Supplementary Information for

Photo-Curable Siloxane Hybrid Material Fabricated by Thiol-Ene Reaction of Sol-Gel Synthesized Oligosiloxanes

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A. Experimental Section

Materials

(3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%, Aldrich) and diphenylsilanediol (DPSD, Gelest) were used as precursors for sol-gel condensation without further purification. Barium hydroxide monohydrate, $Ba(OH_2)\cdot H_2O$ (BH, Aldrich), was used as a catalyst to promote the sol-gel condensation, making basic condition. Also, vinyltrimethoxysilane (VTMS, 98%, Aldrich) and DPSD were used as precursors and *p*-xylene (Aldrich) was added to the solution during the reaction as a solvent for synthesis of vinyl functionalized oligosiloxane. 2, 2-dimethoxy-2-phenyl-acetophenone (BDK, Aldrich) was used to initiate the thiol-ene reaction. The amounts of contents of all reagents as received were used to calculate the chemical composition. In addition, a methacrylate hybrimer was prepared by UV irradiation as previously reported to compare structures derived by typical radical polymerization and the thiol-ene reaction.[S1]

Synthesis of MPO and PVO by sol-gel condensation

Mercaptopropyl-phenyl-oligosiloxane (MPO) was synthesized from organoalkoysilanes, MPTMS and DPSD, by non-hydrolytic sol-gel condensation. Both precursors were mixed with BH as a catalyst (0.1mol% of the total silane compound). The molar ratio of DPSD over MPTMS was 60mol%. After adding DPSD to the solution, a 4 h reaction proceeded to complete the condensation. The solution was stirred with a magnetic stirrer during the reaction at 80°C. Methanol, a by-product derived by condensation between the precursors, was removed by vacuum heating. BH was filtered by a using 0.45*um* pore-sized Teflon filter.

Phenyl-vinyl-oligosiloxane (PVO) was also synthesized by non-hydrolytic sol-gel condensation between VTMS and DPSD. 20wt.% of *p*-xylene was added to the total solution. Other further processes corresponded with the synthesis of MPO.

Fabrication of sulfur hybrid material by thiol-ene reaction

The synthesized MPO and PVO were mixed such that the molar ratio between the thiol group in MPO and the vinyl group in PVO was one. Subsequently, a photo-initiator (BDK) in an amount of 1mol% of the thiol group in MPO was added to the thiol-ene mixture (MPO and PVO).

The thiol-ene mixture was poured and casted in 2mm (transmittance measuring) and 200*um* (dynamic mechanical analysis and thermomechanical analysis) thick glass plates. The casted samples were irradiated with a 365nm mercury lamp (light intensity=85mW/cm^2) in air for 3min. The glass plates were previously coated with HMDS (hexaphenylcyclotrisiloxane, Aldrich) to allow easy detachment of the cured samples. Also, a thin film (thickness=2*um*) of the thiol-ene mixure with 50wt.% of propylene glycol monomethyl ether acetate (PGMEA, Aldrich) was spin-coated at 3000rpm for 30sec on glass to measure the refractive index and a thiol-ene reaction with a mercury lamp was subsequently performed as described above. All prepared samples were heat-treated at 150°C under vacuum for 2h for further densification. The reaction of thiol from MPO with ene in PVO resulted in the phenyl-sulfur hybrimer.

The thiol-ene mixture with 50wt.% of PGMEA was spin-coated as above and cured by the aforementioned method on ITO glass and gold dots were thermally evaporated on the phenyl-surfur hybrimer in order to fabricate a MIM (Au/passivation layer/ITO) structure. This structure was used to measure the electric properties of the phenyl-sulfur hybrimer.

Another sample for photo-pattering was prepared according to the following procedure. A thiol-ene mixture with 50wt.% of PGMEA was spin-coated at 100rpm on glass for 30 sec and heat-treatment of 100°C was applied for 10min to evaporate the solvents. The sample was then selectively exposed for 10s with a mercury lamp using a patterned photo-mask. After UV irradiation, the film was developed in *n*-propylacetate for 30sec and residual material was washed out with acetone and deionized water.

