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(Meth)Acrylate Vinyl Ester Hybrid Polymerizations

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Abstract

In this study vinyl ester monomers were synthesized by an amine catalyzed Michael addition reaction between a multifunctional thiol and the acrylate double bond of vinyl acrylate. The copolymerization behavior of both methacrylate/vinyl ester and acrylate/vinyl ester systems was studied with near-infrared spectroscopy. In acrylate/vinyl ester systems, the acrylate groups polymerize faster than the vinyl ester groups resulting in an overall conversion of 80% for acrylate double bonds in the acrylate/vinyl ester system relative to only 50% in the bulk acrylate system. In the methacrylate/vinyl ester systems, the difference in reactivity is even more pronounced resulting in two distinguishable polymerization regimes, one dominated by methacrylate polymerization and a second dominated by vinyl ester polymerization. A faster polymerization rate and higher overall conversion of the methacrylate double bonds is thus achieved relative to polymerization of the pure methacrylate system. The methacrylate conversion in the methacrylate/vinyl ester system is near 100% compared to only ~60% in the pure methacrylate system. Utilizing hydrophilic vinyl ester and hydrophobic methacrylate monomers, polymerization-induced phase separation is observed. The phase separated domain size is on the order of ~1 μm under the polymerization conditions. The phase separated domains become larger and more distinct with slower polymerization and correspondingly increased time for diffusion.

Introduction

The photopolymerizations industry is dominated by the use of (meth)acrylic monomers due to their desirable polymerization kinetics and wide range of potential polymer properties. There is, however, a continual drive to develop new photopolymerizable systems with advantageous properties that address the various limitations associated with acrylic systems. One of the most distinct limitations of (meth)acrylic systems is oxygen inhibition. Most commonly, nitrogen blankets and high initiator concentrations are utilized to overcome oxygen inhibition in (meth)acrylic systems. In these cases the nitrogen blanket prevents oxygen diffusion into the network or the rate of oxygen diffusion is overcome by a high initiation rate. Additionally, additive chemistries have been developed that consume dissolved oxygen to reduce the effects of oxygen inhibition¹⁻⁴. There has also been significant work addressing the polymerization characteristics and polymer properties of thiol-ene systems as an alternative to acrylics. Due to their thiyl radical-mediated step growth mechanism, thiol-ene systems result in significantly reduced oxygen inhibition, reduced polymerization shrinkage stress, and a variety of other unique characteristics⁵⁻⁹.

An alternate route to reduce the effects of oxygen inhibition is the use of vinyl esters. Vinyl ester systems containing thioether linkages have recently been shown to exhibit significantly reduced oxygen inhibition¹⁰. However, when homopolymerized, vinyl ester systems exhibit relatively slow polymerization rates. When copolymerized with acrylate systems, the vinyl ester/acrylate systems result in both reduced oxygen inhibition and rapid polymerization rates. Vinyl ester systems have also been shown to copolymerize with thiols, resulting in systems that are both very rapid and uninhibited by oxygen^{10,11}.

In this work, vinyl esters are polymerized with methacrylates resulting in a hybrid polymerization between two radically polymerizing systems. The system is unique because both stages of the hybrid polymerization proceed via a radically mediated chain growth polymerization mechanism. Traditionally, hybrid polymerization systems utilize two different polymerization mechanisms to implement the hybrid polymerization mechanism. Hybrid polymerization systems are utilized as a means to combine the polymer properties of two different systems and to achieve unique polymer properties unattainable with either individual polymer system. One common example of a hybrid polymerization system is interpenetrating polymer networks (IPNs). IPNs are frequently formed by the polymerization of two different types of monomers that polymerize via different mechanisms, for example, radical and cationic¹²⁻¹⁵. Curing kinetics of (meth)acrylate/epoxy IPNs have been studied and in some cases been shown to exhibit phase separation upon thermal curing¹⁶⁻¹⁸. Hybrid two-stage polymerizations have also been studied for methacrylate/vinyl ether systems wherein the polymerization occurs via a combination of both radically mediated methacrylate polymerization, which involves minimal direct vinyl ether copolymerization, and a distinct cationic homopolymerization of the vinyl ether¹⁹⁻²⁰. As a practical advantage, hybrid polymerization systems wherein one component of the polymerization remains unreacted during the initial stages of the reaction have also been shown to result in reduced polymerization shrinkage stress in both thiol-allyl ether-methacrylate²¹ and thiol-ene/epoxy systems²².

