To my family and all my friends
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<td>tris-(8-hydroxyquinoline)</td>
</tr>
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<td>BDDVE</td>
<td>1, 4-butanediol divinyl ether</td>
</tr>
<tr>
<td>BDT</td>
<td>butanedithiol</td>
</tr>
<tr>
<td>BP</td>
<td>benzophenone</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DDDY</td>
<td>dodecadiyne</td>
</tr>
<tr>
<td>DDT</td>
<td>decanedithiol</td>
</tr>
<tr>
<td>DDY</td>
<td>1,9-dodecadiyne</td>
</tr>
<tr>
<td>DMPA</td>
<td>dimethoxyphenyl acetophenone</td>
</tr>
<tr>
<td>DPSD</td>
<td>diphenylsilanediol</td>
</tr>
<tr>
<td>ECTS</td>
<td>2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane</td>
</tr>
<tr>
<td>EDT</td>
<td>ethanediol</td>
</tr>
<tr>
<td>EMDS</td>
<td>2-(3,4-epoxycyclohexylethyl) methyldiethoxysilane</td>
</tr>
<tr>
<td>FG</td>
<td>faux glass</td>
</tr>
<tr>
<td>FS</td>
<td>Flory-Stockmayer</td>
</tr>
<tr>
<td>fwhm</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>HHPA</td>
<td>hexahydraphthalic anhydride</td>
</tr>
<tr>
<td>HptDY</td>
<td>heptadyne</td>
</tr>
<tr>
<td>HRIP</td>
<td>High Refractive Index Polymer</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MeHHPA</td>
<td>methylhexahydraphthalic anhydride</td>
</tr>
<tr>
<td>MPTMS</td>
<td>3-methacryloxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
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<tr>
<td>NDY</td>
<td>nonadiyne</td>
</tr>
<tr>
<td>NPB</td>
<td>N,N\textsubscript{2}o\textsubscript{2}i\textsubscript{2}ndi(naphth-2-yl)-N,N\textsubscript{2}o\textsubscript{2}ndiphenyl-benzidine</td>
</tr>
<tr>
<td>ODY</td>
<td>octadiyne</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(amic acid)</td>
</tr>
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<td>PCE</td>
<td>power conversion efficiency</td>
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<td>PDMS</td>
<td>poly-dimethyl-siloxane</td>
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<td>PETMP</td>
<td>pentaerythriol tetra(3-mercaptopropionate)</td>
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<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PVO</td>
<td>phenyl-vinyl-oligosiloxane</td>
</tr>
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<td>RI</td>
<td>Refractive Index</td>
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<tr>
<td>SSL</td>
<td>Solid-state lighting</td>
</tr>
<tr>
<td>TBPM</td>
<td>tetrabutylphosphonium methanesulfonate</td>
</tr>
<tr>
<td>TDET</td>
<td>thiodiethanethiol</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
</tr>
<tr>
<td>TIR</td>
<td>Total internal reflection</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>v</td>
<td>Abbe number</td>
</tr>
<tr>
<td>VTMS</td>
<td>vinyltrimethoxysilane</td>
</tr>
<tr>
<td>$\eta_{IQE}$</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>$\eta_{out}$</td>
<td>Outcoupling efficiency</td>
</tr>
<tr>
<td>$\eta_{EQE}$</td>
<td>External quantum efficiency</td>
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Click reactions using thiols provide highly crosslinked networks with rapid reaction rate in ambient environment such as oxygen and moisture. Thermosets based on thiols show the most ideal homogeneous network arrangement with narrow glass transition regions and extremely low polymerization shrinkage. Click reactions employing thiols can be applied to a variety of applications such as surface science, coatings, optical components, adhesives, photolithography, microdevice fabrication and so on. In this dissertation, we developed various optical applications by using click reactions with thiols.

First, we studied UV curable high refractive index and transparent polymers. In order to overcome limitation of low refractive index of intrinsic polymers, organic-inorganic nanocomposites have been widely used. However, nanoparticles loaded nanocomposites have some limitations such as optical loss and difficult processability which is not compatible with usual processing for polymers such as UV curing and molding. We utilized alkyl dithiol and dialkyne monomer mixtures as a matrix and surface modified TiO$_2$ nanoparticles as a filler. Thiol-yne nanocomposites have the high refractive index $\sim$1.69 and high transmittance over 88 %. Furthermore, the approach
presented herein can easily produce the desired shape by printing or molding methods without side products. It does not require materials clean up, and does not use solvents or high temperature processes.

Microlens arrays are effective methods to improve low out-coupling efficiency of OLEDs. We demonstrated simple fabrication process via printing techniques by using multifunctional thiol and ene as a lens material. Trimethylolpropane tris(3-mercaptopropionate) and tri(ethylene glycol) divinyl ether monomer mixture has low viscosity, high transparency and ~1.5 refractive index. Therefore it is suitable for the lens material and printing process. In order to obtain high contact angle of liquid lens droplets, surface energy of glass substrates was modified with hydrophobic silane coupling agents.

One of the fundamental limitations in the light extraction efficiency of LEDs is the total internal reflection at the interface between high refractive index semiconductors (n=2.5-3.5) and low refractive index encapsulations. Here, we proposed multi layer encapsulation and studied graded refractive index LED encapsulation for minimizing Fresnel reflection and scattering losses. Yellowness index of each layer is calculated after thermal aging to identify thermal stability.

In this dissertation, we presented optical applications such as high refractive index polymer, microlens array for enhancement of outcoupling efficiency for OLEDs, and graded-refractive index LED encapsulation by using thermosets based on thiols in order to provide homogeneous networks with high refractive index and ease of processing for these applications.
CHAPTER 1
INTRODUCTION TO THIOL-ENE AND YNE PHOTOPOLYMERIZATION

1.1 Thiol-Enes Click Reactions

The use of thiols in chemical reactions has been known for 100 years, including various fields ranging from polymer science to biochemistry. Early work on thiol-ene free radical polymerization started the late 1930s.\(^1\) The first large-scale use of thiol-ene radiation curing in the United States was successfully done by Morgan, Ketley and their coworkers.\(^2,3\) However, there were objections to thiol-ene based ultraviolet (UV) curable resins because of the odor and incorrect belief that all thiol-ene coatings were prone to yellowing and discoloration upon weathering. Unfortunately, a large quantity of benzophenone (BP) was used as a photoinitiator and significant light stability problems occurred such as yellowing and discoloration in the cured thermoset network since a portion of BP remained unconsumed at the end of the polymerization and acted as plasticizer and photoreactive species in the network. Therefore, colored byproducts were produced upon exposure to interior or exterior light. However, this problem was overcome by employing cleavage-type photoinitiators. It was possible to use conventional cleavage-type photoinitiators to initiate thiol-ene polymerization and thiols could be effectively combined into acrylate formation to reduce oxygen inhibition and enhance the final film properties.

In 2001, researchers described a new concept for accompanying organic reactions which focused consideration on highly selective, simple orthogonal reactions that do not have side products and give heteroatom-linked molecular systems with high efficiency under various mild reaction environments by the Sharpless et al.\(^4\) Several effective reactions have been grouped under the term click reactions. These reactions are able to
produce a variety of organic materials and functional synthetic molecules. Copper-catalyzed azide/alkyne click reactions have received particular attention with applications extending to the synthesis of biomedical libraries, dendrimer preparation, cross-linking of adhesives for metal substrates among others.\textsuperscript{5-7} Hoyle et al.\textsuperscript{8} focused on the comparably weak bonding between sulfur and hydrogen of thiols because of an excess of chemical reactions with nearly quantitative yields with a capability to initiated by various methods under the mild condition. Two main classifications of thiol reactions have been noted during the last century. Figure 1-1 shows both thiol-ene free radical addition to carbon-carbon double bond and the catalyzed thiol Michael addition to electron deficient carbon-carbon double bond.\textsuperscript{8}

\[
\text{R-SH} + \text{C=C} \rightarrow \text{R-S-C=C-R'}
\]

Figure 1-1. General thiol-ene coupling by a) free radical and b) Michael addition reactions. A single thiol reacts with a single ene in the idealized reaction. (Adapted from [8])

Both thiol-ene reactions provide a quantitative yield, require little or no catalysts, are not susceptible to ambient environment such as oxygen and moisture, have rapid reaction rates and a wide range of thiols and enes are readily available. There are four major thiol types including alkyl thiols, thiophenols, thiol propionates, and thiol glycolates in the literature reports. Free radical and Michael addition reactions are very efficient with these thiols. Any non-sterically blocked terminal ene is able to participate in the radical-mediated thiol-ene reaction. Electron-rich and strained enes such as vinyl ether and norbornene are capable of reacting more rapidly than electron-deficient enes. These four types of thiols and electron-rich and strained enes systems can form ideal
homogeneous network arrangements with narrow glass transition regions and extremely low polymerization shrinkage.\textsuperscript{9,10}

\textbf{1.2 Kinetics of Thiol-Ene Polymerization}

\textbf{1.2.1 Initiation}

Figure 1-2 shows general process of thiol-ene polymerization. Polymerization is initiated by generating thiol radicals from thiol groups. An initial addition of the generated thiol radical to the carbon-carbon double bond (propagation 1) and a consecutive hydrogen abstraction of a thiol group by a carbon-centered radical provide a thiol radical (propagation 2). Radical-radical coupling causes a termination process. \textsuperscript{10}

![Figure 1-2. General thiol-ene polymerization process. (Adapted from [10])](image-url)
One early thiol-ene reaction, diarylketone such as BP employed as an initiator but there were significant issues with long term stability of films when they were exposed to interior or exterior light due to the remaining unconsumed a diarylketone.

![Chemical reaction diagram](image)

Figure 1-3. Mechanism of the initiation process of thiol-ene radical polymerization by DMPA. (Adapted from [11])

Thiol-ene polymerization can also be initiated by the excitation of cleavage-type photoinitiators, which give a benzoyl radical and a tertiary carbon radical by the exposure of light. Figure 1-3 describes the initiation of thiol-ene polymerization by dimethoxyphenyl acetophenone (DMPA).\(^{11}\) Initiation by cleavage-type photoinitiators is more efficient than hydrogen abstraction-type initiator like BP due to higher quantum yields for the generation of reactive radicals. Researchers showed that the rate of the
initiation process is proportional to the square root of concentration of thiol and ene functional groups in a 1:1 molar ratio mixture. \(^{12}\) \(R_{\text{initiation}}\) is the rate of initiation.

\[
R_{\text{initiation}} \propto [\text{RSH}]^{1/2}
\]  

1.2.2 Propagation

Propagation of thiol-ene polymerization consists of the alteration between thyl radical propagation across the ene functional groups and chain transfer reactions by hydrogen abstractions from thiol by the carbon-centered radicals. In an ideal thiol-ene radical reaction, only step-growth reactions, no homopolymerization, occur and the conversion rate reaches 100 %. Hence, the combination of thiol and ene functional groups is the net reaction of the ideal thiol-ene polymerization. \(^{13}\) The addition of thiols to carbon-carbon double bonds is an exothermic process and there is a reaction enthalpy difference depending on the ene species. For electron-rich vinyl ether and electron-poor N-alkyl maleimide, the reaction enthalpies are -10.5 kcal/mol and -22.6 kcal/mol, respectively. \(^{14}\) Propagation rate and conversion reduction is observed at the polymerization of 1,2 substituted internal enes system which is probably due to the reversible addition of the thyl radical to the disubstituted ene \(^{15,16}\) which is shown in Figure 1-4.

![Diagram](image)

Figure 1-4. Reversible process of the thyl radical addition to the internal ene. (Adapted from [10])

Processes of propagation 1 and propagation 2 in Figure 1-2 have the revolving features and their overall rates are required to be equal. If one of the steps is naturally slower
than another, that reaction step becomes the rate-limiting step in the reaction process and concentration differences between the two radical species occurs. The anticipated overall reaction rate (Rp) behaviors are shown in Eq. (2)-(4) in the cases for which 1) the kinetic constants of two reactions are almost equal [Eq. (2)], 2) chain transfer is the slow reaction [Eq. (3)], and 3) the thiyl radical propagation is slow reaction [Eq. (4)].\textsuperscript{17}

\[ k_{ct} \approx k_p \]

\[
\frac{[\text{R-S}^-]}{[\text{R-S-C-C}^-\text{R}^-]} \approx 1 \text{ and } R_p \propto [\text{R - SH}]^{1/2} [\text{R}^- - \text{C} = \text{C}]^{1/2}
\]

(2)

\[ k_{ct} >> k_p \]

\[
\frac{[\text{R-S}^-]}{[\text{R-S-C-C}^-\text{R}^-]} \ll 1 \text{ and } R_p \propto [\text{R - SH}]^{1}
\]

(3)

\[ k_{ct} << k_p \]

\[
\frac{[\text{R-S}^-]}{[\text{R-S-C-C}^-\text{R}^-]} \gg 1 \text{ and } R_p \propto [\text{R}^- - \text{C} = \text{C}]^{1}
\]

(4)

In these equations, \( k_{ct} \) is the chain transfer rate constant, \( k_p \) the thiyl radical propagation rate constant, [R-SH] is the thiol concentration, [R-S\(^-\)] is the thiyl radical concentration, [R-S\(-\text{C-C}^-\text{R}^-\)] is the carbon-centered radical concentration and [R\(^-\text{C}=\text{C}\)] is the ene concentration. In each case, the reaction process is first order overall in the concentration of monomers of thiol and ene. However, the characteristics and reactivity of the radicals and the chemical nature of the thiol and ene functional groups determine the detailed dependence in the reaction steps. Thiols such as alkyl thiols have fewer abstractable hydrogen atoms and will have a tendency to reduce chain transfer rates [Eq. (2)]. Whereas the reaction of allyl ethers is chain transfer-limited and first order in [R-SH], vinyl silazanes are propagation limited and first order in [R\(^-\text{C}=\text{C}\)]. In the ideal case of radical polymerization, norbornene and vinyl ethers have very similar
propagation and chain transfer rates and result in a half order dependence on both the thiol and ene concentrations. In contrast to conventional free radical chain growth polymerization, kinetics of thiol-ene free radical polymerization are very simple in most thiol and ene systems.

1.3 Applications of Thiol-Ene Thermosets

Thiol-ene click reactions can be applied to a variety of applications such as surface science, coatings, optical components, adhesives, photolithography, microdevice fabrication among others. These applications are primarily based on thiol-ene free radical chemistry, the extent of Michael addition reactions is limited.

