



## Fabrication of photo-crosslinkable polymer/silica sol–gel hybrid thin films as versatile barrier films



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### ABSTRACT

Versatile films composed of a photo-crosslinkable thiol-ene (ThE)/silica sol–gel hybrid nanocomposite were prepared using a two-step process. Tetrafunctional thiol and triene monomers were employed as precursors to generate a matrix polymer. Tetraethyl orthosilicate (TEOS) was incorporated as the silica source for the sol–gel process. A two-step process, sol–gel reaction followed by photocuring, resulted in uniform and transparent hybrid thin films. The formation of homogeneous, mechanically stable, and optically transparent films was confirmed and the films were characterized by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyses. The morphological properties of the films were assessed by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The thermal expansion of the obtained membrane films was examined by thermomechanical analysis (TMA). In addition, optical transmission and gas permeation were assessed for high-performance applications.

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### Introduction

Recently, thiol-ene (ThE) systems have shown a high degree of uniformity in their physical properties and exhibit many desirable features [1–5]. ThE systems are based on a combination of multifunctional thiol and ene monomers that undergo photopolymerization (photo-crosslinking) upon ultraviolet (UV) irradiation [6–12]. This simple photopolymerization resulted in a homogeneous and crosslinked polymer network [6]. Accordingly, ThE chemistry has attracted enormous interest due to its high reaction rate and quantitative conversion [13–15]. Compared to conventional polymerization schemes, ThE photopolymerization provides multiple advantages, including high reaction rates under ambient conditions, low shrinkage at high conversion, and versatility in monomer selection [16–20].

Fundamental ThE polymerization is a two-step radical chain process encompassing a propagation/chain transfer leading to a thiol addition across the double bond. Because of

this essentially quantitative conversion, photocured ThE films are highly homogeneous and dense. Dynamic mechanical analysis have confirmed the uniform structure of the ThE network obtained from photopolymerization, which is critical for high performance applications [9]. The photocuring of ThE is efficient and environmentally benign, making it useful for obtaining uniform and stable coatings [21,22], membranes [23–25], and optical elements [26]. This process has been employed extensively in surface modification [27–31], self-healing [32–34], interfacial engineering [35,36], and sensing [37,38] applications.

In spite of these advantages, ThE systems have historically suffered from undesirable mechanical properties and surface hardness due to the flexibility of thio-ether linkages and their relatively low crosslinking density [9–12]. Improvements to the mechanical characteristics of ThE systems are highly desirable, especially for coatings. In previous work, the hardness of UV-curable ThE thin films was increased without sacrificing optical transparency through the introduction of hyperbranched polymers [39]. This enhancement, however, was insignificant to the overall mechanical properties of the material. Conversely, the incorporation of an inorganic clay effectively enhanced the mechanical properties of ThE/clay hybrid thin films [40] but with a deterioration in optical transparency.

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Therefore, a method to produce ThE thin films retaining both their mechanical durability and optical transparency is highly desirable. The addition of a silica network, created via a sol-gel reaction, into a photocurable ThE polymer network is simple, reproducible, and yields a processable material under mild conditions. It is further expected that the resulting ThE/silica hybrid thin films would be favorable for multiple and diverse purposes. Research toward this end has been conducted [41–45], in which thiol-terminated silica precursors were employed for sol-gel reaction and subsequent photopolymerization. In those cases, however, the efficiency of photopolymerization was relatively low because alkoxide groups in the silica precursor reduce the reactivity of thiols toward ene groups. Therefore, selection of both thiols and enes, span of process window, and availability of other additives has been significantly narrow compared with the approach employed in this study. Even worse, the properties of obtained thiol-ene/silica hybrid materials have not been always excellent.

In the present work, silica networks were generated solely from sol-gel reactions using tetraethyl orthosilicate (TEOS). Subsequently, pre-formed silica network was incorporated into the thiol-ene mixture. Photopolymerization proceeded in parallel upon UV irradiation to generate a ThE polymer matrix foundation. That is, the progress of sol-gel reaction was not remarkably suppressed by the presence of other reagents such as thiol and ene. Simultaneously, the photopolymerization of thiol-ene was not hindered by relatively fast hydrolysis and condensation reactions of TEOS. This enhanced the efficiency of both the sol-gel and ThE photocuring reactions. Detailed investigations of the structural, mechanical, thermal, and optical properties of the obtained ThE/silicate hybrid thin films were performed using diverse instrumentation. Finally, the prepared thin films were extensively evaluated for use as barrier films.

