

# Photocurable Tunable Networks

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**Abstract:** *Thiol-acrylate networks were prepared using an amine catalyst that promotes a rapid 1-to-1 Michael addition of thiol to acrylate based on the concentration of the amine catalyst. UV polymerization of similar networks result in networks with both thiol-ene copolymerization and acrylate homopolymerization processes occurring. Kinetic analysis using real-time infrared for the systems involving only photopolymerization show the importance of acrylate homopolymerization. DSC and DMTA data show much narrower glass transition temperatures for the networks prepared with the amine catalyst followed by photopolymerization. Additionally, networks produced using only photocuring had much higher Persoz, but almost equivalent, pencil hardness values.*

## Introduction

There has been recent interest in many applications for the use of thiol-acrylate systems.<sup>1-4</sup> Such systems quickly polymerize as the acrylate homopolymerizes and copolymerizes with the thiol groups with and without photoinitiator. This interesting feature provides unique material properties. It has been shown that certain amine catalysts promote a very rapid and efficient Michael addition of a thiol to an acrylate.<sup>5</sup> The Michael addition reaction is based upon the electron deficient nature of the acrylate. Accordingly, primary and secondary amines in catalytic amounts produce a 1-to-1 reaction of thiol with acrylate showing high conversions (>95%) in short time periods (i. e., 125 s).

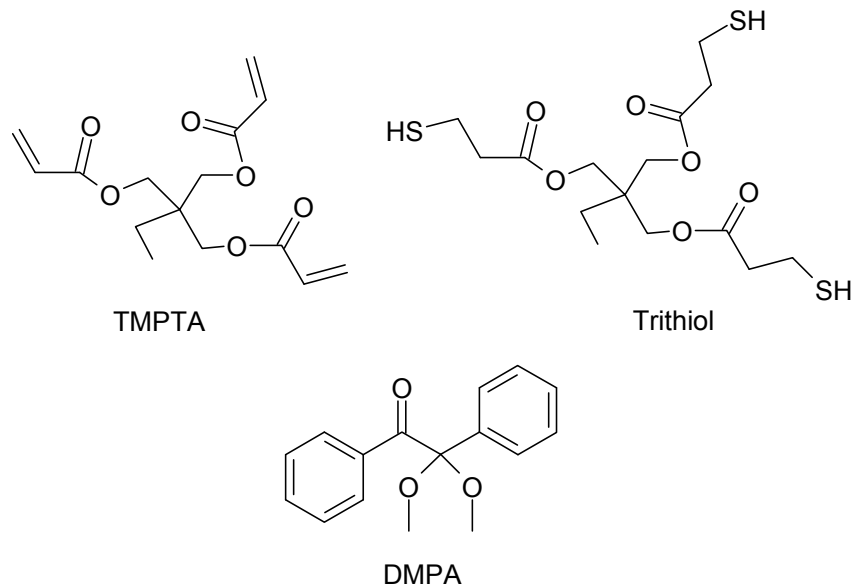
We have investigated photo-induced thiol-acrylate network formation by varying the amount of thiol introduced and using either a simple photocuring process or an amine catalyzed reaction followed by subsequent photocuring. The thiol-acrylate reaction initially reacted prior to photocuring was accomplished by use of an efficient amine catalyst to produce the Michael addition product between the thiol and acrylate. In each system we monitored the reaction progress using FTIR. The mechanical properties of each network were obtained using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Additionally, physical properties such as surface hardness and scratch resistance were obtained for each type of system.

