Photopolymerization of Multicomponent Thiol-Enes: Kinetics, Mechanisms and Properties

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Abstract: *Photocurable thiol-ene monomer systems which are comprised of equimolar concentrations of thiols and enes have recently gained considerable attention as alternatives to conventional acrylate based photopolymerizable systems. Herein, we report a totally new direction in the development of thiol-ene systems which involves the use of thiols in combination with not only traditional enes, but also acrylates in a three component system. This new direction involves simultaneous polymerization processes which allow multicomponent films to be formed by a dual polymerization process. The polymerization kinetics of such a system, which are quite complex, are followed by both real-time calorimetric and infrared analysis. Dynamic mechanical and thermogravametric analysis of the cured films provide insight into the structure and properties of the films formed.*

Introduction

Thiol-ene mixtures have been widely used to vary the physical properties of coatings for many applications. The photopolymerization process gives, in most cases, superior properties to those obtained by means of acrylates and methacrylates. In addition, thiol-ene have inherently rapid rates of polymerization with particularly high reactivity with electron rich vinyl monomers since the thiyl radical is "slightly" electrophilic in character. A particularly attractive feature of thiol-enes involves very low sensitivity towards oxygen inhibition. This is due to the "competitive" hydrogen abstraction from thiols by carbon centered radicals formed during the reaction of an ene and a thiol group.[1-4] Once cured, thiol-enes are characterized by improved homogeneous crosslinking density throughout the thickness of the coating. This is in strong contrast to the very early vitrification in a multifunctional acrylate homopolymerization which eventually leads to formation of an inhomogeneous network. In this investigation, we describe the polymerization consequences of combining thiol-enes and acrylates using

thin film calorimetry and real-time infrared (RTIR) spectroscopy to obtain kinetic data, and DMA and TGA analysis to characterize the resultant film performance characteristics.

Experimental

The following chemical structures as shown in Figure 1 were used throughout the study. All chemicals were used without purification. Propoxylated glycerol triacrylate (Ebecryl 53) was obtained from Cytec. Trimethylolpropane tri(3-mercaptopropionate) was obtained from Bruno Bock in Germany and pentaerythritol triallylether was from Perstorp in Sweden.
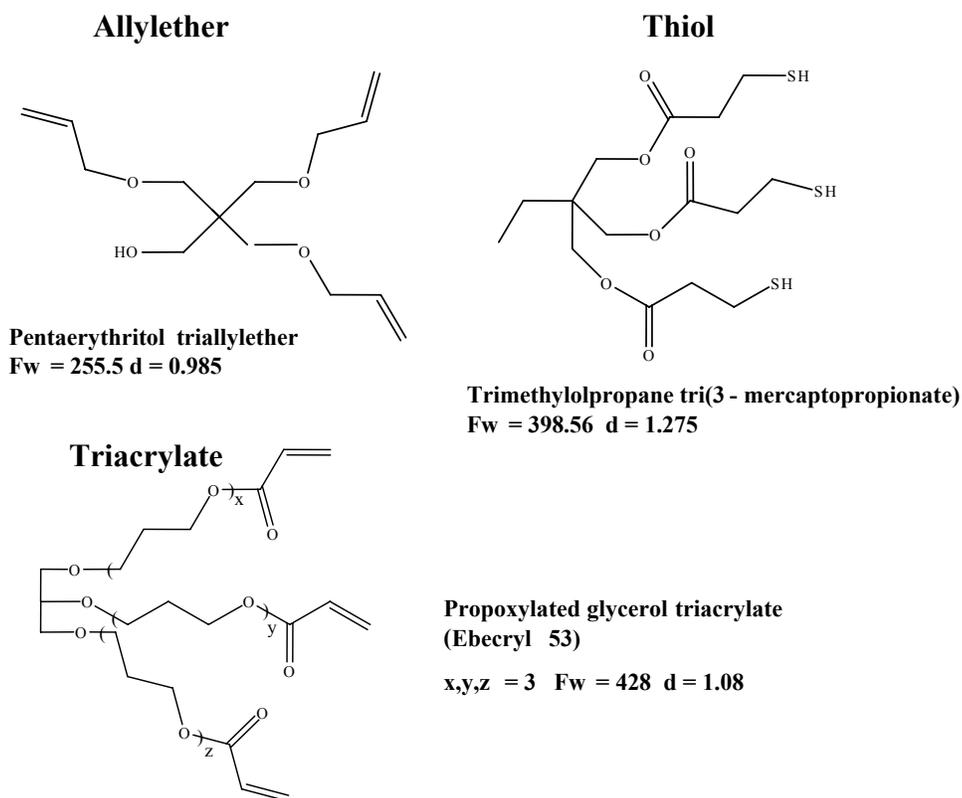
Allylether

Thiol

Pentaerythritol triallylether
Fw = 255.5 d = 0.985

Trimethylolpropane tri(3 - mercaptopropionate)
Fw = 398.56 d = 1.275

Triacrylate

Propoxylated glycerol triacrylate
(Ebecryl 53)

x,y,z = 3   Fw = 428 d = 1.08

Figure 1. Structures of components in thiol-ene/acrylate mixtures.