Characterization

The structure of MPO was estimated by ^{29}Si nuclear magnetic resonance (NMR) spectroscopy using a FT 600MHz (Bruker Biospin, DMX600) instrument. The MPO was diluted in 30vol% of chloroform-*d*. Chromium(III) acetylacetonate was added as a spin relaxation agent of silicon at a concentration of 30mg/L. Fourier transform-infrared (FT-IR) spectroscopy (JASCO, FT-IR 460 plus) was used to confirm functional groups in MPO and the existence of cyclic species in MPO was confirmed by Fourier transform-Raman (FT-Raman) spectroscopy (Bruker, RFS 100/S)

The optical transmittance of the phenyl-sulfur hybrimer, which was fabricated with dimensions of 2cm×2cm×0.2cm (L×W×H), was measured by a UV/Vis/NIR spectrophotomether (Shimadzu, UV3101PC). The refractive index was measured by a prism coupler (Metricon, 2010) at 632.8nm at 25°C. Dynamic mechanical analysis (DMA) of the sample derived by the thiol-ene reaction was carried out using a DMA 2980 dynamic mechanical analyzer (TA. Instruments, Inc., New Castle, DE) by heating the samples from -50°C to 150°C at a heating rate of 2°C/min and at a frequency of 1Hz in air. The dimensions of the sample were set as 4.457mm×2.615mm×0.2mm (L×W×H). A thermogravimatric analysis (TGA) was performed from 30°C to 800°C at a heating rate of 5°C/min in N_2/air using a TGA Q50 (TA. Instruments, Inc., New Castle, DE).

The electric properties such as the dielectric constant and leakage current density were measured using a HP4194A (Aglient Technologies) impedance/gain analyzer and a Keithley 237 source-measure unit (Keithley) in a dark room.

Micrographs of the photo-patterned film were taken by scanning electron microscopy (SEM, Hitachi S-4800). The oxygen permeability was measured by a permeability analysis (MOCON, OX-TRAN Model 2/21) at 23°C and 0% relative humidity. And the water vapor permeability was characterized by a permeability analysis (PERMATRAN-W Model 3/33) under conditions of 100% relative humidity, 37.8°C, and 10sccm of N_2 flow rate. Both sample sizes for measuring the permeabilities were same as 5cm×5cm×0.0115cm (L×W×H).

B. Supplementary figures

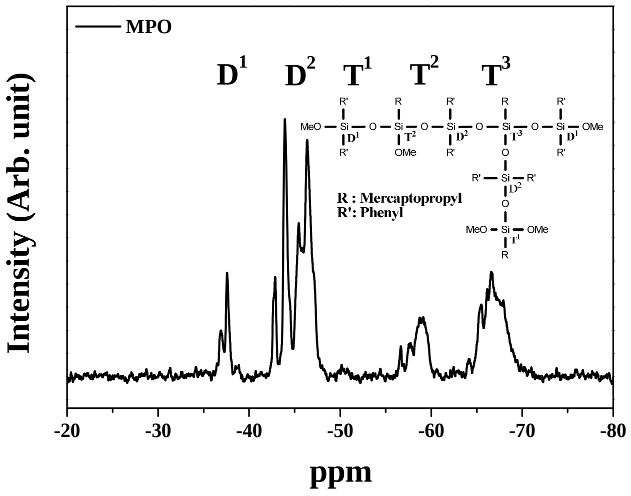

Fig. S1 ^{29}Si NMR spectrum of mercaptopropyl-phenyl-oligosiloxane (MPO). The chemical shifts indicate the Si nucleus species.

^{29}Si NMR spectroscopy is a particularly effective tool to confirm the structure of silicon-based material since different chemical environments of the Si nucleus can be recognized through shifts of the Si resonance line. As shown in Fig. S1, the ^{29}Si NMR spectrum of MPO was obtained and the chemical shifts represent its silicon backbone structure and the degree of condensation (DOC) of MPO can be calculated from dimeric (D) and trimeric (T) species of Si in siloxane bonds by the following equation.[S2]

$$\mathrm{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100 \qquad \text{(S1)}$$

The chemical shifts of D and T species by ^{29}Si NMR spectroscopy are given in Table S1. The calculated DOC based on a result from the ^{29}Si NMR spectrum of MPO is 91.6%. This high value indicates that the non-hydrolytic sol-gel condensation between the two chemical silane precursors is successfully carried out. A transparent and viscous oligosiloxane with thiol groups from MPTMS and phenyl groups from DPSD was prepared for the thiol-ene reaction.

Table S1 Chemical shifts of ^{29}Si NMR depending on the bonding structure of Si in MPO.

