UV Curable Coatings Containing Functional POSS

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Abstract

Nanostructured POSS can be functionalized by incorporating either mercapto propionate or mercapto propionic acid groups onto multifunctional vinyl POSS. The functionalized POSS monomer can be easily formulated into coatings through thiol-ene photopolymerizations. The coatings produced exhibit excellent mechanical integrity and hardness. Real-time FTIR analysis of the functionalized POSS monomer with thiol during its photopolymerization showed that it has a moderate rate of polymerization compared to acrylates. Homopolymerization of vinyl groups on POSS may have taken place from an initial result of PhotoDSC study. Further characterization by DMA, TGA and ion-scavenging will be discussed in the symposium presentation.

Introduction

Photocurable coatings comprised of traditional materials must be formulated properly to give film properties with physical, mechanical and chemical integrity. Of course, there are always considerations that must be made in selecting the various components that comprise a photocurable formulation with respect to balance of properties. When additives are used to improve properties, deficiencies may be encountered along with improvement in target properties. For example, inclusion of nanoparticles in photocurable formulations may result in agglomeration and change in properties such as clarity. It would be advantageous to chemically incorporate polyhedral oligomeric silsesquioxane (POSS) nanoparticles into coatings to improve film properties such as flame retardancy, thermal stability, hardness and hydrophobicity. Despite the fact that POSS particles have an inorganic core that can be functionalized with organic groups, photocurable resins containing POSS chemically bound to the network have not been well studied to date. Herein we will show that indeed POSS nanoparticles can be successfully incorporated into films using thiol-ene photopolymerization by appropriate functionalization and chemical modification.

Photopolymerization of thiol-ene systems and its applications to coatings, adhesives and inks have been investigated since the 1940s. [1-3] Enes with various structures and substitute groups, including vinyl ethers, allyl ethers, conjugated dienes, styrene and acrylates, have been used in these studies. In general, these monomers exhibit high copolymerization rates with thiols due to low oxygen inhibition: this is very advantageous in photocuring processes. In the past, photopolymerization of a vinylsiloxane-thiol mixture has been reported. [4] Taking a lead from this earlier report, in this paper we report the synthesis of a novel POSS monomer (Figure 1) and its use in UV curable coatings. High solubility and compatibility of the POSS in coatings resins is aided by incorporation of the carboxylic acid groups onto POSS molecules, thus facilitate the film formation process. Shown below is a three dimension pictorial of the POSS particles that will be reported on. In the case where R=H, the carboxylic groups should function not only to reduce agglomeration and aid in film formation, but also may serve as sites for ion scavenging of metal ions. UV curing rates for the coatings containing the POSS monomer with a multifunctional thiol was evaluated by Real-Time Fourier

Transform Infared Spectroscopy (RTFTIR) and PhotoDifferential Scanning Calorimetry (photoDSC).

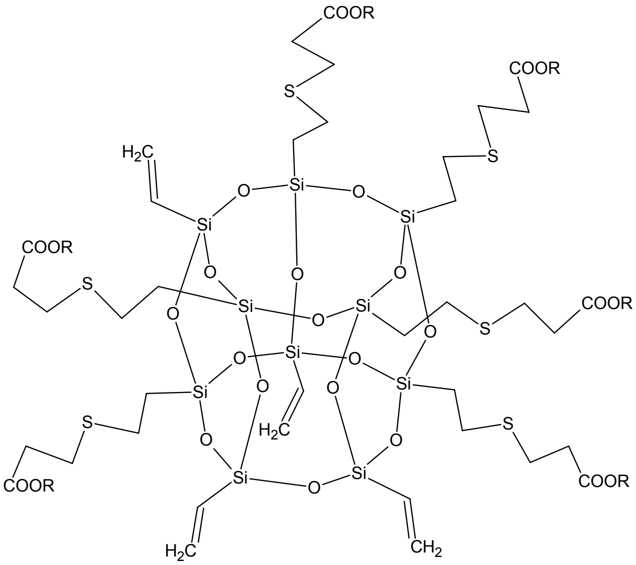


Figure 1. Generic Chemical Structure of Functionalized POSS. R=H designated as POSS **I** and R=butyl designated as POSS **II**.