The RT-FTIR spectra were recorded on a modified Bruker 88 spectrometer, which allowed light penetration to a horizontal sample using a fiber optic cable attached to an Oriel high pressure mercury lamp source. Samples were placed between two NaCl salt plates using a 15 micron teflon spacer. In order to create an oxygen reduced atmosphere and to avoid the evaporation of the low molecular weight acrylates, the gap between the two salt plates was sealed by vacuum grease before positioning of the sample on the horizontal sample holder. The light intensity at the sample was measured by the use of calibrated radiometer (International Light IL-1400). The IR absorption spectra were obtained under continuous irradiation with a scanning rate of 5-10 scans/sec. The acrylate conversion was obtained from the peak at 812 cm^{-1}.

Results and Discussion

Real-Time Infrared Spectroscopy and Calorimetry

We begin by considering the reaction kinetic steps that are likely to occur in polymerization involving ternary systems comprised of a thiol-ene mixed with an acrylate. Note that we only show the propagation and chain transfer steps and not radical-radical coupling which is omitted for convenience. Note that steps (1) and (2) involve addition of a thiol group across with an ene or an acrylate double bond. Step three is simply the free-radical homopolymerization of acrylate double bonds. It would be desirable to evaluate the kinetics of any ternary system by measuring each rate process separately, and in some cases this is possible. For example, if the infrared absorbances corresponding to thiol, ene and acrylate bonds can be separately followed in real time, it is possible to evaluate each process separately. Indeed, reference 5 describes this process.

(1) Insertion of the thiyl radical into any C=C, which in this case can be the allyl or the acrylate.
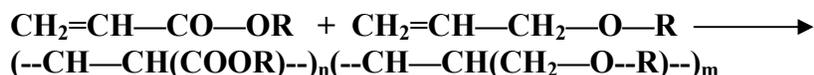
$$RS^{\bullet} + R_3 R_4 C{=}CR_1 R_2 \longrightarrow RS{-}C(R_3R_4)C^{\bullet}{-}R_1R_2$$

(2) Abstraction of a hydrogen from a thiol group by the resultant carbon centered in step 1.

$$RS{-}C(R_3R_4)C^{\bullet}{-}R_1R_2 + RSH \longrightarrow RS{-}C(R_3R_4)CH{-}R_1R_2 + RS^{\bullet}$$

(3) Homopolymerization of the acrylate

$$CH_2{=}CH{-}CO{-}OR + CH_2{=}CH{-}CO{-}OR \longrightarrow ({-}{-}CH{-}CH(COOR){-}{-})_n$$

(4) Copolymeriztion between the acrylate C=C and the allyl C=C (not a significant reaction).

$$CH_2{=}CH{-}CO{-}OR + CH_2{=}CH{-}CH_2{-}O{-}R \longrightarrow$$
$$({-}{-}CH{-}CH(COOR){-}{-})_n({-}{-}CH{-}CH(CH_2{-}O{-}{-}R){-}{-})_m$$

The rates and kinetics of simple thiol-ene systems have been evaluated in a number of publications in the last five years using infrared spectroscopy and other methods.[6-12] Herein, we will next describe the use of two methods for following the kinetics of photopolymerization of ternary thiol-ene/acrylates: real-time infrared spectroscopy and calorimetry. Consider the ternary system involving a 1:1 molar mixture of Thiol-Allylether and Triacrylate. It would be desirable to plot individual conversions for the thiol, the allylether and the acrylate. Unfortunately, deconvolution of the allyl ether C=C and the acrylate C=C IR bands is not possible due to the overlap of the infrared absorption bands for the double bonds of each and the large differences in their extinction coefficients. It is possible, however, to follow in real time the acrylate conversion, even in the presence of the allylether. In Figure 2, the real-time infrared based acrylate conversion curves for a series of Triacrylate and Thiol-Allylether mixtures is shown. The Thiol-Allylether concentration varies from 0 to 50 mole %. From Figure 2, it can clearly be seen that the pure acrylate exhibits a significant oxygen inhibition and reaches a conversion of more than 80 %. The high conversion compared to a more rigid trifunctional acrylate like trimethylolpropane triacrylate is due to the flexible propoxy groups. Interestingly, at low incorporation levels of thiol-ene in the mixture (10 mole %), there is an almost complete disappearance of the oxygen

