

Photocured Films from Thiocarbamates Thiol-Enes: Physical and Mechanical Properties

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Abstract: *The glass transition temperature of thiol-ene polymers can be greatly raised through combining thiol-ene and thiourethane chemistry. The reaction of isocyanates and excess multifunctional thiols yields thiol end-capped oligomers. The multifunctional oligomers are then cured by photopolymerizing with equimolar multifunctional enes under UV light. The resultant films have enhanced properties, such as T_g as high as 93°C and refractive index over 1.6.*

Introduction

Thiol-ene polymerization is an efficient process that leads to the formation of uniform molecular networks with high crosslink density.¹⁻³ However, the glass transition temperatures of the polymeric films prepared by reaction of multifunctional thiols with multifunctional enes are often near or below room temperature. This results from the flexible sulfide linkages introduced into the molecular networks by addition of thiols across the double bonds. The reactive thiol groups can react not only with enes but also with other functional groups, such as isocyanates and carboxylic acids. In the case of reaction of thiols with isocyanates, the resultant Polythio-carbamates have potential use in applications such as optical lenses⁴ and clearcoats for automobiles.^{5,6} Herein we report that by combining the advantages of thio-carbamate and thiol-ene polymers, polythiourethane-thiol-ene (PTUTE) films with enhanced properties, such as high glass transition temperatures and high refractive index can be obtained. Compared to systems utilizing thiols and isocyanates as the base components,^{5,6} the potlife offered by PTUTE systems can be greatly extended because of the stability of the thiol liquid oligomers. The odor problem usually associated with thiols can be greatly modified due to the reduced volatility and concentration of thiols by forming thio-carbamate thiol oligomers with high molecular weight. The result is a system with low overall shrinkage and enhanced physical properties.

Experimental

Toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and dicyclohexyl methane diisocyanate (H12MDI) were obtained from Bayer and used as received. Pentaerythritol tetrakis(3-mercapto-propionate) (TetraThiol) and triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (Triallyl triazine) were obtained from Aldrich Chemical Co. and used as received.

A modified Bruker IFS 88 FTIR spectrometer with a horizontal sample accessory was used to obtain real-time IR (RTIR) spectra. UV light from an Oriel lamp system equipped with a 200 Watt, high-pressure mercury-xenon bulb was channeled to the sample chamber through a fiber-optic cable. Photoinitiated polymerization was performed by exposing a thin sample between two sodium chloride salt plates to continuous UV light. The process was monitored by the FTIR operating at a scanning rate of 5 scans/second. A DSC instrument, TA Q1000, operating at a heating rate of 10 °C/min was used to measure the glass transition temperature. Film refractive index was measured by a Bausch & Lomb ABBE-3L refractometer with 1-bromonaphthalene applied between the sample film and the prism shield. The nuclear magnetic resonance (NMR) spectra were obtained on the Mercury 200 using 5 wt% oligomers dissolved in deuterated-chloroform.

In preparing PTUTE films, first, 2 mmol of diisocyanate, 3 mmol TetraThiol and 10 mL acetone were charged into a one neck flask, and then 1 drop of dibutyl tin dilaurate (DBTDL) was added. The mixture was allowed to react for 4 hours at 60 °C in an oil bath before acetone was evaporated under N₂ flow at room temperature. Then the oligomers were homogeneously mixed with 2.67 mmol Triallyl Triazine and then evenly spread onto aluminum plates. PTUTE films (3 microns) were obtained by exposing the coated plates to the output of a Fusion high intensity UV lamp system with conveyer belt.

Results and Discussion

Structure of three diisocyanates, TetraThiol and Triallyl Triazine are shown in Chart 1. Triallyl Triazine was chosen because its rigidity can help raise the glass transition temperature of resulting films. The general preparation procedure of PTUTE films is shown in Scheme 1 : IPDI is used as an example in this case to illustrate the strategy for film formation. The structure of the oligomer prepared is shown in Chart 2. Its structure is verified by the ¹H NMR chemical shift values in Table 1.

