Photolatent base/radical photoinitiator catalyzed poly(thiourethane)/poly ((meth)acrylate) networks: Dual network formation via radical mediated photopolymerization

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Abstract: *Unique network structures and physical properties have been attained in hybrid polymeric systems. Here, a combination of (meth)acrylates, thiols, and diisocyanates were photopolymerized using a photolatent base/radical photoinitiator. Tetraethylthiiuram disulfide (TED), an iniferter, and TEMPO were added to control the rate of radical polymerization. The effect of TED and TEMPO on the kinetics of thiourethane and thiol-(meth)acrylate reactions was monitored with real-time IR spectroscopy. Kinetic and mechanical characterization indicates that dual T_g networks form simultaneously.*

1   Introduction

Thiol-ene photopolymerizations cure quickly in the presence of air at low light intensities and can produce polymers with a wide range of physical properties depending on the monomers chosen.[1]   In recent years, ternary thiol-ene systems consisting of a thiol with two other components such as vinyl ethers,[2,3] allyl ethers,[4,5] (meth)acrylates,[6,7] or epoxides[2] have been cured by traditional radical or cationic photoinitiators.   These materials have many potential uses as shape-memory polymers,[8] energy absorbing materials,[6] and protective coatings.[9]

Recently, photolatent base catalysts have been developed for traditional two component systems such as 2-pack polyurethanes, thiourethanes, and epoxes.[10]   The combination of traditional step-growth polymerization with addition polymerization, such as a ternary system consisting of an isocyanate, thiol, and (meth)acrylate, may be advantageous because of the two types of kinetics that occur and the physical properties of the resulting networks.   If the kinetics of the radical initiated thiol-methacrylate polymerization is controlled, semi-independent network formation will occur.   Control of the network structure, such as in interpenetrating networks, produces materials with synergistic properties resulting from each network.

It is hypothesized that the physical properties of thiourethane-(meth)acrylate coatings can be adjusted by controlling the kinetics that dominate the initial stages of the polymerization. Therefore, a ternary system comprised of isocyanates, multifunctional thiols, and methacrylates will be studied. TEMPO, and a photoiniferter, tetraethylthiiuram disulfide (TED)

were utilized to control the curing kinetics of each system. TEMPO is a traditional free radical scavenger and TED has been shown to act as a radical terminator in some acrylate and methacrylate photopolymerizations.[11,12]   A comparison between the kinetics and physical properties of the resulting networks will be discussed.

