Thiol−Ene Photopolymerization Kinetics of Vinyl Acrylate/Multifunctional Thiol Mixtures

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ABSTRACT: The photopolymerization of multifunctional thiol (trimethylolpropane tris(3-mercaptopropionate))/vinyl acrylate mixtures as a function of thiol content in the presence and absence of photoinitiators has been investigated using real-time FTIR, thin-film calorimetry, and 2D-COSY NMR. The addition of a multifunctional thiol to vinyl acrylate significantly enhances the conversion of the vinyl double bonds of vinyl acrylate due to the preferential addition of the thiyl radical to the vinyl group. Two separate free-radical polymerization processes, acrylate homopolymerization and thiol/vinyl ester copolymerization, occur simultaneously in thiol/vinyl acrylate mixtures. Thin-film calorimetry and 2D-COSY NMR results are consistent with real-time FTIR results, giving strong evidence for two simultaneous free-radical processes.

Introduction

Because of rapid growth in the field of photopolymerization, considerable research on the fundamentals of the polymerization process using light has been conducted over the past few decades.[1−3] There is no question that the development of new technology is still essential to solving existing problems and improving the final physical and mechanical properties of the films produced. Recent research has focused on the development of new photoinitiation systems with enhanced initiator efficiency,[4,5] measurement of the polymerization kinetics of multifunctional monomers,[4,6−8] and the design of new multifunctional monomers that polymerize rapidly to produce films with outstanding properties.[9−11] Improving the photopolymerization process and developing new monomers are certainly keys to ensuring continued growth of the photopolymerization field.

One particularly interesting aspect of photopolymerization deals with monomers that have two different functional groups. Recently, Hult et al.[12] reported photopolymerization results for a difunctional monomer with a reactive maleimide group and an acrylate. Interestingly, since maleimides have been used as photoinitiators,[13,14] the difunctional maleimide/acrylate reported by Hult et al.[12] polymerized when exposed to light in the absence of an added photoinitiator. In this case, the maleimide not only initiates but also participates in the free-radical polymerization process. Another difunctional monomer with two reactive groups (acrylate and vinyl ester) that can participate in free-radical polymerization is vinyl acrylate. Research on vinyl acrylate polymerization, reported by Fukuda et al. in the early 1970s,[15,16] focused primarily on the polymerization behavior of the two different functional groups and the resultant cyclic polymerization in dilute solution. Recently, Kudyakov et al.[17,18] reported real-time infrared (RTIR) results showing that in bulk the acrylate group homopolymerizes to about 70% conversion before the vinyl ester group begins to react. Vinyl acrylate, like the maleimide/acrylate monomer,[19] can also self-initiate its own free-radical polymerization.

Many photocuring techniques have been developed to enhance overall performance and provide specific properties of photopolymers. Studies have focused on such varied topics as the effect of polymerization kinetics on polymer morphology,[19−21] cationic hybrid curing systems,[22,23] and the development of new monomers.[24] One particularly promising effort deals with photopolymerizable thiol−enes.[25−36] Thiol−ene additions were first discovered by Posner in 1905, and the basic chemistry, polymerization mechanism, and photoinduced reactivity of thiols with various enes have been extensively investigated.[25−28] The thiol−ene reaction is a free-radical chain reaction of a thiol to an ene that proceeds by a step-growth process, i.e., a free-radical addition followed by a chain-transfer reaction. These studies clearly demonstrated that thiol−ene mixtures exhibit significant polymerization advantages including rapid reaction, low shrinkage, little or no oxygen inhibition, self-initiation, and formulation latitude due to the large number of enes that copolymerize with thiols. The final cured films also exhibit excellent physical properties such as good adhesion to substrates. Recently, the detailed photopolymerization kinetics which govern the structure and morphology of thiol−ene photopolymers was reported by Bowman and co-workers.[32−35]

While thiol−ene systems have been examined extensively, much is still to be learned about the differences in reactivity of the thiol with different ene monomers. Herein, we report on the free-radical polymerization of thiol/vinyl acrylate mixtures that have three types of reactive species: acrylates, vinyls, and thiols. When considering such a multicomponent system, it is essential to understand how each component contributes to the polymerization kinetics. The effect of multifunctional thiol on both acrylate and vinyl group conversion of vinyl acrylate has been investigated as a function of

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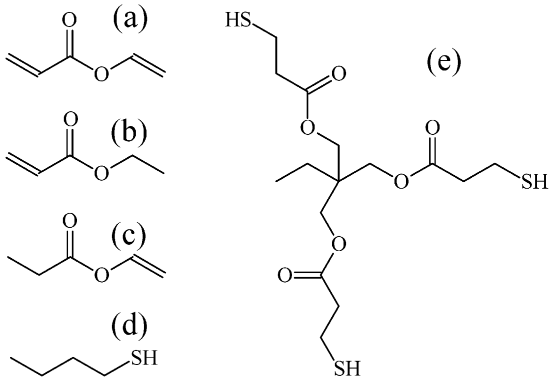


Figure 1. Chemical structures of (a) vinyl acrylate, (b) ethyl acrylate, (c) vinyl propionate, (d) butanethiol, and (e) trimethylolpropane tris(3-mercaptopropionate).

thiol content in the presence and absence of external photoinitiators. Real-time FTIR (RTIR) was used to monitor the effect of the multifunctional thiol on the polymerization kinetics of both functional groups in vinyl acrylate. A thin-foil calorimeter and 2D-COSY NMR were used to provide evidence for a proposed dual free-radical polymerization mechanism. The kinetics of multifunctional thiol/ethyl acrylate and multifunctional thiol/vinyl propionate systems, which serve as models for the multifunctional thiol/vinyl acrylate copolymerization, are also reported.

