Photopolymerization of New Vinyl Ester Monomers

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Abstract: Vinyl esters including divinyl fumarate and ethyl vinyl fumarate, which contain two different conjugated reactive groups, are new unique monomers and have great potential in formulating UV curable systems. The copolymerization kinetics of these vinyl esters with acrylates was studied by using real-time infrared. We also report on their characterization by using techniques including UV-vis, cyclic voltammetry and theoretical calculations. An example of the ability of these unique fumarate monomers to initiate photopolymerization of acrylates in which the monomer initiators are consumed by the polymerization that they initiate is presented for 1,6-hexanediol diacrylate.

Introduction

The pursuit of new photo-reactive monomers is a never-ending task for chemists in the UV curing industry. Vinyl acrylate has been reported to be a very unique monomer with significantly altered copolymerization kinetics compared to traditional acrylate and vinyl ester monomers, and it is photochemically labile and serves as a photoinitiator.[1-3] Significant differences in the addition rates of external free-radicals to the acrylate and vinyl ester double bonds of vinyl acrylate, compared to traditional acrylate and vinyl ester monomers, have been observed.[4] These differences result from the

presence of both acrylate and vinyl groups on the same molecule, presumably due to some type of π-conjugation. Unfortunately, vinyl acrylate has an extremely low boiling point thereby reducing its usefulness in photocurable systems.

Recently we reported the synthesis of ethyl vinyl fumarate, divinyl fumarate and divinyl maleate and their use as self-initiating photoinitiators and commoners. These novel vinyl esters exhibit red-shifted UV absorption compared to vinyl acrylate. Especially, in divinyl fumarate (DiVF -- structure given in Chart I), the electron density and the basic polymerization reactivity of the fumarate and vinyl ester carbon-carbon double bonds were altered compared to their unconjugated analogs. [5, 6]

In this study, we present detailed results for the characterization of a series of monomers including diethyl fumarate, vinyl fumarte and divinyl fumarate. Characterization includes chemical structural analysis via cyclic voltammetry and theoretical calculations. Their use as monomer photoinitiators in a representative practical acrylate photocuring process is given.

Experimental

Materials

Diethyl fumarate (DiEF), vinyl decanoate (VEDC), vinyl propionate (VP) were obtained from Aldrich Chemicals. 1,6-Hexanediol diacrylate (HDDA) was obtained from Cytec. All chemicals were used as received without further purification. Ethyl vinyl fumarate (EVF) and divinyl fumarate (DiVF) were synthesized by transesterification of vinyl acetate with mono ethyl ester fumaric acid and fumaric acid, respectively, in the presence of a palladium catalyst.[5]

Characterization

UV absorption spectra in hexane solution were measured using a Cary 5 spectrometer. Cyclic voltammetric (CV) experiments were performed with a model 990B electrochemical scanning microscope (CH Instruments, Austin, TX). A conventional three-electrode cell was used, with a Pt wire as the counter electrode, an Ag/Ag$^+$ (10 mM AgNO$_3$-0.10 M tetra-n-butyl ammonium perchlorate (TBAP) in CH$_3$CN) as the reference electrode, and a 2 mm in diameter Pt disk electrode or 3 mm glassy carbon (GC) electrode as the working electrode. Acetonitrile (CH$_3$CN, >99.93 %, HPCL grade, Sigma-Aldrich) or dimethyl sulfoxide (DMSO, >99.9%, Sigma) with TBAP (electrochemical grade, Fluka, 0.10 M in DMSO) was used as the electrochemical solvent/electrolyte. Solutions were degassed with high purity N$_2$ for ~15 minutes, and the working electrode was polished with 0.3 μm alumina slurry and then washed and dried before each CV. All experiments were conducted at a room temperature.

Molecular Orbital Calculations

Ab initio molecular orbital theory calculations were performed at the level of second-order perturbation theory (MP2)[7] employing the 6-311+G(d,p) basis set.[8-10] This basis set comprises the standard triple-zeta valence 6-311G split-valence set, d polarization functions on all non-hydrogen atoms and p polarization functions on hydrogen, and additional, diffuse s and p functions on all non-hydrogen atoms. In particular, Mulliken population analyses[11] were performed and molecular orbital energies of frontier orbitals were examined. All calculations were performed using the Gaussian03 program package.[12]

Photopolymerization

The photopolymerization kinetic profiles during the UV-induced free-radical polymerizations were recorded using real-time infrared (RTIR) spectroscopy 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) served as the light source. Conversion rates of each carbon-carbon double bond were calculated according to disappearance of IR absorption bands at 812 cm^{-1} for the HDDA acrylate group.