inhibition effect. Samples with a higher amount of Thiol-Allylether also show an increase in total conversion, i.e., essentially 100 % acrylate conversion is measured for ternary systems with Thiol-Allylether concentrations greater than 40 mole %. A complete kinetic analysis of other ternary systems involving functional groups (e. g. other enes) that are amenable to analysis will be presented at the symposium.
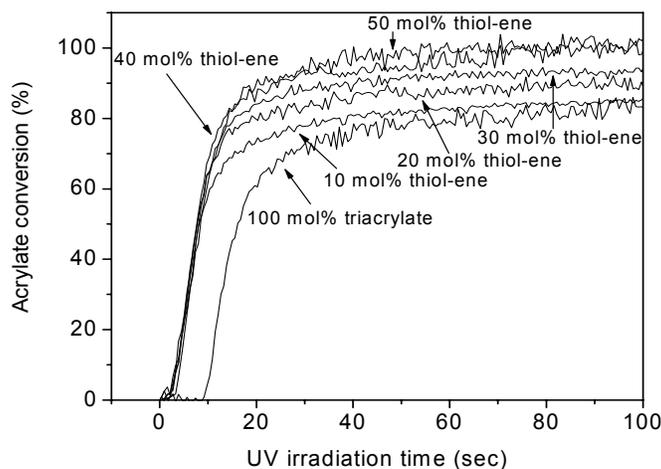
Figure 2. Acrylate conversion as a function of UV irradiation time of Triacrylate with 0, 10, 20, 30, 40 and 50 mole% Thiol-allylether addition measured by RTIR, Light Intensity = 1.87 mW/cm^2.

Next, the polymerization process was evaluated calorimetrically. Exotherm measurements were made on three systems: a pure 1:1 molar Thiol-Allylether mixture, a pure Triacrylate, and a 1:1 molar combination of the Thiol-Allylether and the Triacrylate. Thin-film calorimetric responses for the three mixtures are shown in Figure 3. As can be seen from these exotherms in Figure 3, the exotherm peak maximum rate for the pure Triacrylate is the highest followed by the Thiol-Allylether/Triacrylate mixture in a 1:1 molar ratio. The 1:1 Thiol-Allylether mixture has the lowest peak exotherm maximum. In order to be able to interpret the results of the exotherm measurements, we measured the rates expected for all of the individual steps that can occur including acrylate homopolymerization (-17.7 kcal/mol), addition of a thiol group across an acrylate double bond (-16.3 kcal/mol) and addition of a thiol group across an allyl ether double bond (-18.0 kcal/mol). Obviously the heats of reaction are almost the same for all three cases, but since the addition of a thiol to an ene or acrylate group proceeds by a 1:1 molar reaction, the overall heat that can be evolved will be less per unit volume than for an acrylate homopolymerization. Hence, the heat evolved for the polymerization of the Thiol-Allylether system in Figure 3 (i.e. the total integrated area under the exotherm curve) will be much smaller than for the 50 mole% Thiol-Allylether/50 mole% Triacrylate and Triacrylate systems. This is due to the higher heat content per volume of sample resulting from acrylate homopolymerization steps. Finally, we indicate that there is a slight inhibition period for the Triacrylate polymerization due to oxygen inhibition: this was already noted in the discussion of the infrared results in Figure 2. This inhibition period is not seen for the thiol-ene or thiol-ene/acrylate systems.
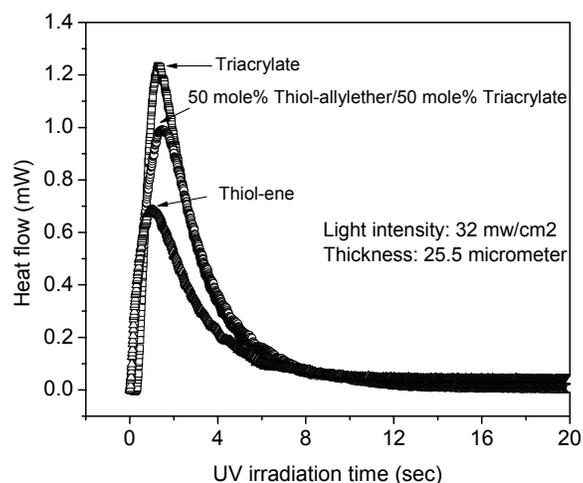
Figure 3. Exotherm plots of Triacrylate, 50 mole% Thiol-allylether /50 mole% Triacrylate and Thiol-allylether. Light Intensity = 32 mW/cm^2.