Experimental Section

Materials. Vinyl acrylate (VA, 98%), trimethylolpropane tris(3-mercaptopropionate) (trithiol, 98%), ethyl acrylate (99%), vinyl propionate (98%), and butanethiol (99%) were obtained from Aldrich Chemical Co. and used without further purification. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was obtained from Ciba Specialty Chemicals. The chemical structures of vinyl acrylate and the multifunctional thiol used in this study are shown in Figure 1 along with monofunctional analogues, ethyl acrylate, vinyl propionate, and butanethiol.

Methods. 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 W high-pressure mercury−xenon lamp source. The real-time FTIR setup has been described in detail elsewhere.[18] Samples were prepared by mixing vinyl acrylate and thiol based on the moles of each functional group. Samples of 10−15 μm thickness were placed between two sodium chloride (NaCl) salt plates. To prevent oxygen diffusion into the cell once polymerization was initiated and suppress evaporation of the vinyl acrylate monomer, the edge between the two salt plates was sealed by vacuum grease prior to positioning the sample on the horizontal sample holder. UV light intensity at the sample was measured by a calibrated radiometer (International Light IL-1400). Infrared absorption spectra of samples were obtained upon continuous UV irradiation at a scanning rate of 5−10 scans/s. The acrylate and vinyl double bonds in the vinyl acrylate were monitored at 1625 and 1645 cm^{-1}, respectively, and the thiol group conversion was observed at 2575 cm^{-1}. A deconvolution technique was employed to separate overlapping C=C stretching bands of the acrylate and vinyl double bonds at 1625 and 1645 cm^{-1} so that the individual kinetic profiles of the acrylate and vinyl groups could be simultaneously determined. The acrylate conversions obtained from the deconvolution results were confirmed by comparing with the conversions calculated by measuring the peak height at 812 cm^{-1}, which is generally used to monitor acrylate polymerization.[37]

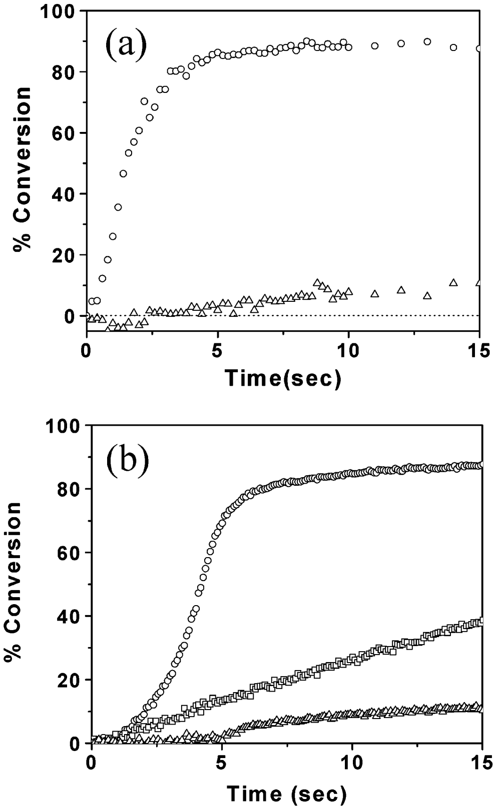


Figure 2. RTIR conversion vs time plots of (a) vinyl acrylate [(○) acrylate and (△) vinyl] photopolymerization without a photoinitiator using an unfiltered UV source and (b) vinyl acrylate [(○) acrylate and (△) vinyl] and (□) ethyl acrylate photopolymerization with 0.5 wt % of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator using 365 nm light. Light intensity is (a) 32 mW/cm^2 and (b) 14 mW/cm^2.

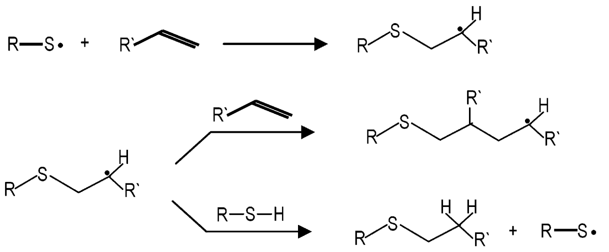
A thin-film calorimeter was used to measure polymerization exotherms of vinyl acrylate and thiol/vinyl acrylate mixtures. This calorimeter is based on a single thin-film heat flux sensor and functions as a self-generating thermopile transducer that measures a physical variable (heat flow) and converts it into an electrical signal (voltage). The measured voltage can be easily converted into watts, however it is not necessary to calculate the polymerization rate since the absolute heat evolved by conversion of the acrylate and vinyl ester bonds in vinyl acrylate is unknown. Also, the fraction of the heat evolved by each double bonds cannot be measured separately. The thin-film calorimeter offers a viable solution to limitations associated with photo-DSC such as measurement of polymerization exotherms of thin films and/or volatile monomers. Applications of thin-film calorimeters are well documented elsewhere.[30,31,38,39]

One-dimensional ^{1}H NMR spectra and a two-dimensional H,H-COSY spectra were recorded on Bruker AC-200 NMR using standard parameters. In both cases, $CDC1_3$ was used as the solvent and tetramethylsilane as the internal standard.

