

From Gas Barriers to High Gas Flux Membranes:

UV-Cured Thiol-ene Networks for Transport Applications

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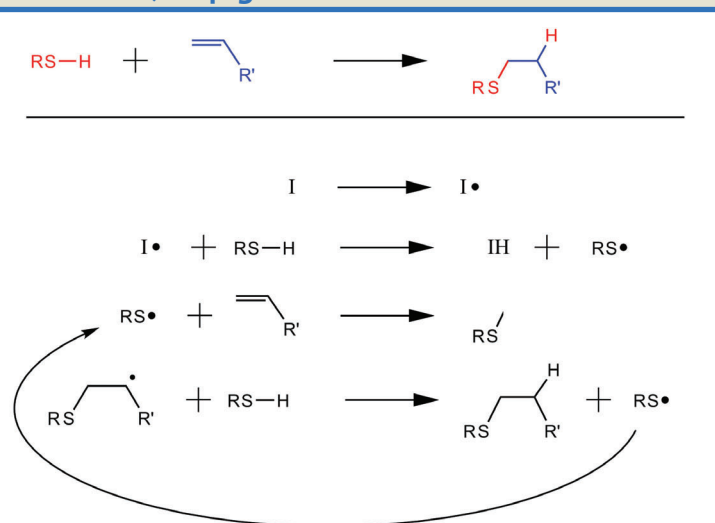
The success of UV curing has been largely determined by its inherent advantages such as high reactive efficiency; eco-friendly formulations that do not emit volatiles; and the possibility of using a variety of processing techniques (i.e., spraying, dipping or rolling of a reactive mixture on a substrate prior to curing which occurs in seconds with UV light).^{1,2} The majority of UV-cured materials used commercially today are acrylates which form network polymers via a

UV-initiated, free-radical chain-growth polymerization mechanism. However, acrylates typically suffer from two inherent drawbacks—shrinkage and oxygen inhibition. Like in acrylates, network formation in thiol-enes often requires free radicals that can be UV-initiated. However, the polymerization mechanism is very different. Polymerization of thiol-enes is a step-growth radical reaction as shown in Figure 1 with a chain transfer step in which carbon-centered radicals abstract hydrogen from thiols, thus regenerating thiyl radicals which continue the polymerization process.^{3,4} Benefiting from this unique mechanism, thiol-ene reactions are practically insensitive to oxygen inhibition. It should be noted that, depending on the electronic character of the ene, the thiol-ene reaction may also proceed via a nucleophile-catalyzed anionic mechanism. The nucleophile-catalyzed anionic addition, called thio-Michael addition, proceeds with electron-poor double bonds such as acrylates.⁵

Thiol-ene networks have been widely studied and are known for their low shrinkage, narrow glass transitions, and overall uniformity as compared to traditional photopolymerized networks. Modularity is another strong advantage of thiol-ene networks. A variety of commercially available thiol and ene

FIGURE 1

Free-radical, step-growth thiol-ene mechanism



This mechanism proceeds for any thiol and any ene, initiated typically with UV light and a photoinitiator (I). Net reaction shown at top in red/blue.

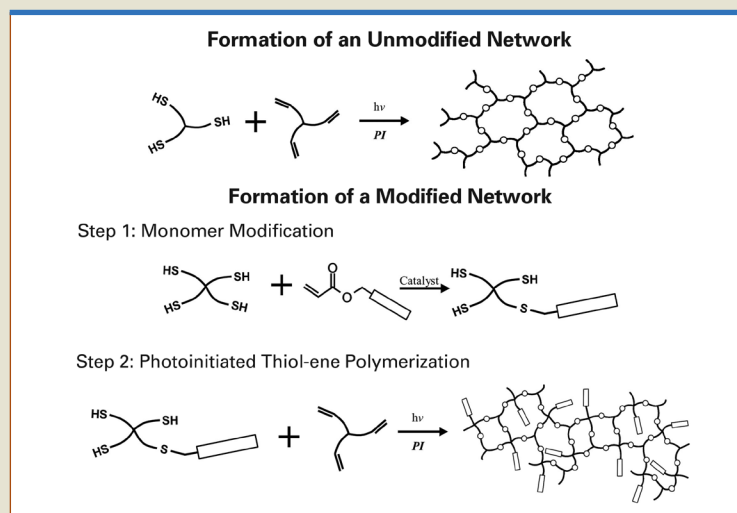
monomers are available. By mixing and matching these components, properties can be tuned to meet specific requirements. The synthesis of new monomers and chemical modification of the existing monomers open up further possibilities.