The thiol-ene reactions is a popular surface modification process due to the ability to use patterns to alter surfaces simply by exposure to light. General approaches, show in Figure 1-5, contain 1) a “grafting to” approach that uses two different thiol-ene polymerization processes, a free radical polymerization and Michael addition polymerization (Figure 1-5 a), 2) a “grafting from” approach that employs initiators including thiol-ene substrates to make the grafting process (Figure 1-5 b), 3) a combination of the above two approaches. Either photo-induced free radical or Michael addition polymerizations are performed in bonding with surfaces (Figure 1-5 c,d).

The thiol-ene reaction has several advantages such as delay in gel point, homogeneous network, and low oxygen inhibition. Those benefits make thiol-ene systems ideal for photolithography and microdevice fabrications. In direct photolithographic applications, thiol-ene reactions are quite effective in the manufacture of nanoscale devices via diverse methods of nanoimprint lithography. A Thiol-ene polymer produced with nanoscale patterns is consequently exposed to a further thiol-ene grafting reaction that further decreases feature sizes.
Because of the high polarizability of sulfur atoms compared to other organic components such as carbon, hydrogen and oxygen, thiol has been incorporated into organic materials and used for optoelectronics. Since 2000, numerous articles and patents applications, especially from Norland Optics photocurable thiol-ene systems, have arisen in a wide range of journals. The applications in optics and optoelectronics of thiol-ene system are very broad and include lens components, flexible display components, photonic crystals, optical waveguides, among others.

Figure 1-5. Several surface modification approaches by thiol reactions: a) “grafting to” approaches that utilize both thiol-ene and thiol-Michael addition coupling reactions, b) a photoinduced “grafting from” approach employing thiyl radicals to initiate acrylate polymerization, c) and d) combinations of “grafting to” and “grafting from” radical reactions and thiol-Michael addition reactions, respectively. (Adapted from [10])
1.4 Thiol-Yne Click Polymerization

In the previous explanation of thiol-ene polymerization, several advantages of thiol-ene crosslinked polymer networks such as nearly ideal, and homogeneous structures were introduced. However, since each ene is able to connect with only a single thiol in the thiol-ene reactions, in order to produce a crosslinked network it is essential to react monomers with more than two enes or thiols. Therefore, the degree of monomer functionality determines the maximum obtainable crosslink density. Likewise, the extent of small molecular replacement or change is also limited by the one thiol-to-one ene nature of the reaction.²⁵ Alkynes are relatively easy to synthesize in various structural configurations and are usually stable until given the chance to react. Therefore, alkynes have been selected as ideal substrates for a wide range of materials applications through Cu-catalyzed Huisgen alkyne-azide reactions. As an extension of other types of highly efficient reactions with alkynes, certain radical-meditated thiol-yne reactions have been investigated by several researchers.²⁶⁻²⁹ Thiol-yne reactions have been explored as a chemical platform for materials synthesis including network film formation, polymer functionalization to control solution properties in water, and synthesis of new highly functional chemical species.

1.4.1 Kinetics of Thiol-Yne Polymerization

Figure 1-6 shows the reaction mechanism of the thiol-yne system. A Yne functional group reacts with a single thiol to produce a vinyl sulfide. Unlike the thiol-ene reaction, a vinyl sulfide can react with a second thiol radical to form a dithioether. Therefore each yne moiety is difunctional in thiol-yne radical polymerization.
Figure 1-6. Reaction mechanism for sequential addition and hydrogen abstraction process of (1) primary alkyne and (2) a vinyl sulfide during thiol-yne step growth polymerization. (Adapted from [26])

Fairbanks and colleagues researched the kinetics and mechanism of the thiol-yne photopolymerization by using 1, 9-dodecadiyne (DDY) and pentaerythriol tetra(3-mercaptopropionate) (PETMP). Almost 80% of thiol functional groups react within the first minute. Consumption of alkyne groups is also relatively fast while the intermediary vinyl sulfide species is generated and consequently consumed during the polymerization (Figure 1-7). During the reaction process, the concentration of vinyl sulfide reaches a maximum at ~0.2 min of UV irradiation, after 0.2 min consumption of vinyl sulfide exceeds its generation due to the thiol addition to alkyne.

The addition of thiol to alkyne and the consequent addition of thiol to vinyl sulfide can be understood by the reactive species balances,

\[
\frac{d[C\equiv C]}{dt} = -k_{p,1}[S'][C = C] \quad (5)
\]

\[
\frac{d[C=C]}{dt} = -k_{p,1}[S'][C \equiv C] - k_{p,2}[S'][C = C] \quad (6)
\]
where $k_{p,1}$ and $k_{p,2}$ are the propagation rate constants for addition of thyl radical to alkyne and vinyl sulfide respectively. If $k_{p,2}/k_{p,1} \ll 1$, the rate of vanishing alkyne is the same as the rates of thiol loss and vinyl generation. Reversely, for $k_{p,2}/k_{p,1} \gg 1$, vinyl sulfides are consumed instantly upon generation. Therefore, significant vinyl sulfides concentration would not be detected. In the stoichiometrically balanced DDY and PETMP system, the rate constant ratio ($k_{p,2}/k_{p,1}$) is decided to be $\sim 3$.\textsuperscript{25}

\begin{equation}
\frac{\partial [C=C]}{\partial [C\equiv C]} = \frac{k_{p,2}[C=C]}{k_{p,1}[C\equiv C]} - 1 \tag{7}
\end{equation}

Figure 1-7. Concentration of reactive thiol (□), alkyne (○) and vinyl sulfide (△) during stoichiometrically balanced DDY and PETMP photopolymerization. (Adapted from [25])

The Flory-Stockmayer (FS) equation is generally utilized to predict the gel-point conversion for a step-growth polymerization between two monomers with degrees of
functionality. In the case of assuming the same reactivity of the alkyne and vinyl sulfide, the gel-point conversion of a stoichiometrically balanced polymerization between tetrathiol and dialkyne is 33%. There is a report demonstrating deviation from the gel-point conversion predicted by FS equation for the step-growth process where subsequent addition to a reactive component has different reactivity.\(^3^0\) In this reference, a higher gel-point conversion was obtained the rate of initial addition was faster than the subsequent addition \((k_{p,2}/k_{p,1}<1)\). The opposite behavior was observed when the rate of subsequent addition was more rapid than initial addition \((k_{p,2}/k_{p,1}>1)\). The observed rate constant ratio \((k_{p,2}/k_{p,1})\) for thiol-yn system was 3 and a gel-point conversion somewhat lower than the Flory-Stockmayer theory. However the rate constant was still of the same order of magnitude and the deviation from the value of the Flory-Stockmayer was likely small. The gel-point conversion from the theory was 33% and it is much higher than methacrylate system of below 5%. Shrinkage stress did not start to grow until the conversion exceeds the gel-point conversion. Therefore thiol-yn network systems were likely to show alike low shrinkage stress behavior as well as thiol-ene system.

1.4.2 Materials Properties of Thiol-Yne Thermosets

Fairbanks and coworkers compared materials properties of thiol-yn to thiol-ene thermosets. In order to make thermosets, they employed tetra-functional thiol, pentaerythriol tetra(3-mercaptopropionate) (PETMP), dialkyne, 1, 9-dodecadiyne (DDY) and diene, 1, 4-butanediol divinyl ether (BDDVE). As a result, the crosslink density of fully polymerized PETMP/DDY is 6 times higher than that of fully cured PETMP/BDDVE network. The full width at half maximum (fwhm) of PETMP/DDY thermosets is almost twice than that of PETMP/BDDVE thermosets. However, this width is still quite narrow compared to network formed by chain growth polymerization. Materials properties of
PETMP/DDY and PETMP/BDDVE networks are presented in Table 1-1. Thiol-yne networks showed higher glass transition and crosslink density than the thiol-ene network. The crosslinked network of thiol-yne system is a promising click-polymerization system as is that of thiol-ene.

Table 1-1. Summary of $T_g$, fwhm, elastic modulus, and crosslink density for PETMP/DDY and PETMP/BDDVE networks. (Adapted from [26])

<table>
<thead>
<tr>
<th>system</th>
<th>$T_g$ (°C)</th>
<th>Tan δ fwhm (°C)</th>
<th>$E'$ at 65 °C (MPa)</th>
<th>calculated cross-link density (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETMP/DDY, 80 °C</td>
<td>48.9 ± 0.9</td>
<td>17.7 ± 0.2</td>
<td>80 ± 1</td>
<td>9.6 ± 0.2</td>
</tr>
<tr>
<td>PETMP/DDY, 25 °C</td>
<td>40.7 ± 0.2</td>
<td>17.7 ± 0.5</td>
<td>69 ± 2</td>
<td>8.4 ± 0.2</td>
</tr>
<tr>
<td>PETMP/BDDVE</td>
<td>-22.3 ± 0.5</td>
<td>9.3 ± 0.3</td>
<td>13 ± 1</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>

1.5 Outline of Dissertation

This dissertation aims to deliver a fundamental background of thermoset materials based on multi functional thiol as well as their important applications. It consists of three chapters about literature reviews on applications and three experimental chapters are followed by reviews. First, Chapter 2 will describe high refractive index polymers, approaches to develop them and their important applications. Chapter 3 will detail general information about organic light emitting diode and light extraction techniques for enhancing low out-coupling efficiency of OLEDs. A range of fabrication techniques of OLED microlens arrays will be depicted in Chapter 3 as well. In Chapter 4, encapsulation of light emitting diode will be delineated based on encapsulation materials and their thermal and optical properties. In Chapter 5, UV-curable low viscosity high refractive index and transparent TiO$_2$-loaded dithiol-dialkyne nanocomposites will be exhibited. The surface modification of nanoparticles for
dispersion and optical properties of nanocomposites will be discussed as well. In order to improve the low out-coupling efficiency of OLEDs, a light extraction method using direct printed microlens arrays will be applied to the OLEDs in Chapter 6. Both the surface treatment of the glass substrate to establish low surface free energy for obtaining high contact angle of thiol-ene liquid lens droplets first and microlens array fabrication via direct printing technique will be explained. In Chapter 7, graded refractive index LED encapsulation will be demonstrated. In order to extract light in LEDs, high refractive index thiol-yne nanocomposites will be employed and low refractive index materials based on room temperature curing silicone will be coated on the high refractive index thiol-yne nanocomposites for index grading and for protecting the thiol-yne film from thermal oxidation. Conclusions and future work will be discussed in Chapter 8.
CHAPTER 2
HIGH REFRACTIVE INDEX POLYMERS

2.1 Introduction

The development of photonic devices has led to increasing interest in high refractive index materials, especially high refractive index polymers. High refractive index polymer materials can be obtained either by substituting low molar refraction to high molar refraction or introducing high refractive index inorganic nanoparticles to the polymer matrix. Applications of high refractive index polymers range from high performance substrates, encapsulation of lighting devices, antireflection coating, photoresists, and microlenses for charge coupled devices. Typical refractive indices of conventional polymers are around 1.30~1.70. However, for example, the encapsulation of LED requires very high refractive index to match the refractive index of the semiconducting layer (n: 2.50~3.50). Epoxy and silicone compound materials for the encapsulation have refractive indices around 1.45~1.55. Therefore, there is significant total internal reflection at the interface between the encapsulation layer and semiconducting layer. Therefore, it is desirable to achieve the refractive index range from 1.80 to 2.50 for this application. In addition to the refractive index, polymer materials must have high transmittance at visible wavelengths for lighting applications.

2.2 Strategies to Increase Refractive Index of Polymers

The Lorentz-Lorenz equation is widely used to anticipate the refractive index of polymers. This equation expresses the refractive index in terms of the molecular refraction $R$, molecular weight $M$, and molecular volume $V$ of the polymer repeating units. $R_M$, the molar fraction can be expressed $R/M$ and $M/V$ can be expressed as the reciprocal of molar volume $V_M$. 
\[
\frac{n^2 - 1}{n^2 + 2} = \frac{R}{M} \rho = \frac{R}{M} \times \frac{M}{V} = \frac{R_M}{V_M}
\]

(8)

\[
\sqrt{\frac{1+2(R_M/V_M)}{1-(R_M/V_M)}}
\]

(9)

From the above equations, employing the moiety of high molar refractions and low molar volumes can be an effective approach towards increasing the refractive index of polymers. Table 2-1 shows the molar refraction of atoms and organic groups of common polymers.\(^{35}\)

Table 2-1. Molar refraction of atoms and organic groups. (Adapted from [35])

<table>
<thead>
<tr>
<th>Group</th>
<th>(R_M)</th>
<th>Group</th>
<th>(R_M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.100</td>
<td>Phenyl (C6H5)</td>
<td>25.463</td>
</tr>
<tr>
<td>C</td>
<td>2.418</td>
<td>Naphthyl (C10H7)</td>
<td>43.00</td>
</tr>
<tr>
<td>Double bond (C=C)</td>
<td>1.733</td>
<td>Cl</td>
<td>5.967</td>
</tr>
<tr>
<td>Triple bond (C≡C)</td>
<td>2.398</td>
<td>Br</td>
<td>8.865</td>
</tr>
<tr>
<td>O (carbonyl) (C=O)</td>
<td>2.211</td>
<td>I</td>
<td>13.900</td>
</tr>
<tr>
<td>O (hydroxyl) (O-H)</td>
<td>1.525</td>
<td>S(thiocarbonyl) (C=S)</td>
<td>7.97</td>
</tr>
<tr>
<td>O (ether, ester) (-C-O-)</td>
<td>1.643</td>
<td>S (thiol) (S-H)</td>
<td>7.69</td>
</tr>
<tr>
<td>F</td>
<td>0.95</td>
<td>S(dithia) (-S-S-)</td>
<td>8.11</td>
</tr>
</tbody>
</table>

2.2.1 HRIP Including Halogens

Halogen materials were used as the substituting components in the early development of HRIP. A series of polymethacrylates containing carbazole rings with lateral substituent of bromine and iodine were studied in an effort to increase the refractive index of polymethacrylates.\(^{36}\) These halogen substituted methacrylates exhibited a range of refractive index from 1.67~1.77 at 589 nm wavelength. However, the optical properties of polymers including halogen components occasionally deteriorate and are not suitable for applications in optical devices. Furthermore, recently, the use of halogen materials has been significantly restricted in electronic devices by the European Union due to the potential environmental pollution.\(^{37}\)
2.2.2 HRIP Including Phosphorus

Phosphonates and phosphazenes groups show high molar refractions by modifying functional groups. Allcock and coworkers developed high refractive index polyphosphonates which have phosphorus-nitrogen backbones. They were able to obtain a high refractive index by attaching side groups with iodinated aromatic groups and the refractive index was reported to be greater than 1.70.

\[
\begin{align*}
\text{Phosphonates:} & \quad n_{633\text{nm}} = 1.58 \\
\text{Polyphosphonates:} & \quad n_{633\text{nm}} = 1.60 \\
\text{Polyphosphonates:} & \quad n_{633\text{nm}} = 1.64
\end{align*}
\]

Figure 2-1. Chemical structures and refractive index of polycarbonates and polyphosphonates. (Adapted from [40])

Polyphosphonates are very similar to polycarbonates in terms of chemical structures. However, by introducing phosphors and attaching aromatic groups, the refractive index can be increased and other properties such as melt stability and fire retardancy were also improved. Figure 2-1 shows the chemical structures and refractive index of polycarbonates and polyphosphonates.
2.2.3 HRIP Including Sulfur atoms

Sulfur atoms have high molar refraction and sulfur containing polymers have been developed for HRIPs. The most common high refractive index sulfur containing polymer is polyimide. High molar refraction groups including sulfur atoms and aromatic groups were substituted to the repeating group of polyimide. They have refractive indices greater than 1.720 and the refractive index increases with increased sulfur concentration of substituting groups. Although sulfur concentration in the polyimide is an important factor for improving refractive index, the degree of molecular packing is also a crucial component. For example, polyimides having bulky moiety such as sulfonyl groups have lower refractive index than polyimides containing linear moiety consisting of sulfur atoms and aromatic groups despite having higher sulfur concentration. This can be explained by the loose molecular packing of bulky sulfonyl groups.\textsuperscript{41-44}

The Abbe number is described as the optical dispersion of the refractive index depending on wavelength. In optic devices, low Abbe number, high dispersion of refractive index, is avoided because it can alter the color of the image and the focal length of lenses. The Abbe number (\(v\)) is determined by the refractive index (\(n\)), molecular refraction (\(R\)), and molecular dispersion (\(\Delta R\)) according to Equation (10).\textsuperscript{45}

\[
V = \frac{6n}{(n+2)(n+1)} \times \frac{[R]}{\Delta R}
\]

From Equation (10), a large refractive index induces a small Abbe number. Typical high refractive index polymers (refractive indices greater than 1.70) have smaller than 20.0 Abbe number.
Sulfur containing polymers having high Abbe number and refractive index are listed in Table 2-2. Researchers have reported improved Abbe numbers while maintaining high refractive index using for example condensed sulfur containing alicyclic rings, polymethacrylates including thiophene, and brominated poly(thiophene methacrylate). These polymers do not reach n=1.70 but have relatively low dispersion with the Abbe number greater than 30.

### 2.3 Organic-inorganic nanocomposites

In Section 2.2, intrinsic methods for improving the refractive index of polymers were discussed. Although refractive indices of polymers can be improved significantly by substituting high molar refraction components, the highest value is limited to less...
than 1.80. Therefore, hybrid approaches which integrate organic polymers as matrixes with high refractive index inorganic nanoparticles as fillers have been introduced in order to achieve much higher refractive indices.

The refractive index of nanocomposites is determined by three factors including the properties of matrixes and nanoparticles and the technique used to incorporating nanoparticles to the matrixes. The refractive index of composites can be predicted by the Maxwell-Garnett effective medium theory. According to Equation (11), the dielectric constant of the nanocomposite sample can be explained from the dielectric constants of the host and inclusion where $\varepsilon_c$, $\varepsilon_h$ and $\varepsilon_i$ are the dielectric constants of the composite, matrix polymer and nanoparticle, respectively and $\phi$ is the volume fraction of nanoparticles.

$$\frac{\varepsilon_c-\varepsilon_h}{\varepsilon_c+2\varepsilon_h} = \phi \left( \frac{\varepsilon_i-\varepsilon_h}{\varepsilon_i+2\varepsilon_h} \right)$$ (11)

It is clear that the higher concentration of high refractive index nanoparticles, the higher refractive index of nanocomposites. However, an overload of nanoparticles has harmful influence to optical properties such as optical losses. Moreover, direct dispersion of nanoparticles into the polymers can induce aggregation of nanoparticles. Therefore, in practice, surface modification of nanoparticles is frequently employed to fabricate well-dispersed nanocomposites. A variety of nanoparticles such as TiO$_2$, ZrO$_2$, PbS, and ZnS have been incorporated into polymer matrixes, TiO$_2$ being the most widely applied in the nanocomposite fields due to beneficial characteristics including nontoxicity, high refractive index, good thermal stability and environmental stability.

Ueda research group developed TiO$_2$-loaded sulfur including polyimide nanocomposites and were able to obtain a refractive index value of greater than 1.80. In this work,
silica was used for enhancing affinity with the polymer matrix and poly(amic acid) (PAA) was selected as the matrix for the photolithography process.

![Chemical structure of poly(amic acid) and SEM images of polyimide-titania nanocomposites and the pattern by photolithography.](image)

Figure 2-2. Chemical structure of poly(amic acid) and SEM images of polyimide-titania nanocomposites and the pattern by photolithography. (Adapted from [51])

The Chen research group also developed high refractive index polymers with a series of TiO$_2$-loaded polyimide nanocomposites. In their study, a soluble PI containing carboxyl endcaps underwent an esterification reaction with titanium butoxide to bond between matrix and fillers. They acquired a 1.82 refractive index with 40wt% concentration of TiO$_2$. Other conventional polymers such as epoxy, PMMA, and polycarbonate have been used as the polymer matrix to obtain high refractive index values. However, those matrixes required much higher degrees of nanoparticle loading due to the nature of the low refractive index of the matrix polymers.

Thermosets based on thiol can inherently have high refractive index due to sulfur atom. In addition, both thiol-ene and thiol-yne networks provide high transparency and
easy processability such as UV curing. In Chapter 5, we will discuss high transparent and high refractive index nanocomposites by using TiO$_2$ nanoparticle as a filler and thiol-yne monomer mixture as a matrix. This approach can easily produce the desired shape by printing or molding methods without side products.
CHAPTER 3
LIGHT EXTRACTIONS OF ORGANIC LIGHT EMITTING DIODES

3.1 Introduction to OLEDs

Global energy consumption is regularly increased every year and approximately ~22% of the total electricity consumed is utilized as lighting in the United States. Conventional light sources such as incandescent light bulbs consume 95% of supplied electricity as a heat and only 5% of the supplied energy is converted into light. The fluorescent tube, which is another traditional light source, has ~20% power conversion efficiency (PCE) but fluorescent tubes contain a certain amount of mercury which is an environmentally hazardous materials and in increased-temperature working conditions around 35°C, power efficiency is reduced by as much as 40~60% compared with the condition at room temperature. If the light source can convert 50% of the supplied electricity into light, it is possible to save up to 650 billion kilowatt-hours per year in the United States. This is equivalent to the amount of energy generated from almost 70 nuclear plants per year in the US. Therefore, there is high demand for efficient lighting sources in order to reduce energy consumption and protect the environment.

Solid-state lighting (SSL) is a highly efficient light emitting device based on semiconducting materials. Conventional LEDs utilize inorganic semiconducting materials and have almost 100% internal quantum efficiency. LEDs have many advantages such as low energy consumption, longer lifetime, and smaller size compared with traditional light sources. Therefore, the market for LEDs has grown rapidly in the past few years. LED applications range from flat panel display appliances, to signals, to automobiles, to illumination.
On the other hand, organic light emitting diodes convert electric power into light by employing organic semiconducting materials rather than inorganic components. In comparison to inorganic LEDs, OLEDs have several benefits although low efficiency and device lifetime and stability issues must still be overcome.

![Illustrations of flexible OLEDs. (above picture) Samsung 4-5 inch AMOLED (below picture) Universal Display Incorporation flexible OLED collaborated with LG. (Adapted from http://www.oled-info.com and http://www.oled-display.net)](image)

Figure 3-1. Illustrations of flexible OLEDs. (above picture) Samsung 4-5 inch AMOLED (below picture) Universal Display Incorporation flexible OLED collaborated with LG. (Adapted from http://www.oled-info.com and http://www.oled-display.net)

First, deposition processes of organic materials are very simple by employing spin coating, inkjet printing, vacuum thermal evaporation and roll-to-roll processes,
compared to inorganic film growth processes such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). Organic materials are more economical than inorganic materials. Moreover, the extremely thin and flexible nature of organic materials make OLEDs applicable for flexible electronic device applications.

From the point of view of display performance, there are also beneficial characteristics of OLEDs compared to liquid crystal display such as a quick response time, a wide viewing angle, a high contrast and low power consumption.\textsuperscript{58,59}

Therefore, OLEDs are a very competitive candidate for flat panel display and the next generation of SSL devices.

3.2 Efficiency Limitations of OLEDs

External quantum efficiency is the number of photons emitted per injected electron. On the other hand, internal quantum efficiency ($\eta_{EQE}$) is defined as the ratio of the total number of photons generated in the device to the total number of electrons injected into the device. $\eta_{EQE}$ is calculated by multiplying the internal quantum efficiency ($\eta_{IQE}$) by outcoupling efficiency ($\eta_{out}$). Although tailoring of the OLED design by for example introducing phosphorescent materials makes the internal quantum efficiency achieve 100%, the external quantum efficiency of the typical bottom emitting-type of OLED is generally limited around 20% due to total internal reflection losses (TIRs) which result from index mismatching at multiple interfaces.\textsuperscript{60,61} The structure of an OLED has a multiple layers consisting of different refractive indices such as a metal reflector, organic layers, indium tin oxide (ITO), and a glass substrate. Therefore, the light generated in the emissive organic layer must pass through multiple interfaces in order to finally escape into the air and during this process the light confronts TIRs as depicted in Fig. 3-2.
Figure 3-2. Exemplar waveguide modes in bottom-emitting OLEDs (BOLEDs); (1) the external modes ($0^\circ \leq \theta \leq \theta_1$), (2) substrate-waveguiding modes ($\theta_1 \leq \theta \leq \theta_2$), and (3) ITO/organic-waveguiding modes ($\theta_2 \leq \theta \leq 90^\circ$).

There are three different types of modes depending on the angle of the emitted light. The light can escape through the glass substrate into the air in the external mode. In substrate-waveguiding mode, generated photons undergo TIR losses at the glass substrate/air interface and these losses are around 20~30%. The third mode is the ITO/organic-waveguiding modes. In this mode, almost 50 ~ 60% of the generated photons are confined since TIR losses occur at the interface between ITO and glass substrate and photons reflected by TIR are trapped near the metal cathode due to the strong localized electric field on the metal cathode.\textsuperscript{62-64} Therefore, it is trusted that only around ~ 20% of total generated photons can contribute to the $\eta_{out}$ in a planar structure BOLED system and this low out-coupling efficiency is main limitation of device performance.
3.3 Methods to Improve Low Out-coupling Efficiency

Several techniques to improve low out-coupling efficiency are proposed by many researchers.

First, researchers have suggested structured and shaped substrates. OLEDs fabricated on 2.2-mm-high square glass mesas with a 3-mm top edge length and a 34° wall angle were developed by Gu et al. and this structure effectively increased the portion of light scattered into the range of critical angle as shown in Figure 3-3 (left image). They also proposed the insertion of a thin film of low-loss, high refractive index dielectric material on the glass substrates before ITO deposition followed by mesa etching.

![Figure 3-3. Schematic illustration of optical ray trajectories of light generated from OLEDs with substrate modifications. The glass mesa substrate (left image) and a thin film having mesh structure (right image). (Adapted from [65] and [68])](image)

Spherically shaped patterns of the glass substrate are suggested to extract substrate waveguiding mode. Macrolens with refractive index matching materials such as polyfluorene (RI ~ 1.55) is also placed on the glass substrates to improve low out-coupling efficiency. The textured meshed structure fabricated using poly-dimethyl-
siloxane (PDMS) was proposed by Cheng et al. for low cost and large scale production (Figure 3-3 right image).

The second approach to enhance low out-coupling efficiency is the introduction of a scattering medium for light extraction into the inside of devices. Yamasaki and coworkers inserted an ordered monolayer of silica microspheres with a 550nm diameter as a scattering medium in the conventional OLED structure. Hexagonally closed packed silica microspheres behave as two dimensional diffraction lattices which behave as strong scattering medium. Silica micro-spheres array were fabricated both inside the device and on the backside of glass substrates as shown in Figure 3-4 and waveguided modes into glass and ITO/organic can be efficiently extracted.  

![Figure 3-4](image-url)

**Figure 3-4.** Schematic illustration of OLEDs with ordered arrays of silica micro-spheres. (Adapted from [69])

The microlens array is also an effective way to improve low out-coupling efficiency for OLEDs. Theoretically nearly 85% enhancement of out-coupling efficiency is possible by employing a microlens array and a 70% of improvement has
been achieved experimentally with an optimized pattern. The microlens array can be fabricated outside of the devices and there is no harmful effect on the electrical device performance. The microlens array can cover large area and fabrication processes can be simple compared to other extraction technique which modifies device structures.

Figure 3-5 illustrates light output scheme with and without microlens.\textsuperscript{74} Reflected light at the interface between the glass substrate and air can be extracted by microlens.

![Figure 3-5. Light output scheme (a) with lens and (b) without lens. (Adapted from [74])](image)

OLEDs can be considered as a one dimensional micro-cavity because the structure of OLEDs is designed to have a total organic film thickness on the order of the wavelength of emitting light.\textsuperscript{75} Weak micro-cavities are constructed with conventional OLEDs structures because of the metal cathode and high refractive index anode.\textsuperscript{76} On the other hand, a strong micro-cavity has a metal mirror and highly reflective dielectric layer such as Si\textsubscript{x}N\textsubscript{y}.\textsuperscript{77,78} OLEDs having tandem structure which is a vertical stack of multiple active regions can yield high enhancements in efficiency.

Photonic crystals are regular dielectric structures which have an energy band gap and thereby prohibit the propagation of a certain frequency range of light. Fujita and coworkers utilized two dimensional photonic crystal structures into OLEDs to improve
ITO/organic wave-guiding modes. Other researchers introduced two dimensional photonic crystal structures between ITO and glass substrates by deposition of alternative layers of SiO\textsubscript{2} and SiN\textsubscript{x}. OLEDs with photonic crystals shows 50% enhancement of light extraction efficiency compared to conventional OLEDs.\cite{80,81}

Sun and Forrest developed a method for extracting wave-guiding modes into the external mode by embedding a low index grid into the OLED active organic layer. The light trapped at the interface between ITO/glass substrate is able to enter into the low index grid and is refracted into the substrate normal direction. There is no effect on the initially emitted photons into the forward viewing cone.\cite{82}

### 3.4 Fabrication Processes for Microlens Array on OLEDs

In the previous section, several methods were introduced to improve out-coupling efficiency of OLEDs. Although these methods can efficiently increase out-coupling efficiency, they require complicated and expensive fabrication processes and modifications of device structures by, for example, the insertion of additional layers into the device. In contrast, microlens arrays can be created through a simple and reliable process to reduce TIR losses over a large area at the glass substrate/air interface.

Several researchers utilized lithography processes in order to fabricate PDMS molding for microlens arrays. Various techniques were employed to produce molds with microlens array patterns such as conventional photolithography, imprint lithography, three dimensional lithography, and soft lithography using polystyrene (PS) beads.\cite{73,82-86} The photoresist was spun on the silicone wafer and via a typical photolithography process, a square plate pattern was produced on the wafer. These plate shaped photoresists were thermally reflowed to have spherical curvature and PDMS was poured on the wafer and thermally cured. However, due to a limitation of the thermal reflow
method, individual microlenses were not hemispherical in shape and showed 0.28:1 ratio of height to diameter. Figure 3-6 illustrates the calculated coupling enhancement factor as a function of the lens height for various lens diameters. The highest value is obtained when the lens has a hemisphere structure.

![Graph](image)

Figure 3-6. Coupling enhancement factor versus lens height for different lens diameter. (Adapted from [87])

Sun and Forrest suggested imprint lithography to make the PDMS microlens array mold. The pattern of hexagonal arrays with a small distance between two photoresist plates was produced by conventional photolithography. The glass substrate with patterned photoresist was wet etched in buffered oxide to obtain an approximately hemispherical shape. PDMS was poured on the glass substrate after removing residual photoresist. In comparison to reflow method, the microlens array avoided gaps between adjacent microlenses and the height to diameter ratio (0.33:1) was improved as well. The three dimensional diffuser lithography technique, which utilizes randomized light,
was employed in order to produce various shapes of microlenses by Chang et al. By controlling parameters of the lithography process, variant shapes of microlenses were able to be fabricated such as conventional convex, hemispherical, and ellipsoidal design.

Although microlens array fabricated by the above methods showed efficient extraction of rays trapped at interface between substrate/air, expensive and complex conventional photolithography and wet-etching processes are regarded as inefficient fabrication methods for generating a reproducible microlens array mold. Therefore, Eom et al. and Nam et al. proposed a soft-lithography process using PS beads as shown in Figure 3-7.  

Figure 3-7. Schematic illustration for hemispherical microlens array formed by the soft lithography method assembled the PS array. (Adapted from [84])
A PS colloidal solution was spin-coated on the glass or SiO$_2$ substrates and PDMS was poured on the substrates containing PS beads arrays. After curing PDMS, a concave PDMS mold was separated by removing the PS array using adhesive tapes. This allowed them to avoid complex photolithography processes for producing the microlens array mold.

Figure 3-8. Schematic illustration of fabrication process via a self assembly approach. (Adapted from [89])

Yu Lu et al. suggested a self-assembly approach to fabricate two dimensional arrays of microlenses. Desired patterns were formed on the glass substrate by typical photolithography and aqueous solution containing monodispersed PS beads was confined within a packing cell consisting of two glass substrates. PS beads were trapped in the cylindrical holes on the patterned glass during capillary flow. By heating PS beads above the glass transition temperature, mushroom shaped microlenses were
obtained and after removing photoresist, hemispherical microlenses were formed by annealing.\textsuperscript{89}

Jun Xia et al. studied a self assembly polymer microlens array as well. They employed a hydrophobic layer on the patterned photoresist by an imprinting technique to prohibit the mixing of prepolymerms from adjacent lens.\textsuperscript{90}

Inkjet printing processes were introduced to produce the microlens array as well. Compared with other methods, inkjet printing has several advantages such as large scalability, simplicity, cost-effectiveness and environmentally friendliness.\textsuperscript{91-93} However, such attempts have produced microlenses with very low diameter to height ratios of approximately 1:0.075. Microlenses with such low contact angles are not suitable for light extraction. Furthermore, sag can occur at the center of the microlenses due to solvent evaporation during fabrication. Consequently, enhancement of light out-coupling efficiency by printed microlens arrays applied to OLEDs has not been demonstrated.

![Figure 3-9. SEM images of microlens array fabricated by inkjet printing process.](image)

Thiol-ene monomer mixtures are suitable for the microlens material for light extraction of bottom-emitting OLEDs due to high transparency; the refractive index is close to glass substrates. In addition, its low viscosity provides thiol-ene compatibility to
inkjet and direct printing processes. In Chapter 6, we will explain microlens array
created by direct printing technique with thiol-ene monomer mixture as lens material for
light out-coupling efficiency enhancement.
CHAPTER 4
ENCAPSULATIONS OF LIGHT EMITTING DIODES

4.1 Introduction to Encapsulations of LED

The light-emitting diode (LED) has received significant interest for illumination applications and displays since it has several beneficial properties such as extended lifespan, low energy consumption, high luminescence efficiency and heavy metal-free. Therefore, the LED market has been dramatically increased in the last few years. 94 Current applications of LEDs are extended to wide areas such as automotive forward lighting, backlight of LCD displays, indicator lamps, signs, and equipments displays.

With increasing demands for high performance, high brightness, of LED, the encapsulation of LED has aroused interest as well. High brightness LED is inevitably exposed to a high intensity UV and a high working temperature. These conditions can occur the accelerated degradation of encapsulation materials usually polymers. Thermal stability of the LED encapsulation requires stable transparency and resistance against to discoloration such as yellowing by thermal aging and thermal degradation. In addition, one of the basic limitations of LED is the light extraction efficiency which is resulted from the huge refractive index mismatch between semiconductors such as GaN or GaP and air. This refractive index mismatch makes the angle of light-escape cone for the semiconductor-air interface to be very restricted. For instance, the light escape cone of AlGaInP is limited by ~17° and trapped light inside of the semiconductor is likely lost by absorption. 95 The light extraction efficiency of both GaN and GaP LEDs was dramatically increased as the refractive index of encapsulant increased, as seen in Figure 4-1. The light extraction efficiency of GaN LEDs increased more rapidly than that of GaP due to a lesser refractive index mismatch with the encapsulation layer.
Therefore, in order to achieve high performance LEDs, the materials for encapsulation of LEDs are required to have the properties such as thermal stability, UV resistance, optical clarity and high refractive index. In addition, it is also required to have good hardness to protect LED chips.

### 4.2 Encapsulation Materials

Epoxy materials have been employed in an extended range of applications such as coatings, adhesives, industrial tooling, and biology. They are also used in electronics and LED encapsulation is a considerable application for transparent epoxy resins. In order to make transparent epoxy, hexahydrophthalic anhydride (HHPA) and methylhexahydrophthalic anhydride (MeHHPA) are utilized as curing agents. 96 These
anhydride epoxy system has several advantages such as manageable treatment, ease of processing due to relatively low viscosity, and long-term storage stability. However, acceleration catalysts such as tertially amine, imidazole, or phosphine are used for epoxy curing due to low reactivity of the anhydride system. These catalysts have a deleterious influence on the optical properties of epoxy including discoloration by either thermal or UV exposure. In addition, anhydride evaporation causes volume shrinkage which leads to internal stress within the packages. 97

Another common material for LED encapsulations is polysiloxane resin. Compared to the epoxy system, cured polysiloxane encapsulation shows impressive thermal resistance to yellowing at high temperature.98 PDMS is the most common product from silicone manufacturers. It has excellent thermal resistance to discoloration even when aging at temperatures up to 200°C. However, PDMS has very low refractive index ~1.4 and the light extraction of LEDs can be limited by the PDMS encapsulation due to the large refractive index mismatch. In order to increase the refractive index, high molar refraction phenyl groups are introduced to polysiloxane. Although phenyl groups can help increase the refractive index up to 1.52, phenyl groups are susceptible to thermal oxidation when in air for long period. 99 Therefore, the development of the high refractive index, transparent, and highly thermally stable materials is very important for the betterment of LED encapsulation technology.

4.2.1 Epoxy-Silicone hybrid resin

Several research groups have investigated silicone-epoxy hybrid resins in order to overcome the limitations of epoxy and silicone materials. Bae and coworkers developed epoxy hybrimers in order to obtain both thermal stability and high refractive index. They synthesized cycloaliphatic epoxy oligosiloxane resin by a simple sol-gel
condensation reaction between 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS) and diphenylsilanediol (DPSD). In order to make the bulk sample for the application of LEDs encapsulations, methylhexahydrophthalic anhydride (MeHHPA, 97%, Aldrich) and tetrabutylphosphonium methanesulfonate (TBPM) were added as a hardener and a catalyst, respectively. Epoxy hybrimer bulk showed good transmittance during thermal aging at 120°C and compared to conventional epoxy resin whose refractive index ~1.52,

Figure 4-2. Fabrication process of cycloaliphatic epoxy hybrimer bulk. (Adapted from [100])

cycloaliphatic epoxy hybrimer bulk exhibited higher refractive index ~1.55 at 632 nm wavelength. Figure 4-2 shows the fabrication process of cycloaliphatic epoxy hybrimer bulk. The researchers developed inorganic-organic hybrid resin as well. Phenyl-vinyl-oligosiloxane (PVO) was synthesized by a sol-gel condensation reaction between vinyltrimethoxysilane (VTMS) and diphenylsilanediol (DPSD). Phenyl hybrimers showed a slight change in transmittance ~6% and yellowness index ~12 after
thermal aging at temperatures up to 200°. Although phenyl groups are susceptible to thermal aging, the strong bonding of the siloxane network and the branched structure in PVO restricts phenyl groups from cleavage from backbone chain. PVO also showed a higher refractive index ~1.56 due to its high phenyl group concentration compared with other polysiloxane materials. The silicone-epoxy resin consisting of 2-(3,4-epoxycyclohexylethyl) methylidiothoxysilane (EMDS) and dimethylidiothoxysilane was developed by Yang et al. In their work, the silicone-epoxy resin was fabricated with different silicone contents by controlling dimethylidiothoxysilane reactions. They found that thermal stability is dependent on both the silicone content in the network and crosslink density. They reported silicone-epoxy resin showed better thermal properties than the commercial LED encapsulation material, 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate. The Morita research group reported on the extension of flexibility of epoxy siloxane. Although epoxy siloxane has promising properties such as photo-thermal stability, its brittleness is a significant issue for encapsulation applications. In order to make longer siloxane segment length, they employed hydroxyl-terminated hydrogenated polybutadiene and were able to obtain better mechanical properties for the packaging application.

4.2.2 Inorganic Particle Loaded Nanocomposites for LED Encapsulations

Inorganic particles such as ZnO and TiO₂ are utilized to improve the refractive index of the encapsulation materials. A highly transparent thermolytic epoxy-silicone which was synthesized by polymerization between the silicone matrix with diglycidyl ether bisphenol-A epoxy as reinforcing materials and ZnO nanowires as a filler to improve the refractive index and modify conductivity. PFPA-silane (N-(3-trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide) was employed to modify
the surface of ZnO nanowires to increase their affinity to matrix packaging materials.

The refractive index of nanocomposites was increased from 1.47 to 1.56 by increasing ZnO nanowires concentration of (0.025~0.200%). Below 0.175% concentration of ZnO, the transmittance of hybrid material was greater than 85% which is adequate for LED packaging.

![Figure 4-3. Three dimensional ray tracing simulation of light extraction efficiency as a function of scattering coefficient of the encapsulation with various absorption coefficients. (Adapted from [95])](image)

High refractive index TiO₂ nanoparticle-loaded epoxy was introduced by Frank et al.⁹⁵ They obtained a refractive index of ~1.67 with 10 wt% TiO₂ nanoparticle content at 500nm wavelength. They also simulated the scattering effect of nanoparticles on light extraction efficiency. For strongly scattering nanoparticles in the encapsulation layer, the optical scattering length is short but light traveling distance is long. If the light traveling distance is longer than the absorption length, photons are absorbed in the
An optimized degree of scattering for improved light extraction efficiency is shown in Figure 4-3. Although the study showed promising results using nanocomposites for increased refractive index, they did not demonstrate optical transparency which is significantly decreased by agglomeration of nanoparticles and thermal stability which is related with discoloration of packaging materials.

Materials for the encapsulation of LEDs are required to be transparent and have high refractive indices. In general, the encapsulation of LEDs is a potting process and thermosetting and UV curable resins are frequently used. UV curable thermosets based on thiol and yne provide a high refractive index and high transmittance. In Chapter 7, we will explain the multi-layer LED encapsulation by utilizing high refractive index thiol-yne nanocomposites.
CHAPTER 5
UV CURABLE HIGH REFRACTIVE INDEX AND TRANSPARENT TiO₂ LOADED
THIOL-YNE NANOCOMPOSITES

5.1 Introduction

The refractive index is one of the most important properties of materials used in optical designs and applications. High refractive index materials are needed for various applications such as ophthalmic lenses, optical adhesives, antireflection coatings, LED encapsulations as well as microlens arrays for CMOS sensors.¹⁰⁶-¹¹⁰

In chapter 2, several strategies to enhance the refractive index of polymers have been reviewed. Although these methods can efficiently increase the refractive index of polymers, there are many limitations to optical waveguiding lenses or encapsulations at the outmost layer of devices. In order to utilize these applications, high transmittance without absorption at all visible regions and processability similar to the usual polymers such as UV curing and molding for obtaining desired shapes are necessary. Since halogens such as bromine and iodine normally lead to colors in the polymer, high refractive index polymers with halogens are restricted for transparent applications. Furthermore, many of the recent regulations for environmental protection limit the use of halogen components due to potential pollution of the environment. Phosphorus containing high refractive polymer has halogen substituent in order to increase the refractive index. Polyimides which are known for good thermal stability, chemical resistance, and mechanical properties can increase the refractive index by 1.76 by including aromatic groups and sulfur moiety. However, because of its orange/yellow characteristic color it is difficult to use it for waveguiding lenses or encapsulations.

Inorganic-organic nanocomposites are developed to overcome the limitation of low refractive index of intrinsic polymers. Several inorganic nanoparticles, such as TiO₂,
ZrO$_2$, Nb$_2$O$_5$, and ZnS have been incorporated into various polymer matrixes to obtain high refractive index nanocomposites. Although high content of nanoparticles in the matrix can deteriorate optical properties of nanocomposites such as optical losses, inorganic nanoparticles-loaded composites can obtain a high refractive index of over 1.80. In order to prevent agglomeration of nanoparticles, typical surface treatments are used to functionalize metal oxide nanoparticles. Silane coupling agents are chemically bonded to the oxide surfaces through condensation reactions with surface hydroxyl groups. Surface treated nanoparticles and polymer matrix are mixed into appropriate organic solvents. Nanocomposite films are obtained after baking and drying.

Currently, there are many references regarding the synthesis, characterization, and applications of nanocomposites. However, there are only a few references on nanocomposites with processability like polymers, high transparency and high refractive index. TiO$_2$, ZnO, and ZnS nanoparticles are dispersed into the epoxy, epoxy-silicone and polycarbonate in order to achieve an easy processable high refractive index nanocomposites. These nanocomposites can be processed by the molding method to obtain desired shapes and an increase in refractive indices of nanocomposites. However, particle concentration was limited to 0.2 wt% due to optical losses from aggregation of particles in the ZnO-loaded epoxy-silicone system and the refractive index was restricted to 1.58. ZnS-polycarbonate nanocomposite showed high particle contents up to 20 wt% but the refractive index was 1.61 due to low refractive index of the matrix polymer.
As introduced in Chapter 1, thiol-yne networks are densely linked and highly uniform with rapid polymerization in mild condition as well as in the thiol-ene system. In order to form a network, thiol-ene system needs greater than two of average functionalities of thiols and enes. Therefore, typically tri or tetrafunctional thiols and enes are utilized to produce networks. On the other hand, in thiols and ynes system, dialkynes are technically tetrafunctional with respect to the addition of thiols and the reaction of dithiols and dialkynes can produce highly crosslinked polymers. A series of dithiol and dialkyne networks were fabricated by Chan et al.27

In this chapter, UV curable transparent high refractive index nanocomposites with 2,2’-thiodiethanethiol and 1,6-heptadiyne monomer mixtures as the matrix and TiO$_2$ nanoparticles as the filler will be demonstrated. 3-Methacryloxypropyltrimethoxysilane was used for the surface treatment of TiO$_2$ nanoparticles to prevent agglomeration. Increase of particle concentrations result in the increase of refractive indices of nanocomposites and the slight decrease in the transmittance of nanocomposites. TiO$_2$-loaded thiol-yne nanocomposites have the high refractive index ~1.683 and high transmittance of 88 %. Furthermore, the approach presented herein can easily produce the desired shape by printing or molding methods without side products. It does not require the clean-up of materials, and does not utilize solvents or high temperature processes.

5.2 Experiment

All dithiols, dialkynes and the photoinitiator, 1-hydroxy-cyclohexyl1-phenyl-ketone, were purchased from Sigma Aldrich and used as received. Dithiols and dialkynes were mixed with 2:1 thiol to alkyne molar ratio or 1:1 functional group ratios for network
formation, because dialkyne is technically tetrafunctional. 2 wt% of ultraviolet active radical generating photoinitiator was added to the monomer mixtures.

Solution of TiO$_2$ nanoparticles (anatase, 5 to 30 nm) in water was obtained from Nanoamor, Inc. Silane coupling agent, 3-methacryloxypropyltrimethoxysilane (MPTMS), was purchased from Fisher Scientific.

The deposition from aqueous solution method was employed for surface treatment of TiO$_2$ nanoparticles. Silane coupling agents were dissolved in ethanol and solution of TiO$_2$ nanoparticles. Solutions were stirred for 10 minutes. The mixture was rinsed with ethanol 3 times, isolated by centrifugation and dried. Dried particles were grinded, dispersed in ethanol, and filtered. Ethanol evaporated in the oven at 60 °C. Particles were mixed into 2,2'-thiodiethanethiol and 1,6-heptadiyne monomer mixtures and ultrasonicated. Solution was placed between the cover glass and hydrophobic glass substrate and exposed to UV-light (365nm, 100mW/cm$^3$) in the duration of 1 minute for polymerization. By removing hydrophobic glass, nanocomposite film remained on the cover glass.

Refractive indices of pure thiol-yne films were measured by the ellipsometer (J. A. Woolam) at visible wavelengths and the refractometer (Reichert Abbe Mark II Plus Refractometers) at a wavelength of 580 nm. Thermogravimetric analysis (TGA) was performed on a thermal analysis system (Mettler Toledo TGA/DSC). Samples of approximately 8mg were loaded and heated up to 800 °C at a rate of 10 °C/minute under air flow of 60 ml/minute. The transmittance of nanocomposite films was measured in UV-VIS spectrometer (PerkinElmer Lambda 750) at a wavelength region from 300 nm to 800 nm.
5.3 The Refractive Index of Thiol-Yne Thermosets

The four dithiols and four dialkynes in Figure 5-1 were utilized to produce a series of thiol-yne networks. The dithiols and dialkynes networks consist of only carbon, hydrogen and sulfur atoms and the refractive index of each polymer can be controlled by changing the weight percentage of sulfur atoms in the networks. The higher

![Chemical structures](image)

Figure 5-1. Chemical structures and abbreviation of dithiols and dialkynes.
sulfur content results in a higher index of refraction due to the characteristic of high atomic refraction of sulfur atoms.

The network consisted of TDET and HptDY has the highest weight percentage of sulfur with 48 %. Among the listed dithiols and dialkynes in Figure 5-1, DDT and DDDY have the longest chain length and the highest molecular weight. Hence, the DDT-DDDY network shows the lowest sulfur content with 22.3 %. Figure 5-2 shows the refractive index versus the weight percent sulfur plots for photopolymerized networks produced from 2:1 alkyl dithiol and dialkyne monomer mixtures. The refractive index of TDET and
HptDY film was measured by both ellipsometer and refractometer and their measured values were 1.623 and 1.621, respectively. Figure 5-3 shows the refractive index of TDET-HptDY film from the ellipsometer.

![Graph showing the refractive index of TDET-HptDY film.](image)

Figure 5-2. Dependence of the refractive index on concentration of sulfur in the photopolymerized networks

The Abbe number is defined as optical dispersion of the refractive index depending on the wavelengths. For the application of optics, high dispersion of the refractive index depending on wavelengths is refrained because it can change the color of the image and the focal length of lenses.

$$V = \frac{n_{587.6\text{nm}} - 1}{n_{486.1\text{nm}} - n_{656.3\text{nm}}}$$  \hspace{1cm} (12)

The Abbe number is determined by Equation (12). As discussed in Chapter 2, a large refractive index induces a small Abbe number. Typical high refractive index
polymers have smaller Abbe number of 20.0 than the ones with high refractive indices over 1.70. However, the film made using TDET and HptDY showed refractive indices 1.6351, 1.6237, and 1.6196 at 486 nm, 589 nm, and 656 nm wavelength. Calculated Abbe number was 40.37 and it is relatively higher than polymers reported as high Abbe number materials.  

Figure 5-3. Measured refractive index of the film made of TDET-HptDY

5.4 Surface Treatment of TiO₂ by Silane Coupling Agent

The direct mixing of nanoparticles into the polymer matrix promotes agglomerations of nanoparticles. Therefore, virtually, the surface of the particle is modified to be suitable for mixing processes. Organic groups attached to the surface of nanoparticles prohibit aggregations and cause a surface polarity adjustable to the medium.
Silane coupling agents have been utilized to form a durable bond between organic and inorganic materials. The typical structure for a silane coupling agent is shown in Figure 5-4. X is a hydrolyzable group typically consisting alkoxy, acyloxy, halogen or amine. Hydrolysis reaction forms a reactive silanol group, which can condense with hydroxyl group on the surface of substrates or fillers. The R group has a functionality that imparts desired properties.

In this work, polymerizable reagent, 3-methacryloxypropyltrimethoxysilane (MPTMS), was used to stabilize nanoparticles and to allow them to be compatible with thiol-ynne monomer mixtures.

![General structure of silane coupling agent](image1)

*Figure 5-4. General structure of silane coupling agent (upper image) and chemical structure of MPTMS (lower image)*
5.4.1 TGA Measurement of Pure TiO$_2$ and Surface Modified TiO$_2$

The amount of attached MPTMS to nanoparticles was estimated from the TGA measurement in Figure 5-5. The weight loss values of untreated TiO$_2$ and MPTMS-modified TiO$_2$ were 7.1 % and 15.3 %, respectively. Weight loss of pure TiO$_2$ is possibly due to adsorbed moisture molecules. It is assumed that the percentage of residue from MPTMS molecules anchored on nanoparticles was approximately 8 %.

![TGA analysis of pure TiO$_2$ and MPTMS modified TiO$_2$.](image)

5.4.2 FTIR Analysis of Pure TiO$_2$ and Surface Modified TiO$_2$

TiO$_2$ nanoparticles were well dispersed in solution of water and ethanol due to electrostatic repulsion. After adding MPTMS into the solution, the translucent solution changed to opaque. This indicates that the surface conditions of nanoparticles were altered by the reaction between nanoparticles and the surface modifier, MPTMS. The
change of surface states of nanoparticles was analyzed using FT-IR. Figure 5-6 shows FT-IR spectra of pure MPTMS, untreated TiO\textsubscript{2} and surface modified TiO\textsubscript{2} by MPTMS. After applying silane coupling agent treatment on nanoparticles, C-O stretching absorption peaks were observed at 1319 cm\textsuperscript{-1}. C=O vibration of \( \alpha,\beta \)-unsaturated ester and C=C double bond peaks were also observed at 1718 cm\textsuperscript{-1} and 1636 cm\textsuperscript{-1}, respectively. These peaks indicate organofunctional group of MPTMS adsorbed on the nanoparticles. At 1180 cm\textsuperscript{-1}, Si-CH\textsubscript{2}-R stretching peaks were observed as well.

![FT-IR spectra of untreated nanoparticle and MPTMS modified nanoparticle](image)

Figure 5-6. FT-IR spectra of untreated nanoparticle and MPTMS modified nanoparticle

### 5.5 Nanocomposites

#### 5.5.1 Composition and Thermal Properties

Nanocomposite films were prepared from MPTMS modified TiO\textsubscript{2} nanoparticles and TDET-HptDY with various particle weight percents. Untreated TiO\textsubscript{2} nanoparticles
were also dispersed into the TDET-HptDY monomer mixtures for comparison. The amount of nanoparticles incorporated into the nanocomposites was measured by the TGA results. Figure 5-6 shows TGA thermograms of the TDET-HptDY polymer matrix and nanocomposites where TY and NCTY are pure TDET-HptDY film and nanocomposite TDET-HptDY film, respectively. 0.7 wt% of cured thiol-yne monomer mixtures remained under the employed TGA condition due to the buoyancy effect which can be observed that a specimen heated in thermobalance. This is, in part, due to the differences in thermal conductivity, density, and heat capacity for the gas and the sample/crucible. At employed condition of TGA measurement, NCTY1 and NCTY2 had particle concentration of 3.33 % and 6.44 %, respectively. NCTY3 and NCTY4 had relatively higher particle content of 8.87 % and 10.67%, respectively.

![Graph](image)

Figure 5-7. TGA results of matrix polymer and nanocomposites.
A slight increase in thermal stability of the nanocomposites was demonstrated by TGA analysis. Decomposition temperatures of nanocomposites increases with particle content. Decomposition temperatures of 10% weight loss was 228 °C, 275 °C, 283 °C for TGA samples of TY, NCTY1 and NCTY4, respectively. The increase in thermal stability was attributed to restrict molecule mobility imposed by nanoparticles. The formation of strong siloxane bonds between silane coupling agents and nanoparticles and the polymerization between thiols and C=C bonds of functional group of silane coupling agent may further enhance the increase in decomposition temperatures.

5.5.2 Optical Transparency of Nanocomposites

![UV-VIS transmittance spectra](image)

Figure 5-8. UV-VIS transmittance spectra of the TDET-HptDY film and nanocomposite films

Optical transparency of nanocomposites is a good measure of dispersibility of nanoparticles in the matrix. The dispersability of TiO<sub>2</sub> nanoparticles in the TDET-
HptDY monomer mixtures was estimated from the transmittance measurement of nanocomposite films with thicknesses of approximately 30 – 35 μm. The agglomeration of nanoparticles to a size larger than several tens of nanometers is a major determinant in possible inducement of the scattering loss of visible lights traveling through a nanocomposite film. Furthermore, a large mismatch of the refractive index between polymer matrix and nanoparticles can result in a large scattering efficiency. The nanocomposite with untreated TiO₂ nanoparticles showed macroscopic phase separation. An analysis of this sample was not performed.

Figure 5-8 shows transmittance of the TDET-HptDY film and nanocomposite films. TDET-HptDY film had very high transmittance ~95% at visible regions and there was almost no change of transmittance from 650 nm to 480 nm. Although introduction of surface treatment on nanoparticles improved dispersion, the optical clarity of nanocomposites with TiO₂ nanoparticles was reduced with increasing weight percent of particles. However, samples with low particle content, NCTY1 and NCTY2, still had approximately 90% transmittance at 650 nm while NCTY3 showed 88% transmittance with a relatively high particle content. Transmittance of NCTY1-3 showed 2 or 3% difference from 650 nm to 480 nm measurements. NCTY4 including the highest particle concentration showed the largest scattering loss at whole visible regions and had 81% transmittance at 650 nm. The occurrence of scattering loss was stronger at short wavelength regions in this sample and the transmittance difference from 650 nm to 480 nm reached to 8%. Unfortunately, TiO₂ nanoparticles act as a photocatalyst by UV light. Refractive index differences can occur through oxidation of polymer materials and particle aggregation.
5.5.2 Refractive Indices of Nanocomposites

The refractive index of composite materials can be predicted by Maxwell-Garnett effective medium theory\textsuperscript{119} and Lorentz-Lorenz approximation.\textsuperscript{120} Maxwell-Garnett effective medium theory is described as Equation (13) and the refractive index of the composite can be calculated by dielectric constants of host and inclusion materials and the Maxwell relation $n^2 = \varepsilon$.

\[
\frac{\varepsilon_c - \varepsilon_h}{\varepsilon_c + 2\varepsilon_h} = \phi \left( \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i - 2\varepsilon_h} \right) \tag{13}
\]

\(\varepsilon_c, \varepsilon_h, \) and \(\varepsilon_i\) are dielectric constants of the composite, host, and inclusion, respectively and \(\phi\) is the volume fraction of the inclusion in Equation (13). Solid line in figure 5-9 is based on the Equation (14) where \(\varepsilon_h\) and \(\varepsilon_i\) are 1.62\textsuperscript{2} and 2.53\textsuperscript{2}\textsuperscript{121} respectively.

Lorentz-Lorenz effective medium approximation is shown in the Equation (14)

\[
\frac{n_c^2 - 1}{n_c^2 + 2} = \phi_{np} \frac{n_{np}^2 - 1}{n_{np}^2 + 2} + \phi_{SCA} \frac{n_{SCA}^2 - 1}{n_{SCA}^2 + 2} + \phi_m \frac{n_m^2 - 1}{n_m^2 + 2} \tag{14}
\]

where \(n_c, n_{np}, n_{SCA},\) and \(n_m\) are refractive indices of the composite, nanoparticle, silane coupling agent (MPTMS) and matrix polymer, respectively. \(\phi_{np}, \phi_{SCA},\) and \(\phi_m\) are volume fractions of the nanoparticle, silane coupling agent and matrix polymer.

Maxwell-Garnett equation and Lorentz-Lorenz equation were plotted with solid and dashed line in Figure 5-9. Samples were measured by the Abbe refractometer at 580nm wavelength. TDET-HptDY had the refractive index \(~1.621\) and it matched with the value (1.623) measured by an ellipsometer. Thiol-yne films were regarded as a bulk substrate sample. Only the top reflected lights on the surface were collected by the detector of an ellipsometer. In this case, films were deposited onto the rough side of a single-side polished silicon wafer and the measurement only contained information from the front.
surface reflection while light reaching the back surface of films were scattered rather than reflected as shown in Figure 5-10 (left image). Therefore, film thickness and

![Graph showing refractive index variation with particle wt%](image)

Figure 5-9. Refractive indices of the TDET-HptDY film and nanocomposites at 580 nm wavelength. Black solid line and red dash line are theoretical assumptions of Maxwell-Garnett equation and Lorentz-Lorenz equation, respectively.

![Ellipsometer sample images](image)

Figure 5-10. Sample species of the ellipsometer; (left image) a bulk substrate and (right image) multi-layer films

uniformity were not important for ellipsometer measurement of a bulk substrate.

However, in order to measure the refractive index of nanocomposite by an ellipsometer,
it is necessary to probe inside the sample like multi-layer samples as shown in Figure 5-10 (right image).

Unfortunately thicknesses of nanocomposite films and surface uniformity were not good enough to be measured by the ellipsometer. Therefore, refractive indices of nanocomposite were measured only with a refractometer. Refractive indices of nanocomposites were increased with increasing particle contents as expected by theories. Refractive indices of NCTY3 and NCTY4 showed 1.6835 and 1.6981, respectively.

5.6 Conclusion

UV curable high transparent and refractive index nanocomposites were successfully fabricated with surface modified TiO$_2$ nanoparticles and high refractive index TDET-HptDY matrix. The polymerizable silane coupling agent, MPTMS, was introduced to improve dispersion of nanoparticles and nanocomposite films which showed high transmittance with particle content up to ~8.8 wt%. Nanocomposite with highest particle contents showed lowest transmittance. Larger transmittance dispersion depending on wavelengths was also observed than that of other nanocomposites which had less than 9 wt% particle contents. It is assumed both particle aggregation and polymer oxidation by TiO$_2$ nanoparticles influence scattering losses and absorptions. Refractive indices of nanocomposites gradually increased with particle contents in the composites. The refractive index of the nanocomposite with 8.8 wt% nanoparticle content was 1.6835 which is relatively higher than reported values such as 1.58 and 1.61.
CHAPTER 6
MICROLENS ARRAYS CREATED BY A DIRECT PRINTING TECHNIQUE FOR LIGHT OUT-COUPLING EFFICIENCY ENHANCEMENT OF ORGANIC LIGHT-EMITTING DEVICES

6.1 Introduction

Organic light emitting diodes (OLED) are electroluminescent devices which have experienced rapid development in the past two decades and have become competitive solutions in illumination tasks requiring a large area light source.\textsuperscript{122} Although nearly 100% internal quantum efficiency of such devices has been achieved using phosphorescent emitting materials,\textsuperscript{60,123} low out-coupling efficiency of around 20% due to total internal reflection (TIR) losses result from refractive index mismatches between the multiple layers of such devices.\textsuperscript{124} Various methods have been proposed to improve out-coupling efficiency such as shaping devices into mesa structures,\textsuperscript{65} making use of a microcavity structure,\textsuperscript{125,126} employing a photonic crystal,\textsuperscript{127} or embedding a low index grid between the indium tin oxide (ITO) and the organic layer.\textsuperscript{82} Although these methods can increase the out-coupling efficiency, they require complicated and expensive fabrication processes and modifications of device structures such as the insertion of additional device layers. In contrast, microlens arrays can be created through a simple and reliable process to reduce TIR losses over a large area at the glass substrate/air interface. Several different methods for fabricating microlens arrays have been reported, such as using imprint lithography and wet etching of a silicon substrate to create a microlens mold,\textsuperscript{70} three dimensional diffuser lithography utilizing randomized light to form various shapes,\textsuperscript{83} liquid crystal droplet microlens array,\textsuperscript{128} microlens array mold from microporous polymer film by casting of polymer solutions under humid conditions,\textsuperscript{129} melting a self-assembled two-dimensional polystyrene array,
and a soft lithography based method in which a colloidal monolayer of polystyrene spheres serves as a mold template. These approaches are all technically complicated and/or expensive.

A direct printing technique is an attractive alternative method for fabrication of microlens arrays due to its relative simplicity, low consumption of lens materials, and the ability to control array pattern and positioning. Printing techniques are familiar and relatively mature and a well-supported industrial infrastructure makes printing techniques a promising method of simple and cost effective microlens array fabrication. Several research groups have attempted to fabricate microlens arrays using the inkjet printing technique. However, such attempts have produced microlenses with a very low diameter to height ratio of approximately 1:0.075. Microlenses with such low contact angles are not suitable for light extraction. Effective microlenses should be as nearly hemispherical as possible. Furthermore, sag at the center of microlenses due to solvent evaporation during fabrication has been a problem. Consequently, enhancement of light out-coupling efficiency by printed microlens arrays applied to OLEDs has not been demonstrated.

In this Chapter we present a process for the fabrication of large area microlens arrays having a high diameter to height ratio (1:0.41). These arrays were printed using a substrate surface modification technique employing a hydrophobic silane coupling agent to control the microlens shape. Several hydrophobic silane coupling agents were tested to find one that would achieve a high contact angle for the lens material. The surface properties of a glass substrate were modified by three different silane coupling agents in order to find the lowest critical surface tension, which can be determined using a
Zisman plot. \cite{131} We employed a solventless multifunctional thiol and ene monomer mixture as a lens material to obtain a nearly hemispherical lens shape without sag at the lens centers. The photopolymerization of a mixture of multifunctional thiol and ene is an efficient method for rapid production of film and thermoset plastics. A thiol and ene monomer mixture is suitable as a microlens material due to its transparency, similar refractive index to a glass substrate, and adaptability to printing techniques because of its low viscosity. Using such a printed microlens array we have been able to obtain a 30% enhancement of light out-coupling efficiency without observing changes to the emission spectrum.

6.2 Experiment

(Heptadecafluoro-1, 1, 2, 2-tetra-hydrodecyl) trimethoxysilane, polydimethylsiloxane(methoxy terminated), and octyl trichlorosilane were obtained from Gelest as hydrophobic silane coupling agents. Deposition from aqueous solution was employed for surface treatment of glass substrates. Silane coupling agents were dissolved at 2 wt% concentrations in water. Cleaned glass substrates were dipped into the solution and removed after 2 minutes of agitation. Silane layers were cured at 110˚C for 10 minutes. DI water (surface tension of 73 mN/m), glycerol (64 mN/m), ethylene glycol (48 mN/m), 1,2 dichloroethane (33 mN/m), acetone (23 mN/m), hexane (18 mN/m) (Fisher) were selected as test liquids for a wetting experiment to determine the lowest surface critical tension that could be obtained for modified surfaces. A goniometer (Rame-Hart) was used to measure contact angles produced by the six test liquids on glass surfaces modified by each of the silane coupling agents.

The silane coupling agent having the lowest critical surface tension determined by a Zisman plot was applied on an ITO sputtered glass substrate using a chemical
vapor deposition method to achieve better uniformity than deposition from an aqueous solution. In a closed chamber, substrates were supported above a silane reservoir with a vapor pressure of 5 torr at 80°C for various deposition times varying from 5 minutes to 8 hours.

The lens material was a monomer mixture of trimethylolpropane tris(3-mercaptopropionate) and tri(ethylene glycol) divinyl ether. Multifunctional thiol and ene were mixed in a 2:3 molar ratio to match the number of functional groups for complete conversion. This solution was formulated with a 2 wt% ultraviolet active radical generating photoinitiator, 1-hydroxycyclohexylphenyl ketone (acros organics). The refractive index and transmittance of the film of the thiol and ene mixture were measured by ellipsometry (J.A. Woolam) and with a UV-VIS spectrometer (PerkinElmer Lambda750) respectively.

Deposition of the microlens array was conducted with a model 3Dn-450-HP direct write instrument (nScrypt, Inc.) as shown in 6-1. Materials dispensing was controlled by air pressure fed to a syringe. The liquid lens material was pushed into a chamber and then pushed out through a dispensing tip. The chamber was connected to a gantry which contained a series of motors allowing movement in the x, y, and z dimensions. A software interface was used to convert CAD or other design specifications into a series of commands that stepped the motors in sequence to draw desired lens array patterns. Controllable variables included the size of the tip, the chamber valve opening distance relative to the sealed position, air pressure, and deposition speed. The rheology of the material being dispensed also affects deposition quality. For microlens array deposition, a tip with an inner diameter of 100μm and outer
diameter of 240μm was used at a relative valve opening distance of 2.2 mm, and an air pressure of 1.5 psi.

Figure 6-1. Deposition of microlens array by the direct write instrument

Printed microlens arrays were exposed to UV-light (365nm, 100mW/cm³) for 10 seconds for polymerization. Scanning electron microscopy (SEM, JEOL 6335F) was employed to analyze the geometry of the resulting microlens arrays and the contact angles of individual lenses.

In order to measure the optical effects these lenses would provide, fluorescent organic light emitting diodes (OLED) were fabricated on glass substrates with the microlenses preprinted on the opposite side, allowing for no change to the standard OLED fabrication. All devices were fabricated using vacuum thermal evaporation at a pressure of 3.0 x 10⁻⁶ Torr or less. Devices consisted of tin doped indium oxide (ITO)
pre deposited on glass with 50 nm \( N,N\text{-odi(naphth-2-yl)}-N,N\text{-ndiphenyl-benzidine} \) (NPB) and 50 nm \( \text{tris-(8-hydroxyquinoline)} \) (Alq\textsubscript{3}) as hole transport and emission layers respectively. A 1 nm CsCO\textsubscript{3} interlayer followed by 80 nm Al was used for electron injection into the device. The device area defined by the cathode was either 4 mm\(^2\) or 1 cm\(^2\). Devices were characterized with and without microlenses using an Ocean Optics Jaz spectrometer to measure enhancement and emission spectra. A 400 mm diameter optical fiber was used to capture the emitted light. All measurements were conducted at ambient room conditions.

Lens array deposition was conducted using Microdrop\textsuperscript{®} MD-series inkjet printing methods as well as direct printing techniques. A dispenser head nozzle with a diameter of 50\( \mu \)m, which dispensed approximately droplets with a liquid volume of 90 pl, was used at a nozzle temperature of 40° C, a driving voltage of 200 V, and a distance from substrate to nozzle of 75\( \mu \)m. Labview software was employed to automate the process of microlens array fabrication. In order to measure the diameter and height of printed lenses, a Wyko optical profilometer was utilized.

**6.3 Surface Treatment on Substrates of OLEDs by Silane Coupling Agent**

**6.3.1 Zisman plots of hydrophobic SCAs**

Critical surface tension is useful in determining wettability of solid surfaces with a range of liquids. A liquid with a surface tension below the critical surface tension of a solid will spread on the substrate (i.e. 0° contact angle). The critical surface tension is determined by plotting the cosine of the contact angle versus surface tension of different test liquids and extrapolating to 1. Typically hydrophobic behavior is observed for surfaces with a critical surface tension less than 35 mN/m. Aliphatic hydrocarbon substituents or fluorinated hydrocarbon substituents are the hydrophobic components
which enable silanes to introduce surface hydrophobicity. Surfaces with a critical surface tension below 20 mN/m resist wetting by hydrocarbon oils and are regarded as oleophobic as well as hydrophobic.

Figure 6-2. Zisman plot and the critical surface tension of (a) (heptadecafluoro-1, 1, 2, 2, -tetra- hydrodecyl) trimethoxysilane (b) polydimethylsiloxane(methoxy terminated) (c) octyl trichlorosilane

In order to determine the critical surface tension of a surface modified by a silane coupling agent, Zisman plots were constructed after measuring the contact angles of six test liquids. Water has the highest surface tension, 73mN/m, among the test liquids and the contact angles of water on the three surfaces were all above 90˚. Contact angles of the test liquids decrease as the surface tension of the liquids increased, as described by Young’s equation.\(^ {132} \) Hexane, having the lowest surface tension, 18mN/m, among the test liquids was not able to resist surface wetting on the surface modified with octyl trichlorosilane. However, hexane showed contact angles of 14.48˚ ± 1.14˚ and 34.4˚ ± 2.06˚ on surfaces altered by polydimethylsiloxane(methoxy terminated) and (heptadecafluoro-1, 1, 2, 2, -tetra- hydrodecyl) trimethoxysilane, respectively. Figure 6-2
shows Zisman Plots constructed from measured contact angles of test liquids. The calculated critical surface tension of a surface with (heptadecafluoro-1, 1, 2, 2, -tetra-hydrodecyl) trimethoxysilane is 9.29 mN/m, polydimethylsiloxane(methoxy terminated), 11.68 mN/m, and octyl trichlorosilane, 20.29 mN/m. All selected silane coupling agents introduce very hydrophobic as well as oleophobic surfaces with critical surface tensions below 20mN/m.

6.3.2 Vapor phase deposition of SCA

(Heptadecafluoro-1, 1, 2, 2, -tetra- hydrodecyl) trimethoxysilane, having the lowest critical surface tension, was selected for the device fabrication. We can visually observe slight non-uniformities on the surface of a glass substrate after coating with a silane coupling agent from an aqueous solution because defects can result from solvent evaporation. Although a wetting experiment with droplets a few millimeters in diameter is not affected by small surface defects, these defects could alter the lens shape or contact angle of a microlens thus damaging the microlens array geometry. In order to obtain a uniform surface on glass substrates, the silane coupling agent was applied using a chemical vapor deposition method in a heated vacuum chamber. A hydrophobic surface is achieved if the hydroxyl groups of a substrate are capped by silane and surface is effectively shielded by the hydrophobic entities of the silane coupling agent. If residual hydroxyl groups are exposed then the surface will not be completely shielded, decreasing surface hydrophobicity. Vapor phase deposition time was varied in order to confirm that the silane coupling agent had effectively screened the surface of the glass substrate.

Figure 6-3 shows the change of contact angle of the microlenses on the modified surfaces resulting from various silane vapor deposition times. On a bare glass substrate
a multifunctional thiol-ene monomer mixture does not have resistance to wetting and individual microlenses have a diameter to height ratio of 1:0.19.

Figure 6-3. SEM cross section images of microlenses on the modified surfaces resulting from various silane vapor deposition times (a) no treatment, (b) 5 minutes, (c) 15 minutes, (d) 30 minutes, (e) 1 hour, (f) 4 hours, (g) 8 hours
The silane coupling agent effectively shields the hydrophilic glass surface even after treatments of short duration; after 5 minutes of deposition the diameter to height ratio increased to 1:0.33. The diameter to height ratio increased slightly to 1:0.39 after 30 minutes surface treatment. A maximum diameter to height ratio of 1:0.41 was measured after a one hour vapor phase deposition and no further increases in the ratio were measured with deposition times of 4 and 8 hours.

6.4 Optical Properties of Thiol-Ene Lens Materials

A film of a multifunctional thiol and ene monomer mixture was deposited on a silicon substrate for measuring the refractive index of the lens material. In order to avoid the effects of film non-uniformity, the film was deposited on the backside of the silicon substrate and the ellipsometry detector only collected light reflected from the top of the film. Figure 6-4 shows the refractive index measured by ellipsometry. At a wavelength of

![Graph of refractive index vs wavelength](image)

Figure 6-4. The refractive index of lens material
486nm, the index of refraction is 1.492, at 589nm it was 1.480, and at 656nm it was 1.473. The Abbe number was calculated as 25.26 using the equation below:

\[ V = \frac{n_{587.6\text{nm}} - 1}{n_{486.1\text{nm}} - n_{656.3\text{nm}}} \]  

A film of a multifunctional thiol and ene monomer mixture was also deposited on a glass substrate to measure the transmittance of the lens material. The transmittance measured using a UV-VIS spectrometer was over 98% across the visible spectrum as shown in Figure 6-5.

Figure 6-5. Transmittance of thiol-ene lens material

**6.5 Microlens array fabrication by direct-printing technique**

For device fabrication, the silane coupling agent was deposited on the ITO sputtered glass substrate for 4 hours using the chemical vapor deposition method. The thiol-ene monomer mixture was then printed on the surface of the modified glass
substrate using direct printing. The outer diameter of the dispensing tip initially interfered with the formation of adjacent lenses in the array resulting in a very low fill.
Figure 6.6. SEM images of a printed microlens array, (a) a top view, (b) an individual lens, (c) 30° tilted view

factor of the microlens array. High air pressure had to be applied so that enough liquid lens materials would flow from the tip in order to obtain larger microlens diameters, thus resulting in a higher fill factor. The distance between adjacent microlenses was set at 400 μm to avoid agglomeration of liquid droplets. An array of 30 lenses by 20 lenses was printed, covering half of the emission area of a large area device. Figure 6.6 shows scanning electron microscope (SEM) images of a printed microlens array: a top view (Fig 6.6. a), a 30° tilted view (Fig. b), and an individual lens (Fig. c). The diameter of an individual lens is 335.4±17.6 μm and the calculated fill factor is 66.8±7.7 %.

6.6 Enhancement of light out-coupling efficiency

The light extraction enhancement of the microlenses was measured on devices 1 cm x 1 cm with half the emitting area covered in the microlens array while the other half remained bare. Figure 6-7 shows the normalized spectral intensity of both the bare
Figure 6-7. The normalized spectral intensity of both the bare OLED side and the lens – enhanced side of a large area device.

OLED side as well as the enhanced lens side. An enhancement factor of \( f = (1.31 \pm 4) \) was observed, and while lower than other reported methods, this enhancement is likely limited by the spacing between lenses which is highly dependent on the printing system used. Further enhancement is likely with finer mechanical control of drop position. Figure 6-8 shows the angular emission pattern of a lens-enhanced 4 mm\(^2\) device compared to both a bare device and an ideal Lambertian light emitting pattern. The lens-enhanced device is shown to be more forwardly directional in its emission pattern than the other two sources. This is believed to be due to redirection of wide angle light into the forward direction by other lenses in the array. Smaller micro lens heights (7 \( \mu \)m), as shown by Sun and Forrest, do not exhibit this effect, but rather show expanded emission at high angles.

Figure 6-8. The angular emission pattern of a lens-enhanced 4 mm\(^2\) device compared to both a bare device and an ideal Lambertian light emitting pattern.
6.7 Microlens array fabrication by inkjet-printing technique

We have fabricated microlens arrays using an inkjet printer in addition to the direct printing system described in Section 6.5. In order to deposit microlens arrays, the glass substrate was first treated with a hydrophobic silane coupling agent using the chemical vapor deposition technique with a deposition time of 4 hours. The substrate was then placed on the sample stage of the inkjet printer and the liquid reservoir was filled with a thiol-ene. Figure 6-9 shows the inkjet printing system consisting of printer head, liquid reservoir, 3D movement actuators and printer controller.

Figure 6-9. Microdrop® inkjet printer with 3D movement actuators.

The distance from the substrate to the dispensing nozzle tip was set by moving the movement actuator 75 μm in the upward z-direction after the nozzle tip had carefully contacted the substrate. If the distance between the substrate and the end of nozzle tip is too far away, an excessive potential energy of liquid droplets prevents stable deposition onto the substrate and air flow influences the positioning of droplets. The
dispensing head consists of a glass capillary which is surrounded by a tubular piezo actuator. The piezo actuator contracts and produces a pressure wave by applying a voltage, resulting in a pressure propagating into the liquid. A small droplet of the thiol-ene monomer mixture left the nozzle by the pressure generated from the piezo device and was deposited on the substrate. The piezoelectric device in the printer head and the movement actuator were controlled using Labview software allowing automatic creation of lens arrays. Figure 6-10 shows SEM (left) and optical microscope images (right) of printed microlens arrays.

![Figure 6-10. Microlens array images created by inkjet printing system. 15° tilted SEM image (left) and optical microscope image (right).](image)

The diameter and height of the printed lenses were measured with a Wyko optical profilometer which is an optical profiler providing three-dimensional surface profile measurements without contact. The measured diameter and height were 73.6 μm and 32 μm, respectively as shown in Figure 6-11. The size of individual microlens created by the inkjet printing technique can be altered by employing various nozzle diameters. In this work, we obtained microlenses having diameters of 73.6 μm with a 50 μm nozzle diameter, which generated droplets with a volume of 90 pl. In comparison with direct printing methods, inkjet printing can produce microlens arrays with better
uniformity because in the direct printing system the dispensing tip must have contact with the substrate. In addition, inkjet printing systems can control lens size using various nozzle diameters. However, the narrow nozzle of inkjet printers can be easily blocked by materials that are easily cured and thus become insoluble due to crosslinking. Therefore, a robust cleaning system is necessary. In this work it was not possible to consistently deposit microlens arrays on OLED devices because of this cleaning issue.

Figure 6-11. Measurement of lens diameter and height by Wyko optical profilometer

6.8 Conclusion

In summary, the microlens array was successfully fabricated on the OLED by a direct printing technique. Surface treatment by hydrophobic silane coupling agent had a significant effect on increase of the contact angle of lens droplets. Thiol-ene monomer mixture was a very suitable for a lens material because it had the refractive index
matched with the glass substrate and high transmittance. In order to dispense lens
droplets, dispensing tip must have contact with the substrate in this direct printing
system. This created slight non-uniformities on the lens array. Further enhancement will
be possible to the employ more precise mechanical positioning system and inkjet
printing system for better uniformity of the lens array.
CHAPTER 7
MULTI LAYER ENCAPSULANT FOR LIGHT EMITTING DIODES

7.1 Introduction

White LEDs have received extensive attention for applications of lighting and displays due to many advantages such as low energy consumption, low driving voltage, long lifespan, and high luminescence efficiency. In the application of LEDs, the roles of encapsulation materials have a great impact on the brightness and life span of LEDs. High brightness LED generates more heat and shortwave radiation which may induce discoloration of encapsulations.\(^{133}\) Thermal stability of the LED encapsulation requires stable transparency and resistance against discoloration such as yellowing of the material by thermal aging and thermal degradation. In addition, one of the basic limitations of LED is the light extraction efficiency which results from huge refractive index mismatch between semiconductors such as GaN (\(n=2.5\)) or GaP (\(n=3.45\)) and encapsulation materials. Total internal reflections at semiconductor-encapsulation interface confine lights inside the LED, which is most likely lost by absorption and heat. Therefore, the light extraction efficiency of LEDs dramatically increased as the refractive index of encapsulant increased.\(^{95}\)

Epoxy resins have been used for encapsulation and packaging materials.\(^{96}\) Anhydride epoxy system has several advantages such as ease of processing, relatively low viscosity, and long-term storage stability. However, acceleration catalysts used for epoxy curing due to low reactivity of the anhydride system leads to a harmful influence on the optical properties of epoxy, including discoloration by either thermal or UV exposure. In addition, anhydride evaporation causes volume shrinkage which leads to internal stress within the packages.\(^{97}\) Another common material for LED encapsulations
is silicone resin. Compared to the epoxy system, cured polysiloxane encapsulation, for example, PDMS shows excellent thermal resistance to discoloration such as yellowing during thermal aging at high temperature even up to 200°C. However, the light extraction of LEDs can be limited by the PDMS encapsulation due to the low refractive index ~1.4 of PDMS. In order to increase the refractive index, high molar refraction phenyl groups were introduced to polysiloxane. Although phenyl groups can help increase the refractive index up to 1.52, phenyl groups are susceptible to thermal oxidation when in air for a long period. Several research groups have investigated silicone-epoxy hybrid resins or inorganic-organic hybrid resin to overcome the limitations of epoxy and silicone materials. They developed thermally stable epoxy hybrimer or phenyl hybrid resin but was limited to the refractive index of ~1.56. Inorganic particles such as ZnO and TiO$_2$ were utilized to improve the refractive index of the encapsulation materials. The refractive index of nanocomposites increased from 1.47 to 1.56 with an increase of ZnO nanowires concentration (0.025~0.200%). Below 0.175% concentration, transmittance of hybrid material was greater than 85% which is adequate for LED packaging. High refractive index TiO$_2$ nanoparticle-loaded epoxy was introduced by Frank et al. Although they did not evaluate transparency of nanocomposites, they obtained a refractive index of ~1.67 with 10 wt% TiO$_2$ nanoparticle content at 500nm wavelength. In Chapter 5, we proposed UV curable high refractive index TiO$_2$-loaded nanocomposites with high transparency. The refractive index of nanocomposite was 1.68 with 88 % transmittance at 600 nm. The thiol-yne monomer mixture as a polymer matrix of inorganic-organic nanocomposites provided high refractive index and ease of processing.
In this Chapter, we will explain the multi-layer LED encapsulation by utilizing high refractive index TiO$_2$-loaded thiol-yne nanocomposite and silicone resin. Graded-refractive index multi-layer encapsulation was employed to minimize Fresnel reflection losses at the interface between air and encapsulation layer. Thermal stability of silicone resin, pure thiol-yne film, nanocomposite, and dual encapsulation layers consisting of nanocomposite and silicone resin was evaluated by transmittance measurement after thermal aging at 120 °C for 120 hours under the air environment. Materials discoloration was calculated based on transmittance results. Both light extraction efficiency and thermal stability can be improved by using double layer encapsulation due to decrease of Fresnel reflection and reducing the chance for nanocomposite to contact oxidation species. In addition, UV curable thiol-yne nanocomposite and room temperature vulcanizing tin based silicone resin are suitable for a potting process which is a general encapsulation of LEDs.

7.2 Experiment

The thiol-yne film and TiO$_2$-loaded thiol-yne nanocomposite were prepared using the method described in Chapter 5. The high refractive index nanocomposite was fabricated with 2,2’-thiodiethanethiol and 1,6-heptadiyne monomer (Sigma Aldrich) mixture as a matrix and TiO$_2$ nanoparticles (Nanoamor, Inc) as a filler. 3-Methacryloxypropyltrimethoxysilane (Fisher Scientific) was used for the surface treatment of TiO$_2$ nanoparticles to prevent agglomeration. Room temperature vulcanizing silicone resin, also known as Faux Glass, was purchased from Silicone Inc. Dual encapsulation layers were prepared by coating the nanocomposite with the silicone resin. Addition cure system using Pt catalyst is susceptible to attack from certain chemical compounds such as nitrogen, sulfur, phosphorous and arsenic.
Contact with these compounds during mixing and manufacturing will result in inhibition of cure. Therefore, condensation curing system using tin catalyst was employed for coating on the thiol-yne nanocomposite film. Solutions of the silicone resin, thiol-yne monomer mixture and TiO₂ nanoparticle-loaded thiol-yne nanocomposite were placed between the cover glass and hydrophobic glass substrate and exposed to UV-light (365nm, 100mW/cm³) in the duration of 1 minute for polymerization. By removing hydrophobic glass, nanocomposite film remained on the cover glass. In order to investigate thermal stability and discoloration by thermal aging, films were placed in the oven at 120 °C for 120 hours under the air environment.

Refractive indices of pure thiol-yne film and silicone resin were measured by the ellipsometer (J. A. Woolam) at visible wavelengths and the refractometer (Reichert Abbe Mark II Plus Refractometers) at a wavelength of 580 nm. Transmittance of samples was measured in UV-VIS spectrometer (PerkinElmer Lambda 750) at a wavelength region from 300 nm to 800 nm.

7.3 Optical properties of encapsulants

In order to study the light transmittance of encapsulation materials, we have prepared films of the silicone compound, thiol-yne network, and nanocomposite on glass substrates. Transmittance of these films was measured by ultraviolet-visible spectrometer in the wavelength of 300-800 nm with the reference as a glass. FG, TY and NCTY were the Faux Glass (silicone resin), TDET-HptDY film and TiO₂-loaded nanocomposite, respectively. FG showed very high transmittance of 99 % and it is assumed that lower refractive index of FG than that of the glass may reduce Fresnel reflection by graded-refractive index. TY and NCTY had transmittance of 95 % and 88 %, respectively. There were no transmittance dispersion depending on wavelengths.
in FG and TY but there was a 4 % transmittance difference between 650 nm and 480 nm in NCTY as shown in Figure 7-1. As discussed in Chapter 5, transmittance dispersion occurred due to oxidation of the polymer and particle aggregations. The refractive index of FG was measured by the ellipsometer and its measured value was 1.397 at 580 nm. The refractive index of TY was 1.621 from the measurement result of Chapter 5. NCTY had an index of refraction of 1.682 measured by the refractometer.

![Figure 7-1. Transmittance of encapsulation materials and the refractive index of FG (inset image)](image)

### 7.4 Optical Total Transmission of Graded-Refractive Index Encapsulations

Light extraction efficiency of LEDs can be improved by using high refractive index encapsulants. Further enhancement is possible by minimizing Fresnel reflection losses at the interface between the air and encapsulation layer. In this study, the low refractive index silicone resin was employed to reduce Fresnel reflection losses at the
nanocomposite-air interface. Fresnel transmission coefficient of normal incidence can be described by Equation (15) for two media,

\[ T_f = \frac{4n_1n_2}{(n_1+n_2)^2} \]  

(15)

where \( n_1 \) and \( n_2 \) are the refractive index of media 1 and 2, respectively. For graded-refractive index encapsulation layers, multiple transmissions and reflections occur at each interface. Total transmittance of graded encapsulation layers can be expressed by Equation (16),

\[ T_{tot} = \frac{4n_0n_1}{(n_0+n_1)^2} \prod_{j=2}^{i+1} \left( \frac{4n_{j-1}n_j}{(n_{j-1}+n_j)^2} \right) \left( 1 - \frac{(n_{j-1}-n_{j-2})^2(n_{j-1}-n_j)^2}{(n_{j-1}+n_{j-2})^2(n_{j-1}+n_j)^2} \right) \]  

(16)

where \( n_0 \) and \( n_{i+1} \) are refractive indices of the semiconductor and air, respectively, and \( n_1, n_2, \cdots, n_i \) are the refractive indices of encapsulation layers following \( n_0 \).

Table 7-1. Total transmittance of no encapsulation, conventional encapsulation (n=1.5), dual encapsulations, and multi-layer encapsulations.

<table>
<thead>
<tr>
<th></th>
<th>GaN n=2.5</th>
<th>GaP n=3.45</th>
</tr>
</thead>
<tbody>
<tr>
<td>No encapsulation</td>
<td>81.6%</td>
<td>69.7%</td>
</tr>
<tr>
<td>n=1.5 single encapsulation</td>
<td>90.2%</td>
<td>81.6%</td>
</tr>
<tr>
<td>n=1.68 &amp; 1.4 dual encapsulations</td>
<td>92.8%</td>
<td>85.0%</td>
</tr>
<tr>
<td>n=1.68, 1.62, &amp; 1.4 multi-layer</td>
<td>93.0%</td>
<td>85.2%</td>
</tr>
</tbody>
</table>

By utilizing multi-layer for encapsulations, total transmittance calculated with Equation (16) can be increased by 2.8 % and 3.6 % for GaN and GaP, respectively, compared with the conventional encapsulation as shown in Table 7-1. These enhancements are only for normal incidence of light. Thus, it is assumed that there may be further improvements for light extraction efficiency because light is emitted to all directions. Figure 7-2 shows calculated transmittance as a function of change in
refractive indices of the encapsulation layer following the semiconductor in dual encapsulation layers, which have the refractive index of 1.4 for the second layer. Optical transmittance is increased as the index of refraction increases due to reduction of Fresnel reflection.

![Graph](image)

Figure 7-2. Optical total transmittance versus refractive indices of the encapsulation layers following the semiconductor in dual encapsulations.

### 7.5 Thermal Stability and discoloration

Thermal discoloration behaviors of encapsulation materials were evaluated. Figure 7-3 shows transmittance spectrum of TY and FG, before and after thermal aging. There is no change of transmittance after thermal aging at 120 °C for 120 hours compared to the FG sample before thermal aging. Silicone resins are well known for excellent thermal stability against yellow discoloration at high temperatures. They have high
thermal stability against discoloration even up to 200 °C, although their applications for the encapsulation of LEDs are limited due to the low refractive index.

Figure 7-3. Optical transmittance spectra of the TY and FG (inset image) samples before and after thermal aging at 120 °C for 120 hours.

Transmittance decreased as aging time increased in the TY sample. Although UV absorption in the sample increased incrementally with aging time, transmittance of thiol-yne network did not change significantly at visible regions after thermal aging for 120 hours. Figure 7-3 presents transmittance variations of the TY film depending on thermal aging time from 0 to 120 hours. There was a slight transmittance change of approximately 3 % at 450 nm between samples of 0 and 120 hours.

Figure 7-4 presents transmittance variations of NCTY depending on the thermal aging times. TiO₂-loaded nanocomposite showed 7 % more transmittance change than the pure thiol-yne film at 450 nm. It can be seen that the photocatalytic degradation of
thiol-yne network was initiated by active oxygen species such as O$_2^-$, HO$_2^-$, HO$^-$ which were produced from O$_2$ photocatalytic reaction of TiO$_2$ while UV polymerization\textsuperscript{136} and thermal aging enhanced the further degradation of the polymer matrix. NCTY also showed much lower transmittance at UV regions which may be explained by both light scattering by nanoparticles and UV absorption by the degradation of polymers resulting in low transmittance.

![Figure 7-4. Optical transmittance spectra of the NCTY sample before and after thermal aging at 120 °C for 120 hours.](image)

Dual encapsulation layers were prepared using silicone resin and NCTY. Silicone resin was coated on the NCTY for graded-refractive index. Thermal stability of these layers was investigated in the same condition. Transmittance of dual encapsulation layers decreased as aging times increased, similar to other samples which had thiol-yne network as a polymer matrix. However, the decrease in transmittance at 450 nm of dual
encapsulation layers was 4 % and less than that of a single NCTY film. Like in a nitrogen environment, it is assumed that the coating of silicone resin can reduce the chance of reacting with oxidation species. In comparison with other films, there was a slight transmittance change of this sample during the 48-120 hours of thermal aging. It is implied that the small amount of oxygen that was dissolved or trapped in the film contribute to fast thermal oxidation following slow thermal oxidation, due to both depletion of oxygen in the film and prevention of exposure to air by the silicone resin.

Figure 7-5. Optical transmittance spectra of the double layers sample before and after aging at 120 °C for 120 hours

Yellowness index was determined based on transmittance spectra of each sample. Equation (17) was utilized to calculate yellowness index where $T_{420}$, $T_{560}$ and $T_{680}$ had transmittance of 420, 560, and 680 nm, respectively. $^{137}$

$$YI = 100 \times (T_{680} - T_{420}) / T_{560}$$

(17)
\[ \Delta \text{YI} = Y\text{I}_{\text{after aging}} - Y\text{I}_{\text{before aging}} \]  

(18)

\( \Delta \text{YI} \) is the change in yellowness index. \( Y\text{I}_{\text{before aging}} \) is the yellowness index of initial state before aging and \( Y\text{I}_{\text{after aging}} \) is the yellowness index after thermal aging for 120 hours.

Figure 7-6 shows yellowness indices as a function of the aging time for silicone resin, thiol-yne film, TiO\textsubscript{2}-loaded nanocomposite and dual encapsulation layers (FGNC). Figure 7-7 shows the changes of yellowness index before and after aging and changes of transmittance at 450 nm of each sample. NCTY exhibited the most serious case of both the discoloration with \( \Delta \text{YI} \) of 15.1 and the change in transmittance at 450 nm. FC showed the most resistance to discoloration from an almost identical transmittance and no change in \( \text{YI} \) during thermal aging. Although \( \text{YI} \) of FGNC (~13.1) was higher than that of TY (~9.4) due to initial high yellowness index of the first layer (NCTY), change in \( \text{YI} \) of FGNC (~7.6) was slightly smaller than that of TY (~8.3).
7-6 Conclusion

In order to reduce Fresnel reflection losses at the interface between air and the encapsulation layer, double layers encapsulation for LEDs was fabricated using high refractive index TiO$_2$-loaded nanocomposite and low refractive index silicone resin. By employing multi-layer encapsulation, total transmittance for normal incidence light can be enhanced by 2.8 % and 3.6 % for GaN and GaP, respectively, compared with the conventional encapsulation. Thus, further enhancement for light extraction efficiency will be possible for light emitted in all directions. Although the nanocomposite showed the most serious discoloration with ∆YI of 15.1 due to the both photocatalytic and thermal degradation of the polymer matrix, double layers encapsulation had better thermal stability than pure thiol-yne sample because coating nanocomposite by the silicone resin reduced the chance of reacting with oxidation species.
CHAPTER 8
CONCLUSIONS

The photopolymerization of mixtures of multifunctional thiols-enes and thiols-yynes is an efficient method for the rapid production of films and thermoset plastics. Reactions of thiol-ene and thiol-yne provide delayed gelation, low shrinkage, high conversion, and uniform crosslink densities with rapid reaction rate in ambient environments such as oxygen and moisture. Click reactions employing thiols can be applied to variety of applications with our focus being on optical applications.

First, high refractive index polymers have received significant attention with the development of photonic devices. There have been many attempts to increase the refractive index of polymers. Among them, the hybrid approaches integrates organic polymers as matrixes with high refractive index inorganic nanoparticles as fillers; the inorganic-organic nanocomposites have been introduced in order to achieve much higher refractive indices compared to intrinsic polymers. In Chapter 5, UV curable transparent high refractive index nanocomposites with 2,2’-thiodiethanethiol and 1,6-heptadiyne monomer mixtures as a matrix and TiO$_2$ nanoparticles as a filler were fabricated. Silane coupling agents, 3-methacryloxypropyltrimethoxysilane, was used for surface treatment of TiO$_2$ nanoparticles to prevent agglomeration. As predicted from effective medium approximations, increases in refractive indices of nanocomposites result from an increase in particle concentration but also a slight decrease in the transmittance of nanocomposites. TiO$_2$-loaded thiol-yne nanocomposites have a high refractive index of ~1.683 and high transmittance of 88%. Furthermore, UV curable nanocomposite can easily produce the desired shape by printing or molding methods without side products.
Second, in planar structure OLEDs, the light outcoupling efficiency is generally believed to be \( \sim 20\% \) due to total internal reflection losses resulting from refractive index mismatches between multiple layers of devices. The microlens array is an effective way to improve low out-coupling efficiency for OLEDs by extracting substrate-air waveguide mode. In Chapter 6, microlens array was created by a direct printing technique and monomer mixture of trimethylolpropane tris(3-mercaptopropionate) and tri(ethylene glycol) divinyl ether was employed as a lens material due to its characteristics such as high transparency and similar refractive index to a glass substrate. In addition, its low viscosity provides thiol-ene compatibility to inkjet and direct printing processes. In order to obtain hemispherical shape of lenses, hydrophobic silane coupling agents were employed to decrease the surface free energy of glass substrates. The surface properties of a glass substrate were modified by three different silane coupling agents in order to find the lowest critical surface tension and it was determined by a Zisman plot. The glass substrate modified with \( \text{(heptadecafluoro-} 1, 1, 2, 2, \text{-tetra-hydrodecyl)} \) trimethoxysilane showed the lowest critical surface tension of \( 9.29 \text{ mN/m} \). In order to obtain a uniform surface on glass substrates, the silane coupling agent was applied using a chemical vapor deposition method in a heated vacuum chamber. Diameter to height ratio of lenses increased from 1:0.19 to 1:0.41 after a one hour vapor phase deposition. The light extraction enhancement of the microlenses was measured on devices with half the emitting area covered in the microlens array while the other half remained bare and an enhancement factor of \( f = 1.31 \pm 0.4 \) was observed. In order to dispense lens droplets, dispensing tip must have contact with the substrate in this direct printing system. This created slight non-uniformities on the lens array. Further
enhancement will be possible to employ more precise mechanical positioning system and inkjet printing system for better uniformity of the lens array.

Lastly, in the application of LEDs, the roles of encapsulation materials have a great impact on the brightness and life span of LEDs. Thermal stability of the LED encapsulation requires stable transparency and resistance against discoloration and high refractive index is an important factor for the light extraction efficiency of LEDs. In Chapter 7, multi-layer encapsulation of LEDs was proposed to reduce Fresnel reflection losses at the interface between air and the encapsulation layer. In order to produce double layers encapsulation, high refractive index TiO$_2$-loaded nanocomposite and low refractive index silicone resin were utilized. By employing multi-layer encapsulation, calculated total transmittance for normal incidence light can be enhanced by 2.8 % and 3.6 % for GaN and GaP, respectively, compared with the conventional encapsulation. Thus, further enhancement for light extraction efficiency will be possible for light emitted in all directions. In order to evaluate thermal stability, transmittance of samples was measured after thermal aging at 120 °C for 120 hours under the air environment. Transmittance of thiol-yne network did not change significantly at visible regions after thermal aging. Although the nanocomposite showed the most serious discoloration with change in yellowness index of 15.1 due to both photocatalytic and thermal degradation of the polymer matrix, double layers encapsulation had better thermal stability than pure thiol-yne sample because coating nanocomposite by the silicone resin reduced the chance of reacting with oxidation species.
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BIOGRAPHICAL SKETCH

Sangjun Lee was born in Seoul, South Korea. He received his B.S in advanced materials science and engineering at Sungkyunkwan University from 1998 to 2005. He served in the Korean Army for 26 months after his freshman year. He joined magnetic materials laboratory as an undergraduate research student.

In 2006, he entered the department of Materials Science and Engineering in University of Florida. He joined to polymer research group in 2007 and spent the next 5 years contributing to the development of applications for transparent thermosets based on thiols, such as high refractive index polymers, microlens arrays on OLEDs, and encapsulations for LED.

Upon completion of his Ph.D. program, he is planning to work at the central research center for LG chemicals in South Korea, where he is going to continue light extraction of OLEDs and inkjet printing processes.