Photo-cured organic-inorganic hybrids for high refractive index materials

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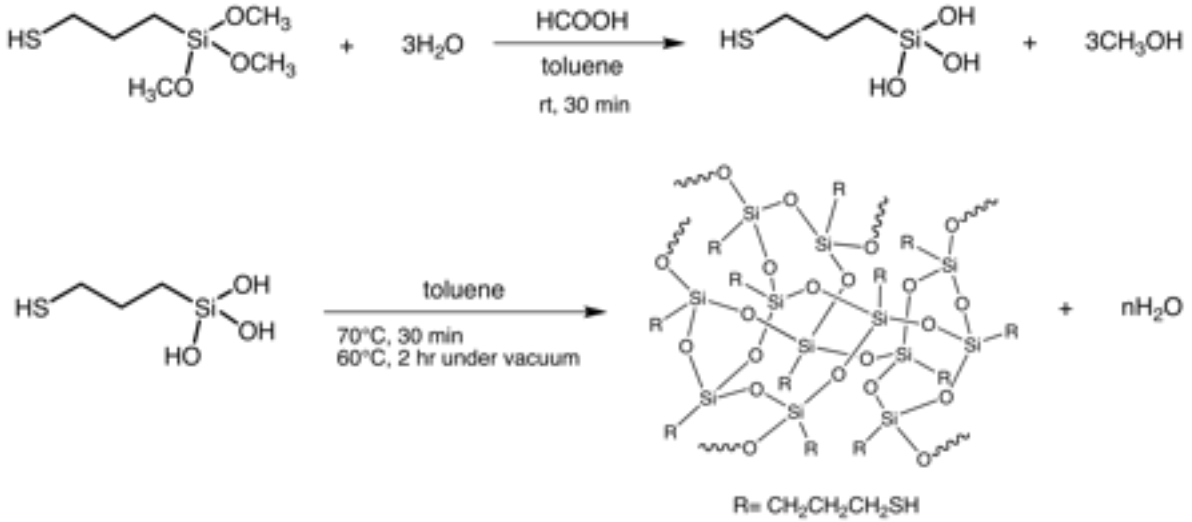
Introduction

Organic-inorganic hybrids are molecularly dispersed nano-composites of organic and inorganic components, which are noted as most attractive materials with improved properties compared to each single materials. These are expected to become new functional materials for versatile advanced applications in many fields. The organic-inorganic hybrids can be prepared by a sol-gel reaction of metal alkoxides and organic polymers, with some interactions such as covalent bonding,[1-5] hydrogen bonding,[6,7] π-π interaction[8] and so on. However, as some amount of alcohol and water are generated by the hydrolysis and condensation of metal alkoxides during a sol-gel reaction for the formation of inorganic components, it is difficult to produce the thicker film of organic-inorganic hybrids because of a generation of crack by shrinking the hybrid materials during the completion of the sol-gel reaction. For resolving this disadvantage, we have studied the preparation of organic-silica hybrids using photo-curable silsesquioxanes which are nano-sized functional materials prepared by the sol-gel reaction of organic substituted trialkoxysilane and expected to generate the novel hybrid materials.[9,10]

On the other, the different combinations of organic and inorganic components have been available in hybrid materials, that there is a great potential for the electrical, optical, structural applications, etc. Especially, as the organic-inorganic hybrid thin films are optically transparent, they are useful optical materials, in which high refractive index is the most important property. It is well-known that organic materials with aromatic ring or sulfur element and inorganic substances such as titania and zirconia have higher refractive index. In this point of view, the refractive index of sulfur compounds is higher than usual organic compounds, so the organic-inorganic hybrids containing sulfur compounds are very interesting optical materials. These hybrids were prepared by a thiol-ene reaction as photo-polymerization containing sulfur elements, which is a radical addition reaction of thiol group to C=C bond. This reaction is an attractive photo-curing system with low shrinkage and no inhibition by oxygen.[11] And this reaction was carried out without any photo-initiators, so it can be prevented from the coloration due to the decomposition of photo-initiators. Therefore, this is a suitable system for optical materials. In this work, the organic-inorganic hybrids were prepared by a thiol-ene reaction using thiol containing silsesquioxanes, and the refractive index of hybrid thin films was evaluated. Furthermore, we investigated to prepare the sulfur containing organic-inorganic hybrid thin films by the simultaneous photo-curing system of thiol-ene reaction and sol-gel reaction using multi thiol compounds and vinyl triacetoxysilane.