Results and Discussion

Before discussing the effect of thiol on vinyl acrylate polymerization, it is essential to first review the characteristics of vinyl acrylate. As reported previously,[17,18] vinyl acrylate has several intrinsic chemical properties which provide significant advantages in photopolymerization processes, including the ability to self-initiate its own free-radical polymerization. Particularly interesting and germane to the present study is the difference in the reactivity of the two functional groups, the acrylate and the vinyl ester, during free-radical polymerization. Figure 2a shows the conversion of the acrylate

Scheme 1. Thiol−Ene Polymerization Mechanism



and vinyl groups of vinyl acrylate upon irradiation without an added photoinitiator. Even in the absence of photoinitiator, where the only mode of initiation is the decomposition of vinyl acrylate upon absorption of a photon of light, polymerization proceeds very rapidly.[17] The acrylate group conversion increases rapidly (within 5 s) after the sample is exposed to light, while the vinyl groups do not polymerize (and then only very slowly) until after the first 5 s of irradiation. Within 7 s, acrylate group conversion reaches about 85% while much less than 10% of the vinyl groups are consumed. This result is consistent with previous reports by Kudyakov and Fukuda et al.[15−17] We next note that the conversion rate of the acrylate group of vinyl acrylate is significantly faster than for ethyl acrylate (Figure 2b) using 365 nm light (vinyl acrylate does not absorb at this wavelength) with an added photoinitiator. Within 6 s, almost 80% of the acrylate double bonds are converted to polymer while only about 15% of ethyl acrylate polymerizes under the same photolysis conditions and irradiation time. Two important conclusions can be drawn from Figure 2. First, the homopolymerization of the acrylate group in vinyl acrylate occurs at a rate about 5−6 times faster than for the polymerization of ethyl acrylate. As discussed in a previous paper[18] on vinyl acrylate polymerization, this is due to either an increase in the propagation rate constant, a decrease in the biradical termination reaction, or a combination of both. Second, little conversion of the vinyl group occurs while the acrylate polymerizes. This apparent homopolymerization of the acrylate gives a linear polymer that is soluble in the monomer and common solvents, as long as the acrylate conversion is less than ∼70%. From these results, it is evident that during vinyl acrylate polymerization the acrylate group polymerizes much faster than the vinyl group. In the traditional copolymerization of acrylate and vinyl ester monomer mixtures, the acrylate double bond polymerizes much faster than the vinyl double bond as indicated by their reactivity ratios, which for the acrylate and vinyl ester are 6.4 and 0.03, respectively.[40,41] There is even a greater difference in reactivities of the acrylate and vinyl ester double bonds in vinyl acrylate. Since the vinyl group is electron-rich, it should preferentially add to thiols by a free-radical chain process, providing the opportunity for the acrylate functionality to polymerize via a homopolymerization process and the vinyl ester group to polymerize by a free-radical copolymerization process with the thiol.

The free-radical chain reaction of a thiol to an ene proceeds by a step-growth process, a free-radical addition followed by a chain-transfer reaction, as illustrated in Scheme 1.[28] The first reaction step in Scheme 1 is simply the addition of a thiyl radical, produced by a chain-transfer reaction, to a double bond to generate a carbon-centered radical. This radical then undergoes either a propagation reaction with a second ene or a chain-transfer hydrogen abstraction reaction, resulting in the generation of another thiyl radical, completing a two-step radical chain process. In lieu of ene homopolymerization, if the functionalities of the ene and thiol are both two or greater, a polymer is formed by the free-radical chain process. In thiol/vinyl acrylate polymerizations, it is conceivable that the thiol can react with both the acrylate and vinyl groups or simply the vinyl group only. The homopolymerization rates of the acrylate and vinyl groups of vinyl acrylate relative to the thiol−acrylate and thiol−vinyl reaction rates are critical kinetic factors in defining which reaction will occur and the overall thiol/vinyl acrylate polymerization mechanism. To provide basic information about the relative reactivities of simple acrylate and vinyl groups with the thiol for comparison with vinyl acrylate, monofunctional analogues of the acrylate and vinyl groups in vinyl acrylate, ethyl acrylate, and vinyl propionate were first reacted with the trifunctional thiol (see Figure 1 for structures of each component). Figure 3a,b shows the conversion vs time plots for the photoinitiated radical chain reaction of 1:1 molar mixtures of thiol/ethyl acrylate and thiol/vinyl propionate with 0.5 wt % DMPA using a 365 nm UV light source. In the presence of the trithiol, the consumption of the vinyl double bonds is much faster than that of the acrylate double bonds. Both vinyl and thiol group conversions in the thiol/vinyl propionate approach high conversion in a very short time period (Figure 3a) while only about 20% of acrylate groups react over the same time period for a thiol/ethyl acrylate mixture irradiated under similar conditions. It is apparent from the results in Figure 3a that about 90% of the vinyl groups react with thiol, while the remaining 10% of the vinyl groups are consumed by free-radical homopropagation. On the other hand, only 40% of the acrylate groups react with the thiol, with the remaining 60% being consumed by homopolymerization. The faster rate for addition of the thiol to the vinyl bond is consistent with its higher electron density.[26,28]

