Structural Influence of Model Ene Reactivity in Photoinduced Thiol-Ene Polymerization of Multifunctional Alkenes

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Abstract

An examination of model monofunctional alkenes using real-time infrared spectroscopy (RTIR) was used to characterize the polymerization mechanism and kinetics of multifunctional thiol-ene systems. Model study results indicate the reactivity of thiol with external enes is rapid and independent of the length of aliphatic hydrocarbon substituted on the ene. However, rates are significantly reduced due to steric affects when the ene is internal, located in the interior of an aliphatic hydrocarbon, and/or by disubstitution of a second aliphatic substituent on an external ene. Internal cis enes rapidly react with thiol but undergo a fast isomerization-elimination sequence generating the trans ene, which proceeds to react slowly with thiol. The reactivity trends in the model study were confirmed in a photopolymerization kinetic investigation of a series of multifunctional thiol-ene systems.

Introduction

Photopolymerizable thiol-ene systems have found use in a variety of industrial applications since the 1970's due to the numerous advantages they offer over traditional acrylate based systems.[1-3] Thiol-enes exhibit fast cure rates, oxygen insensitivity, excellent adhesion, and extremely uniform crosslink densities.[1-6] The thiol-ene polymerization mechanism has been studied extensively and is known to follow a free radical step growth mechanism in which addition of a thiyl radical into a double bond (ene) is followed by chain transfer to thiol.[4] Linear polymer is formed when equal molar mixtures of difunctional ene and difunctional thiol are reacted. A chemically crosslinked polymer is formed when at least one of the components has a functionality greater than two.

Thiol-ene photopolymerizations are incredibly versatile in that products with completely different properties can be easily produced. This distinctive characteristic is the result of having flexibility in the selection of ene monomers capable of participating in thiol-ene reactions. A partial list of enes documented in thiol-ene literature include both electron rich and electron poor enes such as styrene, vinyl ethers, allyl ethers, vinyl acetates, acrylates, norbornenes, and acrylonitrile.[4,7] We note from practical experience in our lab that thiol-ene systems can be tailored to give soft, flexible films or extremely hard, scratch resistant coatings simply by changing the composition of the ene.

Hydrocarbon alkenes are an interesting class of monomer because of the variety of structures commercially available. Types of carbon-carbon double bond found in alkenes that can dramatically influence the reactivity include internal, external, aliphatic, cyclic, conjugated,

nonconjugated and/or substituted enes. In thiol-ene polymerizations, the difference in reactivity between such reactive groups in multifunctional reactants can affect the reactions kinetics, extent of conversion, and crosslink density, all important factors when considering the products final properties. Although some research has been conducted in this field,[4,8-10] a thorough documentation regarding the polymerization mechanism and kinetics of the multifunctional alkenes with thiol is absent. Model studies investigating the structural effect of enes on its reactivity in a thiol-ene system and its implications for the formation of a crosslinked network are the fundamental questions this paper addresses.