UV-curable materials have a broad range of applications.² However, most often they have been used as coatings, adhesives and inks in printing. UV curing has not been widely employed in the gas barrier and membrane fields where the modern market has a strong need for advanced food and electronic packaging materials with the bottom line of cost and barrier efficiency; improved protective coatings; and high gas-permeable polymeric systems which can be employed in the area of gas separation, purification, contact lenses applications, medical related fields and breathable clothing.⁶

Transport of small gas molecules strongly depends on the amount of free volume. Free volume (or unoccupied void space between molecules) allows the hopping of gas molecules through a polymer. In the rubbery or molten state, free volume is dynamic (able to get readily redistributed); while in the glassy state, it is mainly frozen in. As related to the structure of a polymer, free volume is controlled by chain rigidity and secondary forces. Rigid, high T_g polymers (i.e., polyimides, polysulfones and polycarbonates) exhibit high free volume and are often used as gas separation membranes in which high gas permeability is important, in addition to selectivity.^{7,8} Polymers with strong secondary forces (i.e., dipole-dipole interactions and hydrogen bonding) are known to exhibit tight packing (low free volume) and listed as high gas barriers. Examples include polyacrylonitrile, poly(styrene-co-acrylonitrile), poly(vinylidene chloride), poly(vinyl alcohol) and some polyamides.⁹

FIGURE 2

Formation of modified and unmodified networks



Finding a unique material platform based on a similar chemistry route which would allow control of free volume and gas transport characteristics within broad limits has been the goal of our research group for some time. We have demonstrated that thiol-ene-based chemistries can be conveniently employed to have such control over free volume and gas permeability.^{10,11}

This report aims to highlight the methods and advancements made in the modification of thiol-ene networks for the development of high barrier and high flux materials. A baseline of gas transport properties for commercially available UV-curable thiol-ene networks was established in this project; thus, providing a starting point window of gas permeation in thiol-ene networks. After these initial attempts, further efforts were made to expand the window by employing the thiol-acrylate Michael addition reaction. Multifunctional thiols were first derivatized via nucleophile-catalyzed thio-Michael addition reaction using a broad range of commercially available functionalized monoacrylates. Cyano,

hydroxyl and amide, as well as n-alkyl and fluoroalkyl chemical moieties, were explored. Next, modified thiol-ene networks were formed by polymerization of the derivatized thiols with ene monomer under UV light. Figure 2 shows formation of modified and unmodified thiol-ene networks—both displaying trifunctional junction points. Combining the processing simplicity of UV curing with the well-defined and robust thiol-ene modification reactions, this research project reports the first steps toward understanding controlling factors for gas transport in photopolymerized thiol-ene networks.

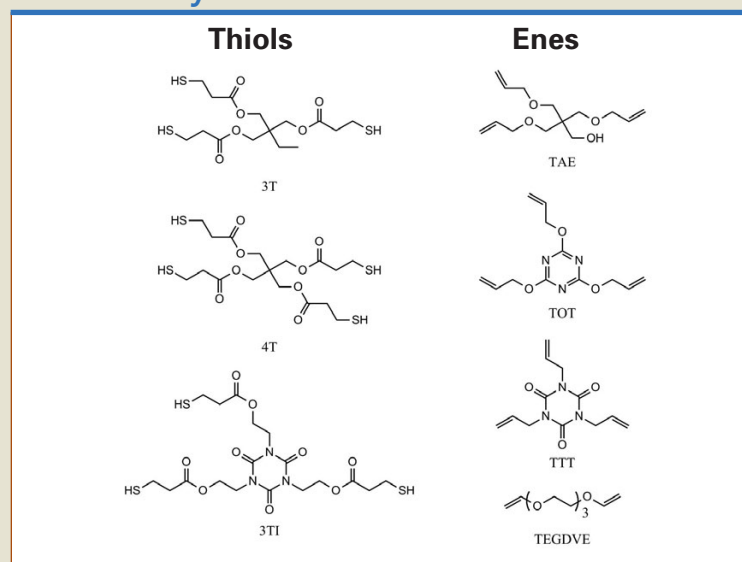
Methods and Results

Preparation of Basic and Modified Thiol-Enes Networks

Commercially available thiol and ene structures are shown in Figure 3. Tri and tetra functional thiol monomers—trimethylolpropane tris(3-mercaptopropionate) (3T), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (3TI), pentaerythritol tetrakis(3-mercaptopropionate) (4T); and di and tri functional ene