Results and Discussion

The chemical structures of all components used in this investigation including DiEF, EVF and DiVF and corresponding models are shown in Chart 1. Characterization techniques of DiEF, EVF and
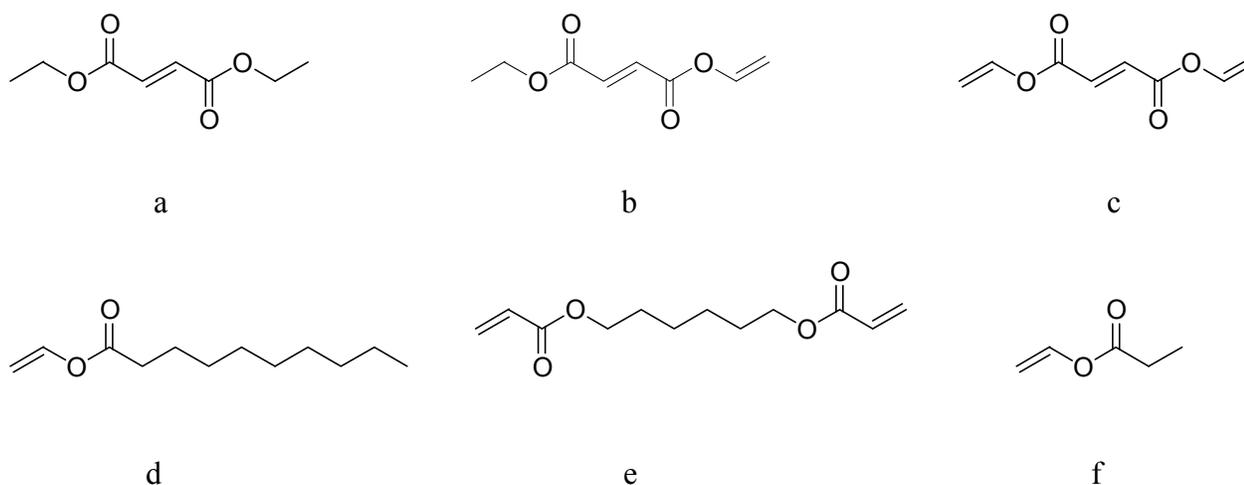
Chart 1. Chemical structure of (a) DiEF, (b)EVF, (c) DiVF, (d) VDEC, (e) HDDA and (f)VPRO

DiVF series monomers were conducted with respect to the electron density of the fumarate and vinyl ester include UV-vis spectroscopy, electrochemical measurement of the reduction (fumarate) and oxidation (vinyl ester) of EVF and DiVF in comparison to DiEF, a dialkyl fumarate and VDEC, a vinyl alkylate, and a Mulliken electron population analyses from molecular orbital calculations of the double bonds and calculation of the LUMO energies. Next, the photopolymerization kinetics of a diacrylate monomer [1,6-hexanediol diacrylate (HDDA)] in the presence of these series monomers is monitored using real-time infrared (RTIR) spectroscopy.

Characterization of DiEF, VF and DiVF: Absorbance and Extinction Coefficients

      As shown in Figure 1, EVF and DiVF exhibit strong UV absorption at wavelengths longer than 300 nm, extending to greater than 350 nm. The red-shift in absorption compared to DiEF is a result of an extended conjugation involving the vinyl ester and fumarate carbon-carbon double bonds and the intermediate carbonyl. Because UV light sources traditionally provide strong intensities at 254, 313 nm, and 366 nm, molar extinction coefficients (ε) at these wavelengths are an important aspect of their overall ability to initiate photopolymerization upon exposure to mercury light. For direct comparison,
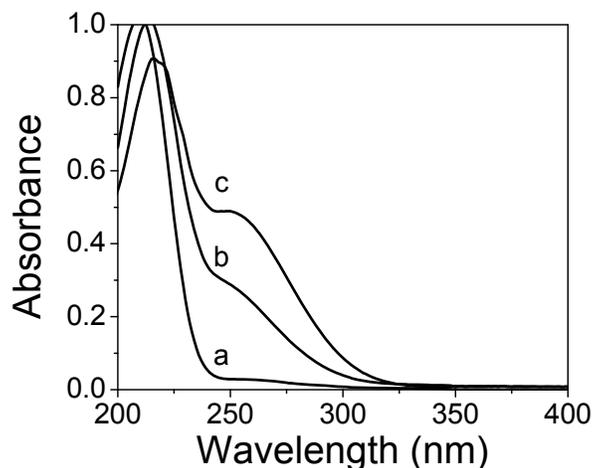
Figure 1. UV absorption spectra of (a) DiEF, (b) EVF and (c) DiVF in hexane solution with equal molar concentration.