A unique characteristic of hybrid polymerizations is that in some cases, independent control of the reaction onset and kinetics for the two polymerization processes enhances the control of any phase separation that is induced. Phase separation can lead to advantageous mechanical properties, including improved toughness or a reduction in polymerization-induced shrinkage stress. Heterogeneous, immiscible polymer blends, involving fully formed polymers, are a common example of structural as well as compositional control of polymer properties. Another type of heterogeneous polymerization involves polymerization induced phase separation (PIPS). PIPS is the process whereby an initially homogeneous solution undergoes phase separation during polymerization²³⁻²⁴. Previously, PIPS has focused mainly on phase separation involving growing polymers and non-reactive species such as thermoplastic prepolymers or liquid crystals²⁵⁻³⁰. PIPS in liquid crystals has received considerable investigation for applications in polymer dispersed liquid crystal displays³¹⁻³⁷. In an alternative example, thermoplastic prepolymers, often referred to as low profile additives, are dissolved in monomers and upon polymerization, the prepolymer selectively segregates, often with one of the remaining comonomers³⁸⁻⁴¹. The instability that drives phase separation is a result of the progressive reduction in polarity and entropy as conversion and molecular weight of the polymerizing species increase. Once polymerization is initiated, non-equilibrium structures form based on the competition between phase separation dynamics, diffusion, polymerization kinetics, and polymer network formation.

Polymerization-induced phase separation can also occur between reactive species. Fluorinated methacrylate monomers exhibit phase separation of growing polymer from unreacted monomer upon polymerization⁴². The polymerization of a fluorinated acrylate produces a phase-separated homopolymer when the fluorocarbon side chains selectively

associate to minimize interactions with the hydrocarbon polymer backbone chains formed during polymerization⁴³. Polymerization-induced phase separation between two different reactive species in a hybrid polymerization where both species polymerize via a free radical mechanism is unique. In this work, such a polymerization is studied by utilizing hydrophilic vinyl ester and hydrophobic methacrylate monomers. Both vinyl ester and methacrylate functional groups polymerize via a free radical mechanism. To enable polymerization-induced phase separation between two or more reactive components, the thermodynamic onset of phase separation must occur relatively early in the polymerization process when significant diffusional mobility still exists and most monomeric species remain free from network attachments. Further, the polymerization kinetics provide control beyond that achieved simply by the thermodynamic incompatibility of the monomers and the polymer/copolymer.

The copolymerization behavior of both methacrylate/vinyl ester and acrylate/vinyl ester systems was studied. The polymerization behavior is monitored with near-infrared spectroscopy where both the (meth)acrylate and vinyl ester functional groups are independently resolvable.

Experimental

Materials

Trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), pentaerythritol tetra(3-mercaptopropionate) (PETMP), trimethylolpropane triacrylate (TMPTA), hexanediol dimethacrylate (HDDMA), decamethyleneglycol dimethacrylate (DMGDMA), vinyl acrylate, and triethyl amine were purchased from Aldrich (Milwaukee, WI) and used as received. 2,2-dimethoxy-2-phenylacetophenone (DMPA/Irgacure 651) was donated by Ciba Geigy (Hawthorne, NY).