Experimental

Materials. VinylPOSS, with an average cage size of ten, was obtained from Hybrid Plastics, Inc. Hexanediol diacrylate (HDDA), ditrimethylolpropane tetraacrylate (SR355) were obtained from Sartomer Company, Inc. Photoinitiators Irgacure 651 and Darocur 1173 were obtained from Ciba Specialty Chemicals Inc. Trimethylolpropane tris(3-mercaptopropionate) (Trithiol), butyl mercapto propionate, mercapto propionic acid and propyl amine were purchased from Aldrich Chemical Company and used as received.

Monomer synthesis. POSS monomer with both vinyl groups and carboxylic acid groups available were synthesized by amine catalyzed Michael addition of thiol and ene groups (Scheme 2). A complete conversion of mercapto propionic acid after 6 hours at room temperature was expected. [5,6] Proton NMR and ^{13}C NMR of the product confirmed the structure for POSS **I**. POSS coupled with butyl mercapto propionate (POSS **II)** was also prepared in a similar fashion so that the targeted average number of residual vinyl groups is four in the product, represented by the structure shown in Figure 1.

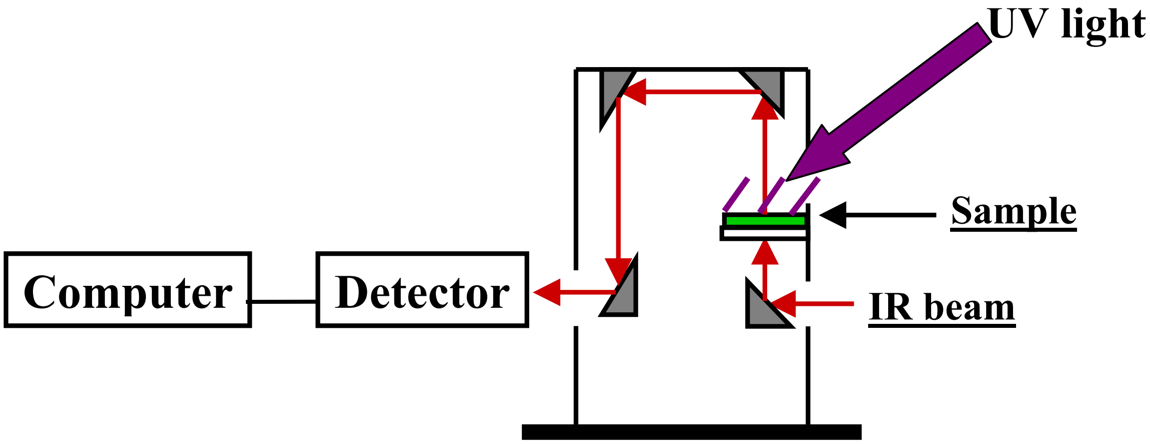
Coatings Preparation Coatings were formulated with variable compositions listed in Table 1. In a typical process, photoinitiator Darocur 1173 was dissolved in a HDDA and SR355 mixture. One of the POSS monomer was then added, heated to 50 °C and sonicated for 30 minutes. Trithiol (see experimental) was then blended in and sonicated for another 10 minutes. Formulations was applied with a thickness of 8 mil on a glass plate and cured under a total energy density of 1.1 J/cm^2 and irradiance of 1.1 W/cm^2 with an H-bulb using a bench-top curing station (Light Hammer-6) from Fusion UV Systems, Inc.

Table 1. Molar composition of monomers for coatings.

Materials	Formulation A	Formulation B	Formulation C	Formulation D
Trithiol	102	86	173	169
HDDA	0	0	135	141
SR355	0	0	67	75
I	210	0	201	0
II	0	206	0	201
Darocur 1173	5	5	9	9

RTFTIR and PhotoDSC. Real time Infrared spectra were recorded using a modified Bruker IFS88 spectrometer. The sample was placed on a NaCl salt plate which stands horizontally in the IR beam path (Scheme 1) to keep liquid sample immobile. UV light was allowed to impinge on the sample from a fiber-optic cable. The sample was coated on a salt plate with such a thickness that an optical density of 0.7 at 1640 cm^{-1} was obtained. A 200 watts high pressure mercury lamp from Oriel Instruments was used as the light source. The UV irradiance was measured with a calibrated radiometer (IL-1400) from International Light. A neutral density light filter was used to obtain a total light intensity of 37.5 mW/cm^2. The infrared absorption spectra were acquired with a scanning rate of 10 scan/s under continuous UV irradiation.

