

Photopolymerization and Physical Properties of Thiol-Vinyl Ether Hybrid

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Abstract: *This paper represents the first example of a thiol-ene free-radical/vinyl ether cationic hybrid system in which thiols copolymerize with vinyl ethers in a rapid radical step growth process followed by vinyl ether cationic homopolymerization. The kinetics of the photopolymerization were investigated. The combination of thiol-ene and cationically polymerized vinyl ether results in networks with thermal and mechanical properties that are combinations of each system.*

Introduction

Hybrid photocuring is an important methodology for achieving multiple property demands placed on radiation cured coatings, gels, and adhesives/pressure sensitive adhesives. Studies of hybrid photopolymerization have primarily focused on overcoming the limitations of polymerization of a single type of system.¹ Hybrid polymerizations involving simultaneous or sequential polymerizations have led to the creation of a variety of novel polymers including interpenetrating polymer networks (IPNs)²⁻⁹ and block copolymer networks.¹⁰⁻¹² In this context, free-radical and cationic photopolymerization have received considerable attention in recent years.¹⁻¹² The primary motivation for such multicomponent hybrid polymerizations has been to develop systems which overcome the limitations of each of the individual systems, e.g. the oxygen inhibition of (meth)acrylate free radical polymerization and water inhibition of ring opening polymerization (oxetanes and oxiranes). Acrylate/epoxide hybrid photopolymerization

systems exhibit reduced oxygen sensitivity as well as hardness and flexibility enhancement in the resultant polymer matrix.^{2,3,13} It has been shown in methacrylate/vinyl ether hybrid systems that the moisture sensitivity of cationic photopolymerization can be reduced.⁵

There has been a revival of interest in thiol-ene photopolymerization in the past 5 years due to its relatively low oxygen inhibition, highly uniform network density and low shrinkage.¹⁴ It has been recently reported that the photocured ternary thiol-ene-acrylate networks characterized by simultaneous photopolymerization of free-radical step growth (thiol-ene and thiol-acrylate) and free-radical chain growth (acrylate homopolymerization) processes, exhibit high impact energy absorption.¹⁵ In this presentation, we report results for a thiol-vinyl ether hybrid photopolymerization system that involves multiple sequential rather than simultaneous polymerization processes: a loose but uniform low crosslink density thiol-vinyl ether network created by a rapid free radical polymerization is followed by a cationic addition polymerization resulting in a marked increase in network density and formation of unique photocured materials.

Experimental

Tris[4-(vinylxy)butyl] trimellitate (TriVinyl) and trimethylol propane tris(3-mercaptopropionate) (TriThiol) were obtained from Aldrich Chemical Co. and Brono Bock, respectively, and used without further purification. The chemical structure of TriVinyl and the TriThiol used in this study are shown in Scheme 1. The photoinitiator, CYRACURE® UVI 6974, triarylsulfonium hexafluoroantimonate salts mixed with propylene carbonate, was obtained from Ciba Specialty Chemicals. TriThiol-TriVinyl mixtures were prepared by blending the trithiol into the trivinyl ether based on molar functional group concentration. The amount of UV initiator, UVI 6974, in each case, was 2 wt%. Real-time infrared spectra (RTIR) were recorded on a modified Bruker 88 spectrometer designed to allow light penetration to a horizontal sample using a fiber-optic cable attached to a 200 Watt high-pressure mercury-xenon lamp source (obtained from Oriel Co.) with primary wavelengths of 313 and 366 nm and light intensity of 1.87 mW/cm² (ND 2.0 filter). Real-time rheological measurements were performed using a Physica MCR 501 rheometer (Anton Paar, USA) with a Novacure high-pressure mercury lamp with primary wavelengths of 313 and 366 nm and a light intensity of 7.5 mW/cm² (ND 2.0 filter). Molecular relaxations of the films were recorded using a TA Q800 dynamic mechanical analyzer (DMA). DMA was conducted in the tensile mode for 19 x 5.6 mm size samples with thicknesses of 100-150 μm. Films on glass plates (200 μm draw down bar) were photocured on a Fusion curing line system with a D bulb (400 W/cm², belt speed of 10 feet/min, 3.1 W/cm²). Thick samples (1 and 4 mm) were irradiated with low intensity 254-nm low-pressure mercury lamps (0.1 mW/cm²) in air. Samples were then cured on the Fusion curing line.