Photo-cured organic-inorganic hybrids using thiol-silsesquioxanes

The thiol-containing silsesquioxanes could be prepared from the hydrolysis and condensation of mercaptopropyltrimethoxysilane using formic acid as a catalyst. As shown in Scheme 1, the condensation was carried out under reduced pressure for removing methanol, H_20, toluene, and formic acid. The result of preparation is summarized in Table 1. The co-condensed thiol-silsesquioxanes



Scheme 1

(SQ-2) with phenyl trimethoxysilane can provide the higher inorganic component

a b c d

Table 1. Preparation of thiol-silsesquioxanes and their properties.

Silsesquioxane	Components (mol ratio)	Solid contents (%)	Solvents	Viscosity (mPa·s)	-SH equivalent (g/eq)
SQ-1	a	99	None	10000	135
SQ-2	a:b=2:1	99	None	100000	205
SQ-3	a:c=12:1	75	DME	300	190
SQ-4	a:d=15:1	50	DMDG	100	480

DME ： ethylene glycol dimethylether, DMDG：diethylene glycol dimethylether

of thiol-ene cured hybrid material. And the co-condensed thiol-silsesquioxanes (SQ-3 and SQ-4) using zirconium isopropoxide and titanium isopropoxide can produce the higher refractive index hybrids. Triallylisocianate (TAIC) as a multifunctional allyl compound was reacted with thiol-containing silsesquioxanes under UV irradiation, as shown Figure 1. The progress of reaction could be confirmed by reducing SH and allyl peaks in the Raman spectroscopy.

These hybrid materials could make a thick film under UV irradiation and showed high transparency (transmittance >95% through 30μm film thickness). In comparison from the photo-radical cured thin film of multi-acrylic monomer on a PET film, this thiol-ene cured hybrid thin film showed less shrinkage property from the condition of low curling film. These characteristics are very effective for optical applications. The light resistance was superior to the photo-cured acrylate because there was no coloration due to the decomposition of photo-initiators. And also, these hybrid materials had high heat resistance, which the temperature of 5 wt% and 10 wt% loss of SQ-1/TAIC hybrids were was 374 °C and 384°C correspondingly. showed compared to usual thiol-ene cured hybrid materials. In Table 2 summarized their properties, it was found the hard surface and low thermal expansion. As optical properties of thiol-ene cured hybrid materials, refractive index and Abbe number of hybrid thin films are

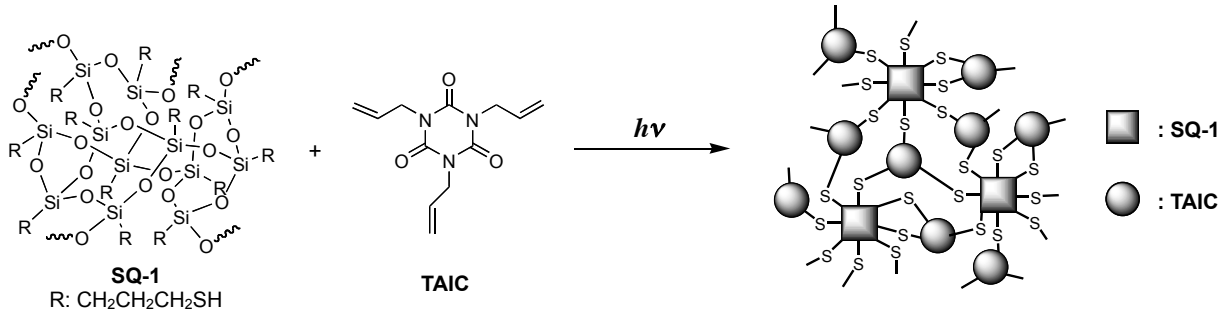


Figure 1. Reaction of sulfur containing nano-hybrid materials from SQ-1 and TAIC.

