carbon of the $\text{Si}-\text{CH}_3$ group and chemical shifts at 126.8 to 131.5 ppm are attributed to carbons of the aromatic ring. The absorptions of the carbons of $\text{C}\equiv\text{C}$ are at 109.4 ppm.

Optical properties

The UV and fluorescence spectra of toluene solutions of the copolymer are given in Figures 4 and 5, respectively, from which one sees a maximum UV absorption in toluene at $\lambda = 284\text{ nm}$ and a maximum fluo-

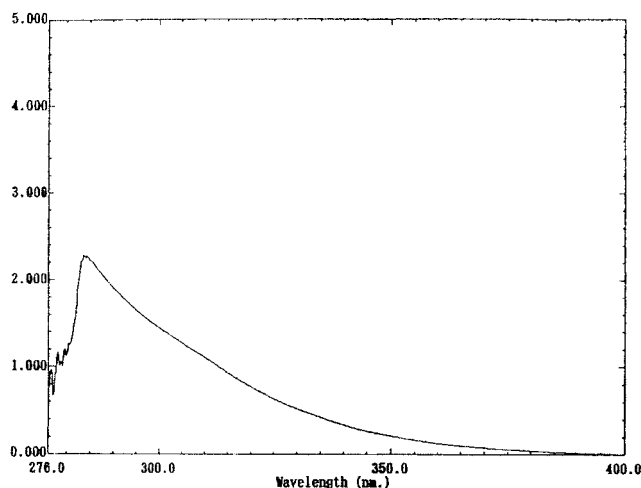


Figure 4 UV spectrum of copolymer in toluene.

rescence emission in toluene at $\lambda = 440\text{ nm}$. Photoluminescence spectra have a half-width of 100 nm. It is predicted that this copolymer would be an excellent candidate for the light-emitting materials in the manufacture of light-emitting diodes.

CONCLUSIONS

It has been shown that the σ - π conjugated copolymer, poly(methylphenyldiethynylsilane-*co*-methyltetraphenylphenylsilylene) can be prepared by a Wurtz-type reductive condensation reaction. The structures of the copolymer were confirmed by FTIR, ^1H -NMR, ^{13}C -NMR, and both UV and fluorescence spectroscopy. The molecular weight was determined to be 18,700, relative to polystyrene standards. The maximum fluorescence emission of the polymer in toluene was at $\lambda = 440\text{ nm}$, and its maximum UV absorption in toluene was at $\lambda = 284\text{ nm}$. It is predicted that this copolymer would be a prime candidate for light-emit-

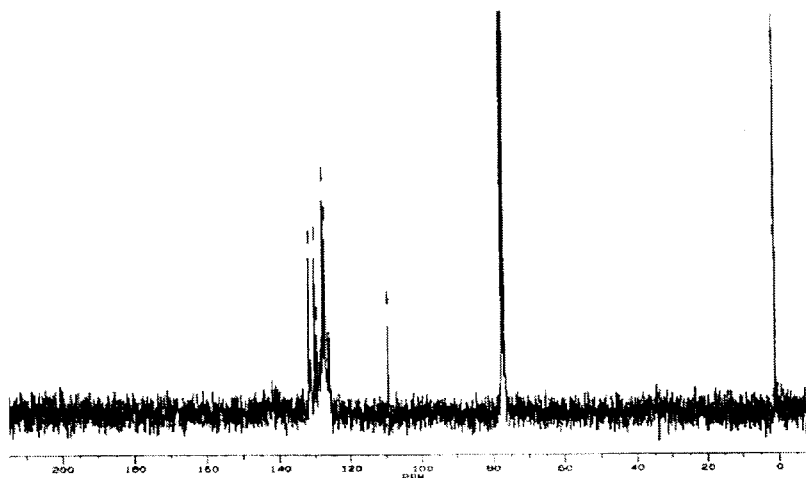


Figure 3 ^{13}C -NMR spectrum of copolymer.

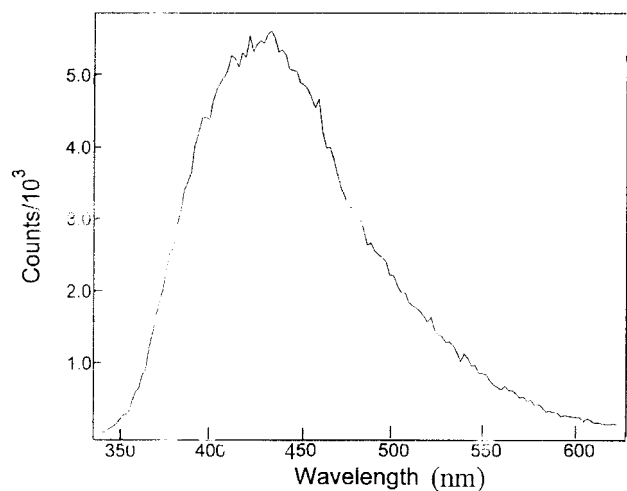


Figure 5 Fluorescence spectra of the copolymer in toluene.

ting materials in the manufacture of light-emitting diodes.

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