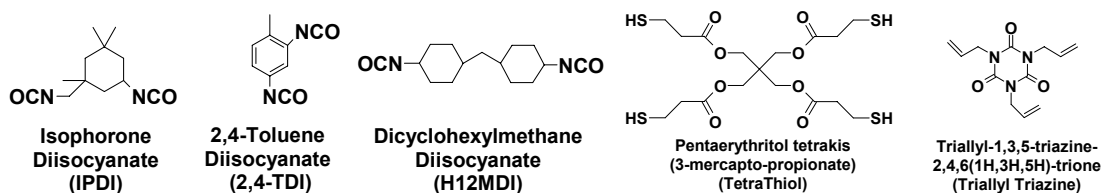
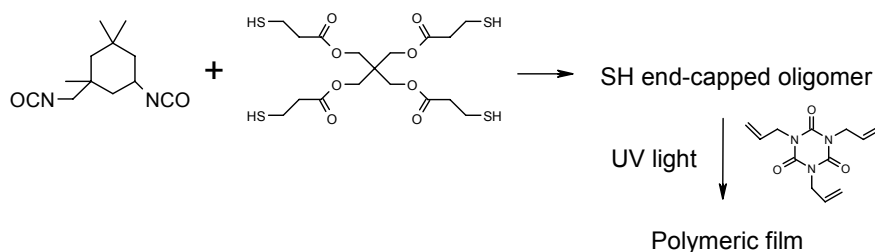


Chart 1. Structures of components used.



Scheme 1. Preparation process of PTUTE films.

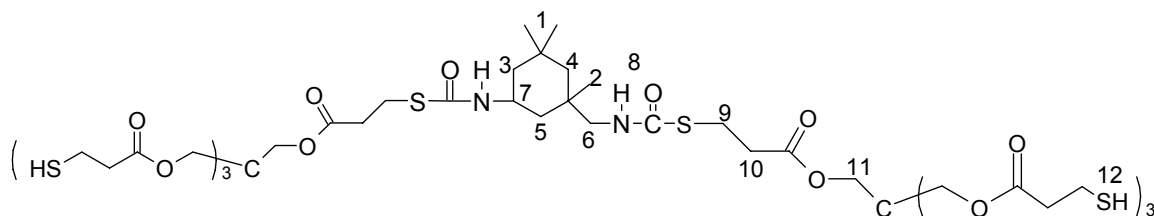


Chart 2. The structure of thiol end-capped oligomer

Table 1. H NMR Chemical Shifts of the SH end-capped oligomer prepared by method 2.

H	1-2	3-5	6-7	8	9	10	11	12
δ (ppm)	0.8-1.1	1.5-1.8	3.3-3.8	5.4-6.9	3.1	2.65	4.1	1.09-1.25

Real time IR spectroscopy was utilized to investigate the kinetics of the reaction of the thiol end capped oligomer and the trifunctional ene. As shown in Figure 1a, the olefinic C-H stretch band at 3083 cm^{-1} and S-H stretch band at 2575 cm^{-1} continuously decreased with the time that the sample was exposed to UV light. By monitoring the S-H band absorbance and applying equation 1 (A_0 and A_t are the absorbance before and after exposure to the output of a high pressure mercury lamp for a span of time t),⁷ the percent conversion of thiol group can be calculated (Figure 1b). A final conversion of 91% was obtained under UV radiation with an intensity of 18.7 mW/cm^2 . This clearly illustrates the high efficiency of thiol-ene photopolymerization at low temperature using a relatively low intensity light source.

