

Monitoring the Kinetics of UV Curing Using *In Situ* Rheology and Real-Time Fourier Transform Infrared Spectroscopy

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Abstract

An *in situ* dynamic rheology technique and real-time Fourier transform infrared (FTIR) spectroscopy were used to characterize the UV cross-linking of a thiol-ene system consisting of trimethylolpropane tris(2-mercaptoacetate) and trimethylolpropane diallyl ether. In order to compare the changes in rheological properties and chemistry of the thiol-ene system during UV curing, the evolving elastic modulus was correlated with the thiol conversion. The thiol conversion increased the fastest during the initial stages of the reaction while the elastic modulus did not have an appreciable value until the thiol conversion reached 0.65. From the Flory-Stockmayer theory of gelation, the critical thiol conversion at the gel point was determined to be 0.71, suggesting that the elastic modulus did not have an appreciable value until the sample is near its gel point. This indicated that large enough cross-linked clusters, with relaxation times comparable to the time scales of the imposed deformation, have to be formed in order for the elastic modulus to have an appreciable value.

Introduction

Various techniques have been used to characterize the kinetics of UV cross-linking in order to gain a more fundamental understanding of how processing conditions and monomer chemistry affect the final material properties. In this paper, we focus on using two techniques, *in situ* rheology and real-time Fourier transform infrared (FTIR) spectroscopy, to monitor the UV curing of a thiolene system. Thiolene photopolymers are used in a number of novel applications, including conformal coatings for printed circuit boards and primary coatings for optical fibers.¹ They have also been used extensively as adhesives for bonding optics.¹

We first use rheology to characterize the UV curing of thiolene polymers. The rheological properties measured during UV cross-linking reflect the kinetics of the evolving microstructure. The extent and density of these cross-links ultimately determine the final mechanical properties of the fully cured polymer. In previous studies,^{2,4} we have demonstrated an *in situ* rheological technique which is able

to measure the evolving rheological properties during UV curing. The evolving rheological properties, when measured under different UV curing conditions, can be used to optimize the curing process.

Another technique which provides a powerful method for probing the UV curing process is real-time FTIR spectroscopy. We have constructed an apparatus which is able to perform real-time FTIR experiments on the thiolene system.⁵ FTIR spectroscopy is able to measure the rate of polymerization directly by monitoring the decrease in infrared absorbances of the reacting functional groups. It is also able to monitor the changes in chemistry and accurately determine the reactant conversion, both of which significantly affect the final material properties of the fully cured polymer. One advantage of the real-time FTIR technique over conventional FTIR techniques is the elimination of dark curing. In conventional FTIR experiments, the sample is first irradiated outside the FTIR spectrometer sample chamber and then placed in the sample chamber for analysis. One problem with such an approach is that the sample may become different from the one obtained directly after irradiation due to the dark curing which may occur during the few seconds required to place the sample in the spectrometer. In real-time FTIR spectroscopy, this problem does not occur because UV radiation is being applied to the sample while the sample is being analyzed.

In this study, we have used both *in situ* rheology and real-time FTIR spectroscopy to monitor the UV curing of a thiol-ene system containing trimethylolpropane tris(2-mercaptoacetate) and trimethylolpropane diallyl ether. For this system, we correlate the changes in chemistry and conversion with the rheological properties. A relationship between macroscopic properties, such as the moduli obtained from rheology, and molecular properties, such as the thiol conversion obtained from FTIR spectroscopy, then gives us a better fundamental understanding of the UV curing process.

Experimental

Thiolene System

For the thiolene system, a stoichiometric amount of a trifunctional thiol, trimethylolpropane tris(2-mercaptoace-

tate), was mixed with a difunctional allyl monomer, trimethylolpropane diallyl ether. Hydroquinone was also added, in the amount of 0.5% by weight of the monomers, to the mixture in order to prevent premature polymerization. Both the thiol and allyl monomers and the hydroquinone were purchased from Aldrich Chemicals and were used as received. Finally, a commercial photoinitiator, Esacure TZT, from Sartomer Inc. was added to the mixture. This photoinitiator contains a blend of methyl benzophenones and the final concentration in the mixture was 1% by weight of the monomers.

In Situ Rheology

UV cross-linking was monitored *in situ* by utilizing a Rheometrics mechanical spectrometer (RMS 800) in conjunction with specially designed parallel plate fixtures. A schematic of the parallel plate fixtures is shown in Figure 1. The thiolene sample was placed between two quartz glass plates, each 20 mm in diameter. These plates were held onto both the top and bottom fixtures by removable screws. A section of the top fixture was cut away, allowing the incident UV radiation to be directed onto the sample via a mirror inclined 45° to the upper plate. The quartz plates were transparent to UV radiation, thus allowing the radiation to reach the sample.

