Photoinitiation and Photopolymerization of Novel Self-Initiating Monomers

Charles E. Hoyle,[1] Tai Yeon Lee,[1] E. Sonny Jonnson,[2] and C. Allan Guymon[3]

1. *University of Southern Mississippi, School of Polymers and High Performance Materials, Hattiesburg, MS 39406*.
2. *Fusion UV-Curing Systems, Gaithersburg, MD 20878*
3. *University of Iowa, Department of Chemical and Biochemical Engineering, Iowa City, IA 52242-1527*

Abstract

Photoinitiation and photopolymerization of novel self-initiating monomers including vinyl crotonate, vinyl cinnamate and ethylvinyl fumarate have been examined. The presence of both a crotonate, cinnamate, or fumarate group and a vinyl double bond in the same molecule significantly affects the UV absorption spectrum as well as the photochemical properties of the monomer. These monomers self-initiate free-radical polymerization, and also photoinitiate the polymerization of other free-radical monomers.

Introduction

Free-radical photocuring is an extremely efficient process for producing crosslinked polymer materials.[1,2] Acrylates have been widely used in photocuring because they polymerize free-radically at rapid rates and give films with a wide variety of desirable properties. Generally, acrylates used in photocuring have more than two acrylate double bonds of equal reactivity on the same molecule to create crosslinked network. The polymerization kinetics of traditional multifunctional acrylates has been studied extensively in the past to provide a fundamental understanding of the photocuring mechanisms. However, free-radical polymerization of monomers with different functional groups in the same molecule that interact electronically to modify the chemical properties of each group has not been examined in great detail. One multifunctional monomer having different carbon-carbon double bonds is vinyl acrylate which has two types of double bonds on the same molecule, an acrylate and a vinyl ester. The acrylate group on vinyl acrylate is much more reactive than the vinyl group and homopolymerizes almost completely while significant concentrations of the vinyl group remain unpolymerized.[3,4] In addition, the acrylate group of vinyl acrylate polymerizes much faster than traditional acrylate monomers. An interesting property of vinyl acrylate is its ability to self-initiate its own polymerization as well as the free-radical polymerizations of other free-radical monomers. [3,4] The self-initiation ability and fast polymerization are a result of having both the acrylate and vinyl ester double bonds on the same molecule, which results in a unique electronic interaction.[4] Due to the fast polymerization rates and self-initiating ability, molecules containing two interactive enes such as vinyl acrylate can provide numerous obvious advantages in photocuring processes.

Herein, we present detailed results of the evaluation of other self-initiating multifunctional monomers comprised of two interactive different ene groups with respect to their initiating efficiency and photopolymerization behavior. The self-initiating ability of these monomers upon irradiation was measured by using these monomers as initiators for the polymerization of traditional acrylate monomers. The difference in reactivity of the two different double bonds was evaluated quantitatively using real-time FTIR (RTIR) spectroscopy. By investigating appropriate model monomer systems, it is shown that it is essential for both ene groups to be on the same molecule in order to attain high polymerization rates and serve as photoinitiators.

Experimental

Materials. Vinyl acrylate, vinyl crotonate, vinyl cinnamate, vinyl acetate, the monoethyl ester of fumaric acid, vinyl propionate, and diethyl fumatate were obtained from Aldrich Chemical Co. 1,6-Hexanediol diacrylate was obtained from UCB Chemicals. 2,2-Dimethoxy 2-phenyl acetophenone (DMPA) was obtained from Ciba Specialty Chemical. All chemicals were used as received without further purification.

Synthesis. Ethylvinyl fumarate was synthesized by transesterification of vinyl acetate and the monoethyl ester of fumaric acid in the presence of a palladium catalyst. $PdCl_2$ (0.5 mmol), AcOLi (48.75 mmol), and $CuBr_2$ (1.5 mmol) were added to 1 mole of vinyl acetate followed by addition of 5 drops of water at room temperature. The reaction mixture was heated to 80 ^oC, and then an acid (0.4 mol) was added. After reaction for 36 hours in nitrogen atmosphere, the mixture was filtered and concentrated under reduced pressure at 50 ^oC. The product was separated by column chromatography. ^1H and ^{13}C NMR (200 mHz) using $CDCl_3$ as a solvent was used to identify product structure. UV absorption behavior of synthesized monomer in hexane solution was measured using a Cary 5 spectrometer. The chemical structure of ethylvinyl fumarate synthesized is shown in Figure 1 along with vinyl acrylate, vinyl crotonate, vinyl cinnamate, and diethyl fumarate.