The conversion of the thiol/ethyl acrylate/vinyl propionate three-component mixture provides further insight into the competitive free-radical chain reactions of thiols with acrylates and vinyl esters. As illustrated in Figure 3c, the three functional components in the reaction mixture composed of an acrylate, a vinyl ester, and a trithiol (1:1:2 molar mixture based on functional group) exhibit almost equivalent conversion rates. In an ethyl acrylate/vinyl propionate mixture, ethyl acrylate reacts much faster than vinyl propionate since the acrylate polymer chain has a low rate constant for reaction with a vinyl propionate and the vinyl propionate polymer chain has a high rate constant for reaction with ethyl acrylate.[18] The lower rate for the thiol−vinyl ester reaction (compared to the results in Figure 3a) probably results from the rapid addition of polymer radical chain ends bearing a terminal vinyl ester to ethyl acrylate which, as seen in Figure 3b and documented in many literature reports, subsequently undergoes an efficient addition of ethyl acrylate monomers before chain transfer to thiol occurs. Considered on a molar basis, and assuming that 90% of the vinyl conversion results from reaction with thiol, our calculations show that the ratios of acrylate groups reacting with thiol to acrylate homopolymerization sequences are almost identical in Figure 3b,c.

On the basis of the results in Figure 3, even though the overall rate for vinyl ester conversion decreases somewhat upon addition of thiol, it would still be

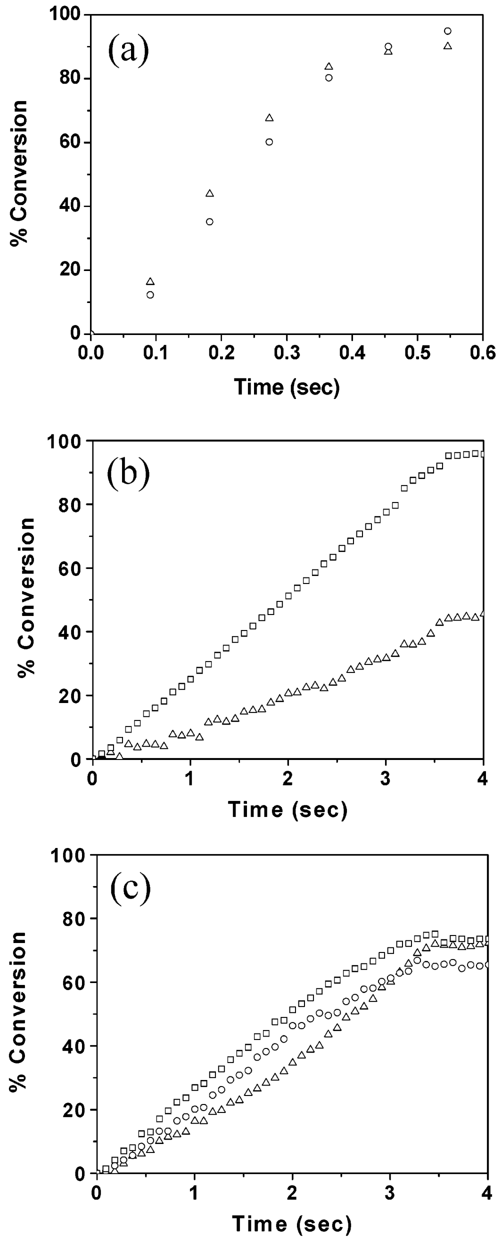


Figure 3. RTIR conversion vs irradiation time plots for the reaction of trithiol/model monomers 1:1 molar mixtures upon irradiation with 0.5 wt % of DMPA using 365 nm light. Shown are (a) trithiol (△)/vinyl propionate (○) and (b) trithiol (△)/ethyl acrylate (□) at 1:1 molar mixture and (c) a 2:1:1 molar mixture of trithiol (△)/vinyl propionate (○)/ethyl acrylate (□). Light intensity is 14 mW/cm^2.

expected that substantial conversion of the vinyl ester groups by a free-radical chain process with thiol would occur in a mixture of thiol and vinyl acrylate. Since the acrylate polymerization rate of vinyl acrylate is much faster than that of ethyl acrylate, one might even expect that the acrylate group in vinyl acrylate will homopolymerize rather than react with thiol. Figure 4 shows plots of acrylate and vinyl ester group conversion vs irradiation time for several thiol/vinyl acrylate mixtures. As expected, addition of thiol to vinyl acrylate significantly enhances the vinyl group conversion. Compared to the results in Figure 2b where the vinyl group conversion is only about 10% after 15 s of irradiation, as little as 20 mol % of thiol results in about 30 mol % vinyl group conversion over the same period of time. By increasing the trithiol content from 20 to 40 mol %, the vinyl conversion increases from about 30% to greater than 80% conversion over the first 15 s, as shown in Figure 4a, with over 90% vinyl bond conversion for a 50 mol % thiol/vinyl acrylate mixture.