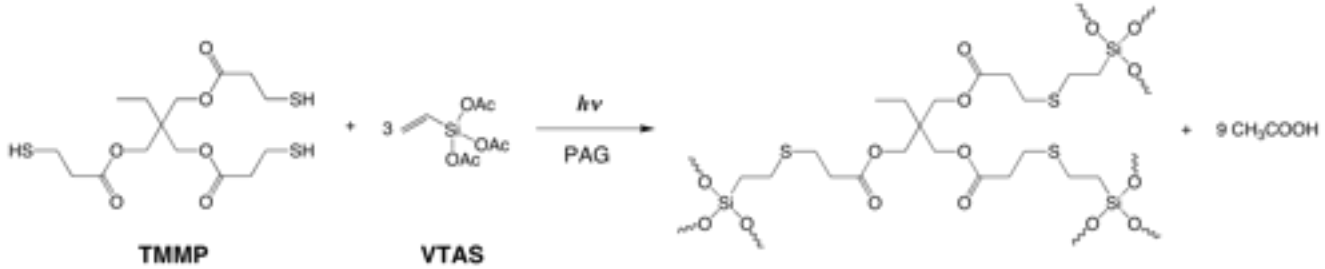
Table 2. Properties of sulfur containing nano-hybrids with thiol-containing silsesquioxane and TAIC.

Silsesquioxane	Water absorption (25°C, 24hr)	Pencil hardness on glass	Coefficient of thermal expansion (ppm/°C) 40-45°C/150-155°C	Refractive index	Abbe number
SQ-1	0.7%	3H	111 / 171	1.55	48
SQ-2	0.7%	3H	102 / 164	1.56	40

relatively high. When paying attention to 1.55-1.56 of the refractive index, a glass fiber composite of SQ-1/TAIC hybrids and a soda glass fiber, which refractive index is 1.56, was formed by the impregnation of glass cloth. After photo-curing the composite, a transparent flexible sheet could be produced with low thermal expansion coefficient, 15 ppm at 100-120°C. These are expected for the transparent optical materials instead of a thin glass sheet.

Photo-cured organic-inorganic hybrid thin film by thiol-ene reaction

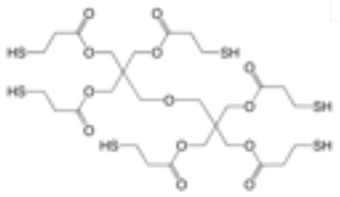
As the materials cured by thiol-ene reaction have high pliability like a rubber, the hybridization with inorganic components such as silica may cause an enhancement of toughness to the flexible film. Therefore, the curing system of thiol-ene and sol-gel reaction was investigated to produce the flexible hard coating materials. The typical reaction is illustrated in Scheme 2, in which trimethylolpropane tris (3-mercaptopropionate) (TMMP) as a multi-thiol compound, vinyl triacetoxysilane (VTAS) as an olefin, and a catalytic amount of photo acid generator (PAG) were used. This Equivalent mercapto and vinyl groups are applied in this reaction. After spin coating on PET and glass, the simultaneous cross-linking reactions were carried out by UV irradiation (300 mJ/cm^2) and post exposure baking at 120 °C for 20 min. Then, the transparent thin films of 5 μm thickness were obtained. And also, the organic-inorganic hybrid with higher silica amount was prepared by the addition of tetraethoxysilane (TEOS) to the above system. The properties are summarized in Table 3. It was found that the addition of TEOS made harder surface and the most interesting result was very high bend performance. When a Mandrel bend test of

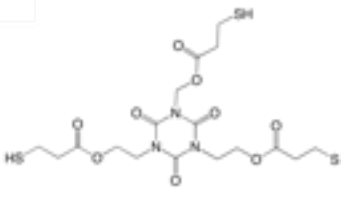


Scheme 2

Table 3. Properties of hybrid thin films prepared by thiol-ene reaction with multi-thiol compounds.

Multi-thiol compounds	TEOS (wt%)	Pencil hardness on PET	Pencil hardness on glass	Mandrel bend test (mm)
TMMP	0	2H	5H	2
TMMP	17	3H	6H	2
TEMPIC	0	2H	4H	2
DPMP	0	2H	5H	2





the organic-inorganic hybrids coated PET film were worked out, the films could be bended around 2 mm mandrel. Therefore, these hybrids have interesting properties of hard and flexible, and they are expected to be new type hard coating materials.

Conclusion

Thiol-ene reaction is one of most effective photo-curing systems. We investigated the preparation of organic-inorganic hybrids by using this reaction and sol-gel reaction, stepwise or simultaneously. Organic-inorganic hybrids were prepared from thiol-silsesquioxanes by the thiol-ene reaction with triallyl compounds. These hybrids formed excellent transparent films, which refractive index were relatively high. The glass composite with same refractive index resulted a flexible transparent sheet. Furthermore, the flexible hard coating hybrid materials were produced by simultaneous thiol-ene and sol-gel reactions of multi-thiol compounds and vinyl triacetoxysilane. These photo-cured organic-inorganic hybrids were promising optical materials.

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