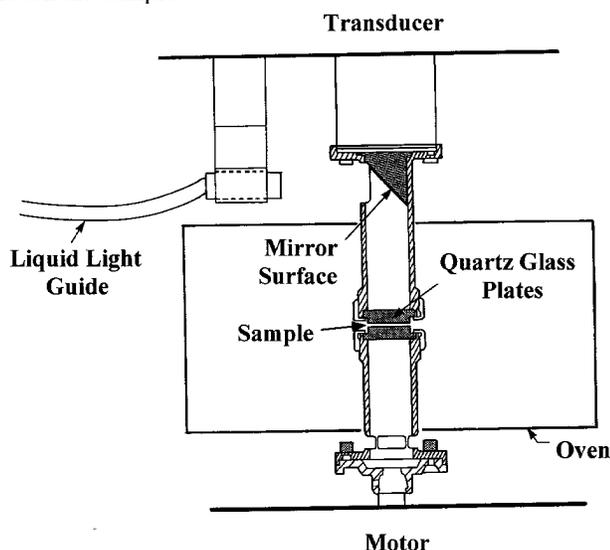


Figure 1. Schematic of the specially designed parallel plate fixtures used in the *in situ* rheology experiments. The UV radiation exits from the liquid light guide and is reflected off the mirror and onto the quartz glass plates. The quartz plates are transparent to UV radiation so the sample, which is placed between the plates, is cured inside the rheometer.

The UV radiation was generated by a 200 W Oriel mercury lamp and the wavelength was maintained at 365 nm by a narrow band interference filter. The radiation intensity was held constant at 0.10 mW cm⁻² for all experiments. Radial variation in the radiation intensity was adjusted to be less than ~ 7%. The thickness for all samples was 0.05 mm and all experiments were performed at 25° C.

A dynamic rheological technique, Fourier transform mechanical spectroscopy (FTMS), was used to monitor the UV curing process. FTMS was used because it is able to simultaneously measure the evolving dynamic moduli at several different frequencies during UV curing. The details of this technique are discussed elsewhere.^{6,7} In dynamic rheological tests, a sinusoidal strain deformation, γ , is applied to the sample at a frequency, ω , and a strain amplitude, γ_0 :⁸

$$\gamma = \gamma_0 \sin(\omega t) \quad (1)$$

The resulting stress, τ_{xy} , on the sample is then measured and is expressed as:⁸

$$\tau_{xy} = G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t) \quad (2)$$

The stress is separated into two parts: one in phase with the applied deformation, which is characterized by the elastic modulus, G' , and one out of phase with the applied deformation, which is characterized by the viscous modulus, G'' . The elastic modulus measures the amount of energy stored by the sample during one oscillation cycle while the viscous modulus measures the amount of energy dissipated during the same cycle. The elastic modulus is particularly sensitive to the microstructure of a material.

Real-Time FTIR Spectroscopy

The schematic of the real-time FTIR apparatus is shown in Figure 2. UV radiation is introduced into the FTIR spectrometer sample chamber by the liquid light guide. The radiation is generated by the same 200 W Oriel mercury lamp used in the rheology experiments. The conditions in the FTIR experiments were matched as closely as possible to the conditions in the rheology experiments. The wavelength of the UV radiation was maintained at 365 nm while the intensity was maintained at 0.10 mW cm⁻². The light guide was positioned at a distance of 6 mm from two 25 mm × 4 mm BaF₂ crystals to insure total UV radiation coverage of the crystals. The light guide was also tilted at an angle of 15° so that it did not block the path of the IR beam. The thiolene sample was placed between the two crystals, along with a 0.05 mm Teflon spacer. All experiments were performed at 25° C.

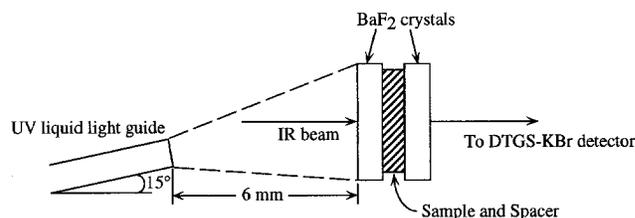


Figure 2. Schematic of the apparatus used in the real-time FTIR experiments. The sample and the Teflon spacer are enclosed between two BaF₂ crystals. The UV light guide is positioned so that it does not block the path of the IR beam.

The FTIR experiments were performed using a Nicolet Magna-IR System 750 spectrometer and a DTGS-KBr

detector. Each IR spectra had a resolution of 4 cm^{-1} and the spectra were obtained one after another in order to ensure that the UV curing process was analyzed in real time. The spectra of the thiol-ene system for three different UV exposure times is shown in Figure 3. The S-H stretching vibration of the thiol functional groups at 2570 cm^{-1} was used to calculate conversions. The aromatic out-of-phase C-H deformation vibration from the methyl benzophenone photoinitiators at 830 cm^{-1} was used as an internal standard since this peak remained unchanged during the course of the experiment.

