

Novel Multifunctional Vinylester Monomers: A New Class of Monomer for Reduced Oxygen Inhibition in UV Curing

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Abstract

New mono- and multifunctional vinyl ester monomers were synthesized by a simple reaction route with high yield. The polymerization behavior of these monomers was also investigated. The most interesting feature of these monomers is the elimination of oxygen inhibition during the free-radical polymerization process. This results in faster photocuring in air of the multifunctional vinyl esters compared to acrylates. Also, significantly enhanced conversions and polymerization rates for vinylester/acrylate mixtures are observed for copolymerizations with acrylates in air. The polymerization kinetics, reduced oxygen inhibition and copolymerization of the multifunctional vinylesters with various monomers are reported.

Introduction

One of the most important factors in determining the chemical and physical properties of photocured materials is the nature of the monomers, i.e, reactivity of double bonds, functionality, and pendant structure.¹ Selecting appropriate monomers can provide cured films with desirable properties and high performance. Acrylates are the primary multifunctional monomers used in photocuring processes due to rapid photopolymerization rates and desirable final network properties. To date, no other monomer type which can compare with the utility of acrylates has emerged, partly due to the requirement of synthesizing high yield, high purity multifunctional monomers.

Unsaturated vinyl esters are known to polymerize by a free-radical mechanism, although the polymerization rates are slow compared to acrylates.² If multifunctional vinyl ester monomers could be synthesized that contain structural moieties beneficial to the final physical properties of photocured films such as flexibility, high refractive index, antioxidant properties, low swelling, and reduced oxygen inhibition, it would provide new opportunities for designing photocured products with improved properties. If different functionality of vinyl esters could be easily synthesized, the network structure and crosslink density of resulting crosslinked films could be controlled to obtain optimum properties. Multifunctional vinyl esters would also copolymerize readily with acrylates and thiols. The development of photocurable multifunctional vinylester monomers would certainly offer formulators new choices for future applications in the photocuring field.

Herein, we describe the high yield synthesis of mono- and multifunctional vinyl ester monomers with up to 16 reacting double bonds and thioether moieties using a reaction route involving the amine catalyzed addition of thiols across acrylate groups. Using photo-DSC and real-time FTIR, the polymerization kinetics of the vinyl esters and the effect of thioether group on oxygen inhibition were investigated. Also, the copolymerization kinetics of multifunctional

vinyl esters with multifunctional acrylates and thiols both in air and nitrogen are reported and compared with both acrylate and traditional thiol-ene copolymerizations.

Experimental

Materials. Ethyl 3-mercaptopropionate, trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis (3-mercapto propionate), vinyl acrylate, ethyl acrylate, pentaerythritol triallyl ether, and diethyl amine were obtained from Aldrich Chemical Co. Trimethylolpropane triacrylate (TMPTA) and 1,6-hexanediol diacrylate were obtained from UCB Chemicals. A 16 functional thiol (Boltorn H20-3MP) was obtained from Perstorp Specialty Chemicals. 2,2-Dimethoxy 2-phenyl acetophenone (DMPA) and 2-hydroxy-2-methyl-1-phenyl-1-propanone were obtained from Ciba Specialty Chemical. The 16-functional thiol was purified by removing residual acids with aqueous sodium bicarbonate. Other chemicals were used as received without further purification.

Synthesis. To synthesize the mono- and multifunctional vinyl ester monomers, an equimolar amount (based on a number of functional group) of thiol and vinyl acrylate was stirred at room temperature. The sample was nitrogen purged, and 1 mole % of diethyl amine was slowly added to the mixture. The reaction was allowed to proceed for about 1 hour which allows high conversion.³ After the reaction was complete, the product was obtained by removing unreacted vinyl acrylate and diethyl amine via vacuum distillation. H^1 NMR (200 MHz) of the products in $CDCl_3$ was used to identify product structures. The chemical structure of mono- and multifunctional vinyl esters synthesized are shown in **Figure 1**.