## Experimental

### Materials

Trimethylol propane triacrylate (TMPTA) and trimethylol propane tris(3-mercaptopropionate) (Trithiol) were obtained from Sartomer Chemical and Bruno Bock, respectively, and used without further purification. The chemical structure of TMPTA and Trithiol used in this study are shown in Chart 1. DMPA,  $\alpha,\alpha$ -dimethoxy- $\alpha$ -phenylacetophenone, was obtained from Ciba Specialty Chemicals. Hexylamine was obtained from Aldrich Chemical Co. and used without further purification. Trithiol-TMPTA mixtures were prepared by blending the Trithiol into the TMPTA based on molar functional

group concentration. The amount of UV initiator used was 2 wt%. The amount of amine catalyst, when used, was 1 mole% of the thiol. Films on glass plates (200  $\mu\text{m}$ ) were photocured on a Fusion curing line (10 passes) with a D bulb (belt speed of 10 feet/min, 3.1  $\text{W}/\text{cm}^2$  irradiance). Films cured with amine catalyst were allowed to fully react for 24 hours before irradiating with UV light.



**Chart 1.** Structures of TMPTA, Trithiol, and DMPA.

### Characterization

Real-time Fourier transform infrared spectroscopy (RT-FTIR) was used to determine the kinetics of the reaction using 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. Photopolymerizations were conducted in a cell prepared by sandwiching the samples between two sodium chloride salt plates at a thickness of  $\sim 20$   $\mu\text{m}$  using an irradiance of  $0.55$   $\text{mW}/\text{cm}^2$  measured with an IL-1400 calibrated radiometer from International Light. IR absorption spectra were obtained under continuous UV irradiation at a scanning rate of 5 scans per second. The characteristic IR absorbance bands used to monitor the disappearance of the reactant and monomer during the photoreactions were ene:  $812$   $\text{cm}^{-1}$  and thiol:  $2570$   $\text{cm}^{-1}$ . The reactant conversions were calculated by integrating the peak heights and areas over time.

Differential scanning calorimetry (DSC) was used to determine the  $T_g$  of cured samples on TA Instrument DSC Q1000. All measurements were conducted under nitrogen at  $10$   $^{\circ}\text{C}/\text{min}$  heating and cooling rates. All samples were heated to  $\sim 50$   $^{\circ}\text{C}$  above the  $T_g$  to remove thermal history before the analysis. Dynamic Mechanical Thermal Analysis (DMTA) was used to determine the thermal transitions and mechanical properties of cured samples on a Rheometric Scientific DMTA V. Persoz pendulum hardness (ASTM D-4366 using BYK-Gardner pendulum hardness tester with a square frame pendulum) values are the average of 6 measurements.