Results and Discussion

This presentation focuses on the hybrid photopolymerization of thiol-ene and cationic systems involving the two components in Figure 1: TriThiol and TriVinyl.

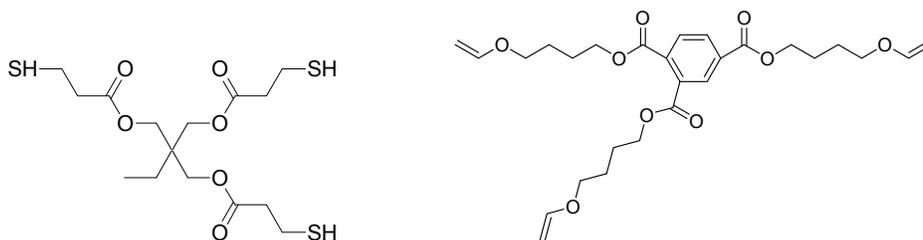


Figure 1. Chemical structures of TriThiol (left) and TriVinyl (right).

Each mixture contained 2 wt % of a cationic photoinitiator triarylsulfonium hexafluoroantimonate that generates both radical and cationic species upon UV light exposure leading to the initiation of both radical and cationic photopolymerization processes.¹⁶ Kinetic analyses conducted with real-time FTIR (RTIR) are shown in Figure 2 where a two-step hybrid photopolymerization involving an initial rapid free-radical thiol-ene polymerization and a subsequent slower cationic polymerization occurs for the 25:75 TriThiol-TriVinyl mixture with an excess of vinyl ether functional groups.

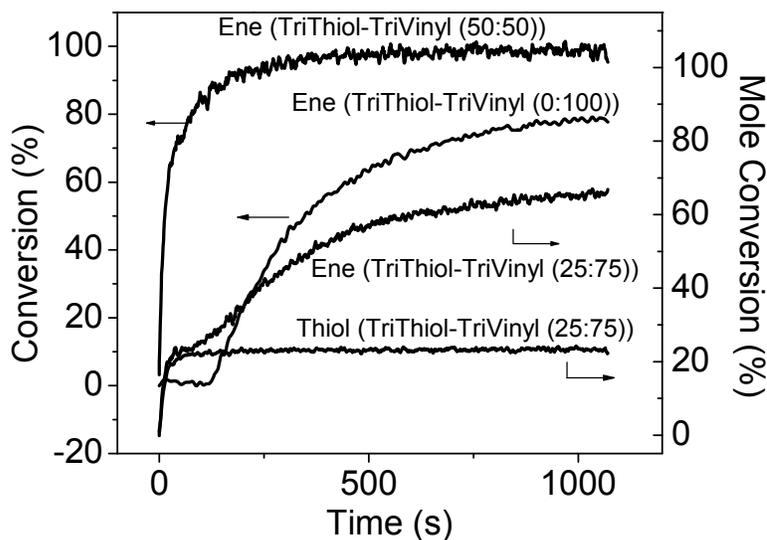


Figure 2. Real-time IR percent conversion/mole conversion versus irradiation time plots of TriThiol-TriVinyl (50:50, 0:100 and 25:75 mol%). Light intensity (full arc) is 1.87 mW/cm².

This two-step process can be verified by the radiation time dependence of dynamic storage modulus and complex viscosity obtained from a real-time rheology measurement which monitors the formation process of polymer gels. The TriThiol-TriVinyl (25 to 75 mol%) system exhibits two sequentially polymerization processes with the building up of both storage modulus and complex viscosity (shown elsewhere).¹⁷

The film prepared from the step growth free radical polymerization of TriThiol-TriVinyl (50 to 50 mol%) exhibits a very narrow glass transition indicating a uniform network, while the network formed from photopolymerization of pure TriVinyl is heterogeneous (Table 1). Compared with the pure TriVinyl network, the TriThiol-TriVinyl (25 to 75 mol%) network exhibits a narrower peak with lower maximum. One of the advantages of this type of hybrid system is that it offers one the ability to tailor the T_g of the hybrid polymer by varying the monomer ratio.

