

The Influence of Hydroxyl Groups on Maleimide/Vinyl Ether Photopolymerization and Film Properties

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Abstract

Monomers containing hydroxyl functionalities are known to have an increased rate of polymerization compared to their non-hydroxy homologues. Photopolymerizations of maleimide/vinyl ether mixtures where the vinyl ether (VE) contained hydroxyl groups were performed in a real-time infrared spectrometer. Due to the hydrogen bonding effect, polymerizations at elevated temperatures of hydroxy containing systems were slower than the corresponding mixture at room temperature, as opposed to the homologues, which showed an increased rate. The final film properties are also affected by hydrogen bonding.

Introduction

Over the last few decades, the areas of microelectronics, coatings, and graphic arts have seen a rapid increase in the use of photoinitiated polymerization,¹ primarily because films with good physical properties are produced rapidly through photocuring.² Of course, the structures of the mono- and multifunctional monomers present in a given formulation greatly affect the final properties, as well as the characteristics of the polymerization process such as rate of cure, network structure, and oxygen inhibition. Monomers that could enhance both the physical properties of the resultant material and the speed of the polymerization are of great interest. Maleimides are one such class of monomers that meet this demand in that they can act as both photoinitiator and polymerizable monomer in the same formulation.³⁻⁷ These monomers leave no residual small molecule photoinitiator in the final product, photobleach as they polymerize, can homopolymerize or copolymerize with electron donors, and, because the substitution on the nitrogen can be easily tailored, are extremely adaptable to any formulation.³⁻⁷

In the late 1980s, Decker, *et al.* synthesized several acrylates containing various functional groups including oxazolidines, dioxolanes, oxetanes, and cyclic carbonates in order to study the relationship between reactivity and monomer structure.⁸⁻¹² When compared to conventional acrylate systems, these functionalized acrylates each showed enhanced rates. More recently, the large effect that certain pendent groups can have on acrylate polymerization rates has been corroborated by Jansen¹³⁻¹⁵ and Bowman^{16,17}. The inclusion of urethanes and amides, both of which are capable of hydrogen bonding, produced monomers that exhibited very high polymerization rates at room temperature, but when heated both the rate and the extent of hydrogen bonding decreased.¹⁵ In our lab, the simplest acrylic hydrogen bonding structures available, hydroxyalkyl acrylates, have been shown at room temperature to have curing profiles more reminiscent of multifunctional acrylates, but at elevated temperature, the rates decrease in direct proportion to the extent of hydrogen bonding, most likely due to the fact that in the presence of hydrogen bonding there is a decrease in the rate of termination.¹⁸

Drawing on our backgrounds in hydroxy containing monomers and in maleimides, we herein report the photopolymerization results for copolymerizations of maleimides with vinyl

ethers containing hydroxyl groups. The relative amount of hydrogen bonding in these systems is determined by sample temperature; therefore, the dependence of polymerization rate and hydrogen bonding on temperature is studied.

Experimental

Materials

4-Vinyloxycyclohexane (CVE), 4-vinyloxybutane (BVE), and 4-vinyloxy-1-butanol (HBVE) were obtained from Morflex. BASF provided (4-vinyloxymethyl-cyclohexyl)-methanol (CHMVE). N-(n-propyl)-maleimide (PrMI) was purchased from Lancaster. The chemical structures and acronyms of the materials used are shown in Figure 1.

