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The kinetics of vinyl acrylate photopolymerization

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Abstract

The photopolymerization of vinyl acrylate has been investigated using real-time FTIR. The acrylate and vinyl groups exhibit different polymerization kinetics with the acrylate functionality polymerizing at a much faster rate. Vinyl acrylate not only self-initiates its own free-radical polymerization, but also photoinitiates the polymerization of mono- and difunctional acrylates. Kinetic studies using a model monomer system indicate that it is essential for the acrylate and vinyl group to be part of the same molecule in order to function as an effective initiator for acrylate polymerization.

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1. Introduction

Acrylates have been widely used as radiation curable resins because of their ability to undergo free-radical photopolymerization at very rapid rates. Acrylates used in photocurable resins are characterized by the presence of multifunctional acrylate double bonds of equal reactivity on the same molecule, at least until one of the acrylate groups has reacted [1–5]. Photopolymerization behavior of these multifunctional acrylates has been fully investigated in the past to provide a detailed understanding of the UV curing mechanism. However, research on the free-radical polymerization of monomers having polymerizable multi-functionalities with differing reactivity has not been examined in great detail.

Vinyl acrylate is a difunctional monomer whose two functionalities display different reactivity in free-radical process. In 1971, the free-radical polymerization of vinyl acrylate in dilute solution initiated by a thermal free-radical and anionic source was reported to involve cyclization as well as traditional radical chain reactions characterized by the addition of unreacted monomer units to the radical chain ends [6]. It was subsequently demonstrated that when high concentrations of vinyl acrylate were used, the intramolecular radical reaction that leads to cyclization was reduced in favor of linear acrylate free-radical polymerization [7]. Under these conditions, the acrylate groups are polymerized almost completely while significant concentrations of the vinyl group remain unpolymerized [6,7]. Recently [8], it was shown that vinyl acrylate polymerizes to high acrylate conversion when exposed to light either in the presence or absence of an additional photoinitiator. In the case of an external phosphine oxide photoinitiator, the rate constant for addition of the primary phosphonyl radical to the acrylate group was about 1.5 times that of addition to the acrylate group of *tert*-butyl acrylate and about 17 times that of addition to the vinyl pivalate. In another report [9], the vinyl acrylate polymerization was followed by photo-DSC. IR analysis after polymerization showed that the acrylate group polymerized to high conversion with little vinyl ester conversion.

Herein, we present a detailed analysis of the photopolymerization behavior of vinyl acrylate without an external photoinitiator using real-time FTIR. The

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difference in reactivity of the acrylate and vinyl groups are quantitatively measured in real-time by deconvolution of the absorption band of the two overlapping peaks from acrylate and vinyl groups. The self-initiating ability of vinyl acrylate upon irradiation was measured by using vinyl acrylate as an initiator for the polymerization of hexyl acrylate. Investigation of appropriate model monomer systems and their comparison with that of vinyl acrylate resulted in a description of the polymerization behavior and clearly demonstrated the requirement of having both the vinyl and acrylate groups on the same molecule to attain high polymerization rates. Possible mechanisms for the initiation by vinyl acrylate upon irradiation are proposed herein.

2. Experimental

Materials. Vinyl acrylate, ethyl acrylate, vinyl propionate, vinyl methacrylate, hexyl acrylate, lauryl acrylate and 1,6-hexanediol diacrylate (see Fig. 1 for chemical structure) were purchased from Aldrich Chemical and used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was obtained from Ciba Specialty Chemicals.

Methods. The kinetic profiles of the UV-induced polymerizations were studied by real-time FTIR. Infrared spectra were recorded on a modified Bruker 88 spectrometer designed to allow light to impinge on a horizontal sample using a fiber-optic cable. A modified horizontal transmission unit was designed to prevent sample flow during each experiment. The diagram depicting the horizontal transmission unit of the real-time FTIR setup is shown in Fig. 2. Monomer samples were placed between two sodium chloride plates with a 15 μm teflon spacer. The two salt plates were sealed at the edges with vacuum grease to prevent oxygen diffusion into the sample and suppress monomer evaporation. A 200 W high pressure mercury xenon lamp (ScienceTech Co.) served as the light source to induce the free-radical polymerization. The UV light intensity was measured with a calibrated radiometer from International Light (IL-1400). The infrared absorption spectra were obtained under continuous UV irradiation at a scanning rate of 5–10 scans/s. The acrylate and vinyl double bonds were monitored at 1625 and 1645 cm^{-1}, respectively. The overlapping absorption bands at 1625 and 1645 cm^{-1} were deconvoluted to enable monitoring of the kinetics of both the acrylate and vinyl groups. % Conversion was calculated using Eq. (1) where A_0 is