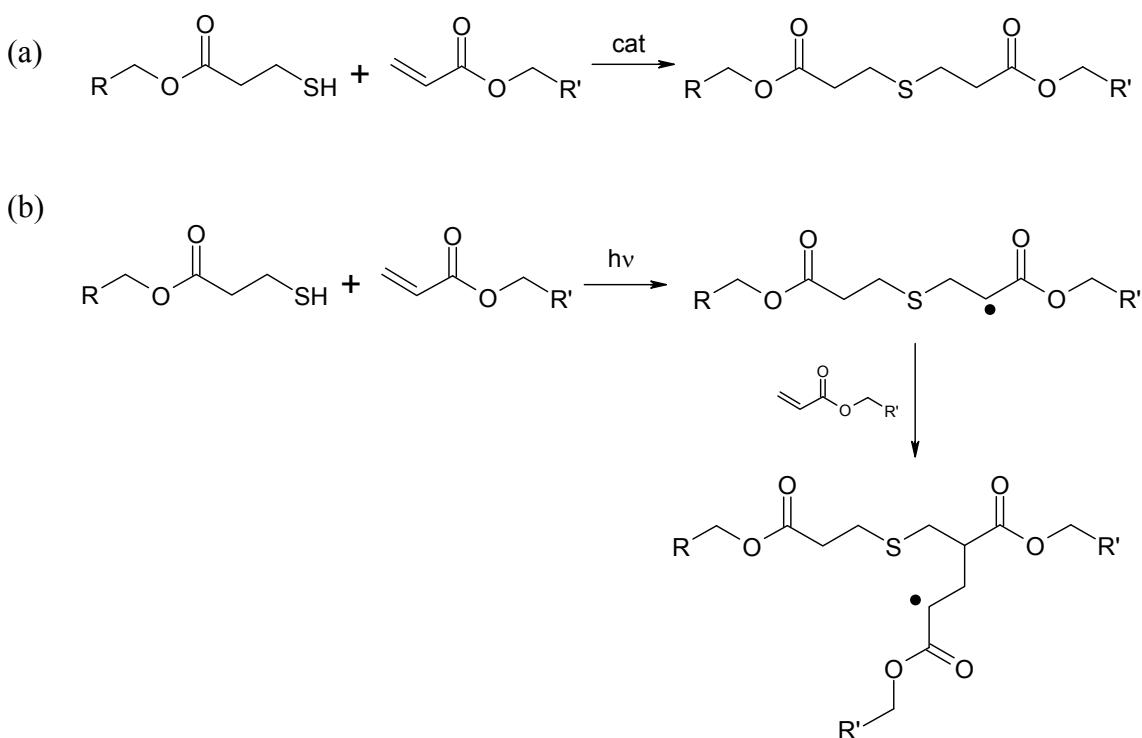
### Film Preparation

Two types of films were prepared. In the first case, Trithiol was mixed with 2 wt% DMPA and/or 2 wt% hexyl amine in the sonicator for 10 minutes in a scintillation vial. This solution was then

mixed with TMPTA in the sonicator for 1-2 minutes until no bubbles remained in the vial. Films (either 500 or 300 micron thick depending upon whether used for DMA or other analysis) made between glass plates with spacers were allowed to cure at room temperature for 24 hours. The samples were then photocured on a Fusion curing line (10 passes) with a D bulb (belt speed of 10 feet/min, 3.1 W/cm<sup>2</sup> irradiance). In the second case, films prepared in the absence of amine were immediately photocured on the same Fusion line system.

## Results and Discussion

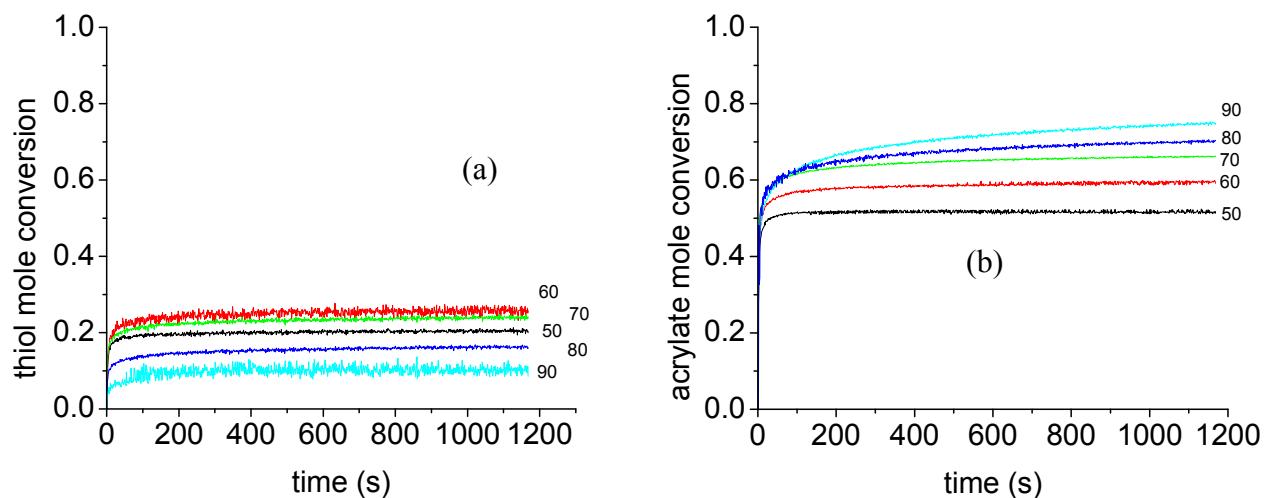
Scheme 1 shows two basic processes for formation of the linkages that ultimately comprise the thiol-acrylate network. In the first case (a), a simple amine catalyzed thiol-acrylate thio-Michael addition occurs by reaction of a thiol functional group with the acrylate ene -- no acrylate-acrylate reactions occur by this catalysis process. In the second case (b), two types of free-radical chain processes occur resulting in either the addition of thiol across an acrylate ene bond to give a sulfide just as for the thio-Michael addition reaction or a free-radical acrylate homopolymerization process.