2   Experimental

2.1 Materials

Glycol di-3-mercaptopropionate (GDMP) and hexane diol diacrylate (HDDA) were obtained from Bruno Bock Chemische Fabrik GmbH & Co. KG and Sartomer respectively and were used to synthesize a thiol terminated oligomer (SH1200). Hexyl amine (98%), purchased from Aldrich Chemical Company, was used to catalyze the thiol-acrylate Michael addition for the synthesis of SH1200. Pentaerythritol tetra-3-mercaptopropionate (PETMP), was provided by Bruno Bock, and was used as the cross-linking agent in thiourethane networks. Hexamethylene diisocyanate (HDI) was provided by Perstorp Coatings and used for the synthesis of thiourethane networks.   Methyl methacrylate (MMA) and trimethyolpropane trimethacrylate (TMPTMA) were purchased from Aldrich Chemical Company and used to form cross-linked methacrylate networks. Irgacure 379 (I379) was provided by Ciba and it was
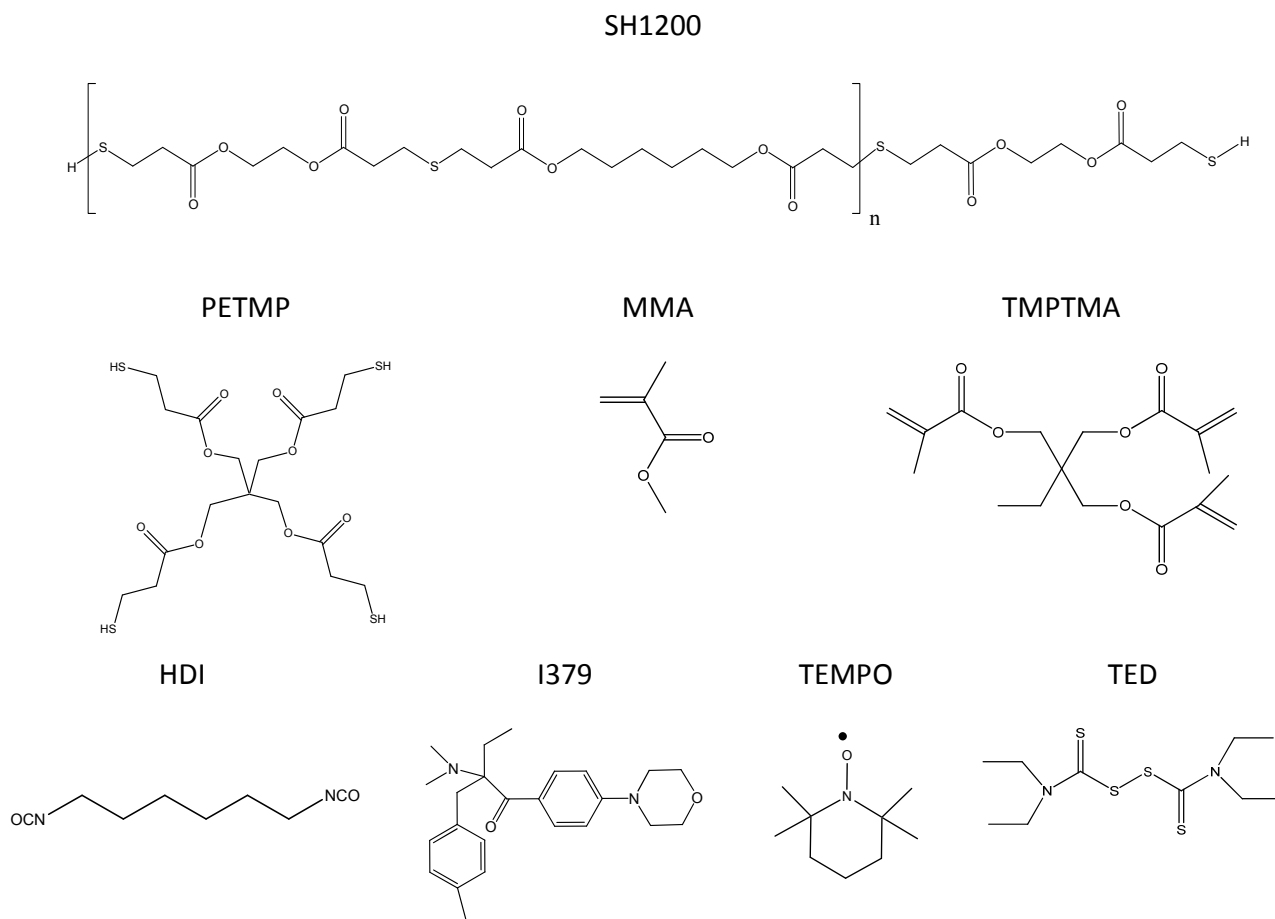
SH1200

Figure 1. Chemical structures of reactants, monomers, catalysts, and radical scavengers.

used to catalyze the thio-urethane polymerization and initiate the photopolymerization of (meth)acrylate networks. TEMPO and Tetraethylthiiuram disulfide (TED), purchased from Aldrich Chemical Company, were used as radical inhibitors during photopolymerization. All reactants, monomers, and catalysts are shown in Fig. 1.

2.2 Synthesis

Synthesis of SH1200.   A 250-mL round bottom flask was charged with GDMP (35.75 g) and a magnetic stir bar. Hexyl amine (0.20 g) was added to the GDMP while stirring. HDDA (22.85 g) was dripped into the GDMP and the temperature was maintained below 40°C. Once all the HDDA was added, the system was allowed to react over night (≥12 hr) to ensure a complete reaction had occurred. ^{1}H NMR confirmed the complete disappearance of the acrylate double bond peaks at 5.7 (q), 6.0 (q), and 6.3 (q) ppm. The molecular weight of the oligomer was determined using titration.

Film preparation. Samples were prepared by dissolving I379 and either TEMPO or TED into the (meth)acrylate formulation comprised of MMA and TMPTMA and HDI. SH1200 and PETMP were added and the solution was stirred and sonicated for 5 min to ensure a homogenous solution was obtained. Each sample consisted of a thiourethane (TU: SH1200, PETMP, and HDI) and a methyl methacrylate (MMA: MMA – 95 wt%, TMPTMA - 5 wt%) portion with a ratio of TU/MMA of 70/30 (by weight). The thiourethane portion was formulated so that there was an equal molar amount of thiol to isocyanate functional groups. I379 was added in either 3 wt% or 1 wt% for kinetics and film preparation respectively. The TEMPO and TED were varied from 0 – 75 wt% of the I379 in each formulation.