$$\%\ \text{Conversion} = \left[\frac{A_0 - A_t}{A_0}\right] \times 100 \tag{1}$$

the absorbance before irradiation and A_t is the absorbance at time t. The dark polymerization behavior of vinyl acrylate was determined by terminating illumination of the samples using a shutter: after converting a given fraction of acrylate groups (approximately 25%), the conversion as a function of dark time was measured with real-time FTIR. UV spectra were obtained on a Cary 5 spectrometer.

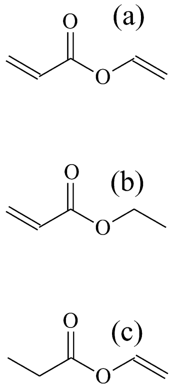


Fig. 1. Chemical structures of (a) vinyl acrylate, (b) ethyl acrylate and (c) vinyl propionate.

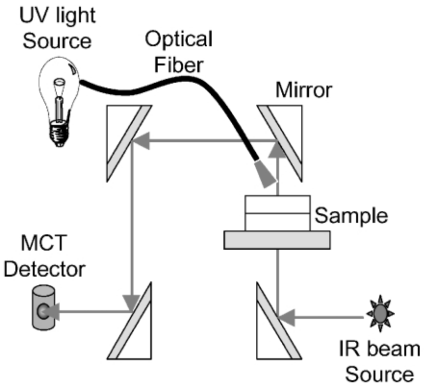


Fig. 2. Diagram of real-time FTIR setup.

3. Results and discussion

The real-time FTIR technique has been widely used to monitor the polymerization profiles of different functional groups simultaneously during polymerization. Details of using real-time FTIR to monitor photopolymerization have been reported elsewhere [10,11]. Monitoring the reactivity of both the vinyl and acrylate functional groups of vinyl acrylate separately is essential in understanding polymerization kinetics upon irradiation. The change in IR absorbance of the acrylate (1625 cm^{-1}) and vinyl ester (1646 cm^{-1}) functional groups over 25 s of irradiation are plotted in Fig. 3(a). It is important to note that the vinyl acrylate polymerization investigated herein was performed without adding an external photoinitiator. Traditionally, the =C–H out of plane band at 812 cm^{-1} has been used to monitor acrylate polymerization. In the case of vinyl acrylate, the intensity of the =C–H out of plane absorption band of the vinyl in the region between 1000 and 600 cm^{-1} is weak and overlaps with the much stronger acrylate double bond peak, thus preventing accurate monitoring of the vinyl group

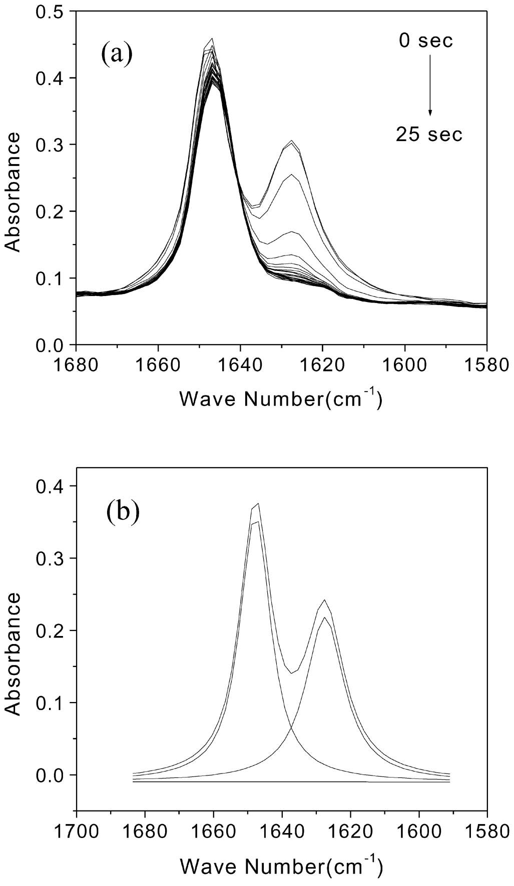


Fig. 3. (a) The IR absorbance change of the acrylate and vinyl group in a vinyl acrylate photopolymerization upon irradiation, and (b) the deconvolution result of 1625 and 1645 cm^{-1} bands.