Mechanical and Thermal Analysis of Films

In order to establish a clear basis for characterizing the networks produced by photocuring thiol-ene/acrylate films, we have chosen to present basic mechanical and thermal decomposition results for a series of films. In Figure 4, the dynamic mechanical analysis (DMA; 1 Hz) tan δ versus temperature results indicate a distinct increase in T_g (temperature at the maximum in the plot) as a function of acrylate content in Thiol-Allylether/Triacrylate systems (see structures of components in Figure 1). As is obvious from the results in Figure 4, the higher the content of Triacrylate the higher is the T_g measured by DMA (1 Hz). In all cases where the Thiol-Allylether content is greater than 10 mole percent, the cured matrices have narrow glass transitions, i. e., the main difference between samples is that the height and width of the tan δ peak will be "lower" and much "broader" as the content of
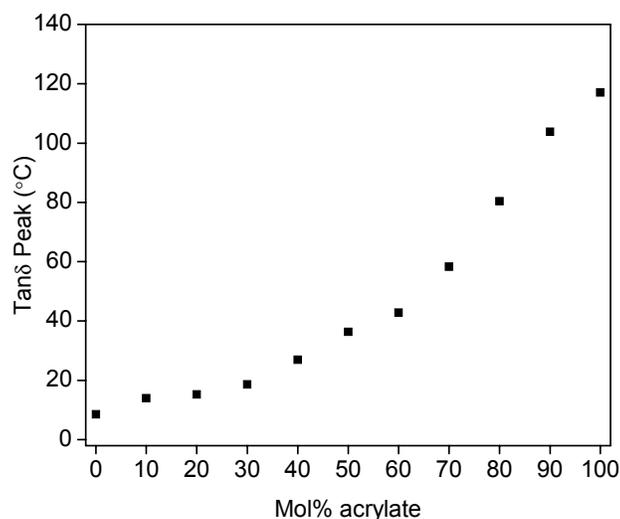

Figure 4. Increase in T_g for Thiol-Allylether/Triacrylate mixtures at various levels of acrylate incorporation in the mixture.

triacrylate increases. Generally speaking, the large height and narrow width of the tan δ peak is good evidence that the there is general overall uniformity of the crosslinking in the Thiol-Allylether /Triacrylate systems. We conclude that the four kinetic steps above are such that the matrices produced are not characterized by a wide inhomogeneous distribution in free volume. This will have important consequences with respect to film properties as will be highlighted in the presentation.

In Figure 5, thermogravametric analysis (TGA) data are shown for the temperature corresponding to 5 wt% weight loss during a TGA ramp in nitrogen for photocured Thiol-Allylether/Triacrylate films as a function of Triacrylate concentration. Addition of Triacrylate results in a decrease in the thermal decomposition onset temperature. Although the actual TGA curves are not shown herein, it is noted that there is a distinct increase in the thermal stability in the decomposition curve at temperatures greater than 450 ^{o}C for samples that contain ~30-80 mol % acrylate. This suggests a higher stability for samples that have substantial thiol-acrylate reactions via steps (1) and (2) in the kinetic scheme where the double bond is an acrylate.
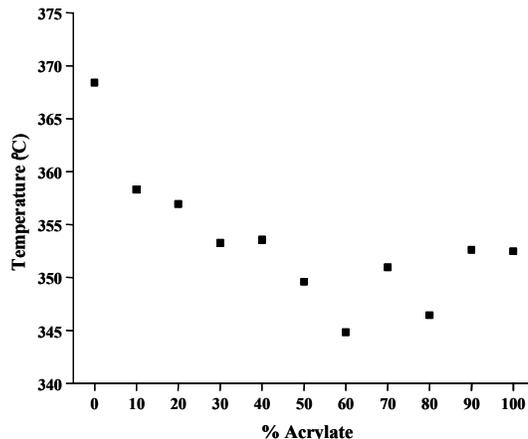

Figure 5. Temperature for 5 wt% weight loss derived from TGA decomposition for photocured Thiol-Allylether/Triacrylate films.

Conclusions

In summary, the photopolymerization of a trithiol-triallyl ether/acrylate proceeds rapidly to give highly crosslinked films. Problems related to the deconvolution of IR signals in these ternary systems prohibit giving actual conversion versus time plots for all components. Exotherm data is consistent with reduced heat per volume being produced for thiol-ene reactions versus acrylate reactions. DMA results indicate that the films have narrow tan δ versus temperature plots with peak maxima that continually increase with acrylate concentration. The temperature for the onset of thermal decomposition in general decreases with increasing acrylate content.

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