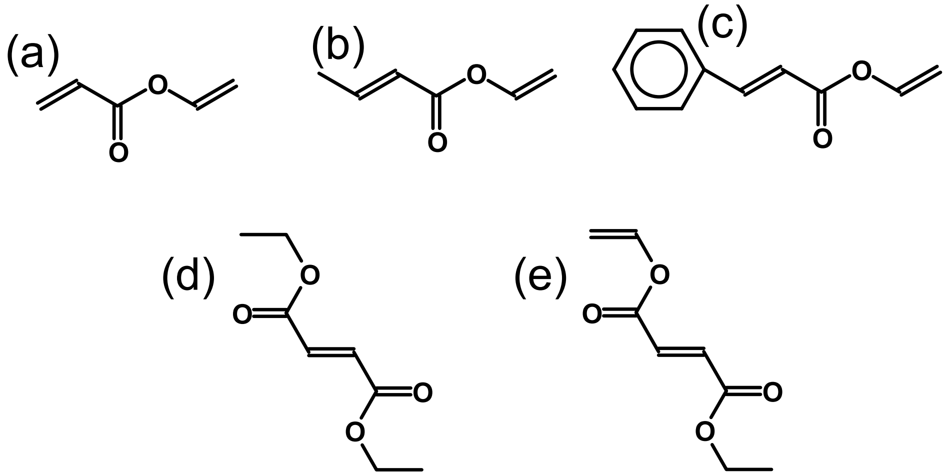

Figure 1. Chemical structures of (a) vinyl acrylate (VA), (b) vinyl crotonate (VC), (c) vinyl cinnamate (VCinn), (d) diethyl fumarate (DiEtF), and (e) ethylvinyl fumarate (VF).

Photopolymerization. Photopolymerization kinetic profiles for the free-radical polymerization of each species were recorded using real-time FTIR (RTIR). Infrared spectra were recorded on a modified Bruker 88 FTIR spectrometer designed to allow light to impinge on a horizontal sample using a fiber-optic cable as a function of irradiation time. A 200 Watt high-pressure mercury-xenon lamp (Oriel Co.) served as the light source to induce the free-radical polymerization. Conversion rates of each carbon-carbon double bond were calculated by recording the disappearance of the following bands: 812 cm^{-1} for acrylate of vinyl acrylate, 885 cm^{-1} for the vinyl of vinyl acrylate or ethylvinyl fumarate, 980 cm^{-1} or 764 cm^{-1} for the fumarate of ethylvinyl fumarate, 980 cm^{-1} for the fumarate of diethyl fumarate.

Results and Discussion

As reported previously,[3,4] the ability of vinyl acrylate (VA) to initiate free-radical polymerization as well as the enhanced polymerization rate of the acrylate double bond of VA are due to the presence of both acrylate and vinyl groups on the same molecule. It would be expected that compounds having similar structure with vinyl acrylate, i. e. two ene groups connected in a like fashion, would also exhibit enhanced double bond reactivity and photochemical properties similar to VA. Since VA is volatile at room temperature and its initiation efficiency is quite lower than traditional photoinitiators, discovery of other similar systems with low volatility and enhanced photochemical reactivity would be advantageous. To this end, we have chosen to evaluate two available monomers vinyl crotonate (VC) and vinyl cinnamate (Vcinn) and one monomer synthesized in our lab, ethylvinyl fumarate (VF). Before presenting results for the photochemical and kinetic results for these monomers, the synthesis of VF is described.

Figure 2 shows H^1 and C^{13} NMR spectra of VF synthesized as described in the Experimental section. The NMR spectra clearly identify the product as VF and attest to its high purity.