Experimental

Materials

The alkenes used in the model study include 1-hexene, 2-methyl-1-hexene, trans-2-hexene, cis-2-hexene, trans-3-hexene, 1-octene, trans-4-octene, 1-decene, trans-5-decene, and ethyl 3-mercaptopropionate (Aldrich). Materials used in the multifunctional thiol-alkene kinetic investigation include 1,6-hexanedithiol, 1,9-decadiene, 1,5,9-decatriene (mixture of cis and trans isomers), and 1,2,4-trivinyl cyclohexane (Aldrich). All chemicals were used as received, without additional purification. The respective chemical structures are shown in Figure 1.
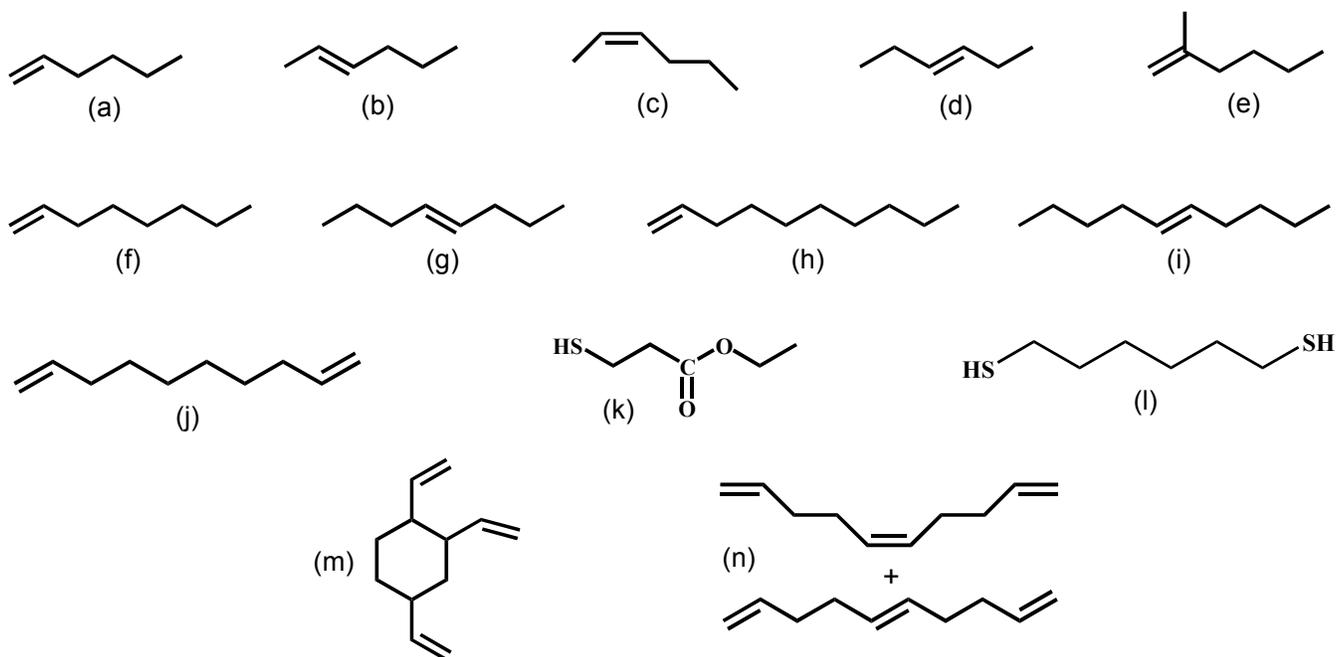
Figure 1.

Chemical structures of (a) 1-hexene, (b) trans-2-hexene, (c) cis-2-hexene, (d) trans-3-hexene, (e) 2-methyl-1-hexene, (f) 1-octene, (g) trans-4-octene, (h) 1-decene, (i) trans-5-decene, (j) 1,9-decadiene, (k) ethyl-3-mercaptopropionate (E3M), (l) 1,6-hexanedithiol, (m) 1,2,4-trivinyl cyclohexane, and (n) 1,5,9-decatriene (mixture of cis and trans isomers).

A Bruker IFS 88 modified to accommodate a horizontal sample accessory was used to collect real-time infrared (RTIR) spectroscopic data of photopolymerizations. Ultraviolet light from an Oriel lamp system equipped with a 200 Watt high pressure mercury xenon bulb was channeled through an electric shutter and fiber optic into the sample chamber. Photoreactions were conducted by sandwiching the sample between two sodium chloride salt plates at a thickness of approximately 20 microns. The salt plate edges were sealed with vacuum grease to suppress monomer evaporation and samples were purged 10 minutes in nitrogen prior to irradiation. All experiments were conducted using a 365 nm bandpass filter and at a light irradiance of 3 mW/cm^2, as measured by a calibrated radiometer from International Light (IL-1400). Infrared absorbance spectra were obtained under continuous UV irradiation at a scanning rate of 5 scans/second. All samples were prepared with equal concentrations of functional groups and contained 1 weight percent of the photoinitiator dimethoxy phenyl acetophenone. The characteristic IR absorbance bands used to monitor the disappearance of reactant/monomer during the photoreactions were as follows; external ene (1640 and/or 910 cm^{-1}), internal trans ene (968 cm^{-1}), internal cis ene (700 cm^{-1}), and thiol (2575 cm^{-1}).