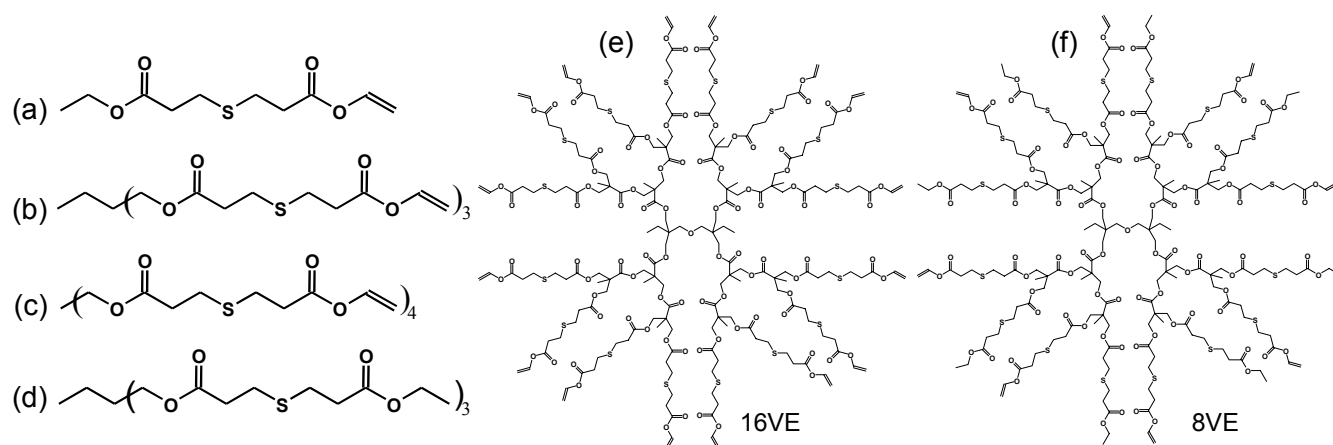


Figure 1. Chemical structures of (a) mono (MonoVE), (b) tri (TriVE), (c) tetrafunctional vinyl ester (TetVE), (d) saturated analogue of trifunctional vinyl ester (S-TriVE), (e) 16-functional vinyl ester (16VE), and (f) 8-functional vinyl ester (8VE).

Photopolymerization. The photopolymerization kinetic profiles in the presence and absence of oxygen during the UV-induced polymerizations were recorded using real-time FTIR (RTIR) and photo-DSC. Using photo-DSC, polymerization exotherms were recorded on a Perkin-Elmer DSC7 modified with a shuttered medium-pressure mercury lamp from Ace glass. Light intensities were measured at the sample pan via a carbon black body absorber. Samples

of 2 μL were injected into the indented pan to give film thicknesses of approximately 200 microns. Polymerization kinetics were also 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. Carbon-carbon double bond stretch peaks were used to monitor acrylate (1635 cm^{-1} and 1618 cm^{-1}) and vinyl double bond (1645 cm^{-1}) conversion of the acrylate/vinyl ester photoinitiated copolymerization. To simultaneously determine the individual kinetic profiles of the acrylate and vinyl groups, a deconvolution technique was employed to separate overlapping C=C stretching bands of the acrylate and vinyl ester double bonds. The thiol group conversion in the thiol/vinyl ester copolymerization was monitored by measuring the peak height of the 2570 cm^{-1} band.

Results and Discussion

Since the branch chains of the MonoVE, TriVE and TetVE synthesized in this study have identical structure, the effect of monomer functionality on polymerization kinetics can be directly compared. Figure 2A shows polymerization kinetics of MonoVE and TriVE in the presence and absence of oxygen. As expected, TriVE polymerizes much faster than MonoVE due to autoacceleration resulting from the formation of a crosslinked network microgel in the initial stages of polymerization. Interestingly, vinyl esters synthesized show little or no oxygen inhibition during free-radical polymerization. Since acrylates undergo significant inhibition in air, it is interesting to compare the polymerization rate of the vinyl ester with multifunctional acrylates in air and nitrogen (Figure 2B). Both multifunctional acrylates (HDDA and TMPTA) polymerize much faster than TriVE in a nitrogen atmosphere. However, TriVE shows only a small decrease in polymerization rate as well as the absence of an induction period in the presence of oxygen, while the polymerization rate of each acrylate is significantly reduced in