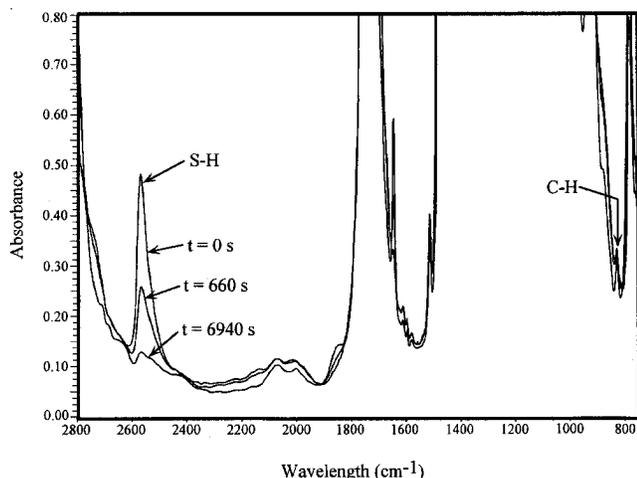


Figure 3. The IR spectra of the thiol-ene system at three different UV exposure times. The S-H stretching vibration at 2570 cm^{-1} is used to calculate the thiol conversion while the aromatic out-of-phase C-H deformation vibration from the methyl benzophenone photoinitiators at 830 cm^{-1} is used as the internal standard

The conversion of the thiol functional group at any time can be calculated by first integrating the unreacted thiol peak at the start of the experiment. At a subsequent time t , the area of the peak can be integrated and the conversion at that time can be determined as follows:

$$x(t) = \frac{A(0) - A(t)}{A(0)} \quad (3)$$

where $x(t)$ is the conversion at time t , $A(0)$ is the normalized area (with respect to 830 cm^{-1}) of the initial thiol peak, and $A(t)$ is the normalized area of the thiol peak at time t .

Results and Discussion

We first used our *in situ* rheology technique to measure the evolving elastic, G' , and viscous moduli, G'' , during UV curing. The elastic and viscous moduli at three different UV exposure times is shown in Figure 4. During the initial stages of the reaction ($t = 780\text{ s}$), the viscous modulus is greater than the elastic modulus throughout the frequency range. This indicates that the sample is still a liquid. At a particular UV exposure time ($t = 1110\text{ s}$), both the elastic and viscous modulus have the same dependence on the

frequency of oscillation. Since Figure 4 is a log-log plot, this means that both moduli scale with frequency to the same power (G' , $G'' \sim \omega^n$). It has been shown by Winter and Chambon^{9,10} that a material exhibiting this behavior is at its gel point. Therefore, our thiol-ene sample has reached its gel point after 1110 seconds of UV exposure. When the sample is exposed to more UV radiation ($t = 6360\text{ s}$), the elastic modulus eventually becomes greater than the viscous modulus and independent of frequency throughout the frequency range. Both of these are characteristics of a highly cross-linked gel. Note that the elastic modulus increases by up to six orders of magnitude during the UV curing process.

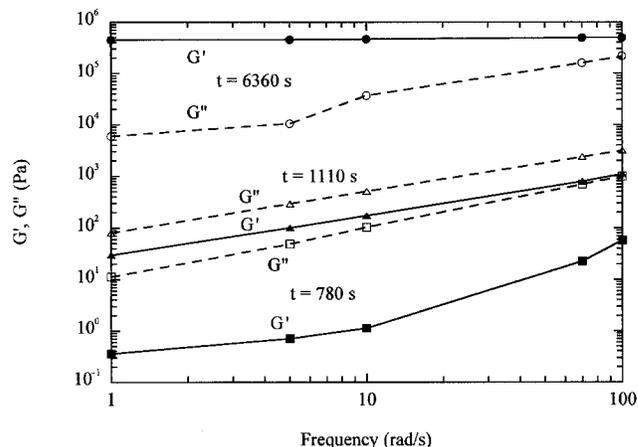


Figure 4. The elastic, G' , and viscous moduli, G'' , of the thiol-ene system as a function of frequency for three different UV exposure times. The viscous modulus is initially greater than the elastic modulus ($t = 780\text{ s}$) throughout the frequency range, indicating that the sample is still a liquid. After 1110 s of UV exposure, the sample has reached its gel point since both moduli have the same dependence on the frequency of oscillation. When the sample is exposed to more UV radiation ($t = 6360\text{ s}$), the elastic modulus becomes greater than the viscous modulus and independent of frequency throughout the frequency range. This indicates that the sample has become a highly cross-linked gel.