Discussion

The persistent demand to produce novel products with superior performance properties regularly drives academic exploration and reasoning. To this end, additional research into thiol-ene photopolymerization mechanisms and kinetics is warranted due to the vast range of physical and chemical properties obtained from these unique systems. The material produced through the reaction of multifunctional thiols and multifunctional alkenes is one underexploited sector within this well recognized field of chemistry. A fundamental understanding of the crosslinking chemistry, polymerization mechanism and polymerization kinetics is necessary to predict and understand the properties of the final product.

Model studies examining the rate of addition of monofunctional thiol to various monofunctional alkenes were conducted in order to determine the structural influence of the ene on the thiol-ene reaction mechanism, kinetics and its subsequent impact on crosslinking reactions. More specifically, the effect accessibility, substitution, and conformation of a carbon-carbon double bond were individually examined. The reactivity of external enes with increasingly larger aliphatic hydrocarbon substituents were investigated in the reaction with a monofunctional thiol, ethyl 3-mercaptopropionate, the results of which are depicted in the RTIR conversion versus time plot depicted in Figure 2(a). It should be noted that alkenes do not homopolymerization due to the electron rich nature of the double bond and the presence of abstractable hydrogens, therefore any ene conversion is assumed to be the result of direct reaction with the thiol. 1-Hexene, 1-octene, and 1-decene displayed equal reactivity with the thiol, achieving complete conversion after approximately 10 seconds irradiation. This indicates that external ene reactivity is unaffected by increasing aliphatic substituent size pendant from the ene. However, addition of a second pendent substituent (disubstitution), as with 2-methyl-1-hexene, dramatically reduces the reactivity. The methyl substituent may reduce the rate of hydrogen abstraction from the thiol by the carbon centered radical, thereby reducing the rate of reaction.

A second model study was preformed to access the affect ene location has on the reactivity with monofunctional thiol. The difference in reactivity between external and various internal enes with trans conformations are shown in the RTIR ene conversion versus time plot