**Scheme 1.** Mechanistic pathways for a thiol-acrylate network formed (a) with a catalyst and (b) with light.

Herein, we show results for samples that were only light cured: the complementary results for samples that were first catalyzed by the primary amine before photolyzing are not represented herein, but will be given in the presentation. From the photopolymerization real-time IR results (samples 50-100% acrylate) in Figure 1 for thiol (Figure 1a) and acrylate (Figure 1b) percent conversion versus time plots, it is apparent that the rate of free-radical acrylate-acrylate reaction induced by UV light is faster than that of the thiol-acrylate free-radical chain process. The final conversions and corresponding mole fractions (given as moles and based on 100 moles total of thiol + acrylate functional groups, i.e., 25

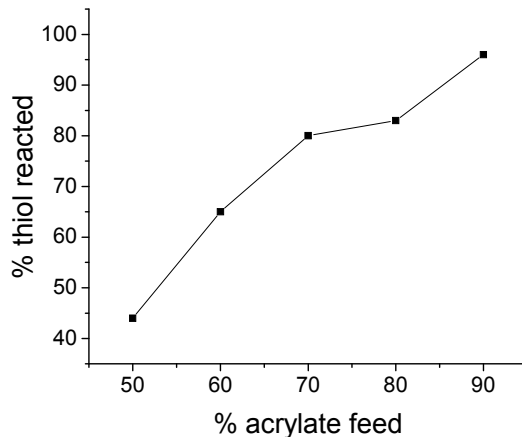
moles represents 25% of all moles in the starting mixture) for all samples are given in Table 1 for ready comparison (Table 1). For samples with greater than 20 mol% acrylate functional groups, this leads to significant unreacted thiol within each system under the conditions employed. As the ratio of acrylate to thiol approaches 50:50, the total amount of thiol incorporated into the networks is only about 43 % while 100 % (i. e. 50 mol%) of acrylate was converted. At a 50:50 molar ratio, it appears that the thiol conversion is the limiting factor to network formation. As the ratio of acrylate to ene concentration increases, an increase in network density occurs. The results in Table 1 shows that a maximum molar percentage of thiol groups incorporated into the network (based upon the total number of moles of functional groups in a give mixture of Trithiol and TMPTA) is exhibited for by 60:40 acrylate to thiol formulation. Even though the amount of thiol reactive groups decreases, the amount of thiol incorporated into the network is at a maximum. Figure 2 clearly illustrates the increase in % thiol as the thiol:acrylate ratio decreases.



**Figure 1.** (a) Thiol and (b) acrylate conversions. Numbers to the right of each curve indicate the feed mole % of each component. Irradiance:  $18.7 \text{ mW/cm}^2$  with 2 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