Photo Differential Scanning Calorimetry was set up using a Perkin-Elmer DSC-7 modified by adding quartz windows to the sample head cover. A 450-W medium-pressure mercury lamp was used as the light source. Light intensity of the full arc was approximately 50 mW/cm^2, with lower light intensity attained by using neutral density filters or changing the distance between the lamp and the sample cells. The actual light intensity used in this experiment was 2 mW/cm^2 using a light filter.

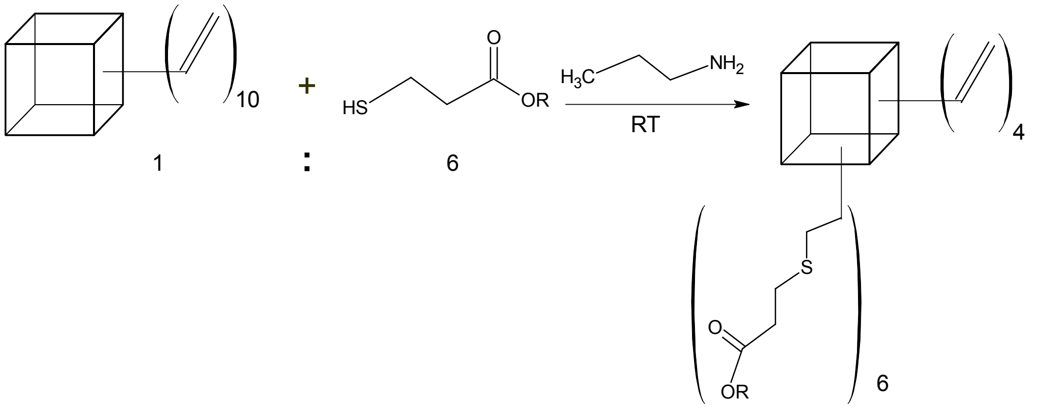


Scheme 1. Schematic Representation of Real Time FTIR Instrumentation.

Results and Discussion

Functionalized POSS Monomers **I** and **II** were prepared as shown in Scheme 2 by an amine catalyzed Michael addition of mercapto propionic acid or butyl mercapto propionate to the vinyl groups of POSS molecules. The product was eluted on silica gel column with THF and ethyl acetate as the eluting solvent for POSS **I** and POSS **II**, respectively. After evaporation of the solvent under reduced pressure, a transparent liquid was obtained and characterized by FTIR and NMR. Shown in Figure 2 are the infrared spectra of both the eluted component in the mixture before the reaction. A decrease in the intensity of the band at 1603 cm^{-1} by half (i.e., an area ratio of 2.1 to1.0) indicates partial conversion of the vinyl double bond leaving an average number of unreacted vinyl double bonds of five.

Proton NMR spectra of the eluted component also showed the presence of both vinyl double bond and mercaptopropionic acid moiety on the POSS cages indicated by the appearance of chemical shifts at 6.2 ppm for vinyl protons and 2.9 ppm for α-carbon protons of sulfide.



Scheme 2. Synthesis of POSS **I** (R=H) and POSS **II** (R=butyl).