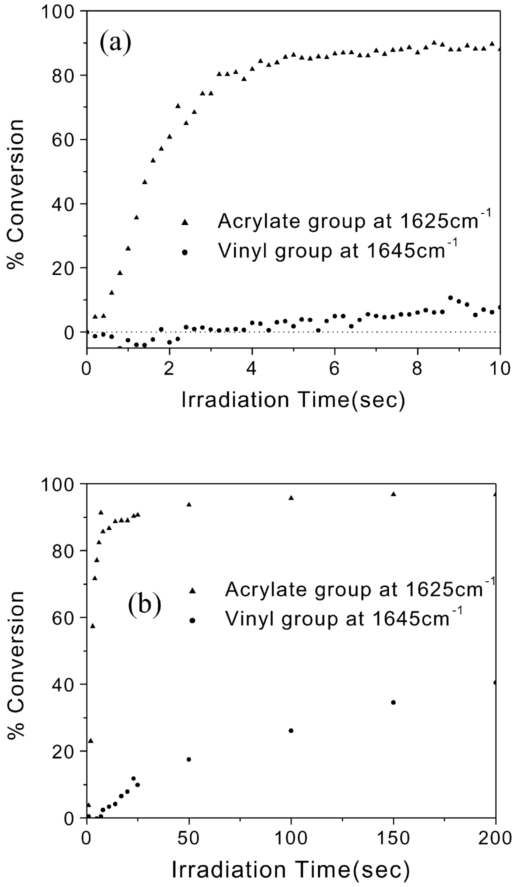
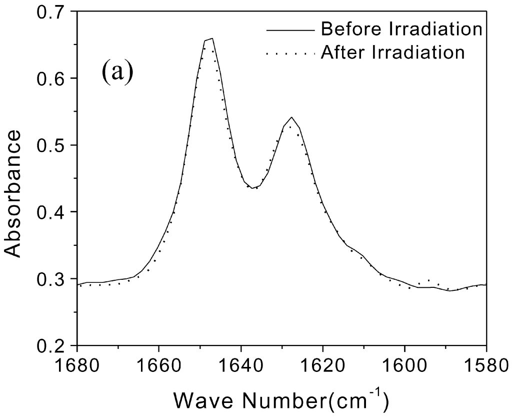


Fig. 4. Conversion of acrylate and vinyl groups within vinyl acrylate as a function of irradiation time without added photoinitiator. Profiles are shown for the initial (a) 10 s and (b) 120 s. UV light intensity is ~35 mW/cm^2.

disappearance. The polymerization kinetics of the vinyl group in vinyl acrylate can best be monitored by deconvoluting the C=C stretching band of the acrylate and vinyl double bonds positioned at 1625 and 1645 cm^{-1}. Fig. 3(b) shows the deconvolution result. The acrylate conversion results measured at 1625 cm^{-1} agree with conversions calculated by measuring the peak height at 812 cm^{-1}. From the results in Fig. 3(a) and (b), it is obvious that the acrylate double bond decreases much faster than that of the vinyl groups upon irradiation, in accordance with Ref. [8].