Table 1 shows the molar extinction coefficients (ε) of DiEF, EVF and DiVF at 254 nm, 313 nm and 366 nm in hexane. Compared with DiEF and EVF, DiVF has much higher ε values at all three wavelengths. The extinction coefficient (ε) at 254 nm of DiVF is about 1.8 and 17 times greater than that of EVF and DiEF, respectively. ε for DiVF is approximately 1.6 and 6 times greater than the value of ε for EVF and DiEF at 313 nm. The n, π^* absorption extinction coefficients at 366 nm are approximately the same for both EVF and DiVF, which are much higher than that of DiEF. The higher ε values at 254 and 313 nm wavelength of DiVF compared with EVF are due to the more extended conjugation afforded by two vinyl ester double bonds, two carbonyls and one fumarate double bond rather than the conjugation involving only one vinyl ester double bond, one carbonyl and one fumarate double bond. The red-shifted absorbance for EVF and DiVF is a unique property for α,β-unsaturated esters which is only found to exist when an unsaturated carbon-carbon double bond is attached to the oxygen ester.

Table 1 Molar extinction coefficients (L/mol·cm) of DiEF, EVF, DiVF at 254, 313 and 366 nm.

	254 nm	313 nm	366 nm
DiEF	407.9	77.7	9.3
EVF	3882.5	300.0	130.4
DiVF	6872.6	485.3	123.9

Characterization of DiEF, EVF and DiVF: Cyclic Voltammetry

Probably the best method of characterizing the electronic nature of the double bonds in a reactive chemical species is to measure its oxidation and reduction profiles. Accordingly, cyclic voltammograms of EVF and DiVF and its monomolecular saturated analog DiEF were recorded in CH_3CN (oxidation at GC) or DMSO (reduction at Pt) at room temperature using a conventional three-electrode cell, with a Pt wire as the counter electrode, an Ag/Ag^+ (10 mM $AgNO_3$ - 0.10 M TBAP in CH_3CN) as the reference electrode, and either a 2 mm diameter Pt or a 3 mm diameter GC electrode as the working electrode.
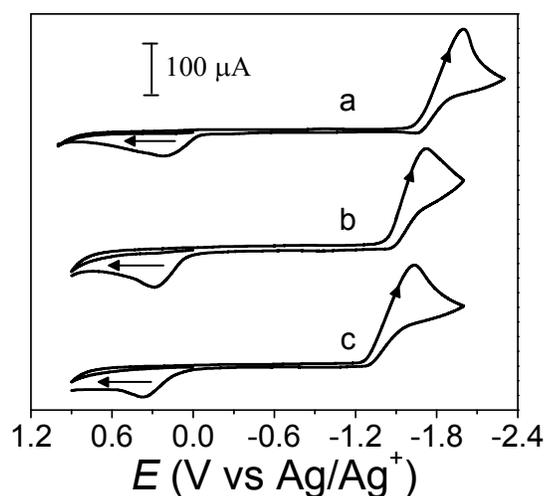
Figure 2 Cyclic voltammograms obtained from a 0.10 M TBAP DMSO solution containing (a) 61 mM DiEF, (b) 60 mM EVF and (c) 83 mM DiVF at 2 mm in diameter Pt electrode with a scan rate of 100mV/s. For clarity, the current axis (Y) was multiplied by 2.6 for (b) and 1.5 for (c).

As can be seen in Figure 2, comparison of the reduction waves of DiVF, EVF and DiEF indicates that it is a little easier to reduce the fumarate group of DiVF than EVF, and in turn much easier than for DiEF. The reduction peak potentials are located at -2.00 V vs. Ag/Ag^+ (Figure 4a) for DiEF, -1.72 V vs. Ag/Ag^+ (Figure 4b) for EVF and -1.63 V vs. Ag/Ag^+ (Figure 4c) for DiVF at a Pt electrode in

DMSO with a scan rate of 100 mV/s. This large difference in the reduction peak potentials clearly indicates that the fumarate double bonds of DiVF and EVF, as expected, are much more electron deficient than DiEF. On the reverse scans, a small re-oxidation wave around -1.7 V vs Ag/Ag^{+} is observed for DiEF, but not for EVF and DiVF. When relatively high scan rates (200-500 mV/s) were employed, the peak ratio of the re-oxidation to reduction was slightly increased for DiEF, however, for EVF and DiVF the re-oxidation wave did not appear with the faster scan rate. The reduction processes are probably attributable to one-electron electrochemical reductions followed by hydro-dimerization chemical reactions.[13] The electro-hydrodimerization products can be further oxidized at peak potential values of +0.21, +0.29 and +0.37 V vs. Ag/Ag^{+} for DiEF, EVF and DiVF, respectively.