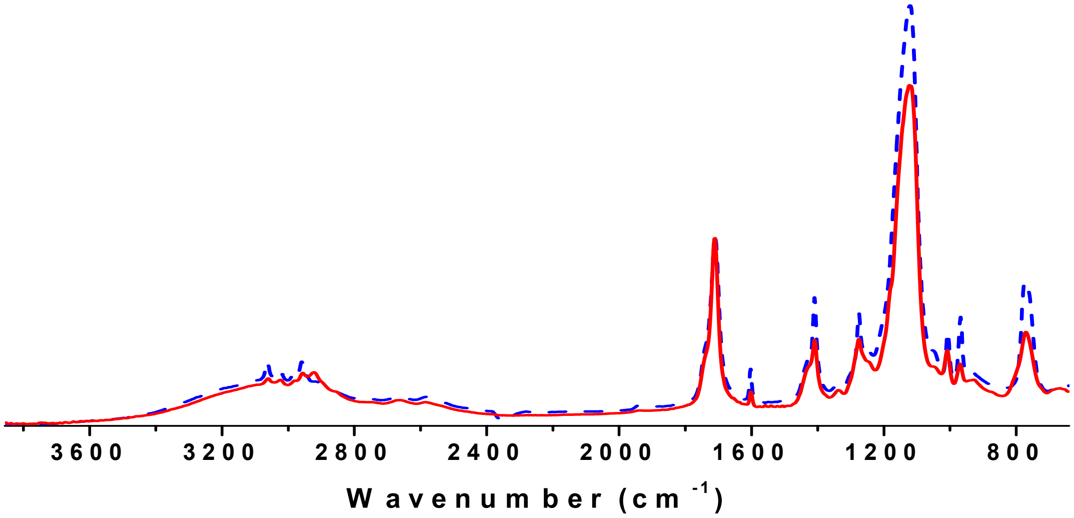


Figure 2. Infared spectra of the mixture of vinylPOSS (with an average cage number of 10) and mercapto propionic acid before and after reaction.

Films were prepared by photocuring of 1:1 mixtures of POSS **I** and POSS **II** with trimethylolpropane tris(3-mercaptopropioniate) (designated as Trithiol) as well as Trithiol:acrylate combinations with POSS **I** and **II** as set forth in Table 1. All the formulations were fully cured on glass plates. The films were stripped off of the glass plate for Dynamic Mechanical Analysis (DMA), Thermal Gravimetric Analysis (TGA) and ion-scavenging analysis after Persoz Hardness measurements were performed. The Persoz hardness results are shown in Table 2. The DMA, TGA and ion scavenging analysis results are not reported in this preprint, but will be presented at the symposium.

Table 2. Relative Persoz hardness of POSS-containing coatings.

Formulation	A	B	C	D
Persoz Hardness	71	94	18	23

The results in Table 2 clearly demonstrate that the films produced using 1:1 combinations of the POSS **I** and **II** (films prepared from formulation A and B) gave much higher Persoz hardness readings that coatings prepared from mixtures which included acrylates as well as Trithiol and POS **I** and **II**. Although not shown, coatings prepared from mixtures with thiol and acrylate only and neither of functionalized POSS monomers gave Persoz hardness values much less than obtained for films prepared from formulations A and B.

The curing rate of the functionalized POSS **I** with Trithiol were evaluated by both RTFTIR and PhotoDSC. Figure 3 shows the conversion of the POSS **I** vinyl double bond with time as well as acrylate double bond conversions for mixtures of two acrylates containing thiols for comparison. Compared with the Trithiol:HDDA mixture, the rate of conversion for vinyl groups on POSS **I** in the Trithiol:POSS I is slower than for the acrylate conversion in the Trithiol:HDDA mixture, and about the same as the initial conversion rate for the acrylate in the Trithiol:di(trimethylolpropane)tetracrylate mixture. Of course, there is substantial homopolymerization of the acrylate and the vinyl groups, and this contributes significantly to the conversions attained. Interestingly, the final conversion of vinyl groups in POSS **I** is higher than that of the acrylate group conversion in the Trithiol: di(trimethylolpropane)tetraccrylate mixture. Note that thiol conversions although not shown, are less in each case than the double bond conversion since both the acrylates and the vinyl groups experience a certain extent of homopolymerization.

Figure 4 shows the PhotoDSC exotherms of **I** cured with various weight percent of Trithiol. Although not shown, at the same weight percent of photoinitiator and cured under the same light intensity, the maximum heat exotherm of HDDA either alone or with Trithiol is much larger than any of the exotherms for the mixtures of Trithiol and POSS I in Figure 4. This result is consistent with the results obtained using Real-time FTIR. Shown in Figure 5**,** the maximum rates of polymerization (Maximum Peak Height) were plotted *versus* Molar Ratio of Trithiol to POSS **I** monomer. If thiol groups reacted with vinyl groups in a one to one molar functional group ratio, then a molar ratio of 1.7 would be expected to give the greatest value for the Maximum Peak Height *versus* Molar Ratio of Trithiol to POSS **I** plot in Figure 5 since the average number of vinyl groups for POSS **I** is ca. 5. The actual value of the molar ratio, however, is approximately 0.3 at which the maximum rate of polymerization reaches its highest value. This was consistent with results from real-time FTIR studies; although not plotted in Figure 3, it was noticed that the thiol conversion is much less than the vinyl conversion for a given irradiation time.