Synthesis

Vinyl ester monomers were synthesized by an amine-catalyzed Michael addition reaction between a multifunctional thiol and the acrylate group of vinyl acrylate. The efficiency of the reaction depends on the basicity of the amine and the electron density of the ene. In amine-catalyzed reactions between vinyl acrylate and thiols, the vinyl double bond remains unreacted and the thiol adds nearly exclusively across the electron-deficient acrylate double bond, forming a thioether linkage, as shown in Scheme 110.

Trivinyl and tetravinyl ester monomers were synthesized by reaction of an equivalent amount of vinyl acrylate with TMPTMP or PETMP (1:1 ratio of thiol to acrylate functional groups) as outlined in Scheme 1 for synthesis of the trivinyl ester (TriVE).

The tetravinyl ester (TetraVE) was synthesized from a mixture of PETMP and vinyl acrylate with equimolar amounts of thiol and acrylate groups (PETMP: 9.77 g, 0.02 mol, vinyl acrylate: 7.87 g, 0.0802 mol). The mixture was stirred at room temperature under a nitrogen atmosphere. Then, 1 mol % of diethyl amine (0.0585 g) was slowly added to the mixture, and the reaction continued for 1 h. Unreacted vinyl acrylate and diethyl amine was removed via vacuum distillation. The purity was determined to be >99% by ratio of peak areas of remaining unreacted acrylate (5.8 - 6.7 ppm) with vinyl ester (a,b,c). The ¹H NMR spectrum of TetraVE is shown in Figure 1a. ¹H NMR (200 MHz, CDCl₃): 7.28 (quart, 1H, ACH), 4.6 (d, 2H, ACHH), 4.9 (d, 2H, ACHH), 2.66 (t, 2H, CH₂), 2.72 (t, 2H, CH₂), 2.82 (t, 2H, CH₂), 2.66 (t, 2H, CH₂), 4.06 (broad signal, 2H, CH₂).

The trivinyl ester (TriVE, Scheme 1) was synthesized by the same basic method as tetravinyl ester. A mixture of TMPTMP (11.96 g, 0.03 mol) and vinyl acrylate (8.85 g,

0.0902 mol) was reacted using 1 mol % of diethyl amine (0.0658 g). Unreacted vinyl acrylate and diethyl amine was removed via vacuum distillation. The purity was determined to be >99%. The ^1H NMR spectrum of TriVE is shown in Figure 1b. ^1H NMR (200 MHz, CDCl_3): 7.26 (quart, 1H, ACH), 4.6 (d, 2H, ACHH), 4.9 (d, 2H, ACHH), 2.64 (t, 2H, CH₂), 2.71 (t, 2H, CH₂), 2.81 (t, 2H, CH₂), 2.64 (t, 2H, CH₂), 4.06 (broad signal, 2H, CH₂), 1.48 (quart, 2H, CH₂), 0.90 (t, 2H, CH₃).

Methods

Fourier transform infrared spectroscopy (FTIR)

studies were conducted using a Nicolet 750 Magna FTIR spectrometer with a KBr beamsplitter and an MCT/A detector. Series scans were recorded, taking spectra at the rate of approximately 2 scans per second. The FTIR sample chamber was continuously purged with dry air. Samples were irradiated with an EXFO Acticure (Mississauga, Ontario) with 320 - 500 nm filter until the reaction was complete, as indicated by the functional group absorption spectra no longer changing. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization. All reactions were performed under ambient conditions.

Carbon-carbon double bond stretching peaks were used to monitor the acrylate (1635 and 1618 cm^{-1}) and vinyl ester (1645 cm^{-1}) group conversion in acrylate/vinyl ester copolymerizations. A deconvolution technique was employed to separate the overlapping double bond stretching bands of the acrylate and vinyl ester double bonds at 1618, 1635, and 1645 cm^{-1} to determine simultaneously the individual kinetic profiles of the acrylate and vinyl ester groups. The acrylate group conversion obtained from the deconvolution results was confirmed by comparing it with the conversion calculated by measuring the acrylate functional group peak height at 812 cm^{-1} , which is not convoluted with the vinyl ester peak. A more detailed analysis of the peak deconvolution method and results are described elsewhere¹⁰. For methacrylate/vinyl ester copolymerization studies, the vinyl ester peak at 880 cm^{-1} and the methacrylate peak at 816 cm^{-1} are individually resolvable.