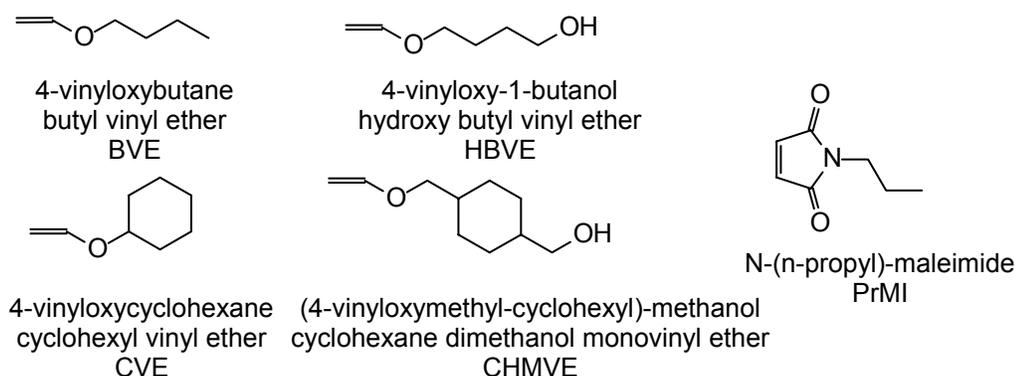


Figure 1. Structures, names, and acronyms for materials used, including common names on which acronyms are based.

Real-Time Fourier Transform Infrared Spectroscopy (RT-FTIR)

A Bruker IFS-88 modified to accommodate horizontal samples was used to take infrared scans in real-time during polymerization. Samples were placed between two polished NaCl plates to inhibit oxygen diffusion and the chamber was purged with nitrogen. The irradiating source was an Oriel lamp system with a 200-Watt high-pressure Hg-Xe bulb. Conversion was determined using the disappearance of characteristic peaks for each species: 1620 cm^{-1} for vinyl ethers and 700 cm^{-1} for maleimides. An independent temperature cell from Harrick Scientific was used to heat the sample with the sample placed between the two salt plates and the seal coated with vacuum grease, then placed in the cell between two o-rings to prevent evaporation.

Results and Discussion

In order to determine the effect of the presence of a hydroxyl functionality on the copolymerization, equimolar mixtures of an aliphatic maleimide, N-(n-propyl)-maleimide (PrMI), with two vinyl ethers, one with an alcohol functionality, (4-vinyloxymethyl-cyclohexyl)-methanol (CHMVE), and one without, 4-vinyloxycyclohexanol (CVE), were prepared. The polymerization was initiated by irradiating the maleimide, and the rate was measured using real-time FTIR at 25°C (Figure 2). The PrMI/CHMVE copolymerization is obviously significantly faster. Also of note is that there is little homopolymerization of the maleimide, *i.e.* the copolymerization dominates.

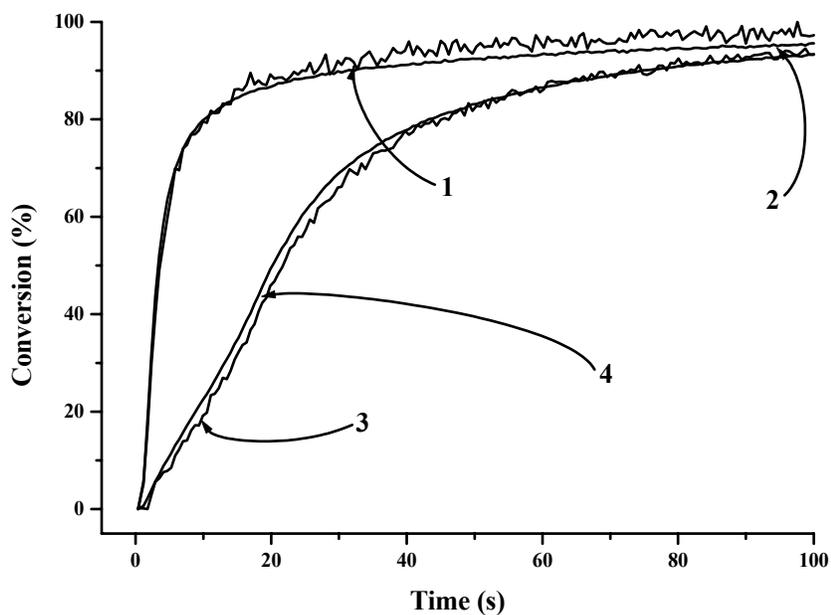


Figure 2. RT-FTIR recordings of copolymerization of 1:1 molar mixtures of PrMI/VE using a high-pressure Hg-Xe lamp. Irradiance $\cong 275 \text{ mW/cm}^2$. Mixtures were sandwiched between two NaCl plates. (1) MI in PrMI/CHMVE mixture, (2) Conv. of VE in PrMI/CHMVE mixture, (3) MI in PrMI/CVE mixture, (4) VE in PrMI/CVE mixture.