Glass plates with a fluoropolymer spacer (0.4 mm thick) between them were then filled with the above formulations and sealed. The samples were cured with a 450-W medium pressure Hg lamp (Hanovia, Fairfield, NJ) at 5 mW/cm^{2} for 20 min on each side to ensure the reaction had reached completion. After photopolymerization, the samples were placed in an oven at 125°C for 4 hr to ensure complete reaction of high T_g MMA networks.

2.3 Characterization

Kinetic analysis.   Real-time FT-IR (RTIR) spectra were recorded on a Bruker 88 spectrometer (Bruker Optics Inc., Billerica, MA) modified to allow for samples to be irradiated.[13] A 200-W high-pressure mercury-xenon lamp source (Newport-Oriel, Irvine, CA) was fitted with a liquid filled light guide to illuminate horizontal samples. Samples were irradiated with 365 nm light at 10.0 mW/cm^{2}. Samples of 10-20 μm thickness were placed between two sodium chloride salt plates. The UV light intensity at the sample was measured with a calibrated radiometer (International Light IL-1400). Infrared spectra were taken continuously at a scanning rate of 5 scans/s. The isocyanate group (2275 cm^{-1}), (meth)acrylate (812 cm^{-1}), and thiol group (2575 cm^{-1}) were monitored to determine reaction kinetics. Samples for RTIR were prepared as previously mentioned in the film preparation section.

Dynamic Mechanical Analysis. Thermal and mechanical transitions were recorded with a Rheometric Scientific DMTA V (TA Instruments, New Castle, Delaware) using a thin film tension clamp. Data was collected from -60 to 150°C at 3 °C/min at a frequency of 1 Hz and a strain of 0.01%.

3   Results and Discussion

3.1 Kinetics of TEMPO mediated systems

Traditionally, the thiol would react with both the isocyanate and methacrylate, yielding low conversions of each. If TEMPO was present, high conversions of each were realized, as shown in Fig. 2, for a 70 wt% TU/30 wt% MMA system with 1.5 wt% TEMPO. The addition of TEMPO inhibited the thiol-ene reaction momentarily and allowed the TU kinetics to dominate the initial stage of the reaction. Afterwards, the polymerization of the MMA took place quickly. Because of the initial presence of thiol, oxygen present in the system is negated[13], and the polymerization of the MMA proceeds quickly when compared to a methyl methacrylate polymerization without thiol present (inset in Fig. 2). These features yield unique networks that can be tuned by controlling the kinetics of each polymerization by the simple addition of a radical scavenger such as TEMPO.
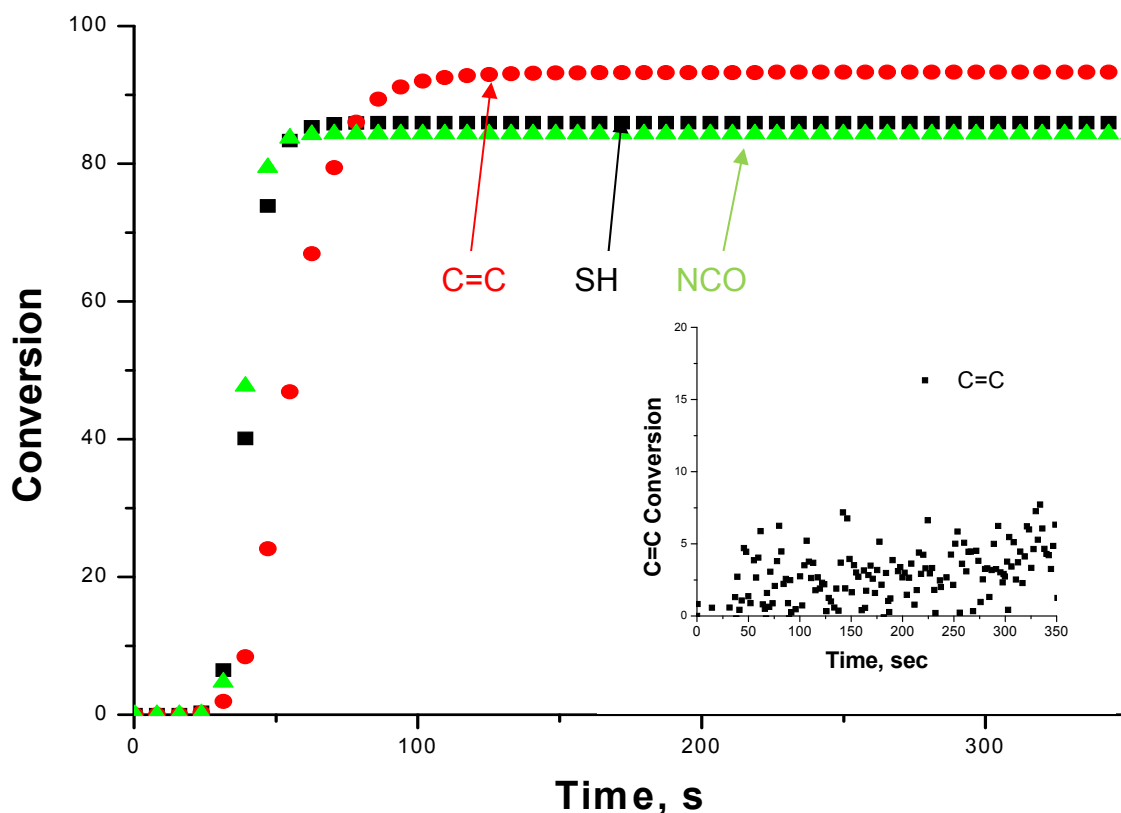

