Electrochemical Synthesis of
Cross-linked Linear Polysilanes

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The authors have found that cross-linked polysilanes can be synthesized by copolymerization of a dialkyldichlorosilane and a bis(dichloroalkylsilyl)alkane. Such cross-linkings restrict the movement of polymer chanins and thus that of the σ-conjugated systems. Synthesis and properties of the obtained polymers are discussed.

Various dialkyldichlorosilanes (monomers for the linear chains) and Bis(dichloromethylsilyl)ethane (cross-linker monomers) were purchased from a commercial source and distilled before use. Dibutyldichlorogermane and bis(dichloromethyl-silyl)butane were synthesized in our laboratory. All the synthetic electrolysis were carried out in a one-compartment cell using 1,2-dimethoxyethane as the solvent and tetrabutylammonium perchlorate as the supporting electrolyte, respectively. After precipitation in methanol, copolymers were obtained in decent yields and Mws were 10000-20000.

In some of the polymers using dibutyldichlorogermane as the monomer for the linear chain, the density of cross-linking points were estimated by means of fluorescent X-ray method. Thus, it was found that when ratio of the two monomers in the electrolyte solution is varied, the density of the cross-linking points in the resulting polymer is controlled.

Three main observations were (1)blue shift in absorption spectrum at room temperature (See Fig. 1), (2)difference in the thermochromic behavior, and (3) suppression of photodecomposition (See Fig. 2).

Among three, the most important is the suppression of photodecomposition. In order to know the reason for the suppression, flash photolysis studies have been carried out. It was found that lifetime of photogenerated silyl radicals was shorter in the cross-linked polymers.

Cross-linking with a shorter alkyl chain gave larger effects to the mother linear polymers. Larger substituent groups on the linear chain showed larger effects.

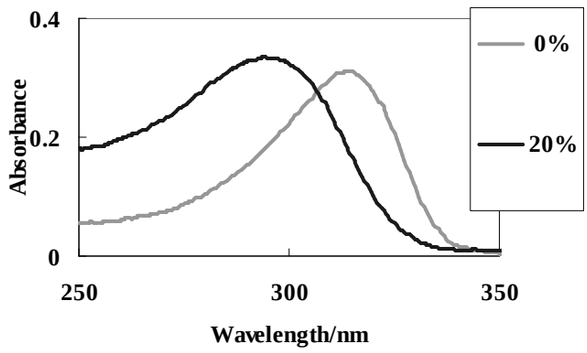

Fig. 1 Absorption spectra of the polymers with and without cross-linking points at room temperature.

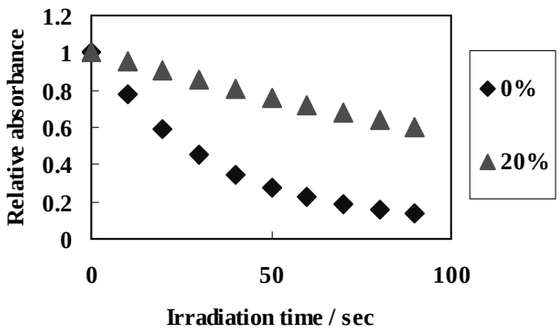

Fig. 2 Time courses of the relative absorbance upon light irradiation of the polymers in pentane at room temperature.