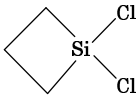
Electrochemical Reduction of Cyclic Dichlorosilanes

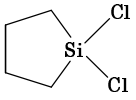
Kazuhiro Yamada, Mitsutoshi Okano
Tokyo Polytechnic University
1583 Iiyama, Atsugi, Kanagawa 243-0297 Japan

It has been well known that electrochemical methods give good results in the synthesis of various polysilanes. The authors' original electrochemical system has been widely applied to various kinds of σ-conjugated polymers, including linear and network polysilanes, polygermanes, and polystannanes. Such efforts of the authors to apply their original system to the synthesis of new σ-conjugated polymers are still continuing.

In this work, cyclic dichlorosilanes were electrochemically reduced in order to obtain new polysilanes. The following two monomers were purchased from commercial sources and used after distillation.



1,1-dichloro-1-silacyclobutane



1,1-dichloro-1-silacyclopentane

According to the method reported earlier, they were reduced electrochemically in 1,2-dimethoxyethane using tetrabutylammonium perchlorate as the supporting electrolyte. A platinum plate was the cathode and a silver wire was the anode.

Electrochemical reduction of 1,1-dichloro-1-silacyclobutane and 1,1-dichloro-1-silacyclopentane gave the corresponding polymers (Mw = 5000 to 8000) in 20-30% yields. The yields were low and Mw's were small compared to those of typical polysilanes, 60-80% and 15000-30000. The resulting polymers had relatively low solubility. Such low solubility may be the reason for the low yields and small Mws. The polymers showed absorption in UV region and indicated the existence of Si-Si bonds and σ-conjugation. However, absorption peaks were hardly observed and the peaks were located in the shorter wavelength region compared to those of typical polysilanes.

Photo-decomposition of the polymers were slow compared to those of typical polysilanes. The absorbance of the polymer obtained from 1,1-dichloro-1-silacyclopenntane decreased by only ca. 3% under photo-irradiation of 600 s, while that of $(Bu_2Si)_n$ decreased by 95% in the same conditions.

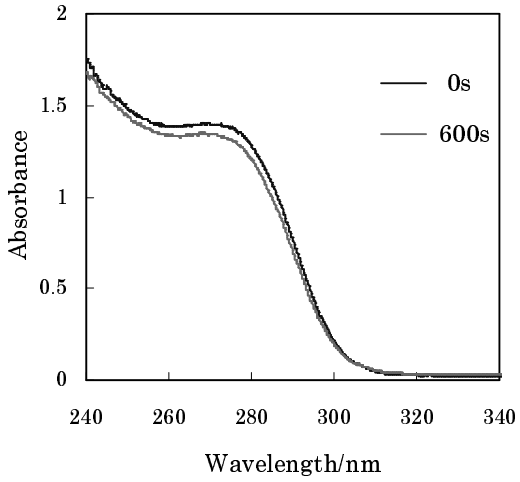


Fig. 1 Photo-decomposition of $(C_4H_8Si)n$ in pentane.