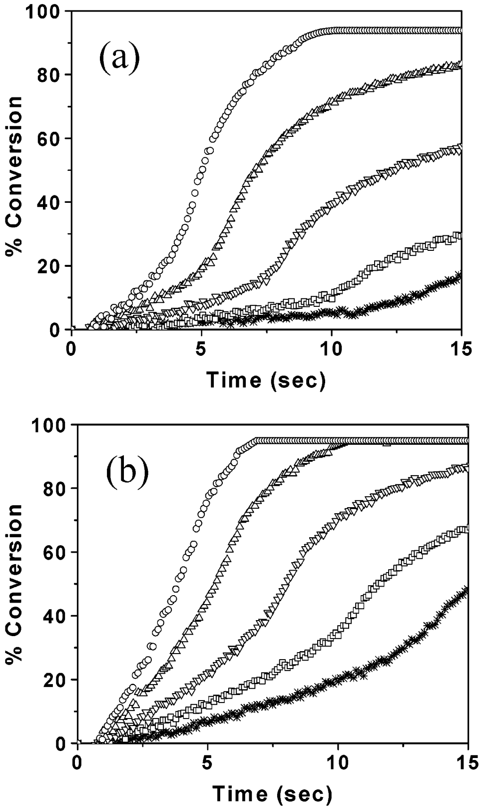


Figure 4. RTIR conversion of (a) vinyl and (b) acrylate groups vs irradiation time of the trithiol/vinyl acrylate copolymerization as a function of trithiol content with 0.5 wt % of DMPA using 365 nm light; thiol content (*) 10, (□) 20, (▽) 30, (△) 40, and (○) 50 mol % based on functional group (total double bond). Light intensity is 14 mW/cm^2.

A particularly fascinating aspect of the vinyl conversion is the sudden increase in the conversion rate vs time plot after a critical conversion is reached for each mixture in Figure 4. This rate acceleration, i.e., a Trommsdorf-like effect, can best be explained by considering the results for acrylate conversion vs time for the same mixtures. Generally, thiol−ene polymerizations show no discernible rate acceleration during the conversion process. The rate of conversion of acrylate over the first 15 s of irradiation drastically decreases upon addition of only 10 mol % thiol functional groups (compare Figure 4 with Figure 2b), but then increases with additional thiol content. The decrease of acrylate conversion upon adding 10 mol % trithiol can be explained by chain transfer of the growing acrylate chain to the thiol. Interestingly, the sudden increase in acrylate group conversion rate for a given thiol content is consistent with a similar increase in the vinyl conversion rate, both occurring at essentially the same photolysis time. As reported in our previous vinyl acrylate work,[18] linear polymer with pendant vinyl groups is formed for acrylate conversions less than about 70% due to an extremely fast acrylate polymerization rate, with little or no vinyl group homopolymerization. In the mixture with thiol present, rapid acrylate homopolymerization thus occurs to give a linear polyacrylate with pendant vinyl ester groups. The amount of polymer formed continually increases with acrylate conversion, and as the "polyacrylate" is formed, the pendant vinyl ester bonds react with the thiol. To understand what induces the rate acceleration in Figure 4a,b, consider eq 1

$$\text{fractional conversion at gel point} = \sqrt{\frac{1}{r(f_1 - 1)(f_2 - 1)}} \quad (1)$$

which defines the gel point for thiol−ene free-radical polymerization, where r is the stoichiometric functional group imbalance, f_1 is the thiol functionality, and f_2 is the ene functionality. The thiol functionality is 3, and initially the vinyl group functionality is only 1. As acrylate homopolymerizes to give the polyacrylate with high vinyl side-group functionality ($f_2 \gg 1$), a critical point is reached, whereupon the concentration of the functionalized polyacrylate is high enough and the corresponding reaction of thiol with the vinyl ester side groups (attached to the acrylate polymer) is large enough for gelation to occur. In each case in Figure 4, the sudden rate acceleration occurs after a total acrylate conversion of about 20−25%. It is obvious that the rate acceleration occurring for both the thiol/vinyl ester copolymerization and the acrylate homopolymerization is a direct result of thiol−vinyl ester gelation.

Next we consider the important question of whether the thiol reacts with both the vinyl ester and the acrylate groups of vinyl acrylate or with only the vinyl ester bond. Figure 5 depicts the relative mole fraction conversion of acrylate, vinyl, and thiol groups. [The total moles of functional groups (thiol, acrylate, and vinyl ester) are taken as 1.0, i.e., the total fraction of moles present as 1.0.] For example, in Figure 5c, both mole concentrations of acrylate and vinyl ester groups are 0.25, and the mole concentration of the thiol group is 0.5. Regardless of the initial thiol content in mixtures with vinyl acrylate, the vinyl group conversion is almost exactly equal to the thiol conversion at any point during the polymerization (see plots in Figure 5a−c). These results suggest that the vinyl ester and thiol groups are undergoing exclusively the thiol−ene step growth reaction, while acrylate groups only homopolymerize with little or no reaction with the thiol.

