COMMUNICATION

Photo-curable siloxane hybrid material fabricated by a thiol–ene reaction of sol–gel synthesized oligosiloxanes†

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The thiol–ene reaction of a sol–gel synthesized oligosiloxane thiol–ene mixture was processed through UV irradiation, resulting in transparency, high refractive index, good thermal stability and especially excellent electrical insulation materials. It provides new strong potential of the thiol–ene system for application in dielectric materials.

Photo-curing is an effective tool that has been applied in numerous applications, such as optical and electric devices.[1–5] The advantages of photo-curable systems have been well documented and include a solvent-free process, a fast and controllable curing system, lower energy consumption than thermal curing, and the possibility of curing at room temperature.[6–9] However, drawbacks of typical photo-polymerization processes have also been noted, with oxygen inhibition, shrinkage, and the formation of heterogeneous networks.[10–15] In particular, oxygen inhibits polymerization, since it reacts with the initiator, and primary and polymer radicals, forming peroxy radicals that terminate further polymerization.

A thiol–ene reaction is a photo-polymerization reaction mechanism that is widely used to reduce oxygen inhibition through a step-growth free-radical process between thiols and enes.[16] The reaction brings about unprecedented characteristics in comparison with other typical radical polymerization techniques.[17] The heteroatom-linked system with efficient properties, as described above, has been classified as click chemistry and was described by Sharpless *et al.* in 2001.[18,19] The properties of the thiol–ene reaction are consistent with the terms of click chemistry.[20–23]

The thiol–ene reaction, which is simple and results in high yields without by-products, has recently received considerable attention for possible new applications. The thiol–ene reaction can be adapted and developed in diverse regions of research and applications such as patterning procedures, functionalized polymers, and biological polymers. In order to extend the thiol–ene reaction to practical applications with unique properties of the thiol–ene system, extensive and diverse research is still necessary.

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However, the thiol monomers used as precursors for synthesizing polysulfides have a pungent odor due to their sulfur content. Considering issues such as thiol odor and shelf-life stability, these issues should be addressed by new synthetic methods.

The multifunctional thiol and vinyl groups, respectively, in an inorganic (oligosiloxane) network prepared by a sol–gel process were used in the thiol–ene reaction between highly condensed oligosiloxanes. The networks of thioether containing sulfur provide distinctive properties to organic–inorganic hybrid materials. The results will first focus on the synthesis of odorless and stable thiol functional oligosiloxanes by non-hydrolytic sol–gel condensation.

The thiol–ene reaction is known to be influenced by the basic structure of the thiol groups, such as alkyl thiols, thiophenols, thiol propionates, and thiol glycolates, as well as three or four multifunctional thiols. Thus, increasing the functionality of the thiol group in the thiol–ene mixture leads to increased thioether network connectivity, adding mobility restrictions to the early polymerization, decreasing oxygen diffusivity, and increasing the thiol–ene reaction rate.[24]

A multifunctional thiol group substituted oligosiloxane (mercaptopropyl-phenyl-oligosiloxane, MPO) was synthesized with chemical precursors by a non-hydrolytic sol–gel process. The hydroxyl groups (–OH) in diphenylsilanediol (DPSD), which are partially negatively charged, facilitate nucleophilic attack to the partial charge of Si in (3-mercaptopropyl)-trimethoxysilane (MPTMS) and the subsequent procedure of hydrogen transition to methoxy groups (–OCH$_3$) yields methanol as a by-product. The generated methanol was removed by
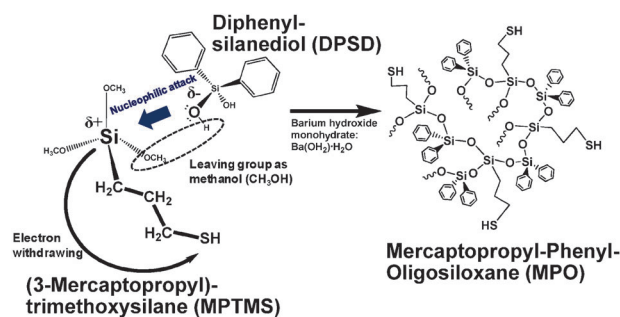
Scheme 1 Non-hydrolytic sol–gel condensation between MPTMS and DPSD, synthesizing MPO.

vacuum heating. Scheme 1 describes the non-hydrolytic sol–gel condensation procedure between MPTMS and DPSD.

