

## Refractive Index Control of Organic-Inorganic Hybrid Film Consisting of Ge-Ge Chain

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### 1. Introduction

Organic-inorganic hybrid polymers are expected to be a new class of optical materials due to the excellent properties such as heat resistance, light resistance, transparency, processability and so on. These features supply the weak points of conventional polymers consisting of aliphatic and aromatic hydrocarbons. The heat resistance, light resistance and transparency are owing to the inorganic component such as Si-O-Si structure. The processability can be controlled by the organic components of the organic-inorganic hybrid polymers. Recently, the POSS (polyhedral oligomeric silsesquioxane) has attracted considerable attentions, which consisting of as a nanometer-sized silica-like cage structure functionalized with various kinds of organic groups. New polymers using the POSS as a building unit of the organic-inorganic hybrids have been developed. The double-decker-shaped silsesquioxane (DDSQ) is a new family of silsesquioxanes consisting of a Si-O-Si cage structure and functional organic side chains.<sup>1-4</sup> The DDSQ has two siloxane rings connected in the shape of double-decker. The DDSQ as a building block provides elegant designs and the controllable reaction for organic-inorganic hybrid materials. The hybridization between organic and inorganic moieties can be controlled by the chemical reaction of the functionalized DDSQ. A unique polymer which has a backbone consisting of a silica-like cage structure (DDPSQ) can be synthesized by hydrosilylation reaction between a hydrosilane-functionalized DDSQ and a vinyl-functionalized DDSQ with a Pt catalyst. In this paper, we studied the control of the refractive index of organic-inorganic hybrid film consisting of DDPSQ and organic germanium polymer (OrGe). The OrGe is consisting of a hyperbranched Ge-Ge chain and organic side chains.<sup>5,6</sup> The OrGe having an element of larger atomic number shows a large refractive index compared to conventional carbon and silicon polymers.<sup>7</sup> The Ge-Ge bond can be converted to Ge-O-Ge bond by photooxidation reaction, which induces the decrease of the refractive index.

### 2. Experimental

DDPSQ (sila-DEC<sup>TM</sup>) was obtained from Chisso Corporation. An organic germanium polymer (OrGe) was obtained by the reaction of germanium tetrachloride using Mg metal in tetrahydrofuran (THF) and the capping reaction of remaining Ge-Cl group by an aryl or alkyl Grignard reagent in THF at the end of the reaction.<sup>5,6</sup> Hybrid polymer films

were prepared by spin coating on a substrate from a toluene solution of the DDPSQ and OrGe. The UV irradiation was carried out using a Hg-Xe lamp with a UV-bandpass filter (60 mW/cm<sup>2</sup>). The refractive index and the thickness were measured by prism coupler (METRICON Model2010).

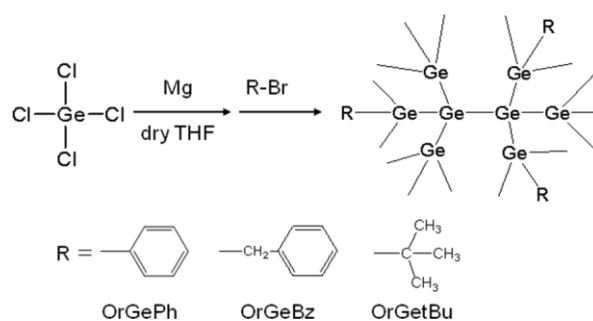


Fig.1 Synthesis of hyperbranched organic germanium polymer (OrGe).

### 3. Results and discussion

The OrGe has a main chain consisting of Ge-Ge bond which shows  $\sigma$ -conjugation along the chain. Such  $\sigma$ -conjugated polymer shows characteristic absorption band in the UV-Visible region. Fig.1 shows the absorption spectra of the DDPSQ/OrGePh hybrid film, where the weight ratio of DDPSQ to OrGePh is 2.

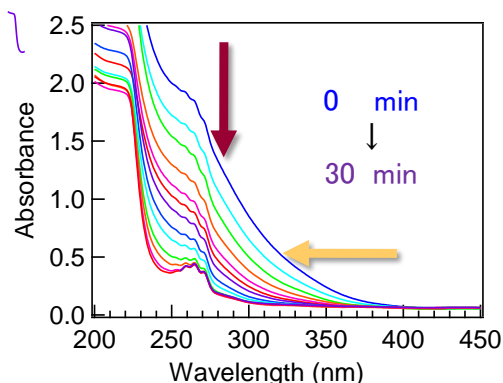


Fig.2 Change of the absorption spectrum of a DDPSQ/OrGePh hybrid film during UV-irradiation.