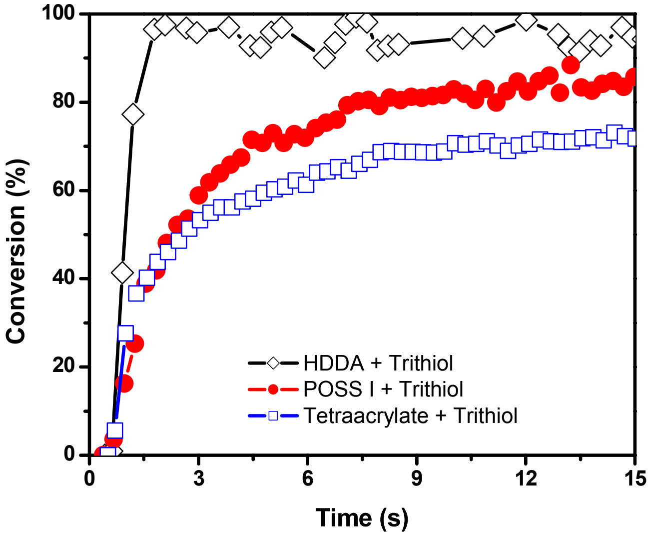


Figure 3. Real-time FTIR of HDDA, **I** and tetraacrylate (SR355) with 5 wt% I-651 and 30 wt% trithiol.

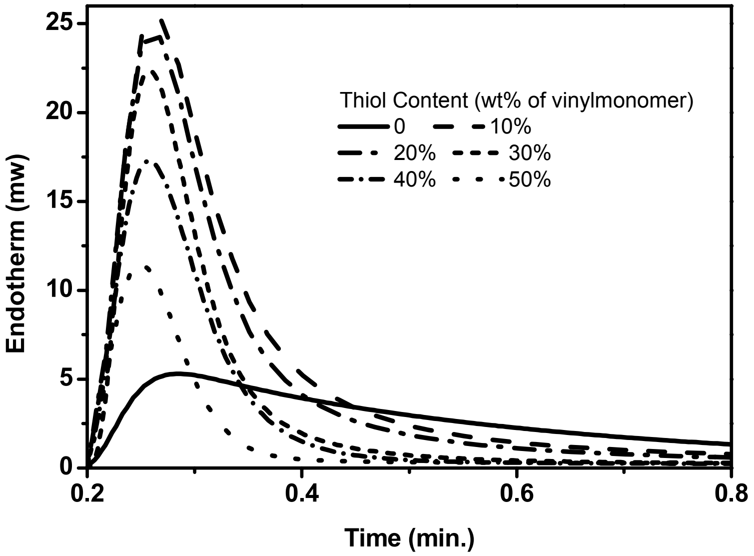


Figure 4. PhotoDSC endotherm traces of **I** cured with photoinitiator I-651 and trithiol at various trithiol content.

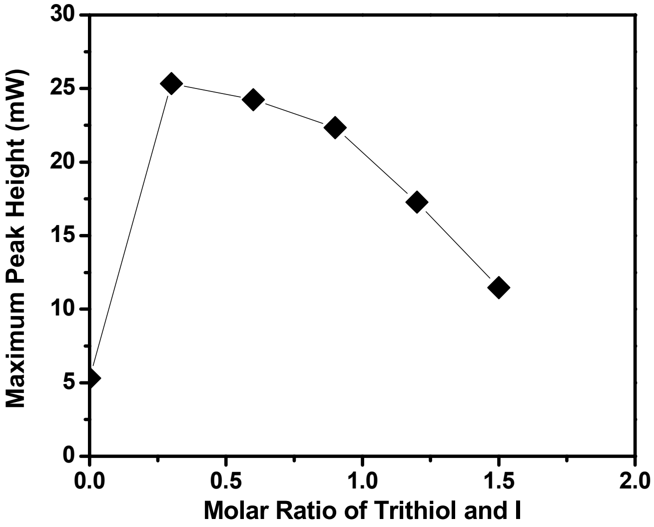


Figure 5. Maximum rate of polymerization *versus* molar ratio of trithiol and **I**.

Conclusions

In conclusion, novel UV curable POSS monomers were conveniently synthesized by amine catalyzed reactions of a vinyl POSS with mercapto propionic acid or butyl mercapto propionate. The monomer showed a moderate curing speed, and may be formulated with multifunctional thiols to produce coatings with excellent hardness. Incorporation of carboxylate or carboxylic acid groups increases compatibility of POSS in coatings, and can potentially provide sites for chelating metal ions for use in ion scavenging.

Acknowledgements

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