pH dependence of the sol–gel process is well known and is one of the critical factors to control the sol–gel process. Barium hydroxide monohydrate was used in this research to promote a weak base atmosphere, which can accelerate the condensation reaction. The sol–gel process is also sensitive to inductive effects of substituents on silicon atoms. The acidity (electron withdrawing ability) of the substituents increases in the following order: $-OPr^i < -OEt < -SH < -OH$.[25] Even though the steric hinderance due to the long alkyl chain in the mercaptopropyl group in MPTMS affects the condensation reaction, the strong acidity of the thiol group (–SH) makes it possible to increase the reaction rate and accelerate condensation. As a result of the inductive effect, highly condensed oligosiloxane with a degree of condensation of up to 91.6% can be synthesized as confirmed by the ^{29}Si NMR spectroscopy (see Fig. S1 in ESI†). Also, oligosiloxane with vinyl groups, phenyl-vinyl-oligosiloxane (PVO), was prepared as a composite of the thiol–ene mixture in this paper and characteristics of PVO were described in detail in a previous work.[26]

The thiol–ene mixture (MPO and PVO) with a photo-initiator (BDK) was cast and photo-cured by a mercury lamp in air, as described in the experimental section in ESI.† If the typical radical polymerization procedure is performed in air, the oxygen scavenges and effectively terminates photo-initiated radicals, resulting in reduction of polymerization while the thiol–ene reaction is not inhibited by air.[24,27–29] Peroxy radicals formed by oxygen with an initiator or other radicals generally are not reactive to further polymerization, but they can abstract hydrogen from thiol groups, generating thiyl radicals for the thiol–ene reaction. As a result of the thiol–ene reaction of the prepared thiol–ene mixture, a thioether bridged organic–inorganic hybrid material, phenyl–sulfur hybrimer, was fabricated. Subsequently, thermal aging at 150 °C under vacuum for 2 h was carried out for further densification.

The homopolymerization between vinyl groups in PVO is restricted by oxygen inhibition in the typical polymerization procedure, as well as by the steric hinderance of PVO, which arises from the short chain length of vinyl groups compared with their bulky branched linear siloxane backbone. Thus, photo-curing in this research cannot promote typical radical polymerization between PVOs, while the thiol–ene reaction is the dominant procedure for photo-curing of the MPO and PVO mixture.

As shown in Scheme 2, the phenyl–sulfur hybrimer was fabricated by identical consumption of thiol and vinyl groups in the thiol–ene mixture of MPO and PVO through a thiol–ene reaction (see Fig. S2 in ESI†). The thiol–ene reaction can be processed by UV irradiation, and this photo-curable property can be exploited for diverse optical and electric device applications. Shown as insets in Scheme 2, micrographs of the photo-patterned phenyl–sulfur hybrimer are taken by SEM. The pattern has approximately 130 μm height and 80 μm width. The photo-cured material fabricated by the thiol–ene reaction also shows high transparency even with high bulk thickness (2 mm) (see Fig. S3 in ESI†).
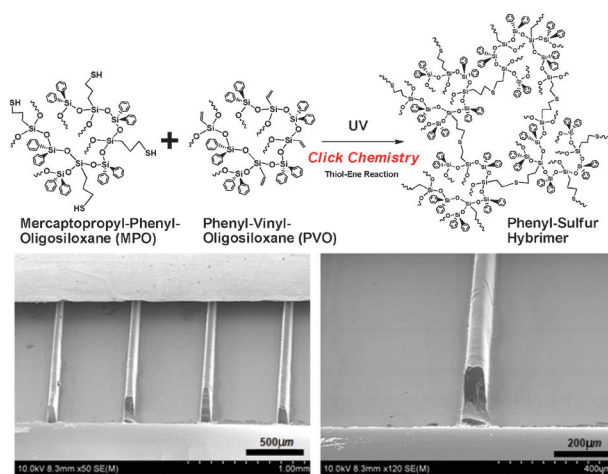
Scheme 2 The thiol–ene mixture of MPO and PVO was cured with BDK as a photo-initiator through the thiol–ene reaction by UV irradiation. The phenyl–sulfur hybrimer was fabricated by thioether cross-linking networks of oligosiloxanes. Insets are tilted SEM micrographs of the photo-patterned phenyl–sulfur hybrimer on a glass substrate.
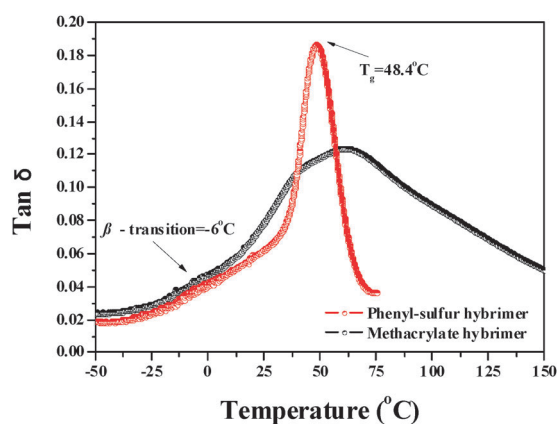

Fig. 1 Tan δ of the phenyl–sulfur hybrimer and the methacylate hybrimer depending on temperature.