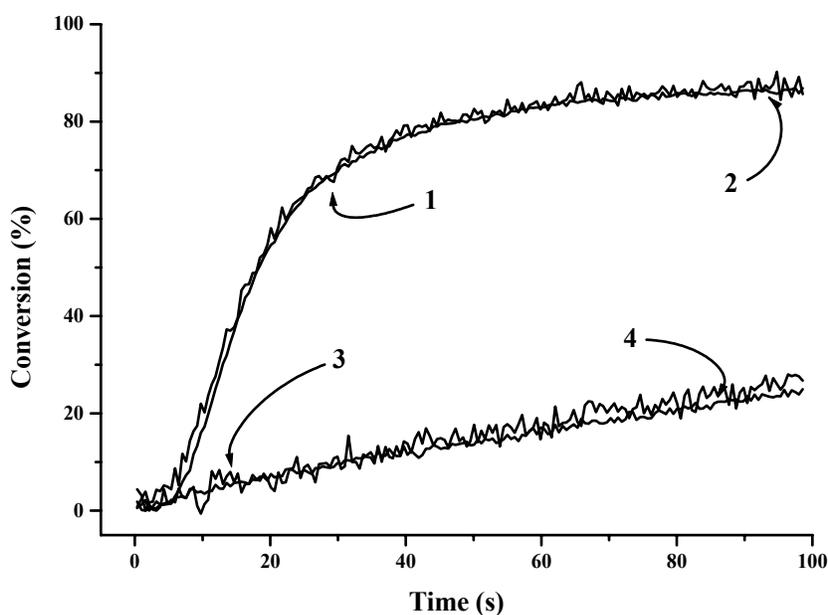


Figure 3. RT-FTIR recordings of copolymerization of 1:1 molar mixtures of PrMI/VE using a high-pressure Hg-Xe lamp. Irradiance $\cong 275 \text{ mW/cm}^2$. Mixtures were sandwiched between two NaCl plates. (1) MI in PrMI/HBVE mixture, (2) VE in PrMI/HBVE mixture, (3) MI in PrMI/BVE mixture, (4) VE in PrMI/BVE mixture.

Unfortunately, CHMVE and CVE are not exact homologues, nor are the homologues for either readily available. This causes a slight problem because maleimide photoinitiation in the presence of a vinyl ether involves an electron/proton transfer process from the α -carbon of the ether. The resulting radical when CVE is the ether is more stable than when CHMVE is used because there is a secondary carbon in CVE, leading to differences in rate of initiation for the two copolymerizations. Therefore, copolymerizations of PrMI with butyl vinyl ether (BVE) and hydroxy butyl vinyl ether (HBVE) were carried out (Figure 3). When HBVE is used there is an even more marked increase in rate than for CHMVE. These polymerizations exhibit nearly a one-to-one copolymerization, which is the case for all the MI/VE copolymerizations reported, so in the remainder of the Figures only the conversion of the maleimide will be shown.

Because the inherent reactivity of a double bond should not be affected by the presence of an alcohol group, some other mechanism must be responsible for the enhanced rates. Both hydrogen bonding and chain transfer to the carbon next to the hydroxyl group have been proposed as possible explanations for rate enhancement in related acrylate systems.^{16,17} If hydrogen bonding is the main factor, an increase in temperature would lead to decreased rates because the extent of hydrogen bonding would decrease at the higher temperatures. To determine the effect that temperature has, polymerizations of the equimolar mixtures of PrMI with the four vinyl ethers were performed at room temperature and at 100°C (Figures 4-7).