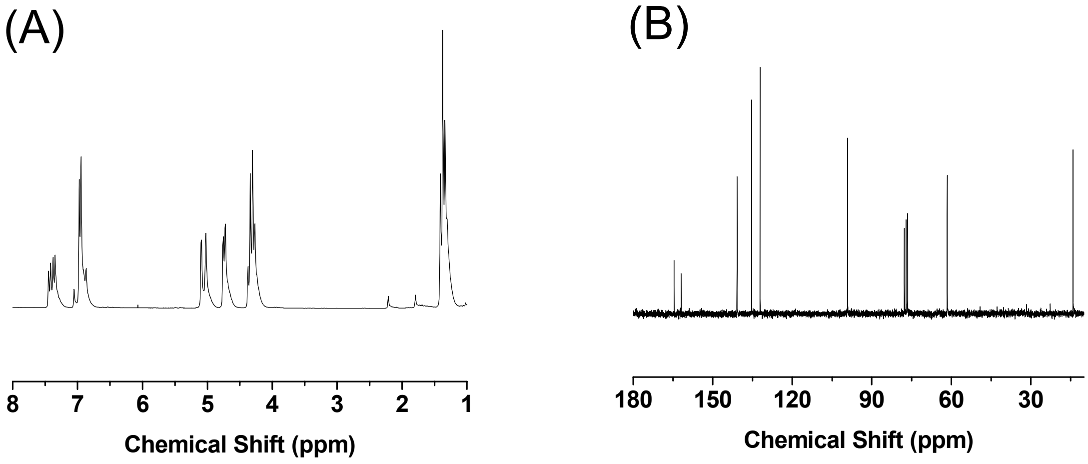

Figure 2. (A) ^{1}H-NMR and (B) ^{13}C NMR spectra of ethyl vinyl fumarate (VF). ^{1}H-NMR δ (200 MHz, $CDCl_3$) 7.36 (quart, 1H, =CH vinyl), 7.0 (s, 1H, =CH fumarate), 5.04 (d, 2H, =CH$\underline{H}$ vinyl), 4.73 (d, 2H, =C$\underline{H}$H vinyl), 4.03 (quart, 2H, CH_2), 1.36 (t, 3H CH_3) ^{13}C-NMR δ (200 MHz, $CDCl_3$) 165 (-OCO-), 162 (-OCO-), 141 (=CH vinyl), 135 (=CH fumarate), 132 (=CH fumarate), 100 (=CHH vinyl), 61 (CH_2), 14 (CH_3).

UV absorption behavior of the monomers shown in Figure 1 are given in Figure 3. As shown in Figure 3A, the UV spectra of the monofunctional analogues of VA, ethyl acrylate, vinyl propionate, and their mixture, shows absorption peak maxima below than 230 nm.

Clearly the absorption of VA and VC are significantly red shifted. For ethyl cinnamate, a large absorption band in Figure 3B ranging from 250 nm to 300 nm is observed due to the presence of the benzene ring. The absorption band of VCinn in this range is red shifted from ethyl cinnamate, commensurate with the shifts noted for VA and VC. This strongly indicates that the presence of the two ene groups on the same molecule where one of the enes is a vinyl ester with the vinyl group attached to the oxygen of the carboxylate: no doubt there is significant conjugation is such arrangements. VF also shows red-shfited UV absorption peaks compared to that of monofunctional analogues, diethyl fumarate as shown in Figure 3C. Interestingly, the absorption of VF is red shifted compared to VA and VC making it an excellent candidate for excitation at longer wavelengths.