The oxidation of DiVF, EVF, DiEF and VDEC was also evaluated in order to establish the electron density of the vinyl ester groups on EVF and DiVF with respect to the vinyl ester double bond on a representative saturated aliphatic vinyl ester (VDEC) and DiEF. Figure 3 (curves b and c) shows the oxidation waves for EVF and DiVF at the GC electrode in CH$_3$CN with a scan rate of 100 mV/s. The oxidation wave for EVF and DiVF (Figure 3b and 3c) has a peak potential value of +2.16 and +2.0 V vs. Ag/Ag^{+}, respectively while the oxidation of DiEF and VDEC never attains a peak within the potential window studied suggesting that its oxidation peak potential is greater than 2.5 V! Hence, we conclude that the vinyl ester groups of DiVF and EVF are much more electron rich than the vinyl ester group of the standard aliphatic vinyl ester VDEC. However, it should be noted that the electron density of vinyl ester double bonds in DiVF is still much poorer than vinyl ether double bonds if compared to the oxidation potential of a triethyleneglycol divinyl ether, +1.41 V vs. Ag/Ag^{+}.[6]
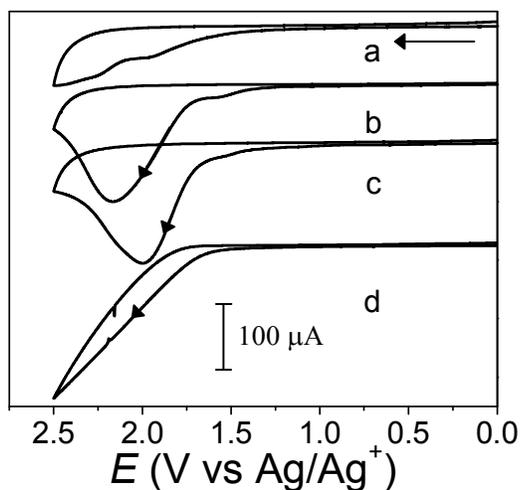
Figure 3 Cyclic voltammograms obtained from (a) 121 mM DiEF, (b) 118 mM EVF, (c) 73 mM DiVF and (d) 85 mM of VDEC in 0.10 M TBAP CH$_3$CN solution at 3 mm in diameter GC electrode with a scan rate of 100 mV/s. For clarity, the current was multiplied by 0.5 for (b) and 0.5 for (d).

Characterization of DiEF, EVF and DiVF: Theoretical Calculations

In order to provide additional evidence for the electron density of the vinyl ester double bonds of EVF and DiVF, theoretical calculations for EVF, DiVF and VDEC were made. A negative population indicates an electron density around that atom greater than the positive charge of that atom's nucleus. Results are presented in Table 2.   Note that the calculations support the conclusions drawn from the oxidation potentials presented above. The vinyl ester double bonds of DiVF are slightly more electron rich than that of EVF, which in turn are more electron rich than that of VDEC. However, the electron density of the vinyl ester double bond of DiVF and EVF are much poorer compared to those of vinyl ether if we compare with Mulliken population of carbons in the terminal vinyl ester double bonds of DiVF and EVF with that of triethylenglycol divinyl ether, which is -0.384.[6]

The population numbers of the carbons in the fumarate double bonds were too small for valid comparisons. Therefore, another result from the calculations was compared. In all of the three fumarates the lowest unoccupied molecular orbital (LUMO) is the *pi* antibonding orbital of the fumarate double bond. The energies for the LUMO in DiVF, EVF and DiEF are 15.41, 21.42 and 27.86 kcal/mol, respectively. While these energies are certainly not quantitative, the trend is irrefutable and indicates that DiVF should be reduced much easier than EVF, which in turn should be reduced easier than DiEF. This is consistent with and provides a rationale for the reduction potentials obtained from cyclic voltammetry.

Table 2 Mulliken population numbers of carbons in terminal vinyl ester double bonds of VDEC, EVF and DiVF.