The % conversion versus time plots of acrylate and vinyl groups are particularly interesting over the first 10 s of irradiation. The conversion profile for this irradiation in Fig. 4(a) clearly shows that more than 80% of acrylate double bonds undergo polymerization within 5 s, leveling off to a very slow increase in conversion with time. The vinyl groups do not begin to react until after 5 s irradiation, with less than 10% conversion being attained in the next 5 s (after 10 s total irradiation time). This result obtained by the real-time IR deconvolution technique clearly demonstrates that the reactivity of the acrylate group is much faster than that of a vinyl double bond and provides a real time quantitative analysis that substantiates previous literature results for thermal initiated polymerization of vinyl acrylate [6–8]. Based on Fig. 4(a), it is reasonable to assume that initially primarily linear polymers result from the selective rapid polymerization of the acrylate group. The vinyl double bonds react much slower and remain as pendant groups. Only after ~85% conversion of acrylate double bonds is reached, do the vinyl double bonds begin to react to form a highly crosslinked network as shown in Fig. 4(b). It should be noted that the conversion of vinyl bonds remains relatively low even after 200 s of irradiation. This behavior can be explained by the inherent low photoreaction of vinyl ester group and the reduction in radical mobility and/or trapped radicals created by the formation of a crosslinked network structure. The formation of a crosslinked network is consistent with Fukuda's [6,7] result for the thermal free-radical polymerization of vinyl acrylate in solution and the results of Kudyakov et al. [8] for neat vinyl acrylate photopolymerization.

To determine the relative efficiency of initiating vinyl acrylate photopolymerization in the absence and presence of an external photoinitiator, vinyl acrylate polymerization with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator was conducted. As shown in Fig. 5(a), vinyl acrylate does not polymerize upon exposure to light



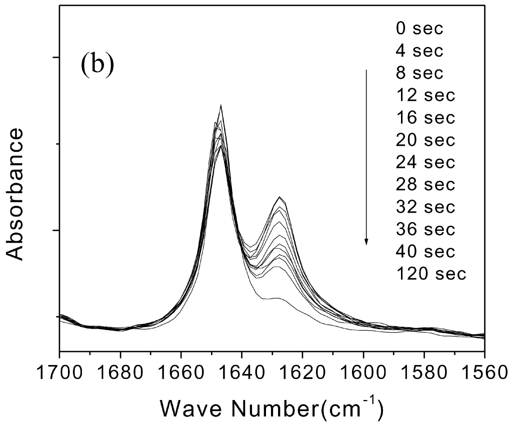


Fig. 5. The IR absorbance change of acrylate and vinyl group during vinyl acrylate photopolymerization with 365 nm UV light (a) without DMPA and (b) with 1 wt% DMPA. UV light intensity is 3.9 mW/cm^2.

filtered with a 365 nm band pass filter. This result is consistent with the UV absorption spectrum of vinyl acrylate which shows absorption in the region between 250 and 300 nm. The polymerization behavior of vinyl acrylate with the DMPA photoinitiator at 365 nm (Fig. 5(b)) is virtually identical to the results shown in Fig. 4(b), with the only difference being a lowered reaction rate due to the low light intensity. Other experiments in our laboratory have demonstrated that the acrylate group reactivity of vinyl acrylate is significantly higher than that of traditional monofunctional acrylate monomers for neat monomer polymerization. The origin of this enhanced rate is under investigation and will be the subject of a future publication.

Additional information is provided when the % conversion of the acrylate group of vinyl acrylate with and without 1 wt% DMPA is examined as a function of irradiation time upon exposure to the full arc of the mercury xenon lamp as shown in Fig. 6. Interestingly, the photoinitiator does not greatly enhance the polymerization process: both the acrylate and vinyl group conversion rates exhibit little or no increase with photoinitiator. These results clearly demonstrate the efficiency of vinyl acrylate in initiating its own polymerization. Investigation of the rate of an acrylate monomer polymerization with and without vinyl acrylate as an initiator should provide further evidence regarding the effectiveness of vinyl acrylate as a photoinitiator. To measure the initiation efficiency of vinyl acrylate, the polymerization of hexyl acrylate was recorded with and without 5 wt% vinyl acrylate as an initiator (Fig. 7). From Fig. 7, it is obvious that by adding only 5 wt% of vinyl acrylate as an initiator, the polymerization rate of acrylate is dramatically enhanced compared to the neat monomer. Additional work in our laboratory demonstrates that vinyl acrylate also efficiently initiates the polymerization of other acrylates (including diacrylates) as well. However, the initiation efficiency of vinyl acrylate on a per weight basis is significantly lower than that of traditional cleavage photoinitiators, i.e. it was found that lauryl acrylate with 5 wt% of vinyl acrylate as an initiator exhibits the same polymerization rate as a 0.05 wt% of DMPA/lauryl acrylate system. The lower efficiency of vinyl acrylate on a per weight basis may be due in part to its low absorbance at wavelengths greater than 300 nm where the mercury xenon lamp has its greatest output.