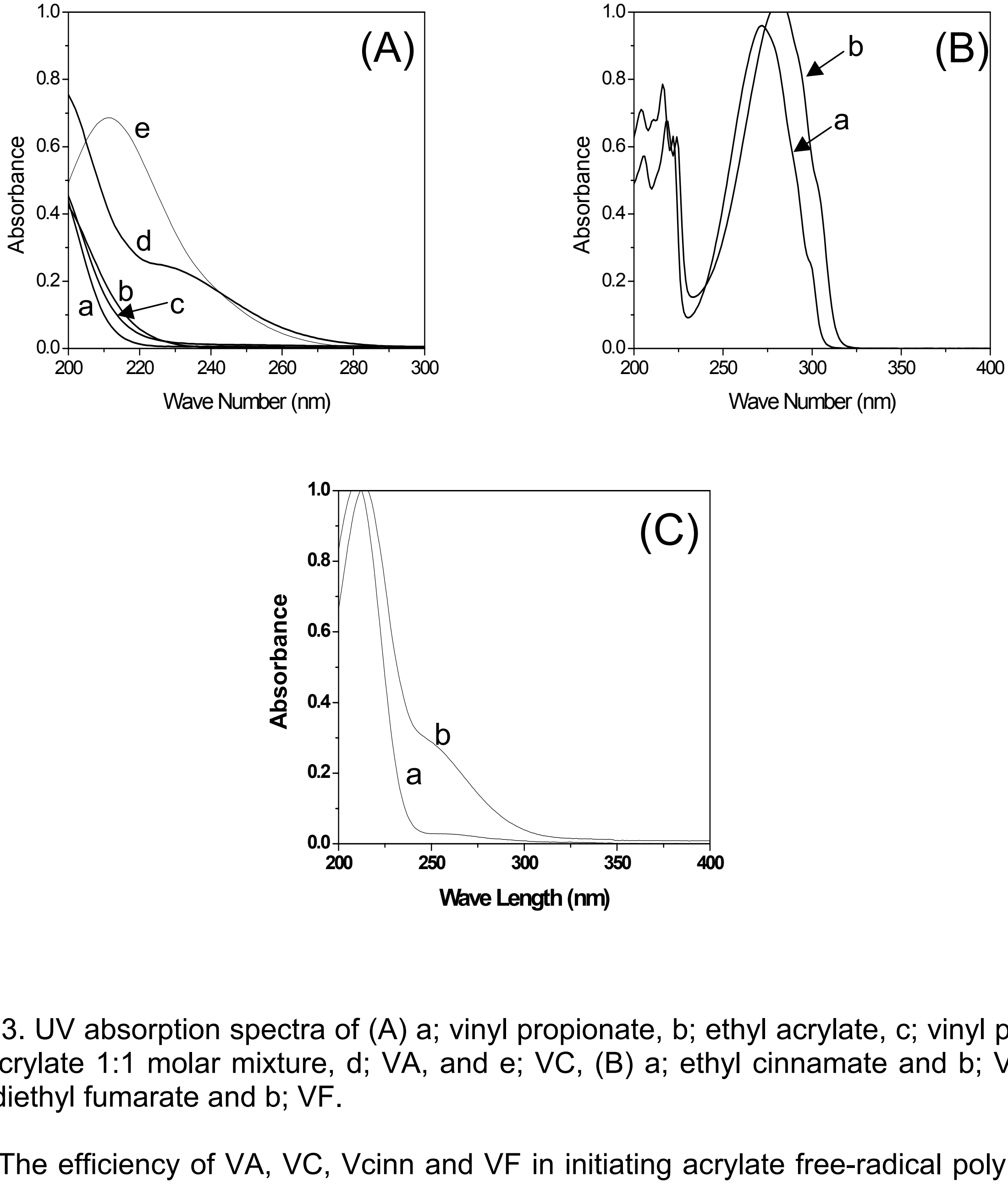

Figure 3. UV absorption spectra of (A) a; vinyl propionate, b; ethyl acrylate, c; vinyl propionate/ ethyl acrylate 1:1 molar mixture, d; VA, and e; VC, (B) a; ethyl cinnamate and b; VCinn, and (C) a; diethyl fumarate and b; VF.

The efficiency of VA, VC, Vcinn and VF in initiating acrylate free-radical polymerization was determined by exposing samples of 1,6-hexanediol diacrylate (HDDA) with each species present to a high pressure mercury-xenon lamp. As shown in Figure 4, HDDA does not polymerize in the absence of a photoinitiator. In the presence of VA and VC, conversions of 60 % are attained (Figure 4). However, it is obvious that initiation efficiency of VA and VC is much lower than that of DMPA. The long induction periods observed when VA and VC are used as photoinitiators is due to a slower initiation rate and inhibition by dissolved oxygen. For Vcinn as an initiator, conversion rate are much higher than those when VA and VC are used as photoinitiators due to the larger UV absorption peaks as shown in Figure 3B. VF also shows better initiation efficiency than VA and VC under the same conditions. However, the initiation efficiency of both VF an Vcinn is still lower than the traditional photoinitiator, DMPA.