in Figure 2(b). When comparing the results from Figure 2(a) and 2(b), it is clear that an external ene is significantly more reactive than an internal trans ene. A 30 fold increase in the time required to reach 50% ene conversion was observed, going from 1 second irradiation for external enes to greater than 30 seconds irradiation for trans-2-hexene. Increasing the substituent size on both ends of the internal ene only further increased the disparity in reactivity. However, once the size of the substituents is greater than or equal to propyl groups, such as with trans-4-octene and trans-5-decene, the ene cannot discern between increasing substituent size and the reaction rate reaches a minimum where further increasing substituent size has no deleterious effect on reactivity. Since the carbon centered radical formed upon insertion into 1-hexene is structurally similar to the radical formed upon insertion into 2-hexene, one might expect the rate of the subsequent thiol abstraction to be similiar. Therefore, thiyl radical insertion into the internal ene must be significantly slower and is the dominant factor in reducing the reactivity of internal enes. Internal enes are plagued by steric crowding around the ene which reduces the thiyl radical accessibility to the ene.
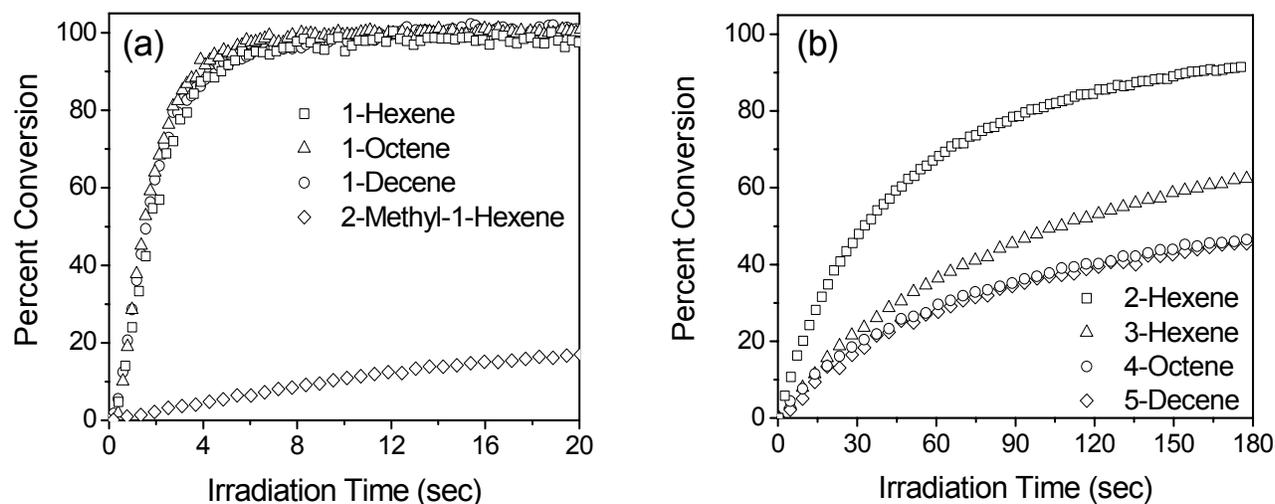
Figure 2.

RTIR plots depicting alkene conversion for 50:50 molar alkene:E3M mixtures. Photoinitiator is 1 wt% DMPA; UV irradiance of 3.0 mW/cm^2. (a) External ene comparison, (b) Internal ene comparison.

Internal enes have restricted rotation about the carbon-carbon double bond and exhibit cis-trans isomerization. It has been previously documented that cis and trans enes isomerize during the thiol-ene reaction as shown in Scheme 1.[8] A thiyl radical will insert into both cis and trans enes, isomerize to the more thermodynamically stable isomer, and finally either hydrogen abstract from a thiol to form the desired thiol-ene reaction product or eliminate the thiyl radical resulting in the regeneration of the alkene. The final reaction conversion and rate are dependent on the ratio between the rate constant of hydrogen abstraction and the thiyl radical elimination rate constant.