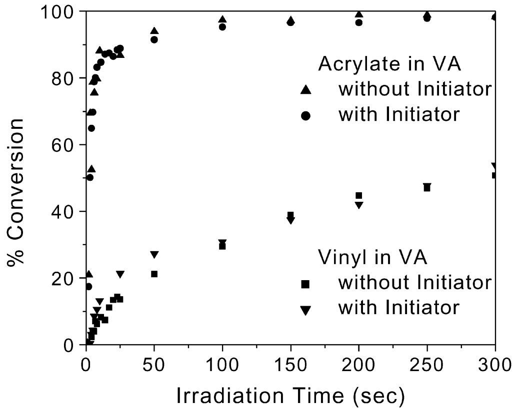


Fig. 6. Conversions of acrylate and vinyl groups in vinyl acrylate with and without 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a function of irradiation time. UV light intensity is ~35 mW/cm^2.

One important question regarding the self-initiated

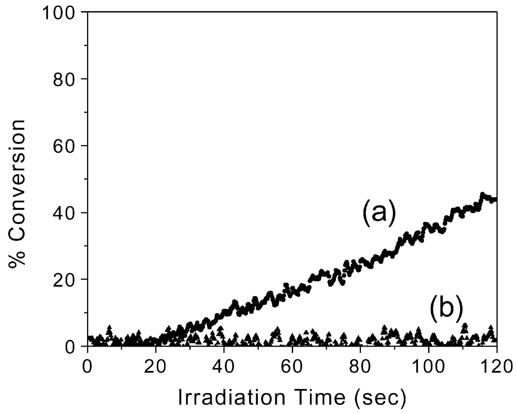


Fig. 7. Conversion as a function of irradiation time in hexyl acrylate (HA) polymerization with and without 5 wt% vinyl acrylate as an initiator; (a) 5 wt% vinyl acrylate, (b) no photoinitiator. UV light intensity is 16.4 mW/cm^2.

polymerization of vinyl acrylate must be answered: is it essential for the vinyl ester and acrylate monomer to be on the same molecule for efficient self-initiated polymerization to take place? The results in Fig. 3 certainly suggest that having an acrylate and vinyl group on the same molecule is essential. The monomers, ethyl acrylate and vinyl propionate shown in Fig. 1, serve as chemically decoupled models of the two functionalities of the vinyl acrylate monomer. By investigating the self-initiated (no external photoinitiator added) homopolymerization of ethyl acrylate and vinyl propionate as well as the copolymerization of a 1:1 molar mixture of the two model monomers, this question can be answered. The % conversion versus irradiation time plots of these systems are shown in Fig. 8(a) and (b). First, we note that the polymerization rate of neat ethyl acrylate is much faster than that of neat vinyl propionate. Second, as shown in Fig. 8(a), the homopolymerization of vinyl propionate and ethyl acrylate both proceed immediately with the onset of exposure to the light source. In contrast, for the 1:1 molar mixture, the vinyl ester group conversion of vinyl propionate is essentially zero until ~50 s irradiation. After this time, the acrylate conversion is about 75% and the vinyl propionate conversion increases continuously as the acrylate conversion levels off after 75–100 s. This behavior can be explained by the low monomer reactivity ratios during the copolymerization of vinyl propionate with ethyl acrylate obtained with a thermal initiator. The r_1 and r_2 values for methyl acrylate/vinyl acetate copolymerization are 6.4 and 0.03, respectively [12,13]. In copolymerization, addition of growing radicals to vinyl double bonds generates unstable high energy vinyl radicals while the addition to acrylate double bonds produces resonance stabilized radicals. Also, chain transfer reaction of vinyl radicals is much faster than acrylate radicals due to lower vinyl radical stability resulting in a reduced polymerization rate of vinyl propionate. Therefore, only after a large portion of ethyl acrylate is consumed, i.e. after achieving a high feed ratio of the vinyl propionate component in the copolymerization system, will the conversion of vinyl propionate increase. This basic result for the 1:1 molar mixture is consistent with the polymerization results for vinyl acrylate. However, the polymerization rate of the acrylate groups in the 1:1 molar mixture of the two model monomers (or for neat ethyl acrylate) is much slower than for the acrylate in the vinyl acrylate as shown in Fig. 4. The conversion of acrylate double bonds in the vinyl acrylate sample reaches 80% in 3–4 s while it takes 70–75 s to attain 80% acrylate double bond conversion in the case of either the ethyl acrylate homopolymerization or the ethyl acrylate/vinyl propionate 1:1 molar mixture. This result clearly demonstrates that having vinyl and acrylate groups on the same molecule is essential for a fast, efficient photopolymerization of the acrylate double bonds.