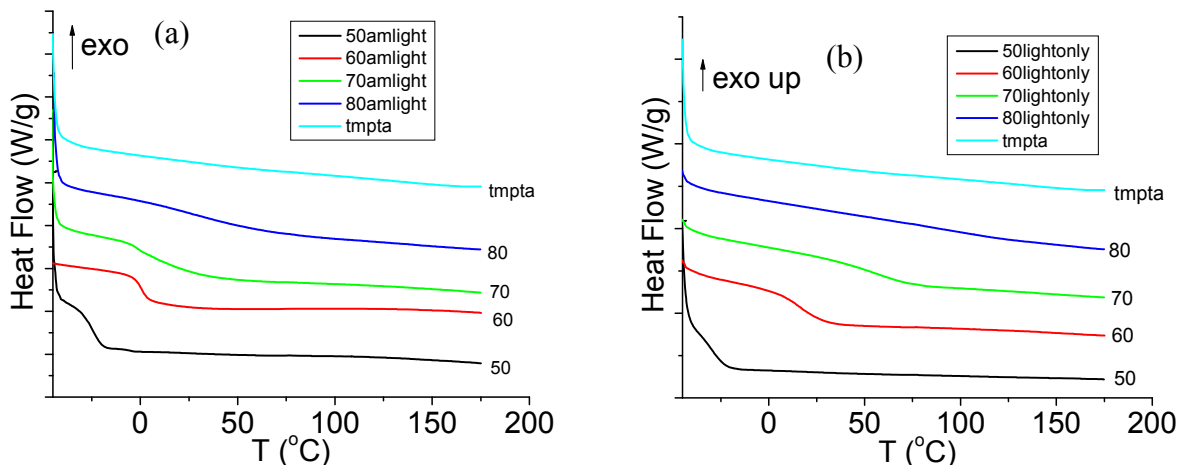
**Table 1.** Feed ratios, acrylate homopolymerization and thiol-acrylate co-polymerization for photo-cured only systems. Irradiance:  $18.7 \text{ mW/cm}^2$  with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

Acrylate Feed (%)	Thiol Feed (%)	Mole Percent in Cured Network	% Acrylate Reacted	% Thiol Reacted
50	50	21.5	100	43
60	40	26	99	65
70	30	24	93	80
80	20	16.6	88	83
90	10	9.6	75	96
100	0	--	72	NA



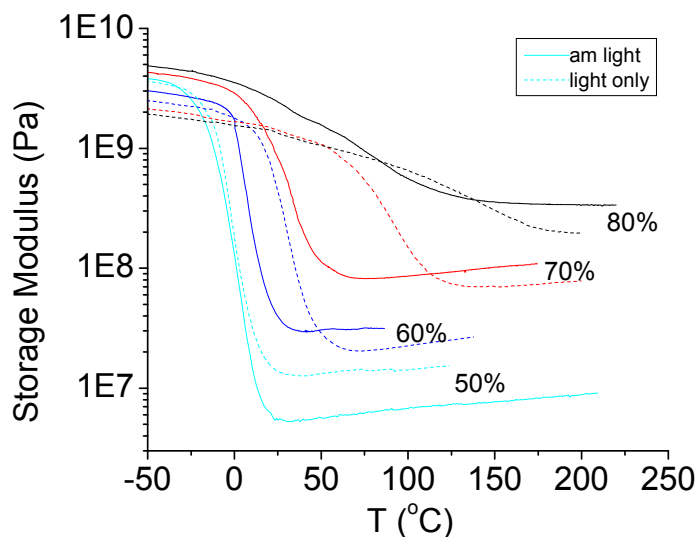
**Figure 2.** Plot of % thiol reacted as a function of acrylate mole% in the photocurable resin.

The results in Figures 1 and 2 and Table 1 clearly indicate the rationale for employing the combination of an amine cure and a photocure for thiol-acrylate mixtures to attain a different processing strategy based upon first reacting all of the thiol functional groups with acrylate groups via a Michael addition process followed by the photocuring process to cure unreacted acrylate. This certainly ensures that no unreacted thiol groups exist in the final cured network: IR results (not shown herein) indeed confirm the supposition that for each formulation in Table 1 (50 - 100 % acrylate) the amine catalyzed curing in each case results in reaction of all thiol groups prior to exposure to the UV light source. DSC analysis of each system (both amine/photocured and photocured) was measured to identify transitions. In Figure 3(a), the  $T_g$  of the photocured 50:50 acrylate:thiol mixture shows the most narrow  $T_g$  of all systems. As the amount of acrylate increases the  $T_g$  broadens and increases, as expected for incorporation of acrylate homopolymer. In Figure 3(b) a similar trend is seen for samples obtained by the sequential amine cure/photocure process, however, the  $T_g$  range for each mixture was narrower and the glass transition temperature lower than the corresponding systems that were only photocured.



