

# Influence of Structure on Photocuring Rate of Ultrafast Monofunctional Diluents.

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## Abstract

The relationship between polymerization of hydroxyalkyl acrylates and chemical structure has been investigated by examination of aggregation (orientation) of monomer and polymer induced by hydrogen bonding. The presence of the OH group significantly enhances polymerization rate of hydroxyalkyl acrylates. Interestingly, these monomers show almost the same curing rate as multifunctional monomers. The relative degree of hydrogen bonding is proportional to the rate of polymerization. This study suggests a rationale for the design of monofunctional diluents for use in UV formulations that will lead to ultrafast polymerization rates and generation of films with unique physical and mechanical properties

## Introduction

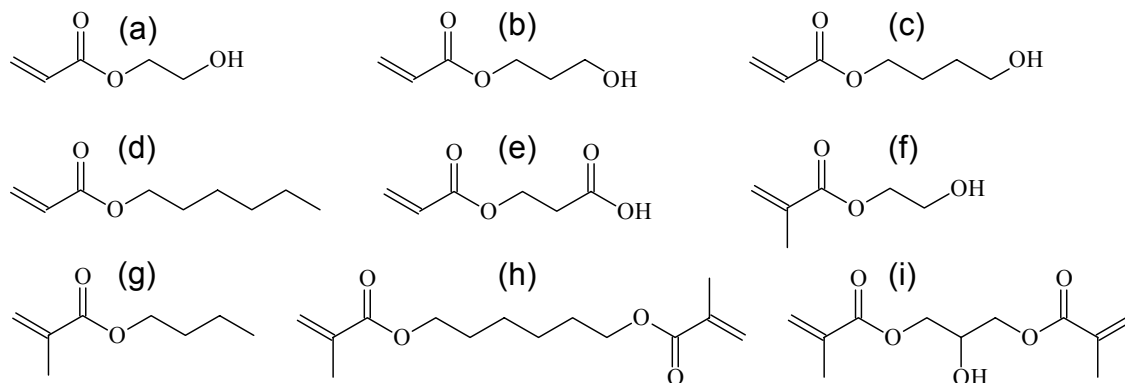
One of the most important advantages in photocuring technology is the simple production of crosslinked films with excellent physical properties and rapid speed.<sup>1,2</sup> Due to the importance of curing speed in photocuring, acrylate monomers have been dominantly used due to their high reactivity compared to other free-radical monomers. Polymerization rate can be influenced by structure and specific functional groups present in monomers. While extensive research has been performed to understand the relationship between monomer structure and the properties of cured films, more research investigating the effect of monomer structure on polymerization rate is required to understand polymerization kinetics of various monomers with different structure and photocuring processes containing these monomers.

The effect of monomer structure on polymerization rate was initially investigated in the late 1980s and 1990s by Decker *et al.* using several model monofunctional acrylates with various pendant groups ranging from cyclic carbonates to oxetanes.<sup>3,4</sup> Each of these modified acrylates exhibited much greater polymerization rates than observed for conventional alkylacrylates. Recently, Jansen *et al.*<sup>5,6</sup> and Bowman *et al.*<sup>7,8</sup> have performed more extensive research on various acrylate monomers. Some proposed mechanisms behind rapid polymerizations involve hydrogen abstraction reactions during polymerization resulting in crosslinked network, dipole moment of monomers, and monomer organization through molecular interactions.<sup>3-8</sup>

Herein, we report polymerization rates for hydroxyalkyl acrylates, hydroxylalkyl methacrylate, and several monomers which can form hydrogen bonds between monomers as well as polymers. These monomers are much simpler in structure than the monomers studied previously, and allow for continuous monitoring of hydrogen bonding during polymerization. The relative degree of hydrogen bonding before, during, and after polymerization is determined as a function of temperature. The effect of hydrogen bonding on polymerization kinetics is also examined.

## Experimental section

**Materials.** Hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), hydroxybutyl acrylate (HBA), hexyl acrylate (HA), 2-carboxyethyl acrylate (CEA), hydroxyethyl methacrylate (HEMA), butylmethacrylate (BMA), 1,6-hexanediol dimethacrylate (HDDMA), and glycerol dimethacrylate (GDMA) were purchased from Aldrich Chemical Co. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was obtained from Ciba Specialty Chemicals. The chemical structures of the monomers used in this study are given in Figure 1.



**Figure 1.** