The Novel Photocurable Network: Urea-tetraacrylate/thiol System

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1. Introduction
Thiol-ene reactions, in both radical and base/nucleophilic reactions, have been introduced as versatile synthetic tools, recently being generalized as thiol click-type reactions and demonstrated to be a powerful method for the fabrication of high performance polymeric materials.\textsuperscript{1-4}

The photopolymerizations of thiol-acrylate systems give networks with broader and indistinct glass transition temperatures due to the large extent of acrylate homopolymerization and resultant inhomogeneous morphology, while amine catalyzed thiol-acrylate Michael addition reaction forms a homogeneous network resulting in very narrow glass transition temperature.\textsuperscript{5}

We reported that the thiol-isocyanate-acrylate ternary system had higher glass transition temperature and refractive indices than the thiol-ene-acrylate system due to the incorporation of thiourethane linkages.\textsuperscript{6}

Urea derivatives formed by the amine-isocyanate click type reaction\textsuperscript{1} have excellent physical/mechanical properties including higher thermal stability, hardness, and abrasion resistance due to stronger hydrogen bonding compared to polyurethanes or polythiourethanes. However, urea-incorporated acrylates have not been reported due to probably the extremely high viscosity and accompanying limitation in applications.\textsuperscript{7}

In this paper, we report the novel urea-acrylate/thiol systems using both free radicals induced by UV light and amine-catalyzed Michael addition reaction. The physical/mechanical and optical properties of the resultant networks were measured in terms of DMTA, hardness, and refractive indices.

2. Experimental
All chemicals used in this investigation are shown in Chart 1.

\begin{center}
\includegraphics[width=0.5\textwidth]{chart1}
\end{center}

Chart 1. Chemical structures of all components.

2.1. Synthesis of Urea-Acrylates
Propylene glycol bis (2-aminopropyl ether)
(DA230, DA400, or DA2000) (10 mmol) was dissolved in CH$_2$Cl$_2$ (~50 wt%), and 1,1-bis (acryloyloxyethyl) ethyl isocyanate (BEI) (20 mmol) was added dropwise at room temperature in a water bath to prevent overheating. The reaction was monitored by the disappearance of isocyanate at 2270 cm$^{-1}$ with FTIR, after which the reaction was continued for another 30 min, and then solvent was evaporated to give urea-acrylate (ideal functionality is 4): BEI-DA230 (7.08 g, 99% yield), BEI-DA430 (8.99 g, 99% yield), and BEI-DA2000 (12.18 g, 99% yield) as a viscous yellow liquid. The structures of the urea-acrylates were confirmed by proton and carbon NMR.

2.2. Synthesis of TUTA
Pentaerythritol tetrakis (3-mercaptopropionate) (tetrathiol) (4.88 g, 10 mmol) and dimethylphenylphosphine (DMPhP) (4.1 mg, 0.02 wt%) were dissolved in CH$_2$Cl$_2$ (10 g), and 2-acryloyloxyethylisocyanate (AOI) (5.64 g, 40 mmol) was added dropwise at room temperature in a water bath to prevent overheating. The reaction was monitored by the disappearance of isocyanate at 2270 cm$^{-1}$ with FTIR, after which reaction was continued for another 30 min, and then solvent was evaporated to give thiourethane-tetraacrylate (TUTA) (10.52 g, 99% yield) as a viscous yellow liquid. The structure of the thiourethane-acrylate was confirmed by proton and carbon NMR.

2.3. Kinetics
Real-time infrared (RTIR) spectra were recorded on a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200 W high-pressure mercury-xenon bulb was channeled through an electric shutter and fiber optic cable in the sample chamber. The characteristic infrared absorption bands (acrylate at 812 cm$^{-1}$, thiol at 2570 cm$^{-1}$, and isocyanate at 2270 cm$^{-1}$) were used to monitor the disappearance of the functional groups during reactions.

2.4. Film preparation and characterization
Urea-acrylate and thiourethane-acrylate films were prepared by using glass molds. Dichloromethane was used as a solvent to reduce the viscosity before film casting. The urea-acrylate (or thiourethane-acrylate) and photoinitiator, 2,2-dimethoxy-1,2-diphenylethanol-1-one (DMPA), (0.5 wt%) were mixed in 20 wt% of dichloromethane, and placed into the glass mold. The mixtures were heated at 60°C for 3 h to evaporate the solvent and then photopolymerized using a medium pressure mercury lamp (light intensity of 23 mW/cm$^2$) for 15 min. The urea-acrylate/thiol network films were prepared by two different curing methods: (1) photocure or (2) amine catalysis at high temperatures. For the first case, DMPA (0.5 wt%) was first dissolved into trithiol followed by mixing urea-acrylate solution (80 wt% in dichloromethane) and then the solution was placed onto the glass mold. The cast solution was heated at 60°C for 3 h to evaporate the solvent and then photopolymerized using a medium pressure mercury lamp system with a light intensity of 23 mW/cm$^2$ for 15 min. All UV-cured films were post-cured at 120°C for 12 h.

In the second case, trithiol mixed with 1.0 wt% of diamine, DA230 was added to urea-acrylate solution (80 wt% in dichloromethane). After casting the sample in the glass mold, the sample was cured at 120°C for 12 h.

Dynamic thermal mechanical properties of the films were measured using a DMTA (MK VI, Rheometrics). Measurements were conducted in the vertical tension mode on samples with dimensions of 10 × 5.0 × 0.5 mm (L × W × T) from -60°C to 300°C at a heating rate of 5°C/min and frequency of 1 Hz with 0.05% strain.

3. Results and discussion
3.1. Synthesis
Urea and thiourethane incorporated tetraacrylate were synthesized via amine-isocyanate and thiol-isocyanate click reactions, respectively as shown in Scheme 1. The urea-acrylates (BEI-DA230, BEI-DA430, and BEI-DA2000) were prepared by reacting BEI with different chain length of diamines (DA series) (Mw = 230, 430, and 2000) in 50 wt% dichloromethane. The reaction is very efficient and more than 99% of the isocyanate was consumed within 5 min monitored by FTIR. No side reactions were observed such as biuret (isocyanate-urea) or aza-Michael addition (amine-acrylate) reaction as verified by proton and carbon NMR analysis. The secondary diamines with propylene oxide repeating units acting as a soft segment prevented the crystallization of urea domains which aided the homogeneity of the reaction medium. Thiourethane-tetraacrylate (TUTA) was prepared by reacting AOI with the tetra-thiol, in the presence of 0.02 wt% DMPhP. Isocyanate was...
consumed within 5 min as verified by FTIR, and the structure of products was confirmed by proton and carbon NMR analysis. Kinetics of the reaction was also monitored with real-time FTIR in 20 wt% of CH₂Cl₂ solution as shown in Figure 1. It clearly showed that quantitative conversion of isocyanate group was obtained during thiol-isocyanate reaction with no acrylate conversion due to the thiol-acrylate Michael addition reaction. This result was consistent with our previous report.⁶

![Scheme 1](image)

**Scheme 1.** Synthesis of (A) urea-tetraacrylates and (B) thiourethane-tetraacrylate

![Figure 1](image)

**Figure 1.** Kinetic profiles of AOI with tetrathiol reaction in the presence of DMPhP (0.02 wt%) in 20 wt% benzene obtained by monitoring the isocyanate peak at 2270 cm⁻¹ and acrylate peak at 812 cm⁻¹.

### 3.2. The effect of hydrogen bonding on physical properties of networks

To investigate the effects of chemical structures and hydrogen bondings on physical properties of networks, crosslinked networks were prepared by photocuring of TUTA (thiourethane-acrylate), PETA (tetra-acrylate) and BEI-DA230 (urea-acrylate). The final conversion and physical properties of the resultant networks are summarized in Table 1. All three networks had relatively broad glass transition temperature regions due to microgel formation which is generally observed in the photopolymerization of multi-functional acrylates. For the multifunctional acrylate homopolymerization, the vitrification occurs at low conversions of acrylate functional groups producing heterogeneous networks. In particular, the conversion of the urea-acrylate was lower than the others due to the stronger hydrogen bonding resulting in higher viscosity, i.e. restricted molecular mobility, at room temperature (curing temperature). The glass transition temperature of the BEI-DA230 network was the highest among three urea-acrylate systems with tan δ maximum at 168°C which is probably due to the higher amount of urea groups resulting in the formation thermally more stable urea domains. The next highest tan δ maximum was the thiourethane-acrylate system (156°C), indicating that the effects of hydrogen bonding of thiourethane linkages are evident and affect the glass transition temperature.