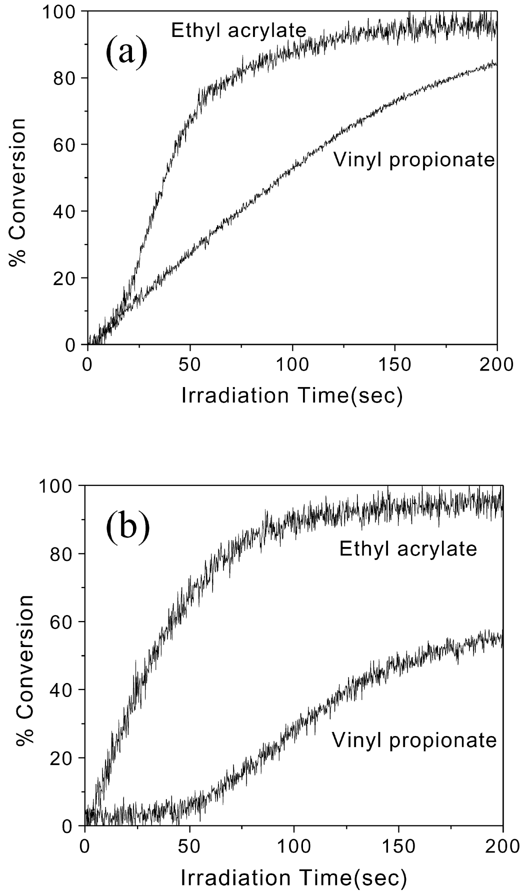
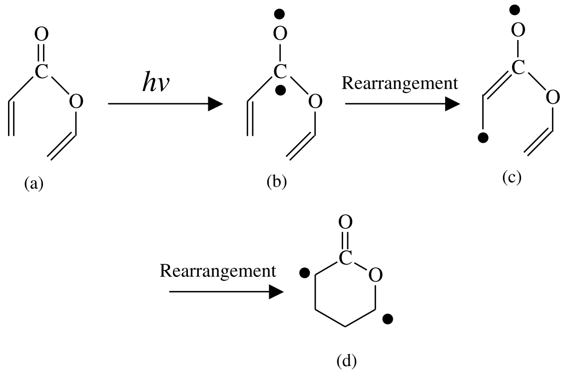
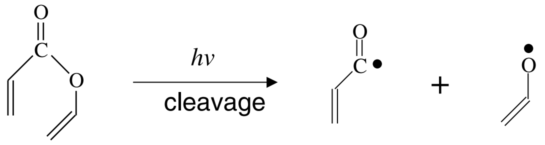


Fig. 8. Conversions of acrylate and vinyl groups (a) for the homopolymerization of ethyl acrylate and vinyl propionate and (b) for the copolymerization of 1:1 molar mixture of ethyl acrylate and vinyl propionate as a function of irradiation time. UV light intensity is ~35 mW/cm^2. No photoinitiator is added.

Two possibilities are suggested for photoinitiation of polymerization by vinyl acrylate. As shown in Scheme 1, the biradical formed by a photoinduced cyclization may be responsible for initiating polymerization. Alternatively, a simple alpha-cleavage between the carbonyl carbon and the oxygen on the ester group may occur (Scheme 2). To date we cannot exclude either possible mechanism. Although initial attempts failed, we are continuing to attempt to trap the initiating radicals. One interesting aspect of the vinyl acrylate monomer with respect to its role in initiating polymerization



Scheme 1. Possible photo-cyclization mechanism for producing radical initiators.