To monitor Phase Separation, samples were irradiated with an EXFO Acticure (Mississauga, Ontario) with 320 - 500 nm filter. Spectra were recorded in transmission mode and transmission versus time was recorded. The use of FTIR to monitor phase separation was first detailed by Bhargava *et al*³¹.

Scanning Electron Microscopy (SEM)

1 mm thick samples were cured between two glass slides. Samples contain 0.1 wt% DMPA and were irradiated at 15 mW/cm^2 with an EXFO Acticure with a 320 - 500 nm filter. Samples were immersed in liquid nitrogen and cut into cross sections. Cross sections were imaged using a low vacuum scanning electron microscope (Jeol JSM 6480LV).

Results and Discussion

Due to the different reactivity of the acrylate and vinyl ester double bonds, it is very interesting to investigate the polymerization kinetics of an acrylate-vinyl ester copolymerization. From Odian⁴⁴, the relative reactivity ($1/r$) of a vinyl ester (vinyl acetate) with acrylate (methyl acrylate) radicals is 0.11, while the relative reactivity ($1/r$) of acrylate with vinyl ester radicals is 10. Based on these values, it is expected that the acrylate component in an acrylate/vinyl ester copolymerization will polymerize much more rapidly than the vinyl ester component. Figure 2 depicts the copolymerization behavior of a 50/50 wt% (70:30 molar) mixture of trimethylolpropane triacrylate (TMPTA) and the trivinyl ester (TriVE). As expected, the acrylate functional groups of TMPTA polymerize much more

rapidly than the vinyl ester functional groups. Hence, the copolymerization of TMPTA/TriVE results in a significant increase in conversion of acrylate double bonds. The final conversion of acrylate groups is approximately 80 %, much higher than for TMPTA homopolymerization under the same conditions (approximately 50 %), while the vinyl ester groups achieve 60 % final conversion. While bulk TMPTA produces a highly crosslinked network at very early stages of the polymerization, in the presence of the TriVE, the TMPTA network is plasticized by unreacted and partly reacted TriVE, which polymerizes more slowly. This dual or hybrid polymerization mode leads to enhanced mobility of the growing chains, resulting in an overall increased polymerization rate, conversion, and crosslink density.

Based on the acrylate/vinyl ester copolymerization results, methacrylate/vinyl ester copolymerizations would also be expected to yield a higher final methacrylate conversion due to an even greater reactivity difference between the methacrylate and vinyl ester groups. The relative reactivity ($1/r$) of vinyl ester (vinyl acetate) with methacrylate (methyl methacrylate) radicals is 0.05 while the relative reactivity value of methacrylate with vinyl ester radicals is 67.44. Due to the stronger homopolymerization tendency of the methacrylate groups, methacrylate/vinyl ester copolymerizations exhibit an even more pronounced two stage curing profile as compared to acrylate/vinyl ester copolymerizations. Figure 3 shows the polymerization behavior of a 50/50 wt% (60/40 molar) mixture between HDDMA and the tetravinyl ester (TetraVE) and a bulk HDDMA system. Initially, in the HDDMA/TetraVE system, the methacrylate groups polymerize rapidly while a negligible amount of vinyl ester polymerization occurs. In fact, vinyl ester polymerization measurably occurs only after approximately 90% methacrylate group conversion is obtained (Figure 4), essentially after nearly all methacrylate double bonds are already consumed. Effectively, this behavior results in two polymerization regimes, with the first regime being a methacrylate dominated polymerization and the second regime being a vinyl ester dominated polymerization. In this hybrid system, the vinyl ester component acts as a solvent during the methacrylate polymerization and results in significantly enhanced conversion (very near 100%) of methacrylate groups. Additionally, the methacrylate polymerization rate in a methacrylate/vinyl ester copolymerization is significantly faster than the methacrylate homopolymerization. The final conversion of a bulk HDDMA homopolymerization under the same conditions is only approximately 60 % (Figure 3).