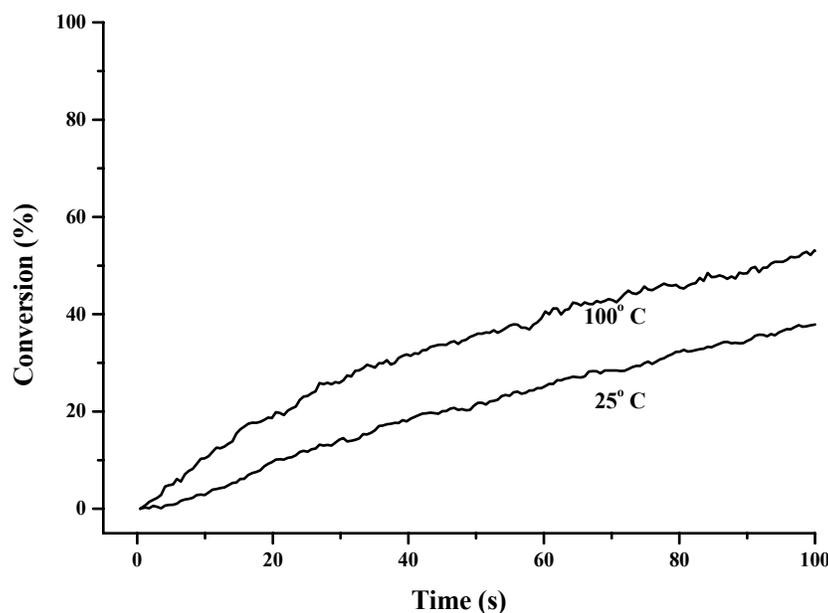


Figure 4. RT-FTIR recordings of copolymerization of 1:1 molar mixtures of PrMI/CVE using a high-pressure Hg-Xe lamp. Irradiance $\cong 275 \text{ mW/cm}^2$. Mixtures were sandwiched between two NaCl plates. Polymerized at 25°C and 100°C.

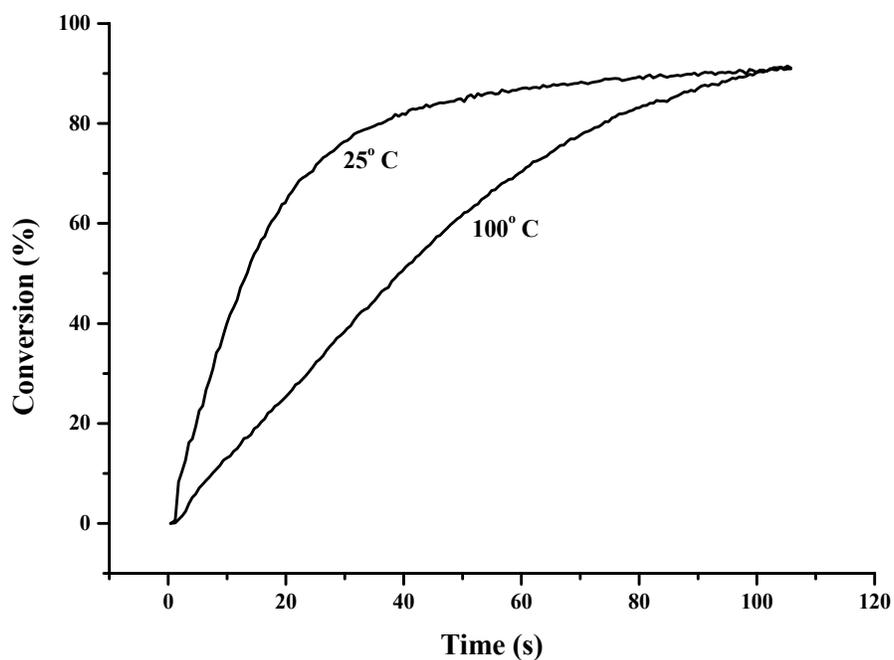


Figure 5. RT-FTIR recordings of copolymerization of 1:1 molar mixtures of PrMI/CHMVE using a high-pressure Hg-Xe lamp. Irradiance $\cong 275 \text{ mW/cm}^2$. Mixtures were sandwiched between two NaCl plates. Polymerized at 25°C and 100°C.

