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Synthesis of σ-π Conjugated Alternating Silylene-Diacetylene Copolymers and Their Optical and Electrical Properties

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New σ-π conjugated alternating silylene-diacetylene copolymers, $-[(SiMe_2)_m-C\equiv C-C\equiv C]_n-$, m=1, 3, 4, and 6, were synthesized by the reaction of α,ω-dichloropermethylated oligosilanes with dilithiobutadiyne, $LiC\equiv C-C\equiv CLi$. The IR spectra clearly indicated the presence of diyne unit in the polymer backbone. The influence of the chain length m of the dimethylsilylene unit in the $-[(SiMe_2)_m-C\equiv C-C\equiv C]_n-$ backbone on the optical and the electrical properties was investigated.

Polysilanes are organometallic polymers that have a Si-Si main chain and an organic side chain. They can be used as functional materials such as photoresists, semiconducting materials, etc.[1)] Recently, many papers concerning the synthesis and properties of polymers that have a regular alternating arrangement of an Si-Si σ unit and π-electron system such as ethenylene,[2)] ethynylene,[3,4)] diethynylene,[5,6)] furylene,[7,8)] and thienylene[9,10)] in the polymer backbone have been reported. Electron delocalization between Si-Si σ bands and π system has been conclusively established in the polymers. Those σ-π conjugated polymers have a disilyl unit in the polymer backbone. However, few studies have been reported concerning the effect of the silylene chain length on the σ-π conjugation. The purpose of our studies is to increase the number of silylene unit in the polymer backbone and to obtain a high σ-π conjugated polymer. The technique[6)] used for the synthesis of new σ-π conjugation polymers, $-[(SiMe_2)_m-C\equiv C-C\equiv C]_n-$, is the reaction of dilithio compound, $LiC\equiv C-C\equiv CLi$, with α,ω-dichloropermethylated oligosilanes. In this paper, we report the synthesis of permethylated silylene-diacetylene copolymers and those optical and electrical properties.

The α,ω-dichloropermethylated oligosilanes were prepared by the reaction of dodecamethylcyclohexasilane with phosphorous pentachloride in *sym*-tetrachloroethane.[11)] The absorption spectra of α,ω-dichloropermethylated oligosilanes are shown in Fig. 1, which shows the significant dependence on the silylene chain length. The absorption maxima and the molar absorption coefficient were ; λmax=219 nm (ε=9200) for m=3, λmax=235 nm (ε=17100) for m=4, and λmax=259 nm (ε=23000) for m=6, respectively, in THF solution. These values are consistent with the literature.[12)] The electron volt of the absorption maximum decreases with increasing chain length as shown in the figure inserted. This means that the σ-conjugation along the Si-Si backbone is enhanced by increasing with the chain length m.

The silylene-diacetylene copolymers were prepared as shown in the scheme. Hexachlorobutadiene was quantitatively converted to dilithiobutadiyne through reaction with 4 equivalents of *n*-BuLi in THF,[6)] and quenching of the resulting solution with α,ω-dichloropermethylated oligosilanes, Cl-$(SiMe_2)_m$-Cl (m=1, 3, 4, and 6), afforded the desired polymers **1-4**, respectively.