Figure 2. RTIR kinetic profiles for conversion of methacrylate double bond, thiol, and isocyanate in a 70 wt% TU/30 wt% MMA, 1.5 wt% TEMPO, and 3.0 wt% I379 system. Inset, is a plot of conversion of the methacrylate double bond in a 100 wt% MMA system.

3.2 Physical properties of TEMPO/TED mediated systems

The physical properties of these systems can be tuned by controlling the kinetics. This can be seen in Fig. 3 below. If no TEMPO is added, a cross-linked network forms comprised of a random mixture of thiol-methacrylate, thiourethane, and homopolymer MMA. This network yielded a single glass transition temperature, represented by the peak of the tan δ curve, as expected. After the addition of TEMPO, the original peak decreased in intensity and a second peak began to appear. This is indicative of the formation of a phase separated network or the formation of independent networks. Also notice that the original glass transition temperature, which originates at ≈30°C, begins to shift to a lower temperature. Because the neat TU network has a glass transition of ≈15°C, this shift indicates that more homopolymer TU network may have formed at higher concentrations of TEMPO.
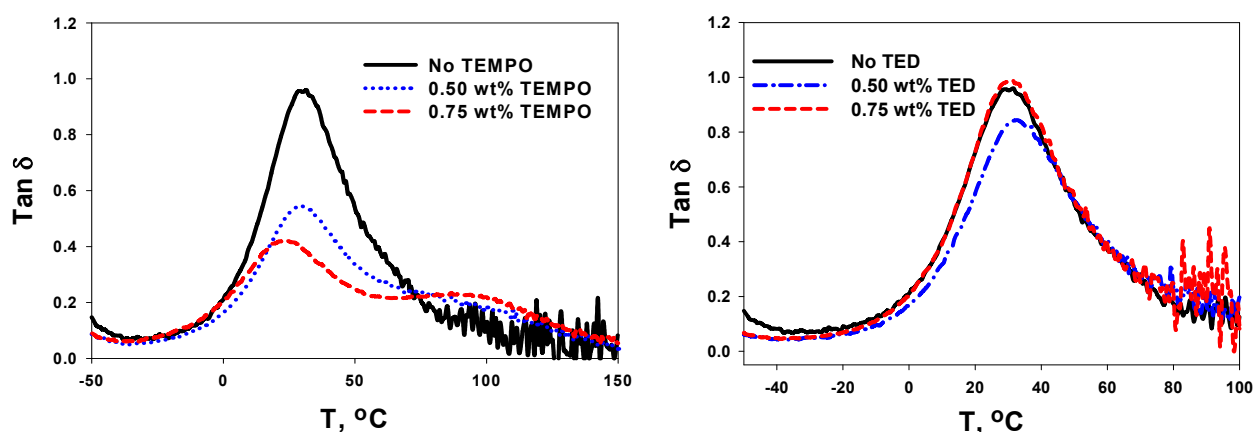

Figure 3. Dependence of glass transition and network development as a function of TEMPO wt% (left) and TED wt% (right) with 1 wt% I379.

Unfortunately, the same trend is not seen in the inexpensive alternative, TED. The glass transition temperature remained constant and a second glass transition temperature was not present, as shown in Fig. 3.

4 Conclusions

It was shown that TEMPO can effectively control the kinetics of MMA polymerization, but TED was unable to control MMA reaction with thiol in these systems. Addition of TEMPO allows for the networks to be tuned to specific properties such as toughness or energy absorption over a wide range of temperatures by adjusting the kinetics of network formation. The method should be applicable to a wide range of monomer combinations yielding unique materials for a variety of applications. In the future, other alternatives for TEMPO will be sought, and focus will be placed on the unique properties which can be developed in these thiourethane /(meth)acrylate hybrid materials.

5 Acknowledgements

6 References

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