FIGURE 3

Commercially available thiols and enes



monomers—tri(ethylene glycol) divinyl ether (TEGDVE), pentaerythritol allyl ether (TAE), 2,4,6-triallyloxy-1,3,5-triazine (TOT), and triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TTT).

Modified tri-functional thiol monomer was synthesized using an amine-catalyzed (diethylamine or dibutylamine) thio-Michael addition reaction between 4T and various functionalized monoacrylates shown in Figure 4 at a 1:1 molar ratio so as to cap an average of one of the four thiol groups per monomer. The final monomer should be a statistical distribution of structures with the trifunctional monomer being predominant. It is noted that the distribution could result in small changes in the macroscopic physical properties of the final networks versus networks formed from a purely trifunctional system. Derivatized thiol monomers were characterized by ^1H NMR.

All studied basic and modified thiol monomers were readily miscible with ene monomers with only mild sonication, resulting in optically

clear, homogeneous liquid mixtures. Freestanding thin films of all thiol-ene network formulations were made by dissolving 1 wt% 1,1-dimethoxy-1-phenylacetophenone (Irgacure 651) photoinitiator into the thiol-ene mixture. This homogeneous mixture was then drawn down onto glass substrates using drawdown bars. Films were cured using a Fusion UV-curing line with a D bulb (400 W/cm² with belt speed of 3 m/min and 3.1 W/cm²

irradiance). Network conversion was monitored by Fourier transform infrared spectroscopy (FTIR). Change in the peak area of thiol –SH groups at 2570 cm⁻¹ (S-H stretch) and ene C=C groups at 3080 cm⁻¹ (vinyl C-H stretch) were measured. Thiol and ene functional groups proceeded in seconds to high conversion (70->90%) at room temperature, and thiol and ene conversions, in all cases, progressed simultaneously. This is indicative of a predominance of the thiol-ene reactions over the ene homopolymerization. Films shown in Figure 6 were all transparent and free of any defects such as bubbles or pinholes. Narrow tan δ at T_g (shown in Figure 5) was indicative of compositional and structural homogeneity of the basic and modified networks.

Oxygen Barrier and Free Volume Measurements

Oxygen is the most widely investigated permanent gas in polymeric materials. It is a vital contaminant of foods and beverages, a detriment to medical and electronic devices, and an important component in technologies such as air enrichment.^{9,12} Oxygen permeation tests were conducted on MOCON OX-TRAN® 2/21 instruments using a

FIGURE 4

Chemical structures of modifying acrylates

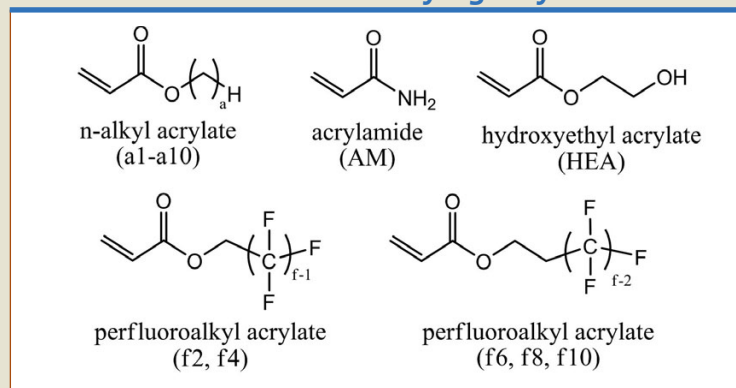
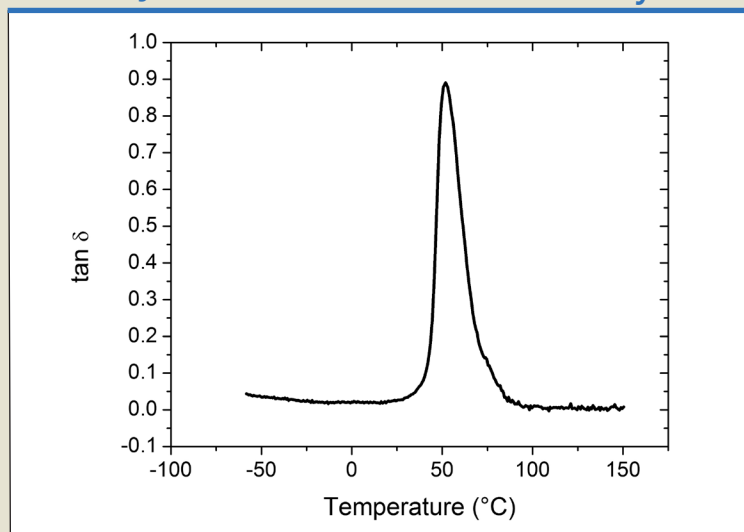