**Figure 3.** DSC scans of networks prepared by (a) amine catalysis first and then photocure, and (b) photocure only. Fusion high intensity lamp, D bulb (400-W/in. input), line speed = 12.2 m/min and irradiance of 3.0 W/cm<sup>2</sup> with 2 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

DMTA data in Figure 4 supports the DSC data in Figure 3 as the onset of the glass transition temperature region was lower and the total transition region broadest for the sample in each case that was cured by the dual amine cure (Michael)/photocure process.



**Figure 4.** Storage moduli ( $E'$ ) of networks prepared by (a) photocure only (.....) and (b) amine/photocure (\_\_\_\_\_). Fusion high intensity lamp, D bulb (400-W/in. input), line speed = 12.2 m/min and irradiance of 3.0 W/cm<sup>2</sup> with 2 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

Table 2 shows the results of the Persoz pendulum and pencil hardness tests. The amine/photocure and photocure only systems showed that in both cases the pencil hardness increased with the amount of acrylate. The Persoz results indicate that the amine/photo-cured networks that

exhibit DSC  $T_g$  values near or less than room temperature (see 60 and 70 % acrylate samples in Figure 3) have the lowest Persoz values.

**Table 2.** Persoz and pencil hardness measurements of films prepared. (Films prepared with less than 20 mol % thiol were too brittle to measure by Persoz pendulum).

## Conclusions

Two processes have been used to cure a thiol-acrylate system, an amine catalyzed thio-Michael addition followed by a photocure and a simple photocure. The resultant film physical, thermal and mechanical properties were characterized. In both cases, increasing the amount of acrylate increased and broadened the glass transition of a given thiol-acrylate mixture. The sequential amine cure/photocure produced films with narrowed glass transition temperature regions and generally lower Persoz hardness values measured at room temperature. Pencil hardness measurements were not apparently a function of the curing process. Ramifications of these and other similar physical property measurements will be discussed in the presentation to provide a framework for thiol-acrylate tailoring film properties by a combination of amine catalyzed Michael additions and free-radical chain processes. Finally, it is noted that although long times were used in the present study for the amine cure reactions in order to ensure high conversion after gelation for the 1:1 molar system, it is noted that in general the amine cured reaction is essentially complete for most of the mixtures investigated here in very short times (typically less than a minute or two). This makes the overall two sequence process quite viable for many applications which would benefit from tuning the properties of films produced from thiol-acrylate mixtures by use of a controlled dual processing methodology.

## Acknowledgements

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## References

- |                               |                                  |        |                    |                             |         |                    |   |
|-------------------------------|----------------------------------|--------|--------------------|-----------------------------|---------|--------------------|---|
| 1. Hoyle,<br>Cole,<br><br>M.; | <b>Amine and<br/>Photo Cured</b> | Persoz | Pencil<br>Hardness | <b>Photo<br/>Cured Only</b> | Persoz  | Pencil<br>Hardness | Charles E.;<br>M.;<br>Bachemin,<br>Kuang, W.; |
|                               | <b>50</b>                        | 73 ± 3 | HB                 | <b>50</b>                   | 74 ± 4  | HB                 |   |
|                               | <b>60</b>                        | 42 ± 2 | 8H                 | <b>60</b>                   | 56 ± 2  | 8H                 |   |
|                               | <b>70</b>                        | 48 ± 4 | 8H                 | <b>70</b>                   | 235 ± 3 | 8H-9H              |   |
|                               | <b>80</b>                        | 72 ± 2 | 9H+                | <b>80</b>                   | 262 ± 3 | 9H+                |   |
|                               | <b>90</b>                        | NA     | 9H+                | <b>90</b>                   | NA      | 9H+                |   |
|                               | -                                | -      | -                  | <b>100</b>                  | NA      | 9H+                |   |
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