Multifunctional enes containing internal carbon-carbon double bonds regularly consist of a mixture of cis and trans isomers. Therefore, acquiring a complete understanding of how the presence of either isomer will affect the polymerization mechanism and kinetics is desired. A model study was performed to examine the phenomenon of cis-trans isomerization within thiol-ene reactions in much greater detail than currently available in literature. Figure 3(a) compares the RTIR conversion versus time plots for the reactions of cis-2-hexene/E3M and trans-2-hexene/E3M. The cis-2-hexene is rapidly consumed in the reaction with E3M, reaching 80% conversion after 30 seconds of irradiation, two times faster than the trans-2-hexene reaction. This confirms that cis enes are less sterically hindered, thus facilitating rapid insertion of the thiyl radical. Interestingly, the conversion of thiol (E3M) does not track the conversion of ene in either reaction and is in fact significantly slower. The insertion-isomerization-elimination sequence discussed in Scheme 1 can explain this phenomenon. Simple insertion of a thiol into an ene to form the thiol-ene addition product dictates 1:1 thiol and ene conversion. However, if isomerization-elimination occurs following insertion into the ene, then the thiol is regenerated but the original ene isomer has been consumed, therefore causing a deviation in 1:1 thiol-ene conversion. It is interesting to note that the thiol is initially converted at a faster rate in the reaction with cis-2-hexene, due to its enhanced accessibility in comparison to a trans ene, yet the final conversion in both reactions are equal. Reactant conversion in thiol-internal ene systems is controlled by the rate constants for two competing reactions after thiyl radical insertion into the ene: hydrogen abstraction from a thiol and thiyl radical elimination. Because the product of thiyl radical insertion into cis-2-hexene and trans-2-hexene are indistinguishable following isomerization to the most thermodynamically stable isomer, the conversions should be equivalent.
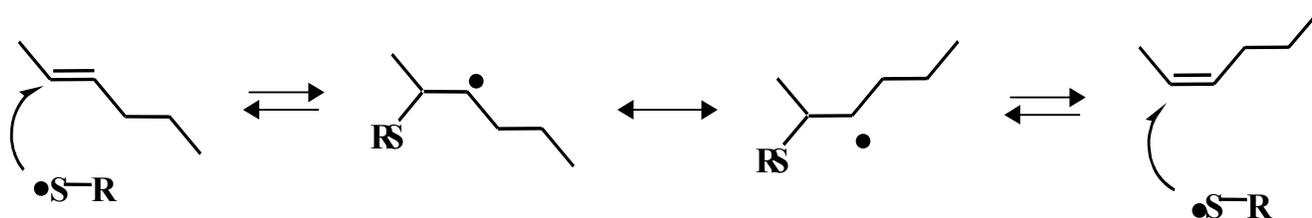
Scheme 1.

Reaction schematic illustrating the cis-trans isomerization during the thiol-ene photoreaction.

Further investigation into the insertion-isomerization-elimination reaction sequence is necessary to supplement the conclusions asserted regarding Figure 3(a). RTIR can provide insight into a chemical reaction by observing both the disappearance of reactive groups and/or formation of products. Figure 3(b) depicts the normalized absorbance values for the cis ene, trans ene, and thiol during the reaction of cis-2-hexene/E3M. Prior to irradiation, the reaction mixture consists of 50:50 molar mixture of ene and thiol, where the ene consists of 97% cis-2-hexene and 3% trans-2-hexene. Following irradiation of UV light, thiol and cis ene are consumed, as indicated by a decrease in IR absorbance. Trans ene formation is signified by an immediate increase in absorbance, reaching a maximum after 25 seconds irradiation. Once formed, the trans ene is slowly consumed by thiol.
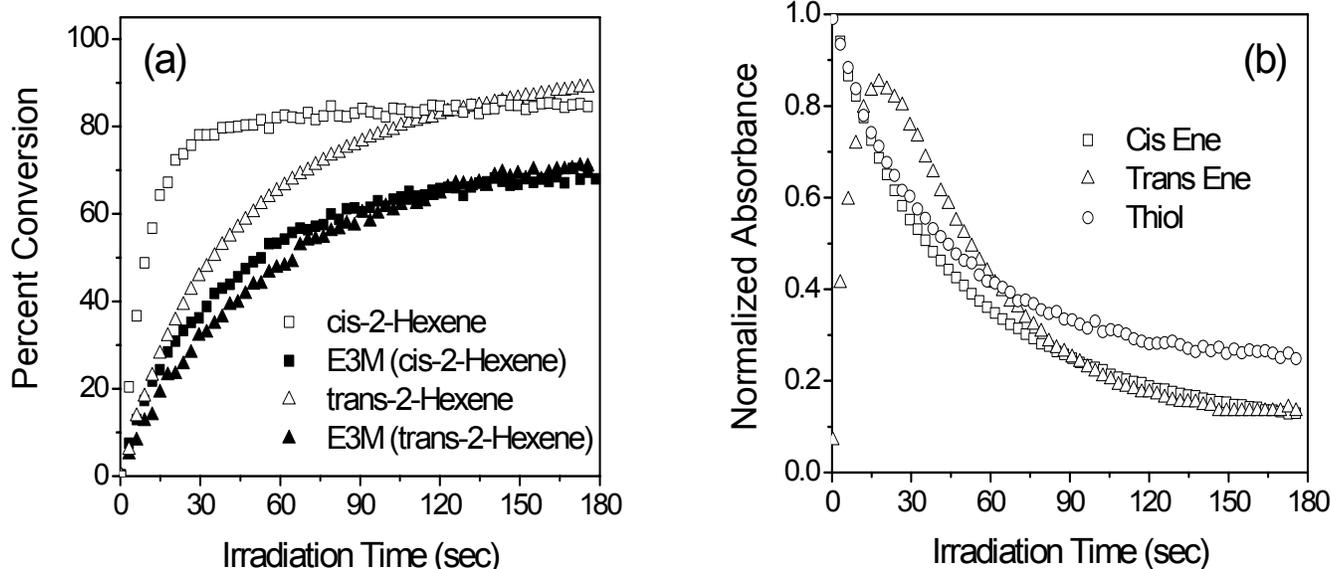
Figure 3.