In both the acrylate/vinyl ester and methacrylate/vinyl ester systems, the vinyl ester monomer solvates the forming polymer network during the early stages of the polymerization. In addition to resulting in higher overall functional group conversion, this solvation effect may result in significant reductions in polymerization shrinkage stress and attainment of improved mechanical properties such as modulus and glass transition temperature.

Polymerization Induced Phase Separation

Due to the two distinct free-radical polymerization regimes, methacrylate dominated polymerization followed by vinyl ester dominated polymerization, the methacrylate/vinyl ester copolymerization systems might be expected to undergo polymerization induced phase separation. To investigate polymerization induced phase separation of methacrylate/vinyl ester systems, two monomers with very different chemical properties, decamethyleneglycol dimethacrylate (DMGDMA) and TetraVE were selected. DMGDMA is a relatively hydrophobic component while the tetravinyl ester is a relatively hydrophilic component.

The DMGDMA/TetraVE monomer mixture is initially transparent but becomes translucent during polymerization, giving preliminary indication that phase separation is occurring.

Polymerization induced phase separation was monitored by observation of the baseline shift of the IR spectra during the polymerization process. The phase separated domains scatter the IR beam in the wavelength range corresponding to the domain sizes and in relation to the degree of phase separation. Figure 5 shows mid and near IR spectral changes versus polymerization time for a 50:50 wt% (70:30 molar) DMGDMA/TetraVE mixture. The transmittance of the double bond peaks ($\sim 3100\text{ cm}^{-1}$ for mid IR and $\sim 6200\text{ cm}^{-1}$ for near IR) decrease due to consumption during the polymerization process. The baseline of the mid IR ($4000 - 500\text{ cm}^{-1}$ or $2.5 - 20\text{ }\mu\text{m}$) transmittance is not affected by the polymerization process. On the other hand, the near IR spectra in the range of ($7000 - 4500\text{ cm}^{-1}$ or $1.4 - 2.2\text{ }\mu\text{m}$) exhibits a significant baseline shift during the polymerization. This spectral data provides evidence that the near IR beam is being scattered by phase separated domain structures formed during the polymerization process.

To monitor the relationship between phase separation and polymerization, conversion of both methacrylate and vinyl ester groups along with transmittance of the near IR spectra at 6500 cm^{-1} are shown in Figure 6. During the first polymerization regime, where the polymerization is methacrylate dominated, the transmittance does not significantly change. Almost immediately following the start of the vinyl ester polymerization, the transmittance dramatically decreases. The phase separation process continues to occur throughout the vinyl ester polymerization. During the later stages of the polymerization, the transmittance exhibits an unexpected increase. The increase in transmittance is likely due to changes in optical density. The optical density is affected by both domain size (relative to the visible light wavelengths) and the refractive index difference between phases. Conversion changes in the two phases are not simultaneous; the refractive index of the monomer-rich phase continues to change, and typically it would increase with continued conversion, thereby reducing the refractive index difference relative to the polymer-rich phase. Also, the interface between phases may become less sharp (more diffuse) with continued polymerization. Both of these effects would lead to increased transmittance as observed in the latter stages of the polymerization in Figure 6.