Table 1. Glass transition temperature and full width at half maximum (FWHM) of TriThiol-TriVinyl (50:50, 0:100 and 25:75 mol%) networks measured with DMA operated at 3 °C/min and frequency of 1 Hz.

	50:50 TriThiol-TriVinyl	25:75 TriThiol-TriVinyl	TriVinyl
T_g (°C)	-6	30	83
FWHM (°C)	18	33	45

From the tensile test (Figure 3), the TriThiol-TriVinyl (25 to 75 mol%) based network exhibits both flexibility in terms of strain at break and rigidity in terms of stress at break compared with each pure system. This clearly demonstrates the ability of the hybrid polymerization to combine the properties of two types of systems.

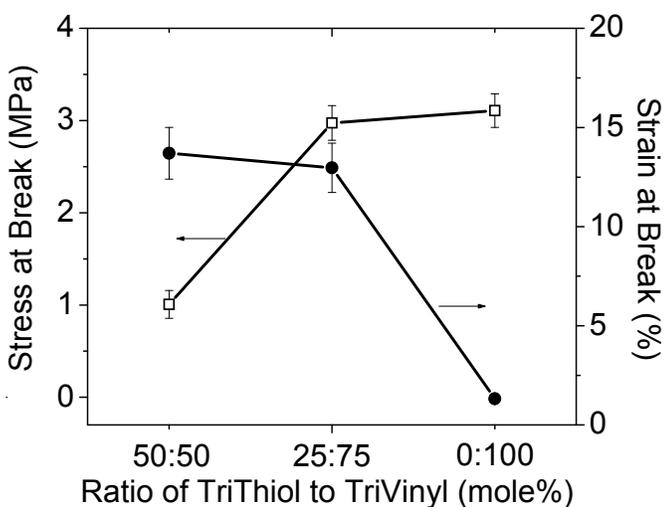


Figure 3. Tensile strain and stress versus ratio of TriThiol to TriVinyl.

As shown in Table 2, TriThiol-TriVinyl (25 to 75 mol%) exhibits much higher toughness in terms of energy to break than both TriThiol-TriVinyl (50 to 50 mol %) and pure TriVinyl. In addition, high energy absorption at room temperature was found for 4-mm plates made from the TriThiol-TriVinyl (25 to 75 mol%) due to the fast relaxation of molecular chains at room temperature as suggested by the position of their Tan δ peak.

Table 2. Mechanical properties of TriVinyl, TriThiol-TriVinyl (25 to 75 mol%) and TriThiol-TriVinyl (50 to 50 mol%)

	TriVinyl	TriThiol-TriVinyl (25 : 75 mol%)	TriThiol-TriVinyl (50 : 50 mol%)
Energy Absorbance (Joule)	0 (cracked)	0.73 (64.6%)	0.15 (13.3%)
Energy to break (N*mm/mm ³)	14.01	128.38	49.79

Conclusion

In summary, real-time infrared analysis shows that the photopolymerization of a TriThiol and TriVinyl mixture with excess vinyl ether proceeds through a rapid thiol-ene radical polymerization and a subsequent cationic vinyl ether polymerization, which is verified by dynamic rheology measurements. The glass transition temperature and the homogeneity of the hybrids can be tailored by varying the TriThiol-TriVinyl monomer ratio. Mechanical and impact measurements of the photocured TriThiol-TriVinyl (25 to 75 mol%) hybrid indicate an energy absorbing, tough material. The results suggest an important strategy for building networks via a hybrid free-radical thiol-ene/cationic-ene polymerization process. Implications for photocurable coatings and a new class of pressure sensitive adhesives will be highlighted in the presentation.

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