RTIR results for 50:50 molar alkene:E3M mixtures. Photoinitiator is 1 wt% DMPA; UV irradiance of 3.0 mW/cm². (a) Conversion versus time plots for the photoreaction of cis-2-hexene/E3M and trans-2-hexene/E3M, (b) Normalized IR absorbance values for the photoreaction of cis-2-hexene/E3M.

Model studies were preformed to provide insight into how various multifunctional alkenes would react during thiol-ene photopolymerizations. To test these results, three structurally different multifunctional alkenes were selected; 1,9-decadiene, 1,2,4-trivinyl cyclohexane, and 1,5,9-decatriene (mixture of cis and trans isomers). Figures 4(a) and (b) show the RTIR conversion versus time plots for the reaction of 1,9-decadiene/1,6-hexanedithiol and 1,2,4-trivinyl cyclohexane/1,6-hexanedithiol. 1,9-Decadiene contains two external enes and thus undergoes a very rapid reaction with the thiol reaching 100% conversion after 30 seconds of irradiation. On the other hand, the trifunctional external ene, 1,2,4-trivinyl cyclohexane, reacts significantly slower, reaching only 50% conversion after 30 seconds of irradiation. Following insertion into the external ene, the resultant carbon centered radical is less accessible, therefore decreasing the rate of hydrogen abstraction and the overall polymerization rate. In addition, the absence of any internal enes prevents isomerization from occurring, and 1:1 conversion of the thiol and ene is observed in both reactions.
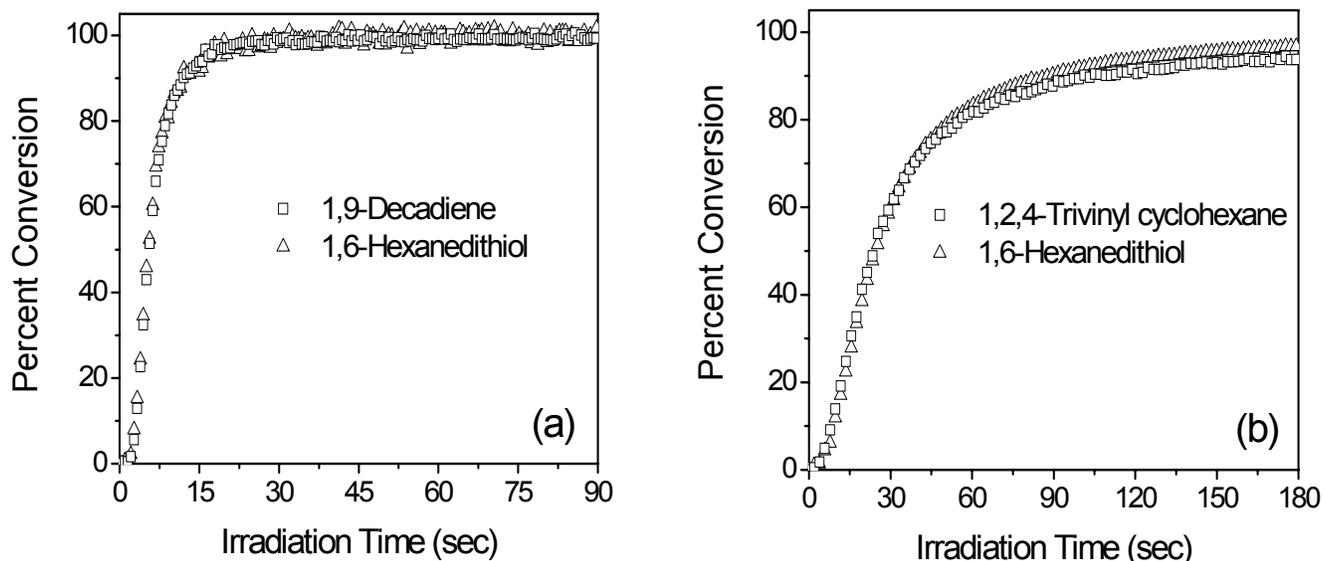
Figure 4.

