

## 論文の内容の要旨

論文題目 Synthesis of Photo-responsive Organosiloxane Materials Containing Azobenzene Groups

(アゾベンゼン基を有する光応答性有機シロキサン材料の創製)

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Photo-responsive materials are gaining increasing attention owing to their potential applications in sensors, actuators, biomedical devices and so on. Azobenzene (hereafter denoted as “azo”) is a typical photo-responsive chromophore that shows photochemical conversion between trans and cis isomers upon UV and Vis irradiations, accompanied by large changes in its molecular size. Azo-containing organic materials showing various photo-responses such as deformations and dynamic motions have been reported. The requirements to achieve such unique properties are as follows: 1) free volume and mobility of azo groups to realize efficient photoisomerization and 2) ordered arrangement of azo groups to amplify the molecular size change into macroscopic scale. Azo moieties in organic polymer systems are unidirectionally aligned, and the flexibility of the polymer chains gives them adequate free volume and mobility. However, organic polymer matrixes suffer the disadvantages of low thermal, chemical, and mechanical stabilities, which should limit their practical applications.

This dissertation describes the syntheses of novel, photo-responsive azo–siloxane hybrid materials that undergo structural changes triggered by photo-isomerization. Organosiloxanes are an important class of inorganic–organic hybrid materials because of their high transparency and stabilities as well as ease in the control of their compositions, structures, and morphologies by a simple process based on polycondensation of molecular precursors. There have been many reports on the azo–siloxane hybrid materials; however, those having ordered structures are very limited. Recently, self-assembly of trialkoxysilylated azo precursors by intermolecular hydrogen bondings has been reported. The resulting products have lamellar structures, but are not photo-responsive probably due to intense H-bondings which inhibit trans–cis isomerization of azos. In Chapter 1, the background and strategies to overcome this limitation are described. The first strategy is based on self-assembly of azo-modified siloxane precursors by weaker interactions. The syntheses and properties of the precursors are described in Chapter 2. In

Chapter 3, the precursors are hydrolysed and polycondensed into photo-responsive, ordered hybrids materials. The second strategy is construction of three-dimensional porous networks where rigid siloxane cages are bridged by azo groups to achieve photo-responsive porous networks (Chapter 4).

In Chapter 2, azo-modified alkoxy silane and oligosiloxane precursors with different geometries (pendant-type, bridged-type, and dumbbell-type) and reactivities (monosilyl groups with different numbers of Si-OR groups and oligosiloxane with Si-H groups) were synthesized and their properties were investigated. The pendant-type precursors, where single mono- and di-ethoxysilyl groups are attached to azo by simple propylene linkers, were synthesized by Pt-catalyzed hydrosilylation of 4-allyloxyazobenzene with  $\text{HSi}(\text{OEt})_3$  and  $\text{HSiMe}(\text{OEt})_2$ , respectively. Red liquids obtained after purification were identified by NMR and MS. UV-Vis spectra of these precursors in THF showed efficient, reversible trans-cis photo-isomerizations. Different numbers of ethoxy groups mean that these precursors have different cross-linking abilities by siloxane formation. It is expected that the free ends of azos in both precursors allow trans-cis photo-isomerization even after polycondensation. The bridged-type precursors, where mono-, di-, and tri-ethoxysilyl groups are bridged by azo, were also synthesized by hydrosilylation of diallyloxyazobenzene with  $\text{HSi}(\text{OEt})_3$  and  $\text{HSiMe}(\text{OEt})_2$ , and  $\text{HSiMe}_2(\text{OEt})$ , respectively. Different from the pendant-type precursors, the bridged-type precursors were obtained as crystalline solids. Such bridged-type precursors can incorporate azos into main frameworks of hybrids. Depending on the numbers of alkoxy groups, the number density and dimensions of Si-O-Si bonds can be varied, resulting in differences in the flexibility of the networks. UV-Vis spectra of these precursors in ethanol showed quick and reversible trans-cis photo-isomerization, while their solid films showed different photo-responsive behaviors. For the precursors with mono- and di-ethoxysilyl groups, after UV irradiation, relative intensity of the peak of cis isomers slightly increased, indicating a trans-to-cis isomerization. Subsequent Vis irradiation induced cis-to-trans isomerization. XRD patterns of these films showed similar lamellar structures. Interestingly, the film of the precursor with di-ethoxysilyl groups showed a reversible crystalline-isotropic phase transition upon UV/Vis irradiation. Melting of this film upon UV irradiation was confirmed by optical microscopy observation. Such photo-induced melting of molecular crystals is a rare phenomenon that should be due to the high mobility of azo groups. The dumbbell-type precursor, where azo is sandwiched by two bulky octasiloxane cages, was synthesized by hydrosilylation of diallyloxyazobenzene with cage-type oligosiloxanes ( $\text{H}_8\text{Si}_8\text{O}_{12}$ ). A thin film with a lamellar structure was obtained by spin-coating of a THF solution of this precursor. Reversible trans-cis photo-isomerizations were confirmed by UV-Vis spectroscopy. Order-disorder transitions were observed upon light irradiations. It was

considered that bulky oligosiloxane cages provided large free volume for trans-cis photo-isomerization of azo moieties even in solid state.