	Mulliken population of carbons in terminal vinyl ester double bond
VDEC	-0.188
EVF	-0.208
DiVF	-0.215

Photopolymerization Kinetics and Initiation Process of HDDA with EVF, DiVF and the Mixtures of DiEF and VPRO: Conversion Rates

To evaluate the effectiveness of DiVF and EVF as an initiator for the polymerization of HDDA, a RTIR analysis of the polymerization process was conducted. HDDA was polymerized in the presence of 5 wt% of DiVF and EVF (equivalent to 5wt% of DiVF), respectively, to evaluate their inherent ability to initiate photopolymerization of HDDA. For comparison, DiEF and VPRO were added in concentrations equal to that of DiVF to determine if a charge transfer complex between vinyl ester and fumarate groups can form and initiate polymerization upon excitation with light. As shown in Figure 4, where all polymerizations were performed between two salt plates with only residual oxygen present, HDDA does not polymerize efficiently in the absence of a photoinitiator or in the presence of a 1:2 molar mixture of DiEF and VPRO (5 wt% DiVF equivalent), while the sample with EVF polymerized moderately and the sample with DiVF polymerizes rapidly. This demonstrates that the presence of both

fumarate unsaturation and vinyl ester groups on the same molecule is essential for initiating polymerization photolytically. The HDDA sample polymerizes quickly, attaining 65 % conversion within 10 seconds with 5 wt% DiVF, however, the HDDA, attained only 30 % conversion with equivalent amount of EVF within the same period of time. The better initiation ability of DiVF compared to that of EVF is consistent with its higher molar extinction coefficients (ε) at 254 and 313 nm. It should be noted that the initiating abilities of DiVF and EVF are actually better than appears in Figures 4, since the concentration of DiVF and EVF decreases steadily by taking part in a copolymerization process as shown in our previous study.[6] It is important to note that the vast majority of conventional photoinitiators remain unreacted after polymerization is complete, while DiVF and EVF readily copolymerize with the HDDA. Although the overall initiation quantum yield for initiation of acrylate polymerization by DiVF and EVF is inherently lower than for the conventional photoinitiators, the ability of DiVF and EVF to be incorporated into the polymer network by virtue of its participation in the free-radical polymerization process that it initiates could be an asset.[6] This point will be discussed in the presentation to highlight the use of DiVF and EVF in photoinitiator free-systems.
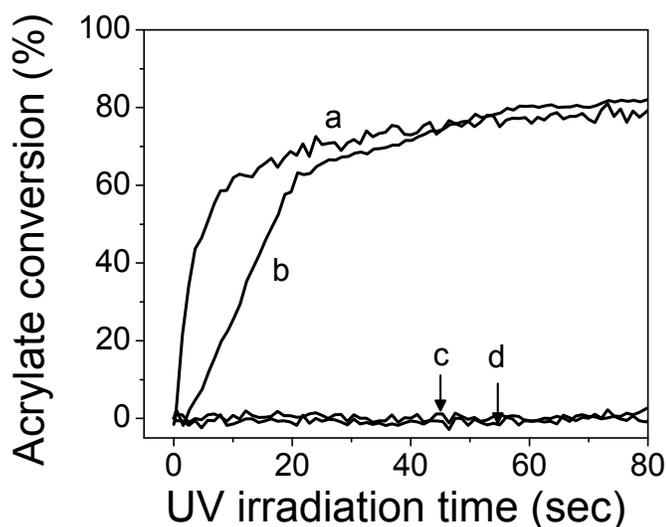
Figure 4 RTIR percent conversion versus time plots of HDDA polymerization in the presence of (a) 5wt% of DiVF, (b) EVF equivalent to 5wt% of DiVF, (c) no photoinitiator, and (d) mixture of DiEF and VPRO equivalent to 5wt% of DiVF. Light intensity (full arc) is 187 mW/cm^2.

Conclusions

Diethyl fumarate (DiEF), ethyl vinyl fumarate (EVF) and divinyl fumarate (DiVF) are a series of unique monomers. The conjugation between a fumarate double bond and one or two vinyl esters of EVF and DiVF provides a distinct red-shifted absorption spectrum that readily results in decomposition upon excitation. The electron densities of the carbon-carbon double bonds in DiEF, EVF and DiVF were characterized by cyclic voltammetry and molecular orbital calculations. The electron density of the

fumarate carbon-carbon double bond in DiVF is lower than that of EVF, which is in turn much lower than the fumarate double bond of diethyl fumarate. Likewise, the electron density of the vinyl ester double bond of DiVF is greater than that of EVF, which in turn is greater than the electron density of the vinyl decanoate double bond. Both EVF and DiVF initiate the photopolymerization of HDDA. The photoinitiation efficiency of DiVF is much greater than that of EVF due to its greater conjugation. Finally, in the presentation the use of such reactive monomers in photinitiator free systems that result in network films with little or no extractable photoinitiating species present will be discussed in detail.

Acknowledgements

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