Electrochemical Synthesis of Poly(dibutylsilane) Cross-linked with Tetramethylene Chain

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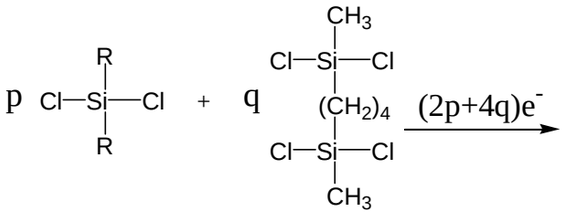
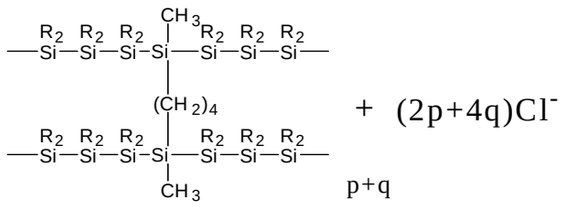
σ-Conjugated polymers such as polysilanes, polygermanes, and polystannanes can be synthesized electrochemically. Copolymers which have Si-Si, Si-Ge, Si-Sn bonds have also been reported. The authors successfully utilized the copolymerization technique to construct a new polysilane structure. Polysilanes cross-linked with tetramethylene chains were successfully synthesized by reducing dialkyldichlorosilanes in the presence of 1,4-bis(dichloromethylsilyl)butane.

Dibutyldichlorosilane was purchased from a commercial source and distilled before use. 1,4-bis (dichloromethylsilyl)butane (cross-linker monomer) was synthesized from 1,4-bis(diphenylmethylsilyl)butane in our laboratory. Electro-copolymerization was carried out in 1,2-dimethoxyethane in the presence of tetrabutylammonium perchlorate as the supporting electrolyte. The cathode was a platinum plate and the anode was a silver wire. Ratio of the two monomers in the electrolyte solution was varied to control the density of the cross-linking points in the resulting polymer.





Copolymers were obtained in decent yields and Mws were 15000-20000.

Photo-decomposition of the cross-linked polymers were slow compared to those of typical linear polysilanes such as $(Bu_2Si)_n$. The absorbance of the cross-linked polymer decreased to ca. 53% of the initial value after the photo-irradiation of 50 s, while that of $(Bu_2Si)_n$ decreased swiftly to 28% in the same conditions.

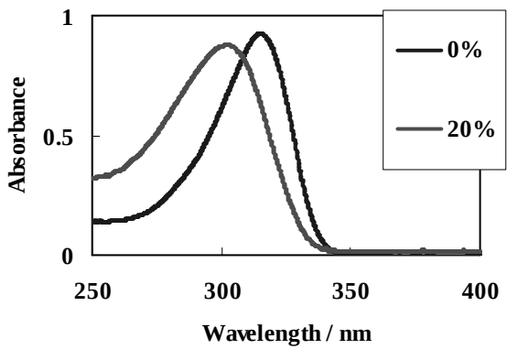


Fig.1 Absorption spectra of polymers with and without cross-linking points at room temperature.