Using *in situ* rheology and real-time FTIR spectroscopy, we have correlated the elastic modulus with the thiol conversion in order to compare the changes in the sample's rheological and chemical properties. The plot of the elastic modulus and the thiol conversion as a function of UV exposure time is shown in Figure 5. During the initial stages of the reaction, the thiol conversion increases very rapidly and reaches a value of 0.65 after 750 s. During this period of time, the elastic modulus still does not have an appreciable value. The elastic modulus begins to increase only after 750 s of UV exposure, but increases very rapidly thereafter. Note that the greatest rate of increase of the thiol conversion does not necessarily coincide with the greatest rate of increase of the elastic modulus. The thiol conversion increases the fastest during the early stages of the reaction while the elastic modulus does not have an appreciable value

until a certain conversion has been reached.

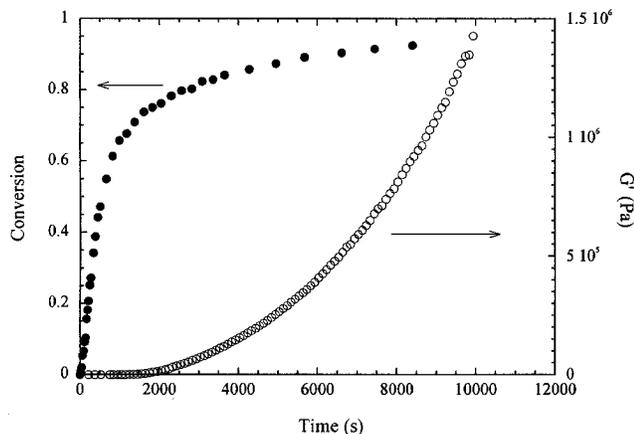


Figure 5. Comparison of the thiol conversion and the elastic modulus as a function of UV exposure time. The thiol conversion increases very rapidly during the initial stages of the reaction while the elastic modulus does not have an appreciable value until a thiol conversion of 0.65 is reached.

In order to explain this behavior, we have to examine the thiol conversion at which the sample has reached its gel point. The critical conversion at the gel point for a thiolene system can be predicted from the classic Flory-Stockmayer theory of gelation. The critical conversion at the gel point, x_c , is expressed as:¹¹

$$x_c = \frac{1}{[r(f_{\text{thiol}} - 1)(f_{\text{allyl}} - 1)]^{1/2}} \quad (4)$$

where r is the stoichiometric ratio of the thiol to allyl functional groups, f_{thiol} is the functionality of the thiol, and f_{allyl} is the functionality of the allyl monomer. Since we have a trifunctional thiol and a difunctional allyl monomer, the critical thiol conversion at the gel point is 0.71. Note that the elastic modulus does not have an appreciable value until the thiol conversion reached 0.65. This suggests that the conversion has to be close to the critical conversion at the gel point in order for the elastic modulus to have an appreciable value. The reason why the elastic modulus can be detected only when the sample approaches its gel point can be explained by examining the cross-linking process occurring in the sample. During the initial stages of cross-linking, only small and separate cross-linked clusters are being formed. These small clusters have very short relaxation times compared to the time scales of the rheological experiments, which in this case range from 1 to 0.01 s (e.g. frequencies of 1 to 100 rad/s). Therefore, we are not able to detect an appreciable elastic modulus during the initial stages of the reaction because the small clusters relax much faster than the time scales of the imposed deformation.^{5,12} However, as the sample is exposed to more UV radiation, more cross-links are being formed and the clusters become larger. Eventually, cross-linking between clusters occur and as the

sample approaches its gel point, large enough clusters with relaxation times comparable to the time scales of the imposed deformation are formed. The elastic modulus then becomes detectable at this point.

Conclusions

We have used an *in situ* rheological technique to monitor the UV curing of a trimethylolpropane tris(2-mercaptoacetate)/trimethylolpropane diallyl ether system. We have also constructed an apparatus which enabled us to perform real-time FTIR experiments on the UV curable thiol-ene system. We then correlated the elastic modulus with the thiol conversion and found that the thiol conversion increased the fastest during the initial stages of the reaction while the elastic modulus can only be detected only after the thiol conversion reached 0.65. The critical thiol conversion at the gel point is predicted to be 0.71 from the Flory-Stockmayer theory of gelation, suggesting that the elastic modulus can be detected only when the sample approaches its gel point. This behavior is explained by comparing the relaxation times of the cross-linking clusters with the time scales of the imposed deformation. When the sample is close to its gel point, large clusters with relaxation times comparable to the time scales of the imposed deformation are formed. It is only after this point when the elastic modulus begins to have an appreciable value.

Acknowledgments

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