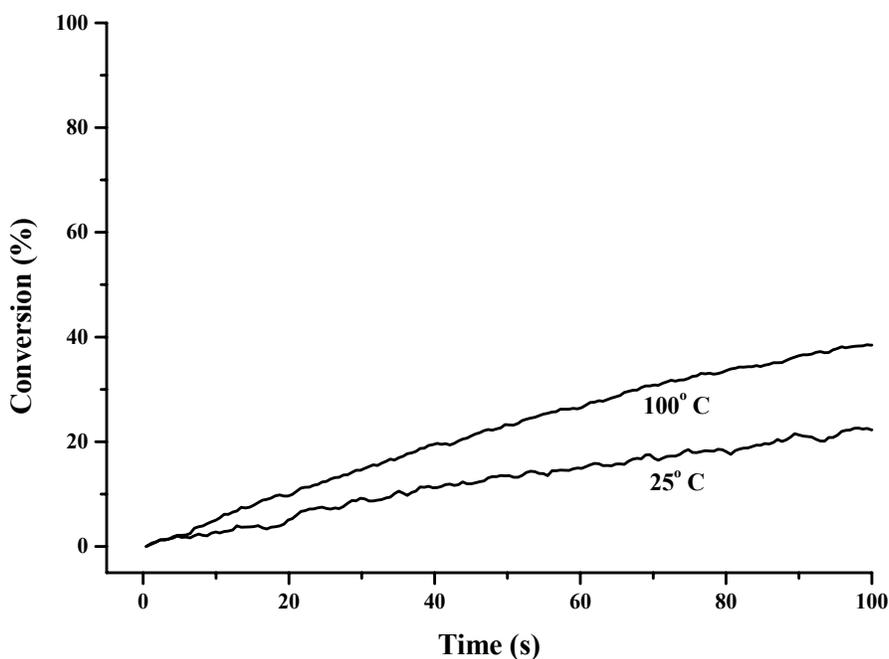


Figure 6. RT-FTIR recordings of copolymerization of 1:1 molar mixtures of PrMI/BVE using a high-pressure Hg-Xe lamp. Irradiance $\cong 275 \text{ mW/cm}^2$. Mixtures were sandwiched between two NaCl plates. Polymerized at 25°C and 100°C.

Systems without a hydroxy functionality, PrMI/CVE and PrMI/BVE (Figures 4 and 6, respectively), which no enhanced rate at room temperature, proceed faster with an increase in temperature, as would be expected for any “typical” system. As seen in Figures 5 and 7, however, at elevated temperature the PrMI/CHMVE and PrMI/HBVE mixtures polymerize slower, though still faster than the non-hydroxy counterparts.

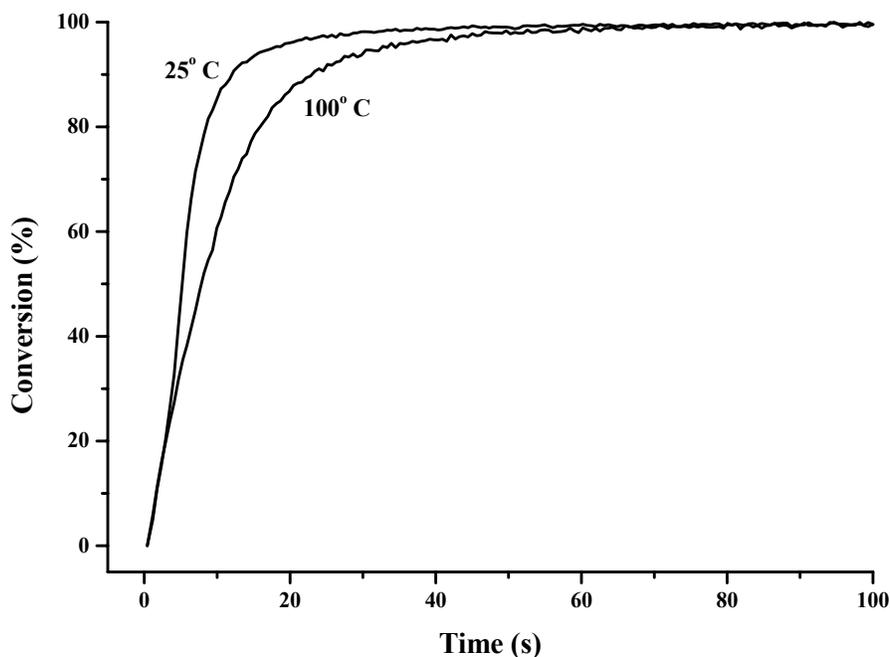


Figure 7. RT-FTIR recordings of copolymerization of 1:1 molar mixtures of PrMI/HBVE using a high-pressure Hg-Xe lamp. Irradiance $\cong 275 \text{ mW/cm}^2$. Mixtures were sandwiched between two NaCl plates. Polymerized at 25°C and 100°C.