RTIR results for 50:50 functional group mixtures of multifunctional ene:thiol. Photoinitiator is 1 wt% DMPA; UV irradiance of 3.0 mW/cm^2. Conversion versus time plots for the photoreaction of (a) 1,9-decadiene/1,6-hexanedithiol and (b) 1,2,4-trivinyl cyclohexane/1,6-hexanedithiol.

The presence of internal double bonds in a multifunctional alkene imposes a complex series of reactions which ultimately results in the formation of a crosslinked network. The commercially available trifunctional aliphatic alkene, 1,5,9-decatriene, consists of a mixture of cis and trans isomers. Figure 5(a) depicts the RTIR conversion of the external enes in 1,5,9-decatriene upon reaction with 1,6-hexanedithiol. As seen in the thiol-ene reaction with 1,9-decadiene, the external enes of 1,5,9-decatriene are rapidly consumed, reaching nearly 100% conversion in 50 seconds. Meanwhile, thiol conversion has reached approximately 68%, indicating the formation of a linear polymer with residual internal enes. Thiol is slowly consumed over the next 300 seconds through crosslinking reactions with the internal ene, ultimately reaching a conversion greater than 85%. Figures 5(b) and 5(c) illustrate in detail the sequence of reactions occurring during the polymerization. Prior to irradiation, there exists a mixture of external enes along with cis and trans internal enes having characteristic IR absorbances at 910, 700, and 968 cm^{-1} respectively. Figure 5(b) depicts the real-time