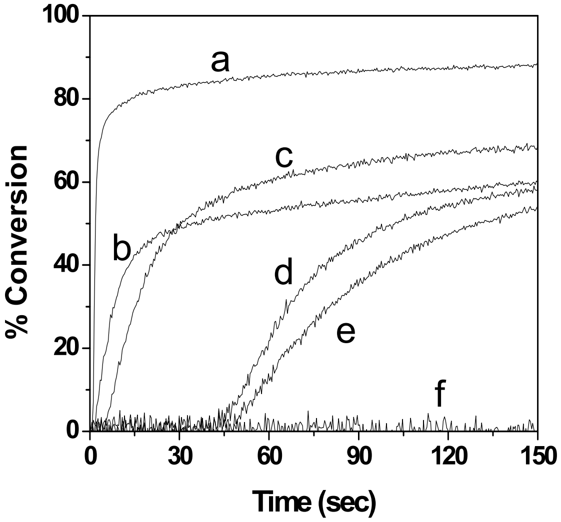

Figure 4. Real-time IR conversion rates of HDDA polymerization in the presence of $3.9*10^{-4}$ mol % of (A) a; DMPA, b; VCinn, c; VF, d; VA, e; VC as photoinitiators and f; no photoinitiator at full UV source. Irradiance is $20mW/cm^2$

In addition to the self-initiation ability of these monomers, their polymerization kinetics are very important if these monomers are to be used as photoinitiators and monomers simultaneously. As mentioned in the Introduction, the reactivity of the acrylate group of vinyl acrylate is much higher than traditional acrylates. On the other hand, VC and VCinn polymerize very slowly probably due to streic hindrance resulting from the presence of methyl and benzyl substituients (data not shown). Interestingly, VF polymerizes rapidly as shown in Figure 6: since the conversion rates are almost identical for the vinyl and the fumarate groups, the polymerization is most likely an alternating copolymerization. This would be expected based on the well-known copolymerization of diethyl fumarate with vinyl esters.[7] For monofunctional analogues, diethyl fumarate and vinyl propionate, homopolymerizations and copolymerizations (of both ene groups) of their mixtures (diethyl fumarate/vinyl propionate 1:1 molar mixture), which are appropriate model systems of VF, are much slower than that of VF (data not shown). We observed that the conversions of the monofunctional analogues are lower than 10% under the same conditions used to polymerize VF in Figure 6. It is expected that, like VA, polymerization rates of VF are enhanced due to the presence of both the fumarate and vinyl groups on the same monomer molecule.

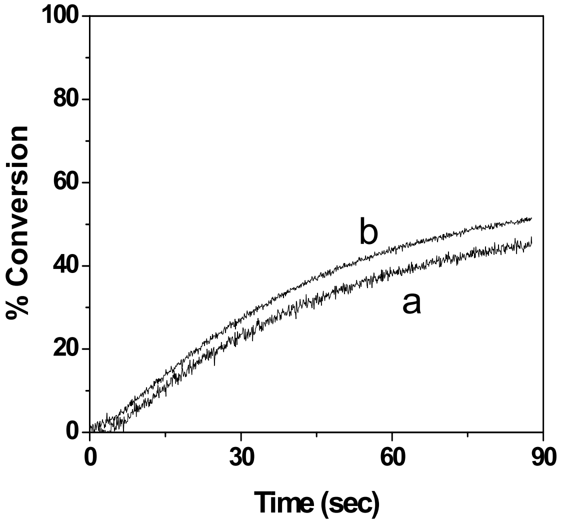

Figure 6. Real-time IR conversion rates of VF in the presence of 1wt % of DMPA at 365 nm. Curve a is fumarate conversion and curve b is vinyl group conversion. Irradiance is 14 mW/cm^2.

Conclusions

Ethylvinyl fumarate was synthesized by a transfication reaction, and the photoinitiation and photopolymerization of ethylvinyl fumarate, vinyl acrylate, vinyl crotonate, and vinyl cinnamate were investigated using real-time IR and UV spectroscopy. As with the acrylate of vinyl acrylate, the presence of the crotonate, cinnamate, and fumarate groups and the vinyl double bond on the same molecule results in a distinct red shift in the electronic absorption spectrum due to intramolecular conjugation. Each of the monomers evaluated also initated acrylate polymerization effectively, with vinyl fumarate being the most efficient. The polymerization of vinyl acrylate and ethylvinyl fumarate exhibit faster polymerization rates than their monofunctional analogues.

Acknowledgements

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