FIGURE 5

Narrow T_g of thiol-ene networks measured by DMTA

continuous-flow testing cell method (ASTM D3985). All measurements were conducted at 23°C and 0% RH. When oxygen flux was too high to measure with MOCON, a constant-volume, variable-pressure (ASTM D1434-82), custom-built apparatus was employed. The experimental methodologies are described elsewhere.^{13, 14} Positron annihilation lifetime spectroscopy (PALS) is widely used in the characterization of free volume of polymers.¹⁵ PALS involves measurements of the lifetime of positrons injected into a polymer sample from a positron-emitting nucleus, generally Na²². The lifetime (τ_3) of the long-lived orthopositronium (positron/electron pair) o-Ps species were used to extract information about the average size of molecular holes. The o-Ps lifetime (τ_3) can be related to the radius of a spherical cavity. The average free volume of a hole (V_h) can then be calculated as $V_h = 4/3\pi R^3$.

Results

In order to establish a baseline in properties, the oxygen transport

characteristics of basic thiol-ene films were evaluated. These basic networks feature the 3T trifunctional thiol monomer copolymerized with four different ene monomers of varying functionality and rigidity—TEGDVE, TAE, TOT and TTT. TEGDVE (the least rigid monomer) is difunctional, while TAE (also a

flexible monomer) is trifunctional. Isomeric TOT and TTT enes have basic triazine and isocyanurate structures and are more rigid trifunctional ene monomers. The trifunctional thiol 3TI and tetrafunctional 4T were also copolymerized with TTT to increase the network rigidity and the glass-transition temperature. Oxygen permeability of the basic thiol-ene films measured at room temperature in units cc(STP) cm m⁻² day⁻¹atm⁻¹ varied broadly from 13.8 (3T-TEGDVE) to 0.021 (3TI-TTT). The lowest permeability observed for the basic networks corresponded to the oxygen barrier about tenfold better than that (0.38) for poly(ethylene terephthalate),¹⁶ the most common resin used for carbonated drinks packaging. Oxygen permeability correlated remarkably well with T_g for both the rubbery and glassy networks as shown in Figure 7. This correlation displayed a classic V shape. The minimum in oxygen permeability was found for samples whose glass transitions were near room temperature. These samples exhibited a minimum in free volume. At room temperature, rubbery and

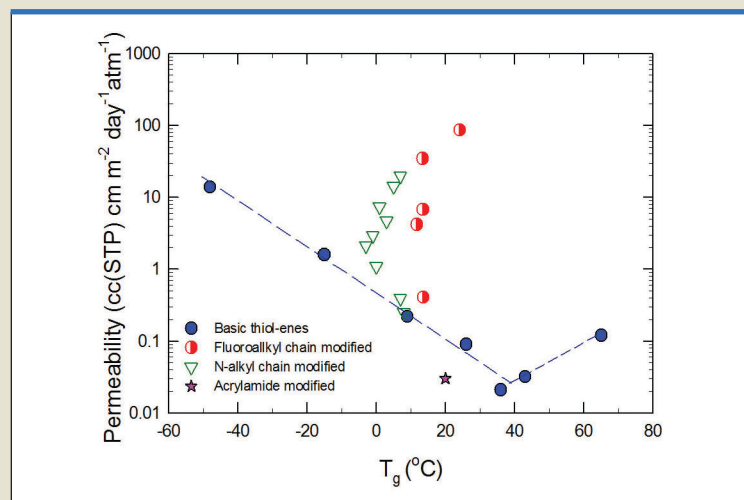
FIGURE 6

UV-Cured thiol-ene films are transparent, robust and malleable



FIGURE 7

Oxygen permeability of basic and chemically modified thiol-ene networks



glassy networks with subsequently lower and higher T_g in turn were more permeable. These samples exhibited maximums in free volume.