By adding together the vinyl and acrylate functional molar conversions at any given time, the total double-bond conversion vs time plot shown in Figure 6 is attained for the sample with 50 mol % thiol (taken as a representative example). Taking the derivative of the combined double-bond conversion vs time plot results in the polymerization rate (in terms of s^{-1}) vs time plot. The increase in the rate which occurs at about 4−5 s, as explained previously, is due to the gelation process. Figure 7 shows the photopolymerization exotherm of the 50 mol % thiol sample measured on a thin-film calorimeter. A thin-film calorimeter was used since it has the distinct advantage over photo-DSC in that polymerization exotherms of volatile samples, such as vinyl acrylate, can be monitored. The polymerization exotherm in terms of millivolts, which is directly proportional to the polymerization rate, is almost identical to the rate vs time plot in Figure 6 obtained from the RTIR analysis of the polymerization (except for the irradiation time scale, which results from differences in the sample configuration and light source used). The autoacceleration in the exotherm plot observed for the 1:1 thiol/vinyl acrylate mixture after 4−5 s exposure is certainly consistent with and confirms the RTIR results in Figure 6. On the other hand, vinyl acrylate homopolymerization (Figure 7b) does not show rate acceleration. As explained in Figure 2, acrylate group homopolymerizes up to about 90% conversion, and then the vinyl groups start to slowly polymerize. This results in no polymerization rate acceleration.

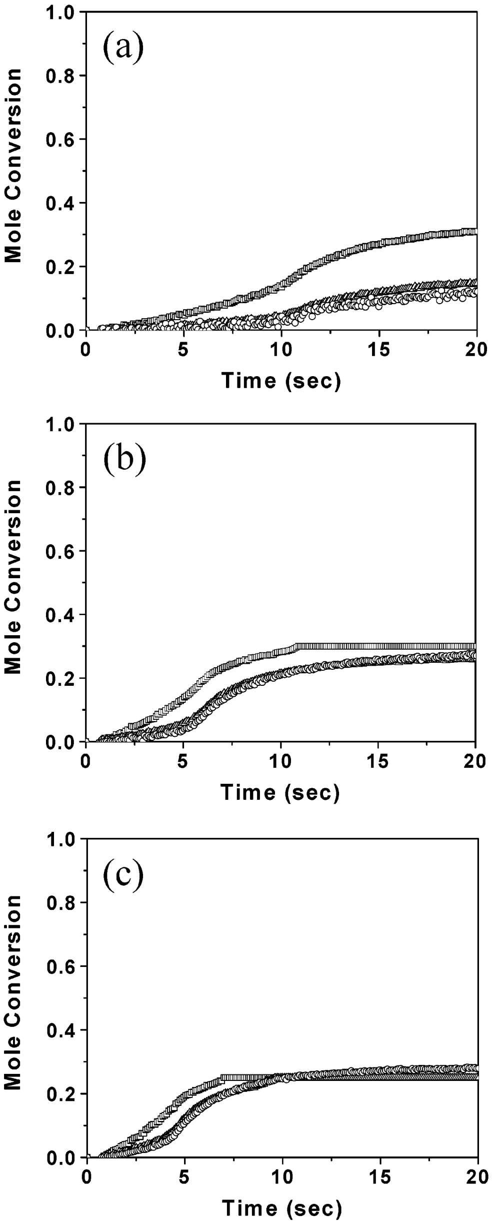


Figure 5. RTIR relative mole conversion of acrylate, vinyl, and thiol groups vs irradiation time of trithiol/vinyl acrylate mixtures with 0.5 wt % of DMPA using 365 nm light. Shown are results for (a) 20 mol % thiol, (b) 40 mol % thiol, and (c) 50 mol % thiol mixtures based on functional group (total double bond); (□) acrylate, (△) vinyl, and (○) thiol group. Light intensity is 14 mW/cm^2.

As mentioned previously, vinyl acrylate self-initiates free-radical polymerization.[17,18] Therefore, even without an external photoinitiator, the thiol/vinyl acrylate mixture polymerizes at a rapid rate with almost identical polymerization kinetics (Figure 8) as observed for the same mixture with a photoinitiator (Figure 6). The autoacceleration in Figure 8 occurs at almost the same conversion as in Figure 6 where a photoinitiator was used. Any differences in the exotherms in Figures 6 and 8 can be attributed to differences in the self-initiation

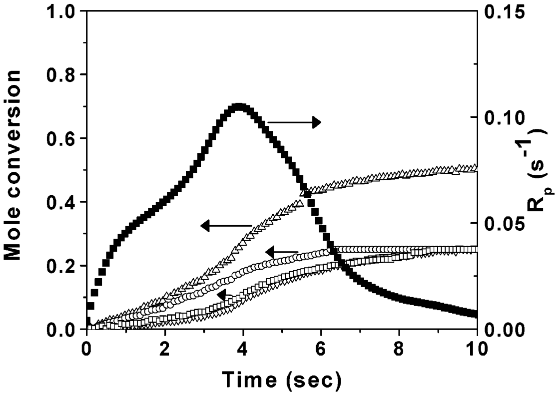


Figure 6. RTIR polymerization rate (■) and conversion of total double bonds (acrylate plus vinyl) (△) as well as (○) acrylate, (□) vinyl, and (▽) trithiol conversions for trithiol/vinyl acrylate mixture (50 mol % trithiol based on functional group) as a function of irradiation time with 0.5 wt % DMPA using 365 nm light. Light intensity is 14 mW/cm^2. Time zero in plot was adjusted by ∼0.7 s to account for experimental offset in data analysis.