The refractive index of the network prepared with TUTA was the greatest, 1.5504, which is the effect of incorporation of sulfur.

The hardness of all three tetracrylates was very high since all three acrylates were densely crosslinked glasses at the room temperature.

### Table 1. Conversion (mol%) and physical properties of photopolymerized (at 23 mW/cm²) urea-, thiourethane-acrylates, and tetrafunctional acrylate (BEI-DA230, TUTA, and PETA).

<table>
<thead>
<tr>
<th></th>
<th>Acrylate core structure</th>
<th>Pendulum Hardness</th>
<th>Pencil Hardness</th>
<th>Refractive Index</th>
<th>DMTA tan δ max(°C)</th>
<th>Acrylate conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEI-DA230 (urea)</td>
<td>3.09</td>
<td>9H</td>
<td>156</td>
<td>1.5110</td>
<td>100</td>
<td>62.9</td>
</tr>
<tr>
<td>TUTA (thiourethane)</td>
<td>2.65</td>
<td>9H</td>
<td>156</td>
<td>1.5504</td>
<td>100</td>
<td>78.5</td>
</tr>
<tr>
<td>PETA (pentaerythritol)</td>
<td>3.54</td>
<td>9H</td>
<td>156</td>
<td>1.5005</td>
<td>100</td>
<td>88.5</td>
</tr>
</tbody>
</table>

### 3.3. Physical properties of the urea-tetraacrylate/thiol networks

Urea-tetraacrylate/thiol networks were prepared by photo cure method. Physical properties are summarized in Table 2. As the amount of acrylate feed in the initial formulation increased, the glass transition temperature regions became broad and the glass transition temperatures increased due to the increased amount of acrylate homopolymers. Glass transition temperature and rubbery modulus decreased as the thiols content increased (Table 2 and Figure 2), i.e. the
amount of acrylate homopolymer decreased and flexible thioether linkage increased.  

3.4. The effect of hydrogen bonding on physical properties in amine cured systems

To attain high glass transition temperatures and more uniform networks, equimolar amounts of thiol were reacted with urea-acrylate by using amine catalysis method at high temperature (120°C) that proceeds to stoichiometric reaction between thiol and acrylate. The DMTA plots of these networks are shown in Figure 3, and physical properties are shown in Table 3.

FWHM value (15°C) of the networks indicated that uniform network structures were produced. The glass transition temperature (57°C) was higher than the TUTA networks because urea linkages exhibit higher hydrogen bonding than thiourethane linkages. Indeed, the results obviously demonstrated that incorporation of the strong hydrogen bonding of urea linkage into the network is very useful to attain higher glass transition temperature and thermal stability.

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## References


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**Table 2.** Physical properties of urea-acrylate (BEI-DA430) with trithiol by using photo cure (at 23 mW/cm²) method.

<table>
<thead>
<tr>
<th>System No.</th>
<th>C=C/SH (mol%)</th>
<th>Pencil Hardness</th>
<th>Refractive Index</th>
<th>DMTA tan δ max (°C)</th>
<th>Modulus at 150°C (MPa)</th>
<th>FWHM (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100/0</td>
<td>9H</td>
<td>1.5011</td>
<td>117</td>
<td>471</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>83.3/16.7</td>
<td>9H</td>
<td>1.5086</td>
<td>117</td>
<td>124</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>71.5/28.5</td>
<td>9H</td>
<td>1.5101</td>
<td>88</td>
<td>46</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>62.5/37.5</td>
<td>8H</td>
<td>1.5225</td>
<td>69</td>
<td>36</td>
<td>32</td>
</tr>
</tbody>
</table>

**Figure 2.** Dynamic mechanical properties of urea-tetraacrylate BEI-DA430 with trithiol films (systems 1–4) prepared by photolysis at 23 mW/cm².

**Figure 3.** Dynamic mechanical properties of networks prepared by equimolar of BEI-DA230 or TUTA with trithiol by using amine catalysis at 120°C.