Species	Chemical shift (ppm)
D^0	-29~-34
D^1	-36~-38
D^2	-42~-47
T^0	-49~-51
T^1	-57~-61
T^2	-65~-69

The FT-IR peaks of the thiol groups (2570cm^{-1}) in MPO and vinyl groups (1600cm^{-1}) in PVO disappeared after the thiol-ene reaction from the initial mixture state, as shown in Fig. S2.[S3, S4]

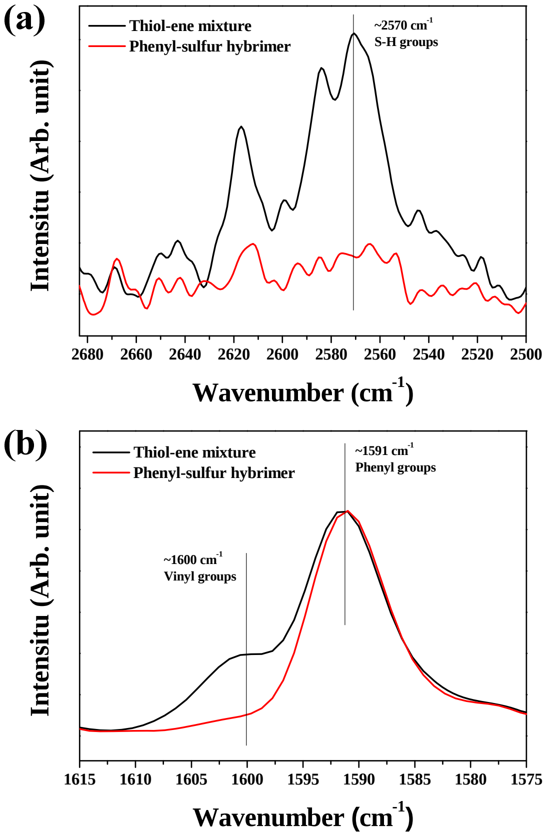

Fig. S2 FT-IR analysis of thiol-ene mixture (MPO and PVO) and phenyl-sulfur hybrimer. (a) thiol groups approximately at 2570cm^{-1} disappeared after the thiol-ene reaction and (b) vinyl groups at around 1600cm^{-1} were also used for the thiol-ene reaction, resulting in reduction of the intensity of peaks at around 1600cm^{-1}.

The phenyl-sulfur hybrimer was fabricated as a thin film (2*um*) and in bulk (2mm) form to measure its optical properties. The high atomic refraction of sulfur and high electronic polariziability of phenyl groups in the material produce high refraction (n=1.5847, at 632.8nm, 25°C). As shown in Fig. S3, the casting material with a bulk shape and 2mm thickness shows high transmittance (80.7% at 450nm). The inset in Fig. S3 exhibits the transparency of the phenyl-sulfur hybrimer. The sulfur embedded in siloxane chains by the thiol-ene reaction yielded a high transparency with high refractive index. The thiol groups are available to photo-cure the oligosiloxane for application as optical materials and also simultaneously increase the refractive index due to their sulfur content.

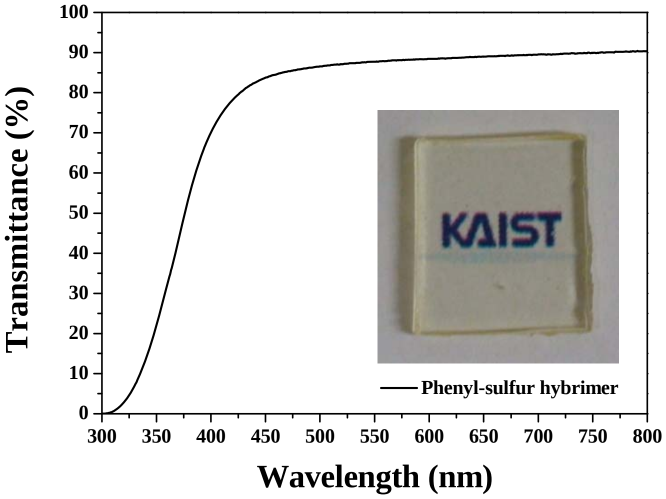

Fig. S3 Transmittance of the phenyl-sulfur hybrimer depending on wavelength. The inset shows the transparent bulk sample with 2mm thickness.

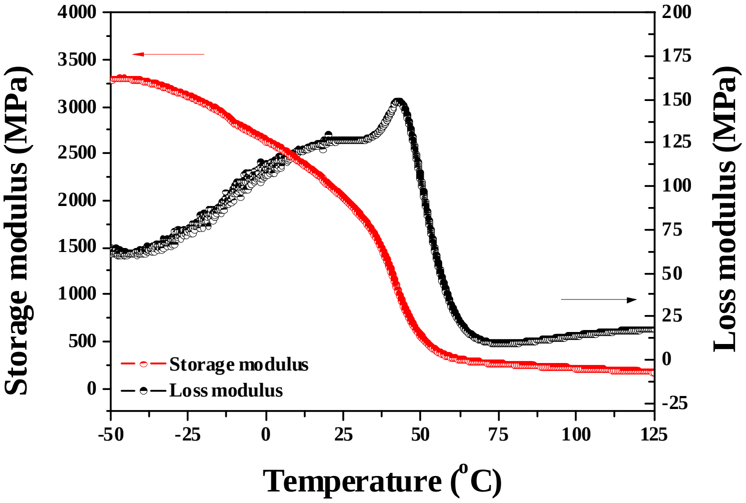

Fig. S4 The storage modulus and the loss modulus of the phenyl-sulfur hybrimer depending on temperature by dynamic mechanical analysis (DMA).