The tan δ determined by dynamic mechanical analysis (DMA) of the phenyl–sulfur hybrimer is plotted in Fig. 1 with that of the methacrylate hybrimer,[30–32] the structure of which is formed by typical radical polymerization. The tan δ of the phenyl–sulfur hybrimer shows a narrow glass transition temperature range compared with the methacrylate hybrimer, since thioether networks have a more uniform structure than structures in methacrylate networks. One of the unprecedented properties of the thiol–ene system is the narrow width of tan δ which represents its homogeneous structure.

The β-transition (−6 °C) is shown in both the tan δ graphs of phenyl–sulfur and the methacrylate hybrimer due to incorporation of oligosiloxane. The main glass transition temperature of the phenyl–sulfur hybrimer is approximately 48.4 °C due to the thioether networks. The storage modulus and loss modulus are plotted in Fig. S4 in the ESI.†

The electric properties of the phenyl–sulfur hybrimer were demonstrated, as shown in Fig. 2. We have focused on the properties that can extend thiol–ene systems for application in further diverse fields. The following dielectric constant and
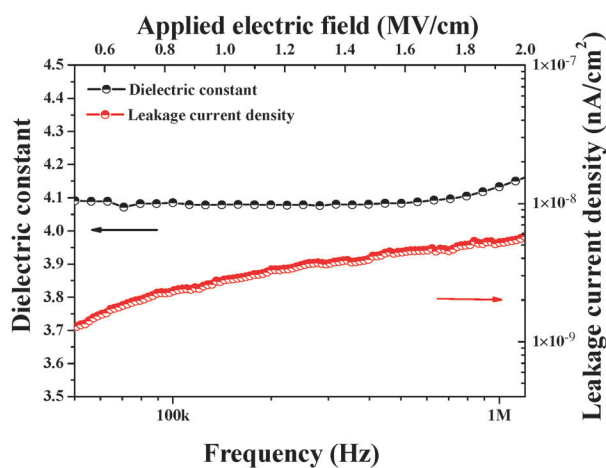
Fig. 2 The dielectric constant and the leakage current density of the phenyl–sulfur hybrimer depending on frequency (Hz) and the applied electric field (MV cm^{-1}).

low leakage current density properties of the newly fabricated thiol–ene system reveal strong potential for the extension and development of thiol–ene systems.

The dielectric constant of the phenyl–sulfur hybrimer is 4.134 at 1 MHz, and the leakage current density is 2.79 nA cm^{-2} at 1 MV cm^{-1} as shown in Fig. 2. The leakage current density represents the dissipated current in the phenyl–sulfur hybrimer film as the passivation layer between the metal contacts of the source or drain and ITO pixel electrodes in thin film transistors for display applications. The low value of leakage current is a result of highly condensed oligosiloxane and especially the homogeneous structure of thioether networks formed by the thiol–ene reaction. The leakage current density of the phenyl–sulfur hybrimer is much lower than that of soluble polymers such as poly(4-vinylphenol), which was reported to have a relatively high value of around 100 nA cm^{-2} at 1 MV cm^{-1}.[33] It is also lower than the values of previously reported siloxane-based materials.[34–36] The uniformity of the structure caused by high cross-linking density with siloxane networks prevents leakage current in the film. Also, the high dielectric constant value is due to high refraction of the sulfur content and high electronic polarizability of the phenyl groups.

In Table S2 in the ESI†, the optical, thermal, and electrical characteristics of the phenyl–sulfur hybrimer are summarized including low water vapor and oxygen permeability compared to other polysiloxane materials. These unprecedented properties of the hybrid material fabricated by the thiol–ene reaction present a solution for limits on applications of typical photo-curable materials.

In summary, a thiol–ene mixture was prepared by sol–gel process synthesized oligosiloxanes. The mixture was then photo-cured to fabricate a novel hybrid material. Excellent insulating characteristics with a high dielectric constant were demonstrated for the first time. We confirmed the new properties of the sol–gel derived thiol–ene system for application in dielectric materials.

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