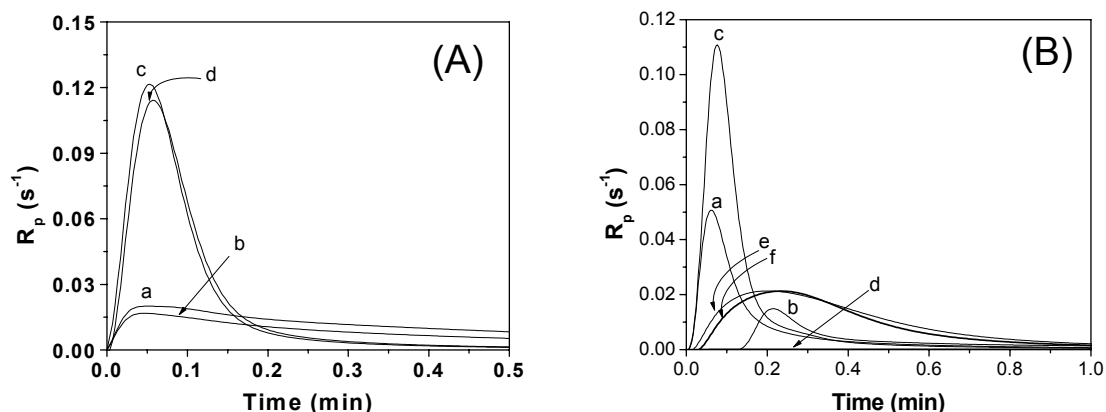


Figure 2. (A) Polymerization rate (R_p) of MonoVE (nitrogen (a) and air (b)) and TriVE (nitrogen (c) and air (d)), and (B) TMPTA (nitrogen (a) and air (b)), HDDA (nitrogen (c) and air (d)), and TriVE (nitrogen (e) and air (f)) with 1.0 wt% of DMPA. Irradiance is 75 mW/cm^2 for (A) and 6.8 mW/cm^2 for (B).

air due to oxygen inhibition. This results in slower polymerization rates for the acrylates than vinyl esters with comparable functionality. Andrzejewski *et al.*^{4,5} reported similar results for

di(meth)acrylates containing the thioether group. The reduced oxygen inhibition of the vinyl ester monomers synthesized can be explained by rapid oxygen consumption involving the thioether groups as suggested by Andrzejewski *et al.*⁵ The hydrogens on the α -carbon of thioether can readily be abstracted by a peroxy radical due to the high polarizability of the sulphur atom which enhances stabilization of the α -carbon centered radical through $p_{\pi}-d_{\pi}$ bonding and electron-sharing conjugation ($R-S-C\cdot-R \rightleftharpoons R-S\cdot=C-R$).⁶ The carbon centered radical produced reacts with oxygen to produce another peroxy radical. The chain reaction for oxygen consumption continues until the oxygen concentration in the sample reduces the oxygen level to where polymerization is not inhibited.

From the results in Figure 2, it is reasonable to expect that when acrylates copolymerize with one of vinyl esters in air, the polymerization rate should increase due to rapid consumption of oxygen by thioether groups of the vinyl esters. Figure 3 shows the effect of adding TriVE on TMPTA polymerization in air. Pure TMPTA has a long induction period and polymerizes slowly as shown in Figure 3A. Addition of TriVE to TMPTA results in an increase in polymerization rate and conversion as well as a reduced induction period. It should be noted that addition of 22 mol % of TriVE results in a polymerization exotherm in air comparable to that observed for TMPTA in nitrogen. To provide evidence for reduced oxygen inhibition by thioether linkages, Figure 3B shows the effect of a saturated analogue of TriVE (acronym S-TriVE, Figure 1) on TMPTA polymerization. Interestingly, addition of S-TriVE has the same effect as TriVE on TMPTA polymerization except, there is a slightly smaller increase in polymerization exotherm compared to TriVE since S-TriVE is a non-polymerizable species.