In Chapter 3, ordered azo-siloxane hybrid films were prepared by hydrolysis and polycondensation of the precursors shown in Chapter 2, and their photo-responsive properties were investigated. To obtain ordered structures, self-assembly of the hydrolyzed precursors, having Si-OH groups, or solid-liquid reaction of the precursor films have been employed. Hybrid films were prepared by hydrolysis of the pendant-type precursors in THF, HCl and H<sub>2</sub>O mixtures, followed by spin-coating on glass substrates and heating. Self-assembly and polycondensation of the hydrolyzed precursors were realized by this simple procedure. XRD and TEM analyses revealed lamellar structures with different arrangements of azo groups. UV irradiation on these films induced either a slight decrease or increase in the d-spacings depending on the difference in the arrangement of azo groups. Thus, by utilizing the precursors with different numbers of alkoxy groups, different tendencies of structural changes were observed. Such behavior was caused by partial trans-cis photo-isomerization of azo moieties, as evidenced by UV-Vis spectra. Lamellar films were also prepared by co-hydrolysis and polycondensation of the pendant-type precursors with tetraethyl orthosilicate (TEOS). These hybrid films had smooth surface and therefore higher transparency than those prepared without TEOS. In addition, the structures of the films were varied by co-condensation. Their UV-Vis spectra showed higher degrees of trans-cis photo-isomerization of azo moieties than those prepared without TEOS, although no change of the XRD peaks was observed. After soaking in dioxane, the lamellar structures were maintained but showed large increases in the d-spacings. By co-condensation with TEOS, the changes of the arrangement of azo facilitated the intercalation of solvent molecules, which would be important for the creation of smart adsorbents. It was found that bridged-type precursors had an ability to form lamellar hybrid films by direct hydrolysis of the precursor films in HCl aqueous solutions or by spin-coating of the hydrolyzed solutions. XRD patterns showed that these hybrid films had lamellar structures with different d-spacings. UV-Vis data showed that photo-isomerization was nearly inhibited for the film derived from the precursor with triethoxysilyl groups, whereas partial trans-cis isomerizations were observed for those derived from mono- and di-ethoxysilyl precursors. This fact suggests that azos have relatively high mobility in the Si-O-Si networks with lower degrees of cross-linking. The film derived from di-ethoxysilyl precursor showed structural change from the lamellar structure to a disordered structure upon UV irradiation. Subsequent Vis irradiation did not recover the original peaks; however, after several days of storage under ambient conditions, the lamellar structure recovered. A lamellar hybrid film was obtained by solid-liquid reactions of dumbbell-like precursor film with an aqueous solution of Et<sub>2</sub>NOH.

Hydrogen gas was generated when the reaction proceeded. FT-IR spectra after the reactions showed the progress of hydrolysis and polycondensation. The XRD peaks of the film disappeared after UV irradiation, and recovered after subsequent Vis irradiation, thus confirming a photo-induced reversible order–disorder transition. The UV–Vis spectra after irradiations showed reversible decrease and increase of the peak for trans isomers, indicating the occurrence of reversible trans–cis isomerization. These results indicated the ease of photo-isomerization of azos that are sandwiched by bulky oligosiloxane cages.

In Chapter 4, porous, three-dimensional azo–siloxane networks were synthesized by hydrosilylation of diallyloxyazobenzene with cage-type siloxanes ( $\text{H}_8\text{Si}_8\text{O}_{12}$ ) in toluene. After the reaction, an orange-colored wet gel was obtained. Solid-state  $^{29}\text{Si}$ -NMR analysis of the dry gel showed hydrosilylation proceeded with a relatively higher degree of reaction. Unfortunately,  $\text{N}_2$  adsorption measurement showed that the product had very low surface area, which was probably due to the flexibility of propylene linkers formed between azo and D4R units. Actually, large shrinkage of the network upon evaporation of the solvent from the wet-gel was observed. The obtained dry gel underwent reversible swelling–deswelling behavior upon soaking in toluene and air-drying. Neither dry gel nor wet gel exhibited obvious photo-responsive properties, which may be because UV/Vis light absorption of azos can only occur in a thin surface layer of these materials. Morphology control of the materials into thin films or nanoparticles should be important.

In conclusion, azo-modified alkoxy silane and oligosiloxane precursors with different geometries (pendant-type, bridged-type, and dumbbell-type) and reactivities (alkoxysilyl groups with different numbers of alkoxy groups and an oligosiloxane with Si-H groups) synthesized as described in Chapter 2. They showed reversible trans–cis photo-isomerizations in dilute solutions. For the precursor films, reversible crystalline–isotropic phase transition and order–disorder transitions were observed. In Chapter 3, hybrid films with lamellar structures were prepared from these precursors by hydrolysis and polycondensation. Some of them showed novel photo-responsive properties such as reversible d-spacing change and order–disorder transitions upon UV/Vis irradiations. It was found that the molecular structures that allow mobility of azo-groups were crucial. In future, to achieve more dynamic changes of the structures and properties by light stimuli, fine control of the structure from molecular scale to meso or macro scale is needed. Control of the macroscopic morphologies of products into free-standing films, nanogels, nanofibers or hierarchical structures is promising approaches. Also, more systematic materials design and devices design are also necessary for practical applications of this class of photo-responsive hybrids.