Scheme 2. Possible cleavage mechanism for producing radical initiators.

is its red-shifted absorption spectrum compared to simple acrylates and vinyl esters. As shown in Fig. 9, the UV–Vis absorption spectrum of vinyl acrylate extends to 300 nm with a shoulder at 230 nm that is not present in either ethyl acrylate or vinyl propionate model monomers. Although in this spectral region, impurities can never be ruled out, we believe that this spectrum is essentially that of vinyl acrylate. Such a red-shifted absorption as shown in Fig. 9 is indicative of extended conjugation involving the acrylate and vinyl ester species (see Ref. [8]). One additional result for the vinyl acrylate photoinitiated polymerization shown in Fig. 10 may have mechanistic implications. Fig. 10 shows the acrylate conversion in vinyl acrylate versus time after shuttering the UV light at 25% conversion for two different samples; one sample was polymerized to 25% conversion using the full arc (attenuated) without a photoinitiator and another with a photoinitiator at 365 nm. In both samples, the conversion and polymerization rates before terminating the UV light were almost identical. After removal of the initiating source, the polymerization rate and conversion drastically decrease because termination reactions dominate the polymerization. As shown in Fig. 10, the conversion of acrylate groups of the self-initiated vinyl acrylate during the dark polymerization is about 5% compared to the dark conversion of about 3% achieved when a conventional photoinitiator was used. This behavior may have its origins in the type of polymer chain growth initiated by each initiator species as well as the structure and molecular weight of the growing polymer chains, which could of course alter termination kinetics and account for the observed results

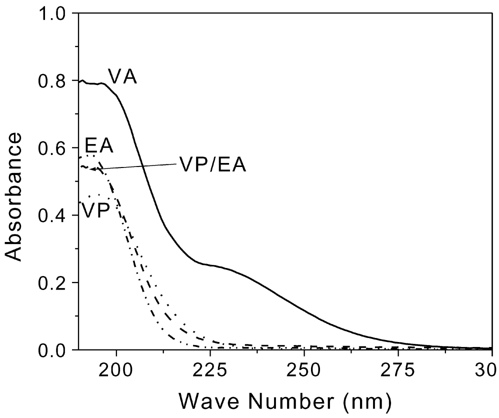


Fig. 9. UV–Vis absorption spectrum of vinyl acrylate (VA), ethyl acrylate (EA), vinyl propionate (VP), and vinyl propionate/ethyl acrylate 1:1 molar mixture (VP/EA).

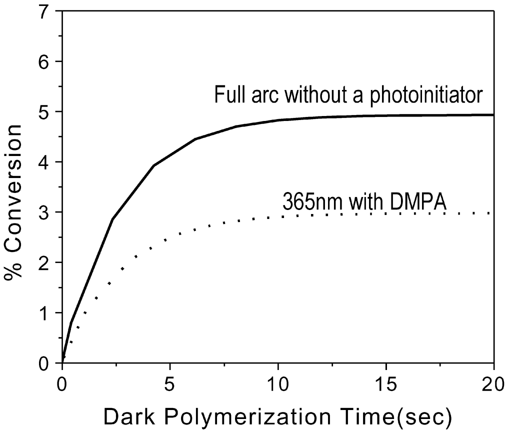


Fig. 10. Conversion of the acrylate double bonds in vinyl acrylate as a function of dark polymerization time after shuttering UV light at 25% conversion. Polymerization was initiated using full arc of UV light without photoinitiator and 365 nm UV light with 1 wt% DMPA. UV light intensity is 16.4 mW/cm^2.

4. Conclusions

The photopolymerization kinetics of vinyl acrylate has been investigated using real-time FTIR. The acrylate groups of vinyl acrylate undergo rapid polymerization upon irradiation. On the other hand, the vinyl group polymerization is much slower, occurring only after ~85% acrylate conversion. The reactivity of the acrylate group of vinyl acrylate is also much faster than common acrylate monomers. A low concentration of vinyl acrylate shows a notable ability to initiate radical polymerization of an acrylate monomer upon irradiation, although the initiation efficiency on a per weight basis of vinyl acrylate is lower than with conventional photoinitiators. Comparisons with monofunctional analogues demonstrate that having both the acrylate and vinyl group on the same molecule is essential for achieving the rapid polymerization rate of the acrylate group.

Acknowledgements

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