The main mechanism of rate enhancement seems to be hydrogen bonding as opposed to chain transfer, as evidenced by the fact that the rate decreases in hydroxy containing monomers with increasing temperature. Dimeric aggregate species can occur through intermolecular hydrogen bonding¹⁹⁻²¹ by either hydroxyl-hydroxyl associations (Figure 8a) or hydroxyl-carbonyl associations (Figure 8b), or even larger aggregates can be produced (Figure 8c). Monomer associations can greatly affect polymerization rates as shown in our previous work with acrylates.¹⁸ Interestingly, maleimide/vinyl ether polymerizations involve two comonomers either of which can contain an alcohol functionality.

A preliminary study of films made using these monomer systems shows that mixtures containing a hydroxyl functionality have much better adhesion to a glass substrate. Further film studies will be conducted to determine the extent of property enhancements due to hydrogen bonding in these polymers.

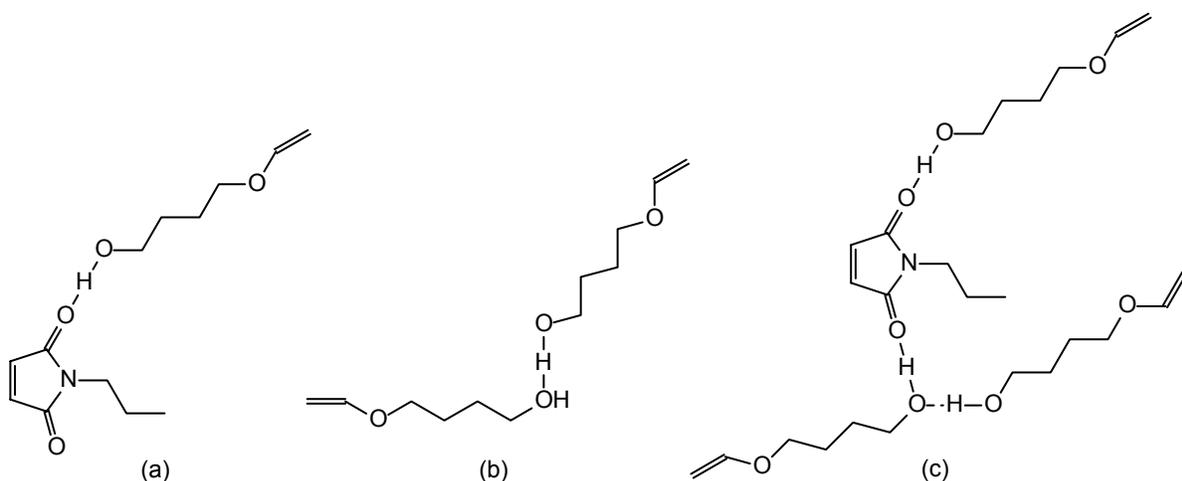


Figure 8. Possible hydrogen bonding in a PrMI/HBVE system.

Conclusions

The role of hydrogen bonding in the photopolymerization of hydroxy containing maleimide/vinyl ether systems has been investigated. Comonomer systems which contain a hydroxyl functionality have been shown to proceed at higher rates than those containing no alcohol groups. Both the degree of hydrogen bonding and the rates of polymerization decrease when the temperature is raised, unlike systems where no hydrogen bonding is possible. Hydrogen bonding also has an effect on the properties of the films produced from the copolymerization of the vinyl ether and maleimide: hardness and adhesion are affected by the hydrogen bonding.

Acknowledgments

We acknowledge Fusion UV Systems, Inc. and Albemarle Corporation for assistance in this research.

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