For polymerization induced phase separation, the polymerization rate is an important factor that dictates the phase separation because it controls the available time for diffusion and hence formation of the phase separated domains. If the polymerization is rapid, the components have limited diffusion time to phase-separate into larger, distinct domains. Figure 7 shows conversion versus time for the DMGDMA/TetraVE mixture polymerized at 1, 15, and 50 mW/cm^2 . There is clearly a significantly increased polymerization rate, and hence reduced time available for diffusion and phase separation, as the irradiation intensity is increased. The time to reach 90% of the final conversion is ~ 380 seconds at 1 mW/cm^2 , ~ 70 seconds at 15 mW/cm^2 , and ~ 50 seconds at 50 mW/cm^2 . From observation of the near and mid IR spectra of Figure 5, it is expected that the phase separated domains are on the order of one micron in size. Figure 8 shows SEM images of the DMGDMA/TetraVE mixture polymerized at irradiation intensities of 1, 15, and 50 mW/cm^2 . The sample polymerized at 1 mW/cm^2 clearly shows a phase separated morphology with domains on the size scale of $\sim 1\text{ }\mu\text{m}$. The sample polymerized at 15 mW/cm^2 exhibits a less distinct phase separated morphology on the size scale of $\sim 1 - 2\text{ }\mu\text{m}$. The degree of phase separation decreases with increasing irradiation intensity as observed by a less distinct morphology for the samples polymerized at 15 and 50 mW/cm^2 .

Conclusions

Copolymerizing vinyl ester monomers with acrylate and methacrylate comonomers results in significantly enhanced final conversion and polymerization rates relative to the bulk acrylate or methacrylate systems. Uniquely, copolymerization of methacrylate and vinyl

ester monomers results in two distinct polymerization regimes. The first regime is a methacrylate dominated polymerization regime where the vinyl ester acts as a solvent or diluent and the second regime is a vinyl ester dominated polymerization regime. With the appropriate choice of vinyl ester and methacrylate monomers, the two distinct polymerization regimes can be designed for polymerization induced phase separation between the two reactive species. The phase separation morphology is controlled by both the monomer components and the polymerization kinetics.

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Scheme 1.

The amine catalyzed reaction between thiol (TMPTMP) and vinyl acrylate monomers to give TriVE.

Figure 1.
 ^1H NMR spectrum of tetrafunctional vinyl ester (tetravinyl ester) and trifunctional vinyl ester (trivinyl ester).

Figure 2.

Conversion versus time for (o) acrylate and (□) vinyl ester groups in a TMPTA/TriVE system (70:30 molar mixture) and bulk homopolymerization of TMPTA (—s). Samples are irradiated at 14 mW/cm² and contain 1.0 wt% DMPA.

Figure 3. Conversion versus time for (o) methacrylate and (□) vinyl ester groups in a HDDMA/TetraVE system (1:1 weight %) and in a bulk homopolymerization of HDDMA (—). Samples are irradiated at 15 mW/cm² and contain 0.1 wt% DMPA.

Figure 4. Methacrylate-Vinyl Ester conversion plot of a 50:50 wt% HDDMA/TetraVE mixture. Samples are irradiated at 15 mW/cm^2 and contain 0.1 wt% DMPA.

Figure 5. Percent transmittance versus wavenumber of a 50:50 wt% DMGDMA/TetraVE in (a) near IR at 0, 7.5, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, and 30.0 seconds of irradiation, and (b) mid IR at 0, 10, 20, and 35 seconds of irradiation. Samples are irradiated at 15 mW/cm² and contain 0.1 wt% DMPA.

Figure 6.

Percent transmittance (—) at 6500 cm^{-1} and methacrylate ($\square$) and vinyl ester (O) functional group conversion of a 1:1 (wt %) DMGDMA/TetraVE mixture versus polymerization time. Samples are irradiated at 15 mW/cm^2 and contain 0.1 wt% DMPA.

Figure 7. Methacrylate functional group conversion versus time for a 50:50 (wt %) DMGDMA/TetraVE system polymerized at (□) 1 mW/cm² and (○) 50 mW/cm². Samples contain 0.1 wt % DMPA.

Figure 8. SEM images of a 50:50 (wt %) DMGDMA/TetraVE system polymerized at (A) 1 mW/cm², (B) 15 mW/cm², and (C) 50 mW/cm². Samples contain 0.1 wt% DMPA.