Figure 7 also shows oxygen permeability behavior of the modified networks. Acrylamide modification of 4T-TTT network, as expected due to incorporation of strongly “attractive” moieties, led to noticeable (about one order of magnitude) reduction of oxygen permeability as compared to the basic thiol-ene systems with similar T_g . In contrast, incorporation of strongly “repulsive” moieties such as n-alkyl and, in particular, fluoroalkyl functional groups resulted in remarkable increases of oxygen permeability. This behavior was shown to depend strongly on alkyl chain length where the networks with longer alkyl units exhibited larger oxygen permeability. A magnitude increase of oxygen permeability up to three orders was observed in our experiments. Interestingly, the glass transition temperature of the modified networks was practically independent on the alkyl chain length; thus, mainly

defined by the crosslink density of the backbone network that was similar in each case.

Probed by PALS, an increase in free volume size was anticipated from incorporation of n-alkyl and, in particular, fluoroalkyl moieties. Indeed, a drastic increase of the molecular free volume size was observed for the

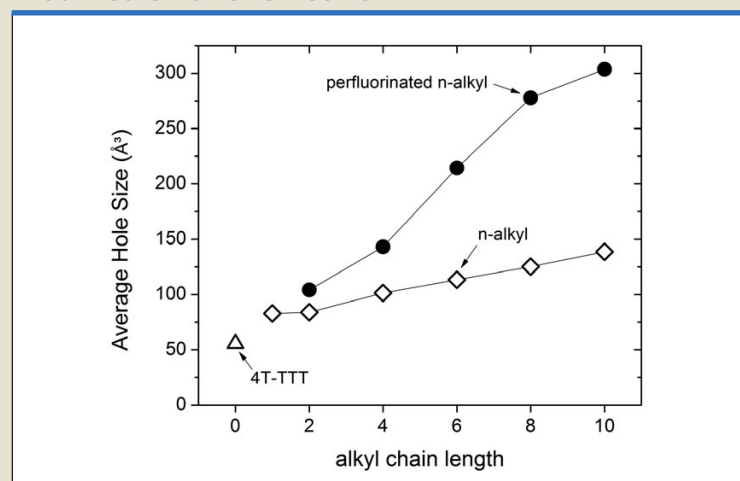
modified networks as one can see on Figure 8. Similar to oxygen permeability, free volume size showed a correlation with alkyl chain length. More than a twofold increase of free volume size, compared to basic thiol-ene systems, was possible to attain after n-alkyl chain modification and a fivefold increase after the incorporation of maximum length fluoroalkyl chain moieties.

Conclusions

Oxygen permeability was initially determined for a variety of photopolymerized thiol-ene networks. Until now, such information was absent from the literature despite its importance. Basic thiol-ene network formulations showed a broad range of oxygen permeabilities. Some of the networks were fairly oxygen-permeable and some demonstrated an excellent oxygen barrier. Oxygen permeability of basic networks showed a correlation with T_g . Then, an interesting approach based on thio-Michael addition of various functionalized acrylates to a tetrathiol monomer was employed to chemically modify the networks. This modification technique enabled a study

FIGURE 8

Average hole volume versus alkyl chain length for modified thiol-ene network



on how different functional groups embedded in a uniform network affect oxygen barrier properties and free volume. Of particular interest was the introduction of primary amides, n-alkyl and fluoroalkyl groups as dangling appendages which resulted in especially low and, in contrast, high gas permeability, respectively. The use of thiol-ene networks as a platform to investigate the systematic effect of functional groups on network properties has far-reaching implications. This method enables manufacturers to broadly tailor gas transport characteristics for a variety of applications. ▀

Acknowledgements

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