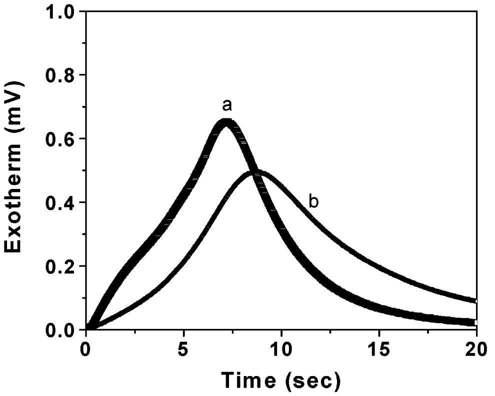


Figure 7. Thin-film polymerization exotherms of a 50 mol % trithiol/50 mol % vinyl acrylate mixture (a) and vinyl acrylate (b) with 0.5 wt % DMPA using 365 nm light. Light intensity is 6.8 mW/cm^2.

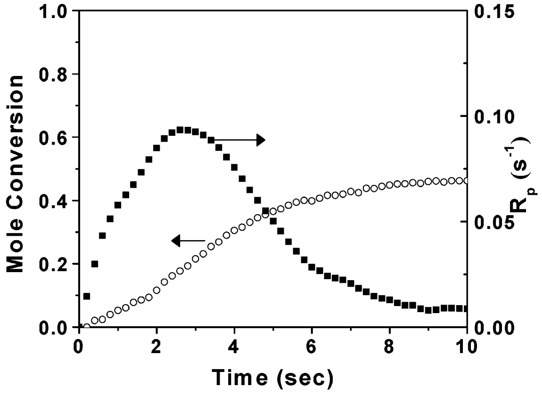


Figure 8. RTIR polymerization rate (■) and conversion of total double bonds (acrylate plus vinyl) (○) of trithiol/vinyl acrylate mixture (50 mol % trithiol based on functional group) without a photoinitiator using unfiltered UV light source. Light intensity is 20 mW/cm^2.

process vs the photoinitiation process resulting from photoinitiator decomposition. In the absence of photoinitiator, initiation involves excitation of vinyl acrylate and thiol groups, both of which constantly decrease in concentration as the polymerization proceeds. In essence, this decreases the concentration of initiator much more than would be observed with an external photoinitiator.

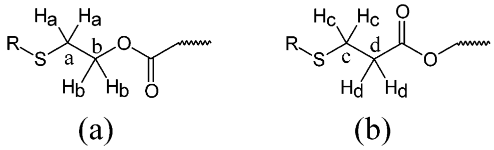


Figure 9. Chemical structures of the products produced by thiol addition to (a) vinyl group and (b) acrylate groups of vinyl acrylate.

A final and intriguing question concerning the trithiol/vinyl acrylate polymerization process still remains. The results in Figure 5 show the same conversion rate for both vinyl and thiol groups for samples with three different compositions. As mentioned previously, this suggests that vinyl groups are consumed only by reaction with thiol, while the acrylate participates exclusively in homopolymerization. This, of course, involves essentially two separate free-radical polymerization processes occurring simultaneously, accompanied by chain transfer from the acrylate radical to the thiol. While the results in Figure 5 are compelling in support of the two self-propagating free-radical chain processes, additional chemical structural evidence would be extremely valuable. To support the suggestion of the dual free-radical polymerizations, we investigated whether thiol adds only to the vinyl group or to both vinyl and acrylate groups using the 2D H-COSY NMR technique. For this study, butanethiol (a monofunctional thiol) was used both to prevent the formation of a cross-linked network and to simplify NMR spectral interpretation. The use of buthanethiol is necessary as 3-mercaptopropionate, the direct monofunctional analogue of the trithiol, causes severe difficulties in resolving the NMR spectra of the products due to the similarity of its structure with the product (Figure 9b) produced by thiol addition to the acrylate. For the butanethiol/vinyl acrylate mixture, two possible products resulting from addition of thiol to acrylate and vinyl double bonds are shown in Figure 9. The structure in Figure 9a corresponds to the product that would be formed by thiol addition to the vinyl double bond while the structure in Figure 9b is the product that would result from thiol addition to the acrylate double bond. In COSY NMR, within 2−3 bonds, cross-peaks exist in the 2-D COSY spectrum when there is spin−spin coupling between hydrogens; thus, connectivity between carbons a and b (or c and d) in Figure 9 can be proven by analyzing the 2-D COSY spectrum of the product formed between butanethiol and vinyl acrylate. A 1:1 molar mixture of butanethiol and vinyl acrylate was photolyzed with a 365 nm light source (approximately 1 mW/cm^2) for about 30 s. The resultant mixture was analyzed by NMR. The 1D ^{1}H NMR spectrum, shown with the 2D COSY spectrum in Figure 10a, indicates the presence of unreacted vinyl moieties ($\delta = 4.65, 4.95$), the butyl group of butanethiol (CH_2: $\delta = 2.44, 1.65, 1.33$; CH_3: $\delta = 0.96$), and the b and d hydrogens (b: $\delta = 4.2$, d: $\delta = 2.6$). NMR peaks due to a and c hydrogens (Figure 9) cannot be resolved since they have almost identical chemical shifts ($\delta \sim 2.72-2.82$). However, one can clearly see a cross-peak between a and b hydrogens, while no cross-peak between c and d hydrogens is observed. This strongly supports the absence of the thiol adduct with the acrylate bond and the previous suggestion of two separate free-radical process occurring in thiol/vinyl acrylate mixtures. Different results are