The decrease of the broad absorption band and the blue shift of the absorption edge can be assigned to the decrease of the  $\sigma$ -conjugation length of the OrGePh by photooxidation.

tion of the Ge-Ge bond. The UV-irradiation causes the cleavage of the Ge-Ge chain and the insertion of oxygen. The formation of the Ge-O-Ge bond was confirmed by FT-IR spectra. Fig.3 shows the FT-IR spectra of the DDPSQ/OrGePh hybrid film before and after UV-irradiation. The increase of the band around 850  $\text{cm}^{-1}$  can be assigned to the formation of the Ge-O-Ge bond. The insertion of the oxygen also caused the increase of polymer film thickness.

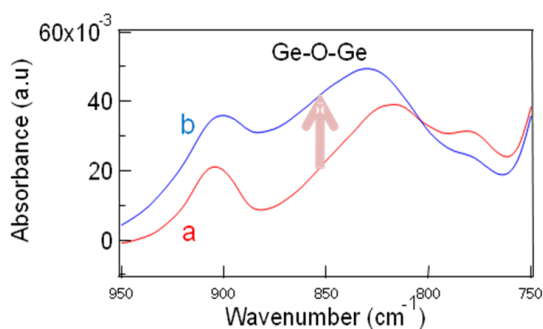


Fig.3 FT-IR spectrum of a DDPSQ/OrGePh hybrid film before (a) and after (b) UV-irradiation.

The refractive index of a DDPSQ/OrGe hybrid film can be controlled by the photooxidation of the Ge-Ge bond. The refractive index changes of the hybrid films consisting of OrGes with various organic side chains are shown in Fig.4. The DDPSQ/OrGePh hybrid film shows the decrease of the refractive index from 1.583 to 1.544 by the UV-irradiation for 5 min and a constant value after 5 min. The DDPSQ/OrGeBz and DDPSQ/OrGetBu hybrid films also show similar decrease of refractive index changes by UV-irradiation although the values of the refractive index depend on the organic side chains of the OrGe. The order of the initial value of the refractive index is as follows: OrGePh > OrGeBz > OrGetBu. The OrGe with an aromatic side chain has the larger refractive index. Another noticeable feature in Fig.4 is the difference of the refractive index after UV-irradiation for 30 min. Especially, DDPSQ/OrGetBu hybrid film showed remarkable low refractive index compared to others. The value is lower than that of DDPSQ ( $n = 1.520$ ). This can be explained by the elimination of the organic side chains and the formation nanoporous structure by UV-irradiation, which was confirmed by the decrease of the absorption band of tert-butyl group in FT-IR spectra and the decrease of the film thickness during UV-irradiation.

#### 4. Conclusions

The refractive index of an organic-inorganic hybrid film consisting of DDPSQ and OrGe was controlled by UV-irradiation using the photooxidation of the Ge-Ge chain of OrGe. The organic side chain of the OrGe influenced the refractive index value and the amount of change by photooxidation.

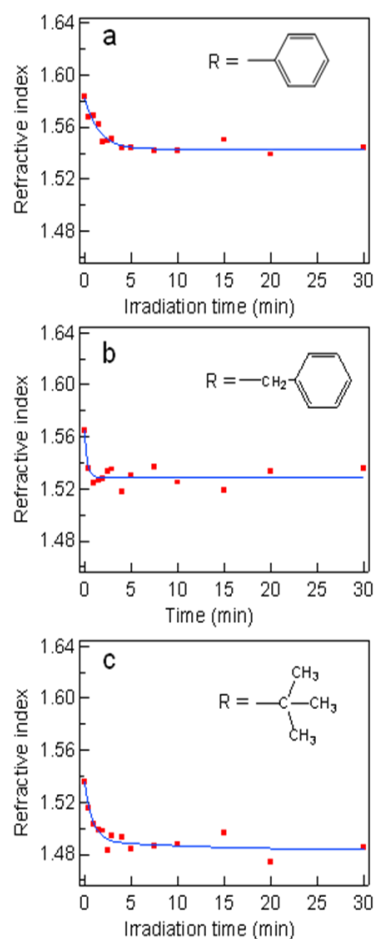


Fig.4 Refractive index changes by UV-irradiation for DDPSQ/OrGePh (a), DDPSQ/OrGeBz (b), and DDPSQ/OrGetBu (c) hybrid films.

#### Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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