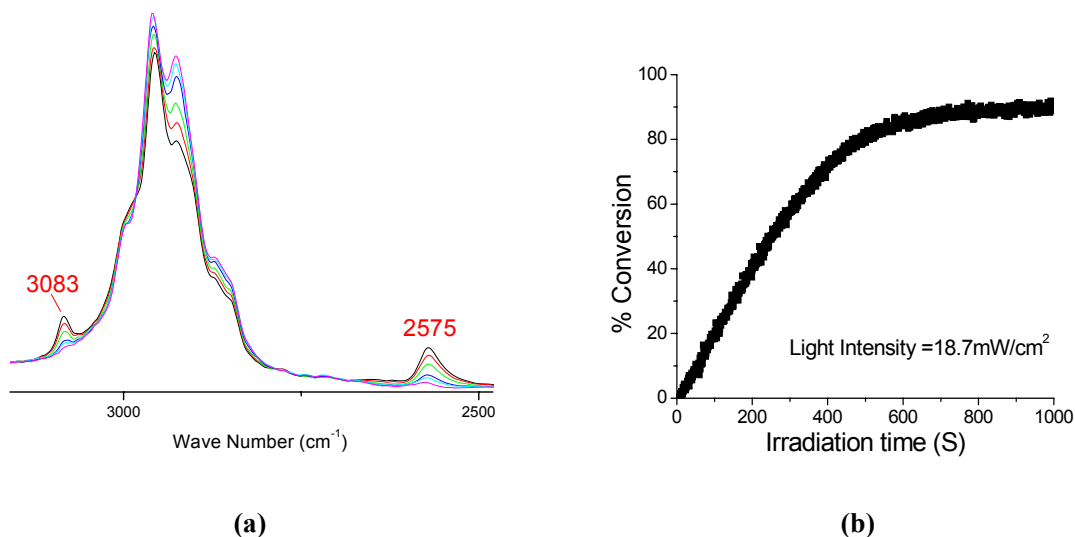


Figure 1. (a) RTIR spectra of thiol in thiol-ene photopolymerization (b) Percent conversion of thiol group as a function of irradiation time.

The glass transition temperatures of the PTUTE films determined by DSC are shown in Figure 2. As the UV energy dose applied increases, the glass transition temperature increases. This results from the increase of crosslink density and higher conversion of the polythiourethane-thiol-ene system with UV dose. The PTUTE films prepared from IPDI and H12MDI have glass transition temperature as high as 93 °C and 91 °C, respectively. Due to the uniform cross link density associating with thiol-ene polymers, the glass transition region of these films were much narrower than that of acrylate based photo-cured polymers. In additional work, we have obtained evidence that suggests that the high glass transition temperatures partially result from contributions of urea structure leading to enhanced hydrogen bonding. The reaction of the NCO group and H₂O, which is an impurity in acetone, probably results in the formation of the urea linkages. The urea structure was suggested by a peak with a higher ¹H NMR chemical shift value of the amide proton than in the ¹H NMR of the urethane structure. A similar observation was made in the report in reference 8.

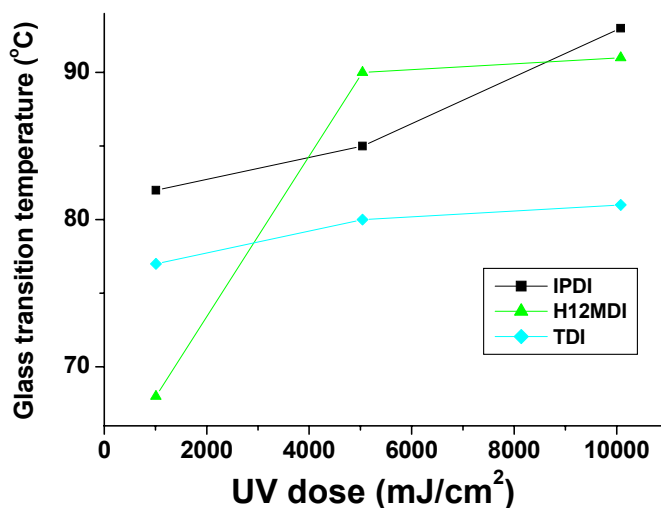


Figure 2. Glass transition temperature of PTUTE films as a function of UV dose.

Finally, we report that the PTUTE films have refractive indices over 1.6. This value is higher than many generally used optical polymers, such as polycarbonates (refractive index = 1.59) and polymethyl methacrylate (refractive index = 1.49), and suggests a large number of uses in both the coatings and optics industries. Additional structure-property correlations will be made in the conference presentation for all systems investigated.

Conclusion

Polythiourethane-thiol-ene films, with high glass transition temperatures and high refractive indices, were prepared from TetraThiol, Triallyl Triazine and diisocyanates. The films have potential use in optical applications as well as thermally stable films. The preparation procedure in which urea structures were introduced into the film yielded high T_g films. The methods decided herein for fabricating PTUTE films has many advantages, including increased potlife, low odor and low overall shrinkage. The physical and mechanical properties of the films will be discussed in the presentation.

Acknowledge

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