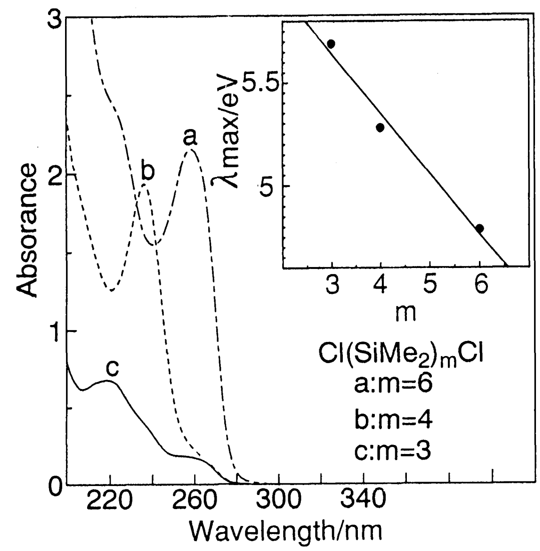
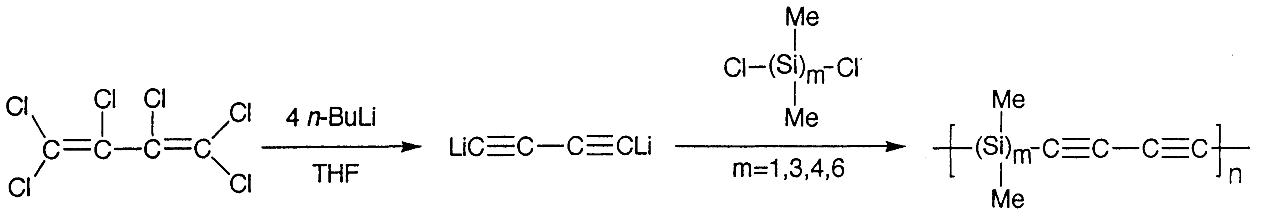


Fig.1. Absorption spectra and the plot of λ_{max} vs. chain length m for α, ω – dichloropermethylated oligosilanes, Cl-$(SiMe_2)_m$-Cl, in THF at room temperature.



1: m=1 , **2**: m=3
3: m=4 , **4**: m=6

The absorption spectra from the UV-visible to the IR region were measured by the diffuse reflectance technique using the copolymer samples mixed with KBr powder (0.2 wt%). The IR absorption spectra were measured using a JIR-100 FT-IR spectrophotometer. Since the FT-IR instrument is a single-beam instrument, the actual procedure of recording the absorption spectra involves recording a background spectrum with a reference and a spectrum with the sample, and calculating the ratio of the latter to the former spectrum. The electronic absorption spectra were measured by a Hitachi U-3400 spectrophotometer with a diffuse reflectance apparatus equipped with an integrating sphere of 60 mm inner diameter. The intensity of diffuse reflectance spectra is represented by the Kubelka-Munk function F(R), which is proportional to the absorbance. The electrical conductivities of the polymer powders were measured using the apparatus consisting of two pistons made from stainless steel which serve as electrodes and a Teflon cylinder (5 mm inner diameter). A sample was pressed at 20 kg/cm^2 (~2 MPa) by static weight, and a high voltage was applied between the two pistons. The conductivity measurements were performed with a Takeda Riken TR 8651 electrometer. All measurements were carried out at room temperature.

The characteristics of the silylene-diacetylene copolymers in this study are summarized in Table 1. Ishikawa and his co-workers have recently reported that 1,2,5,6-tetrasilacycloocta-3,7-diynes undergo anionic ring-opening polymerization to give poly[(disilanylene)ethynylenes] with high molecular weights.[13)] However, all the copolymers in Table 1 are dark colored powders that were hardly soluble in organic solvents, such as benzene, THF, DMSO, and chloroform ; therefore molecular weights of these copolymers were not determined. These insoluble copolymers should be due to stiffness of the main chain, relatively high molecular weight. It would be expected by replacement of methyl groups with flexible substituents such as *n*-hexyl which increases the solubility of the polymers.

Table 1. Characteristics of silylene-diacetylene copolymers

Polymer	Yield/%	IR $\nu_{C\equiv C}$/cm^{-1}	Optical band gap Eg,opt/eV	Conductivity x 10^{12}/S · cm^{-1}
1	79	2173, 2213	0.56	8.8
2	67	2057, 2181	0.53	11.8
3	62	2059, 2172	0.41	20.0
4	43	2086, 2166	0.33	32.1

The IR spectra of the silylene-diacetylene copolymers in the region from 400 to 4000 cm^{-1} are shown in Fig. 2. The presence of the C≡C bond and Si atom in the polymers can be confirmed by the IR spectra : An absorption band due to C≡C stretching is seen at 2050-2220 cm^{-1}. Compared with ordinary C≡C stretching, this band is shifted by about 50 cm^{-1} to the low wavenumber side owing to the presence of silylene unit in the adjacent position. Further, a band characteristic of deformation of the C-H band adjacent to Si around 1250 cm^{-1} and a band due to Si-C stretching at 770-900 cm^{-1} are observed. The IR spectra show absorptions at 1050 cm^{-1}, indicating the presence of siloxane unit, which would be formed from hydrolysis of the chlorosilyl group remaining in the resulting polymers during work-up.