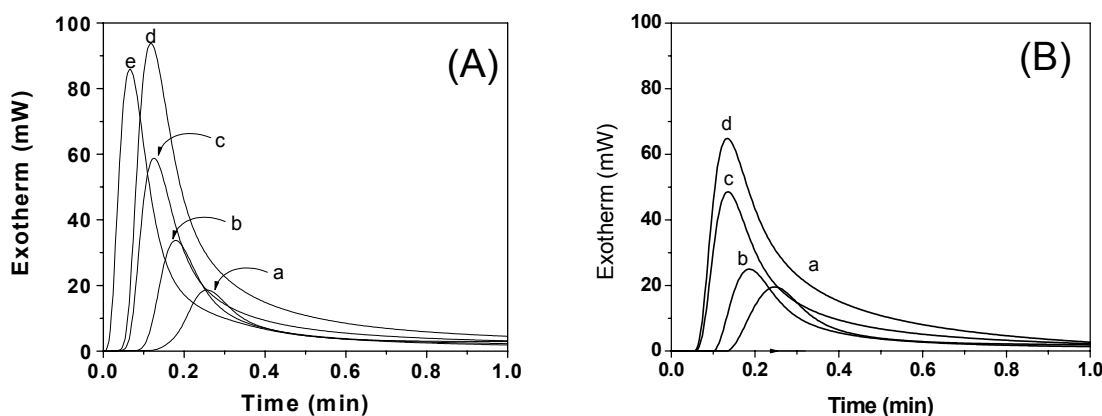


Figure 3. Polymerization exotherm measured by photo-DSC of (A) TMPTA/TriVE mixtures (TriVE mole content; (a) 0%, (b) 4.5%, (c) 15%, (d) 22% in air, and (e) 0% in nitrogen) and (B) TMPTA/S-TriVE mixture (S-TriVE content; (a) 0%, (b) 4.5%, (c) 15%, (d) 22%) in air with 1.0 wt% of DMPA. Irradiance is 2.45 mW/cm² for (A) and 2.6 mW/cm² for (B).

Since no quantitative analysis of the extent of conversion of each functional group (acrylate and vinyl ester) can be obtained from the photo-DSC results, the conversion rates of both functional groups are separately monitored using RTIR. Figure 4 shows the conversion as a function of time for acrylate in nitrogen and air for three samples with increasing concentration of TriVE in TMPTA. In an inert nitrogen atmosphere, the pure TMPTA shows a final acrylate conversion of ~44 mol%. When 15 and 30 mol % TriVE are added to TMPTA,

both the polymerization rate and the final percent conversion of acrylate groups in nitrogen increase significantly. When 30 mol % of TriVE is added to TMPTA, the calculated total double bond conversion (acrylate and vinyl ester groups) is approximately 65%, which is much greater than that of pure TMPTA. The increase of acrylate conversion with increasing TriVE content can be explained by the plasticizing effect of the vinyl ester. Due to the higher reactivity, the acrylate will polymerize much faster than the vinyl ester group. In the presence of oxygen, pure TMPTA achieves less than 5 % conversion due to oxygen inhibition as shown in Figure 4B. The acrylate conversion rates for the 15 % and 30 % TriVE samples are greatly enhanced compared to pure TMPTA in air, consistent with photo-DSC results.

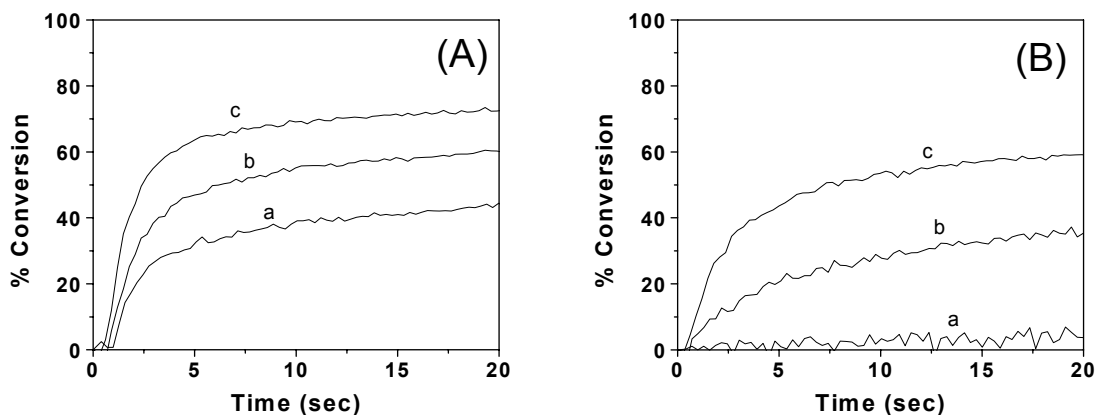


Figure 4. TMPTA double bond conversion in TMPTA/TriVE mixtures in (A) nitrogen and (B) air as a function of TriVE content with 1.0 wt% of DMPA at 365 nm; TriVE mole content a: 0 %, b: 15 %, c: 30 %. Irradiance is 14 mW/cm²; 365-nm filtered light.