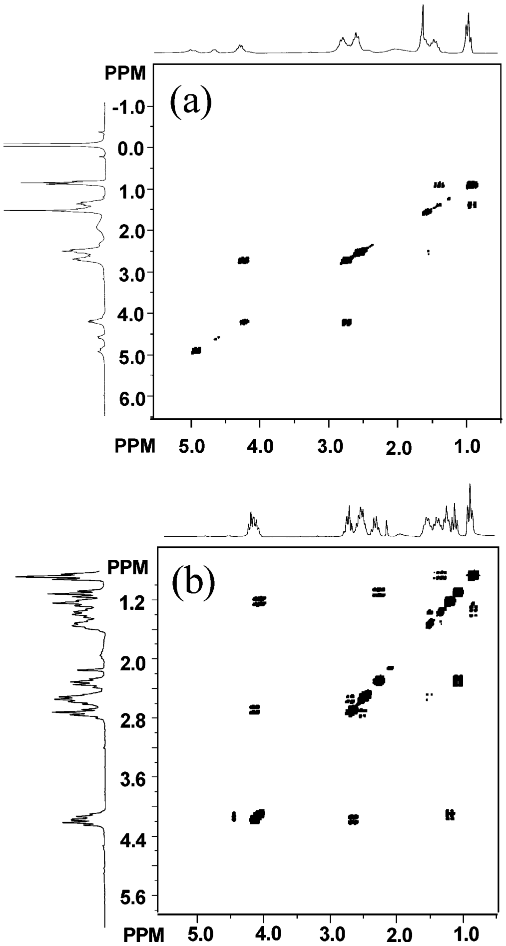


Figure 10. 2D COSY NMR spectra of photolyzed mixtures: (a) butanethiol/vinyl acrylate (50 mol % buthanethiol based on functional group) and (b) butanethiol/ethyl acrylate/vinyl propionate (2:1:1 molar ratio).

observed upon analysis of the products of a photolyzed model butanethiol/ethyl acrylate/vinyl propionate three-component mixture. As shown in Figure 10b, cross-peaks are observed for a and b hydrogens as well as c and d hydrogens (Figure 9), indicating the presence of products between butanethiol and both ethyl acrylate and vinyl propionate. The results in Figure 10 are compelling evidence that thiol/vinyl acrylate polymerizes by two separate free-radical propagation processes.

The apparent total absence of thiol addition to the acrylate bond of vinyl acrylate might be expected due to the different chemical nature of acrylate double bonds in vinyl acrylate compared to traditional acrylates. The presence of an acrylate and a vinyl group on the same molecule dramatically enhances the polymerization rate of the acrylate double bond, as shown in Figure 2b. This enhanced homopolymerization rate can be one reason for the absence of thiol addition to acrylate double bonds. However, the change in electron density of the acrylate group resulting from the presence of the vinyl group in vinyl acrylate may also contribute to the absence of free-radical thiol addition to the acrylate. Interestingly, in associated work, we observed by way of reaction rates of the amine-catalyzed thiol−Michael addition reaction that the electron density of the acrylate of vinyl acrylate is lower than that of ethyl acrylate. In amine-catalyzed reactions, it is know that more electron-deficient ene double bonds undergo faster thiol addition reactions than electron-rich double bonds.[42,43]

Thiol addition to ethyl acrylate occurs in several minutes, while thiol addition to the acrylate group of vinyl acrylate is so rapid in the presence of a catalytic amount of primary amine that the reaction cannot be monitored under normal mixing conditions. This attests to the drastic change (lowering) of the electron density on the acrylate group in vinyl acrylate. The more electron-deficient acrylate double bonds should thus result in slow thiyl radical addition due to the electrophilic character of the thiyl radical, and consequently no thiol adduct with the acrylate group of vinyl acrylate would be expected. As we have already stated, the thiol−acrylate free-radical process was not observed.

Conclusions

The effect of thiol on the polymerization kinetics of vinyl acrylate has been investigated using real-time FTIR, thin-film calorimetry, and 2D-COSY NMR. Addition of a multifunctional thiol comonomer to vinyl acrylate results in enhanced vinyl group conversion via a selective addition of the thiol with the vinyl ester. The kinetic chain length of the acrylate homopolymerization of vinyl acrylate is reduced by chain transfer to thiol. An autoacceleration of two simultaneous free-radical processes, acrylate homopolymerization and thiol/vinyl ester copolymerization, occurs when a critical concentration of polyacrylate with pendant vinyl ester functional is reached, and the requisite extent of reaction between the pendant vinyl ester and thiol groups is attained. Thin-film calorimeter results are consistent with the RTIR results. 2D-COSY NMR analysis of photolysis products of both buthanethiol/vinyl acrylate and butanethiol/ethyl acrylate/vinyl propionate mixtures provides strong evidence for the two separate simultaneous free-radical processes.

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