The storage modulus and the loss modulus of the material produced through the thiol-ene reaction without homopolymerization, determined by a dynamic mechanical analysis (DMA), are given in Fig. S4. The storage modulus, which represents the elastic portion of the material, is approximately 3300MPa at glass state, and approximately 183MPa at rubbery state. There is a rapid decrease in the storage modulus around the glass transition temperature (48.4°C). The resulting networks between the siloxane back-bone of oligosiloxane and thioether generate a broad loss modulus graph at the region of the glass state while a sharp loss modulus graph is shown in the material with only polysiloxane or thioether networks. This indicates that the material derived by thiol-ene reaction of oligosiloxanes is homogeneously bridged with both oligosiloxane and thioether networks.

In Table S2, the properties of the phenyl-sulfur hybrimer are summarized including the oxygen and water vapor permeabilities and 5wt.% loss temperature by TGA. Its oxygen and water vapor permeabilities are higher compared with typical polydimethysiloxane values (1.6×10^{24}cc mil/m^2·day and 3.14×10^3gm mil/m^2·day, respectively).[S5, S6] The TGA results reveal that the 5wt.% loss temperature is approximately 364/374°C in N_2/air. This high thermal stability is enhanced by siloxane networks and high cross-linking density of thioether.

Table S2 The characteristics of the phenyl-sulfur hybrimer.

Property	**Unit**	**Value**
Refractive index	n, at 632.8nm, 25°C	1.5847
Transmittance	%, at 450nm	80.7
5wt.% loss temperature (TGA in N_2/air)	°C	364/374
50wt.% loss temperatrure (TGA in N_2/air)	°C	-/597
Residue at 800 °C (TGA in N_2/air)	wt.%	53/36
Glass transition temperature (DMA)	°C	48.4
β-transition (DMA)	°C	5.7
Oxygen permeability	cc mil/m^2·day	1.98×10^3
Water vapor permeability	gm mil/m^2·day	1.35×10^2
Dielectric constant	ε	4.134
Leakage current density	nA/cm^2	2.79

As shown in Fig. S5, the TGA graphs in N_2/air of the phenyl-sulfur hybrimer are plotted. The thermal decomposition in air was slow down compared to the thermal decomposition in N_2. It can be explained by condensed phase oxidation of the phenyl-sulfur hybrimer resulting in further tight crosslinking of the molecules with increasing thermal stability.[S7, S8]

However, 50wt.% loss temperature was low in the case of TGA in air due to thermal-oxidative decomposition of organic components. And silica (36wt.%) by oxidation was left as a white residue after TGA. On the other hand, TGA in N_2 has 54wt.% of a black residue (silicon carbide) after TGA.[S7, S8]

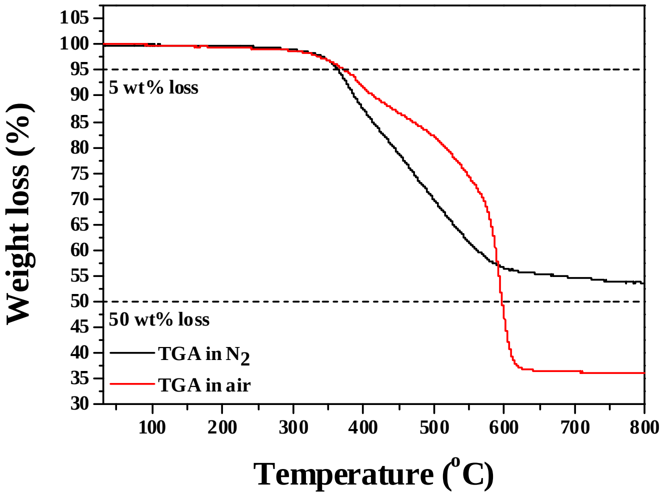

Fig. S5 The thermogravimatric analysis (TGA) graphs of the phenyl-sulfur hybrimer in N_2/air.

C. References

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