Two other highly functional vinyl ester monomers also enhance TMPTA polymerization. Herein, we briefly describe the polymerization kinetics of 8- and 16-functional vinyl esters with TMPTA at a relatively high UV light intensity. The polymerization rate of pure 16VE is comparable to TMPTA as shown in Figure 5. It is interesting that the final conversion of 16TV is almost same as the final conversion for TMPTA. This behavior can be explained by the flexible chain structure of the 16VE monomer. For 8VE, the polymerization rate is slower than for 16VE, but the final conversion is higher due to its lower functionality. Since multifunctional vinyl esters with a wide variety of functionalities can be made using the synthesis described in this paper, it should be possible to create polymer networks with a wide variety of properties.

Vinyl esters rapidly copolymerize with thiols by a two-step free-radical step growth polymerization process due to the high electron density of the vinyl ester double bonds. Figure 6 shows RTIR percent conversion versus time plots for conversion of the trithiol with the triallyl ether (a traditional ene) and TriVE. It is obvious that the rate of polymerization of the 1:1 trithiol/TriVE molar mixture is faster than the 1:1 trithiol/triallyl ether mixture. As with any thiol-ene polymerization, the rate is not inhibited to any great extent by oxygen.^{7,8} The results for the thiol-ene reaction involving TriVE is particularly interesting due to the rapid rate of polymerization and high degree of conversion attained in air and nitrogen.

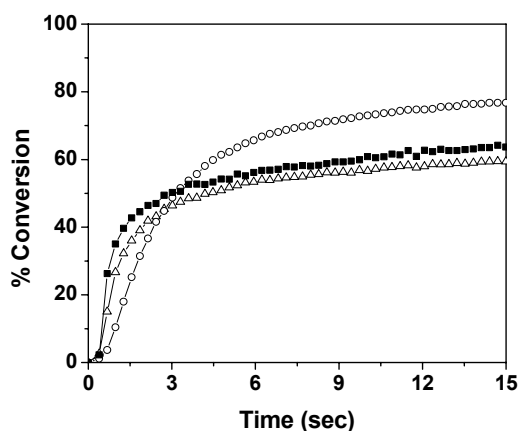


Figure 5. RTIR conversion of (■) TMPTA, (△)16VE, and (○) 8VE with 1.0 wt% DMPA. Irradiance is 200 mW/cm².

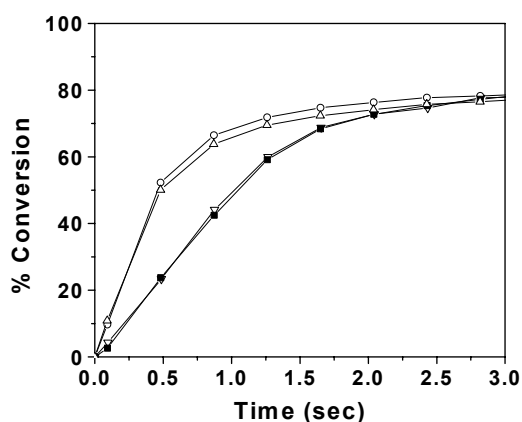


Figure 6. RTIR conversion of 1:1 molar mixture of TriVE/thiol ((○) nitrogen and (△) air) and triallyl ether/thiol ((▽) nitrogen and (■) air) with 1.0 wt% DMPA. Irradiance is 14 mW/cm².

Conclusions

Novel mono- and multifunctional vinyl ester monomers containing thioether groups were synthesized via an amine catalyzed Michael addition reaction between vinyl acrylate and multifunctional thiols. In nitrogen, the vinyl esters exhibit slower polymerization rates than corresponding acrylates. On the other hand, the polymerization rates of the vinyl esters are faster than those of acrylates in air due to significant reduction in oxygen inhibition. The reduced oxygen inhibition results from rapid oxygen consumption via a repetitive hydrogen abstraction/oxygen scavenging reaction involving the α -carbon on the thioether groups. Addition of the vinyl ester to TMPTA results in an enhanced overall double bond conversion in both nitrogen and air. In the early stages of polymerization, the vinyl ester acts as a plasticizer to enhance acrylate conversion. Addition of a trifunctional thiol to the multifunctional vinyl esters results in a very efficient thiol-ene reaction.

Acknowledgements

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