## Experimental

### Materials

Tetrafunctional thiol-[pentaerythritol tetrakis(3-mercaptopropionate)], trifunctional ene-[1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione], photoinitiator-[Irgacure 754], and TEOS were purchased from Aldrich (Milwaukee, WI, USA) and used as received. Fig. 1 shows the chemical structures of thiol and ene molecules used in this study.

### Formation of ThE/silica hybrid thin films

Fig. 2 shows a schematic diagram detailing the formation of hybrid thin films. Thiol (0.8 g) and ene (0.528 g) were mixed using a mechanical method and dissolved in acetone to produce solution A. The solvent was evaporated at room temperature under vacuum for approximately 20 min and the remaining solution was degassed subsequently for approximately 5–10 min. Then, a trace amount of photoinitiator (Irgacure 754) was added to the obtained solution and mixed with mild magnetic stirring to prevent polymerization. In a separate vessel, TEOS (0.2 g) was dissolved in a small amount of acetone and mixed with a trace amount of acetic acid to generate solution B. The solution was stirred for 1 h to promote the hydrolysis and condensation of TEOS, resulting in a silica network. The residual solvent was dried and the two solutions were mixed under mild stirring to produce thin film precursor solution C.

An amount of solution C was poured between two glass plates that had been coated with alumina film. The distance between the plates was controlled by the thickness of a spacer material. The film preparation apparatus (D in Fig. 2) was inserted into a UV

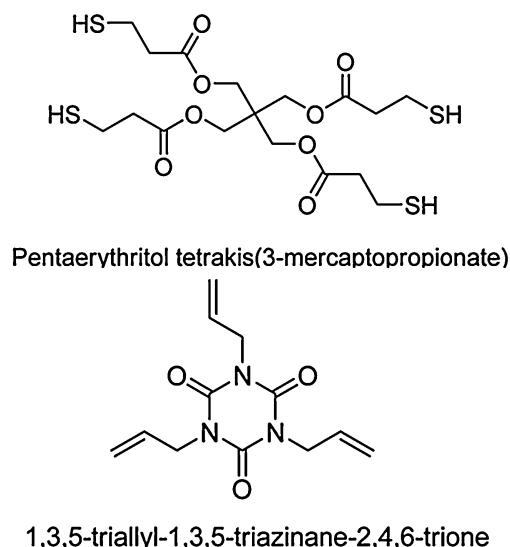


Fig. 1. Chemical structures of (a) tetrafunctional thiol and (b) trifunctional ene monomers.

(5–10 mW/cm<sup>2</sup>) curing chamber. The precursor solution was cured under irradiation for 10–30 min and post-cured at 60 °C without UV irradiation for at least 6 h to promote the formation of a silicate network. The obtained films were detached from the apparatus manually.

### Instrumentation

Differential scanning calorimetry (DSC) thermograms were recorded on a Texas Instruments (Dallas, TX, USA) TA2010 differential scanning calorimeter at a heating rate of 5 °C/min under nitrogen from room temperature to 200 °C. Thermomechanical analysis (TMA) curves were acquired with a Texas Instrument (Texas, USA) TA Q400 with an applied force of 0.05 N from room temperature to 150 °C. X-ray diffraction (XRD) diffractograms were collected with a Rigaku D-max/3C X-ray diffractometer (Tokyo, Japan) at 10°/min. Surface morphology was monitored with a Digital Instruments Dimension 3100 atomic force microscope (AFM; Digital Instruments, Santa Barbara, CA, USA) in tapping mode. Transmission electron microscopy (TEM) micrographs were obtained with JEM-200CX equipment (Jeol, Tokyo, Japan) with an acceleration voltage of 200 kV. To prepare a TEM sample, the hybrid thin film precursor solution (solution C) was spin-coated onto a silicon wafer bearing a 250-nm silicon oxide layer. The silicon oxide layer was then etched away with an aqueous solution of 3 wt% hydrofluoric acid (HF). The presence of polymeric network can prevent the loss of sol-gel silica network in the hybrid film during sample preparation. The separated thin film was retrieved with a copper grid. Light transmittance in the visual range (360–740 nm) was measured with a CM3600d spectrophotometer (Minolta, Osaka, Japan). The measurement time was approximately 2 s.

To assess the performance of the obtained ThE/silica hybrid thin films as barriers, the permeabilities of water vapor and oxygen were measured with Aquatran model 1 and Oxytran 2/21 instruments, respectively (Mocon Inc., Brooklyn Park, MN, USA). A continuous-flow testing cell method approved by the ASTM (D3985) was used. All measurements were carried out at 20 °C and 0% relative humidity. For this experiment, water vapor/oxygen was the test gas and inert nitrogen was the carrier gas in this study. For measurements of oxygen permeability, helium might be considered a more desirable carrier gas because of its low molecular

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