disappearance of the external enes and the internal trans ene. As expected, the external ene peak at 910 cm^{-1} rapidly disappears, whereas the trans ene reacts at a significantly slower rate. Examination of the trans ene at 968 cm^{-1}, as shown in Figure 5(c), clearly indicates the insertion-isomerization-elimination reaction sequence attributed to internal enes. Trans ene IR absorbance initially increases as cis isomer is rapidly consumed and then subsequently reacts with the thiol.
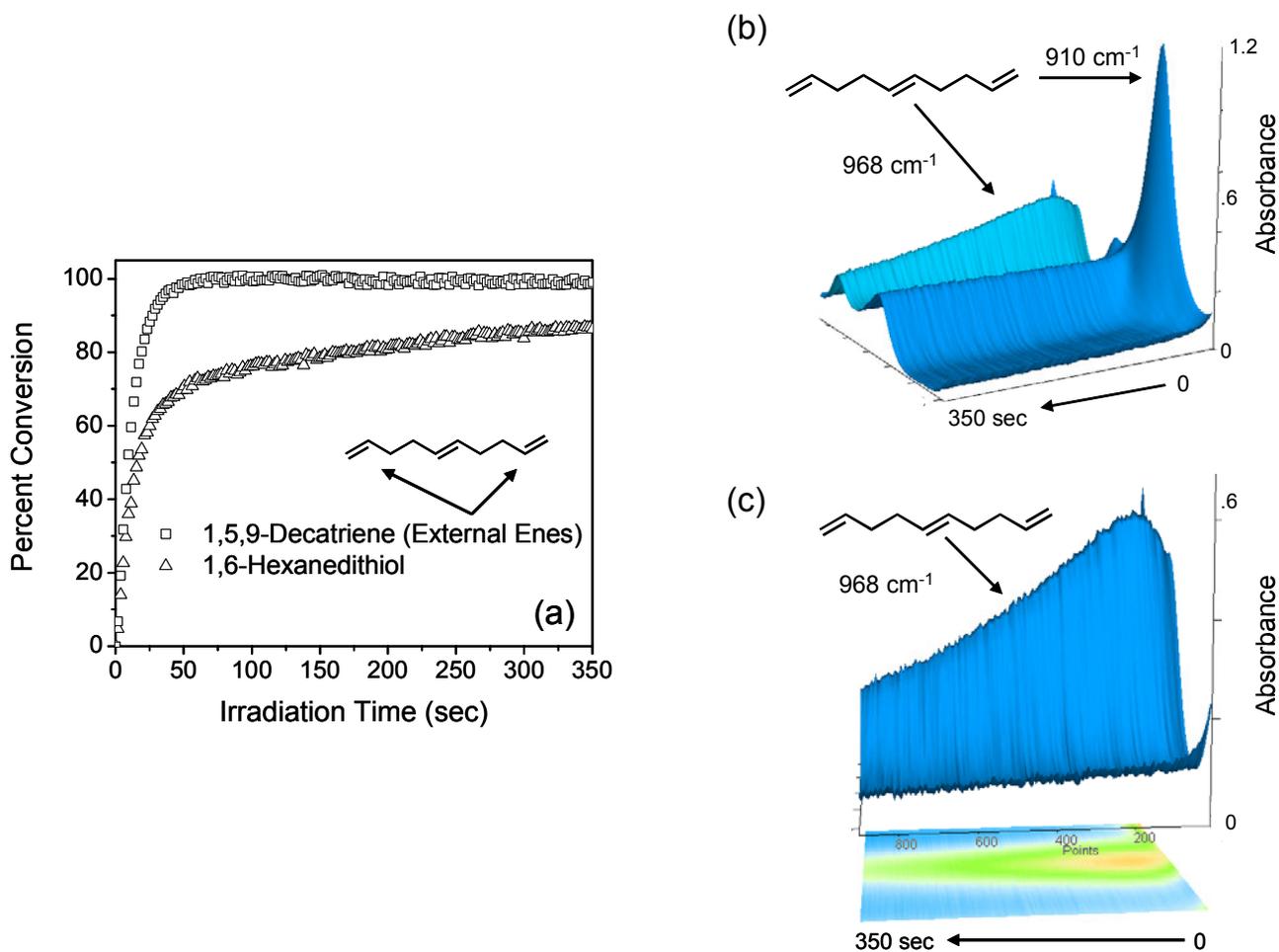
Figure 5.

RTIR results for a 50:50 functional group mixture of 1,5,9-decatriene/1,6-hexanedithiol. Photoinitiator is 1 wt% DMPA; UV irradiance of 3.0 mW/cm^2. (a) Conversion versus time plots for the external enes of 1,5,9-decatriene and thiol, (b) IR absorbance of the internal trans ene at 968 cm^{-1} and the external ene at 910 cm^{-1} as a function of time, (c) IR absorbance of the internal trans ene at 968 cm^{-1} as a function of time.

Conclusions

RTIR was used to examine the polymerization mechanism and kinetics of thiol-alkene photoreactions. A series of model studies illustrated the significant impact accessibility/location, substitution, and conformation all have on the reactivity of alkenes. Understanding the structural influence on reactivity will play an important role in the future development of novel materials based on thiol-alkene systems.

Acknowledgements

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