

Synthesis and Optical Properties of Polysilanes containing Anthryl Groups

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1. Introduction

Polysilanes contain σ -conjugated silicon-silicon bonds in the polymer backbone. Changing the substitutions can control the backbone structure. Interesting optical properties characteristic of σ -conjugated polysilanes have been known to change by the backbone structures. Polysilanes with various substituent groups have been synthesized as the advance in the synthetic technique. However, little is studied about optical properties of polysilanes containing anthryl groups.

In this paper, we report synthesis and optical properties of linear and network polysilanes containing anthryl groups. The effect of various substitution groups and backbone structures, and UV irradiation on the heat treatment of polysilanes thin films was investigated by measurement of absorption spectra.

2. Experimental Section

Linear and network polysilanes with anthryl groups in Fig. 1 were synthesized by the Wurtz coupling method. The samples were obtained in the form of powder. Thin films were prepared by spin-coating from a toluene solution on solid substrates. The spin-coated films were heated at a constant temperature for a constant time under reduced pressure. After the heat treatment, the thin films were cooled to room temperature. The spectral changes of the thin films after the heat treatment were investigated using UV-Vis-NIR absorption spectroscopy, in air at room temperature.

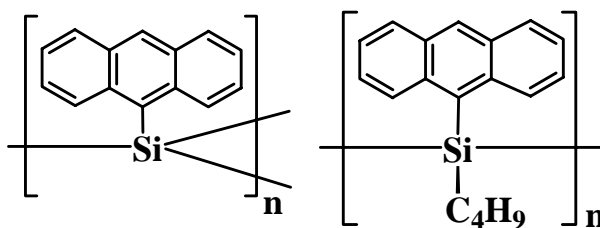


Fig. 1. Chemical structure used in this study.

3. Results and Discussion

Spectral Changes by Heat Treatment

Figure 2 shows the change in absorption spectra after heating thin films of network poly(9-anthrylsilyne) at various temperatures under reduced pressure. The absorption around 5 eV decreases gradually with increasing heating temperature. At 500 °C, the absorption edge shifts to lower energy. The absorption spectra show broad absorption up to 1 eV with increasing heating time at 500 °C. The polymers show the electronic states characteristic of amorphous semiconductors, which are characterized by a Tauc gap energy. The color of the thin films changes from pale yellow to brown, indicating the decrease of the Tauc gap energy. We investigated the effect of the substituent groups on heat treatment of thin films of network polysilanes. For the polymers with phenyl groups as side chains, the absorption decreases gradually with the increase in heating temperature and disappears finally. The shift to lower energy of the absorption edge is not observed by heat treatment of thin films. On the other hand, the absorption spectra of the polymers with naphthyl group show a similar

behavior as the anthryl ones. However, as compared with anthryl ones, the absorption edge shifts to lower energy gradually with the increase in heating time at 500 °C. It is found that the spectral changes by heat treatment depend on the substitutions of side chains of network polysilynes.

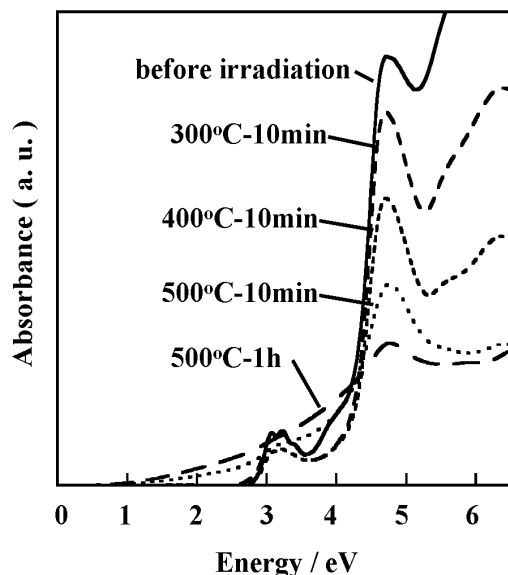


Fig. 2. Absorption spectra in heat-treated thin films of poly(9-anthrylsilyne).

Effect of Backbone Structures and UV irradiation

We investigated the effect on backbone structure of polysilanes and UV irradiation on heat treatment. Figure 3(a) shows the change in the absorption spectra of thin films of linear poly(butyl-9-anthrylsilane) when the film was heated at 500 °C for 10 min under reduced pressure. A similar shift to lower energy of the absorption edge is observed, independence of backbone structures of polysilanes with anthryl groups. The spectral changes of heat treatment after UV irradiation are shown in Fig. 3(b). The absorption around 3 eV due to anthryl groups decreases on UV irradiation. When heating thin films after UV irradiation, the absorption edge shifts to lower energy than that of heat treatment without UV irradiation. In addition, the absorption intensity of low energy becomes large. This is due to the difference in film thickness between thin films of heat treatment without and after UV irradiation

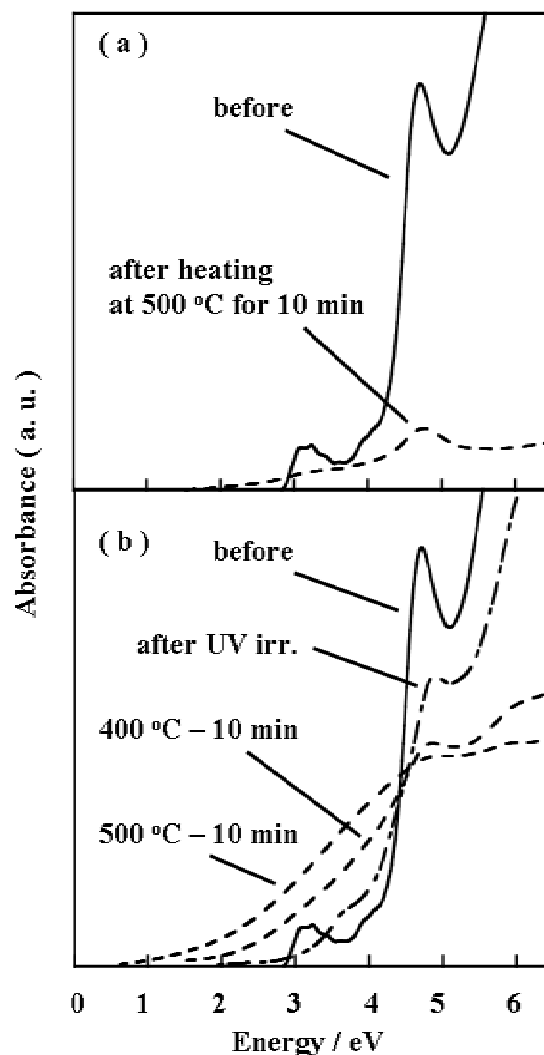


Fig. 3. Absorption spectra in heat-treated thin films of poly(butyl-9-anthrylsilane).

4. Conclusion

Linear and network polysilanes with various substitutions were synthesized. We have demonstrated that the substitutions bonded to polysilanes, the backbone structure of polysilanes, and UV irradiation play an important role in spectral changes by heat treatment of thin films.

Acknowledgements

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