The band gap in σ-conjugated polysilanes is about 4 eV in contrast to a typical band gap of almost 8 eV for a saturated carbon skeleton. Figure 3 shows the diffuse reflectance spectra of the silylene-diacetylene copolymers. The absorption tail of the diffuse reflectance spectra extends to approximately 1700 nm. The Eg,opt was

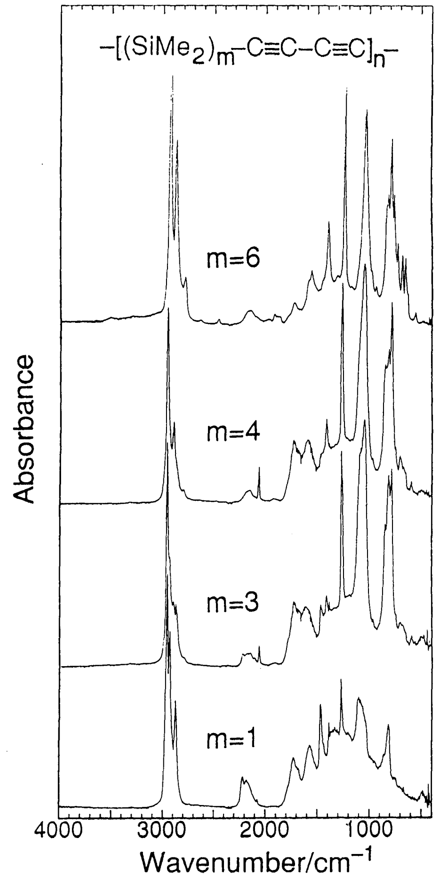


Fig.2. The IR spectra of silylene-diacetylene copolymers.

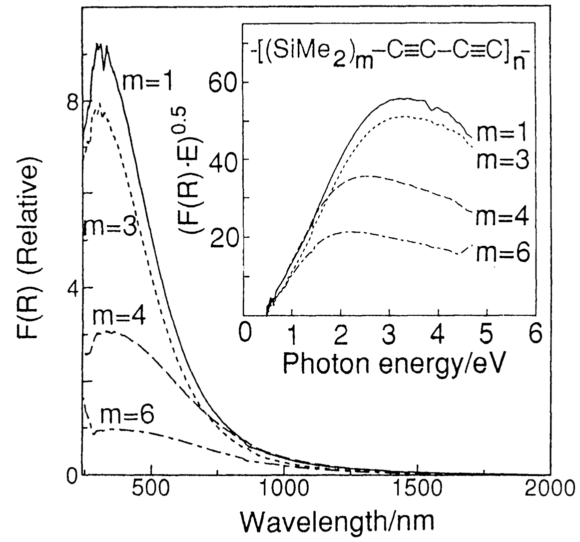


Fig.3. Diffuse reflectance spectra and the plot of (F(R) · E)$^{0.5}$ vs. photon energy for silylene-diacetylene copolymers.

determined by Tauc plots shown in the figure inserted in Fig. 3. The Eg,opt of the silylene-diacetylene copolymers are included in Table 1. It is noteworthy that Eg,opt decreased with the number of dimethylsilylene unit, and the minimum Eg,opt (0.33eV) was observed for m=6. Presumably, this feature corresponds to the increase of the σ-π conjugation, which was enhanced by the σ-conjugation of silylene chain.

The electrical conductivities, the undoped compressed-pellet samples, were in the range of 10^{-11}-10^{-12} S • cm^{-1} at room temperature, which is in the insulator range. Comparison of the electrical conductivity values in Table 1 shows that the electrical conductivity increases apparently with increasing the number of dimethylsilylene unit. In conclusion, the data from Eg,opt and the electrical conductivity suggest that the σ-π conjugation occurring through overlap with the π-electron system and the σ-conjugated chain is enhanced by increasing with the number of silicon atom in the silylene-diacetylene copolymer backbone.

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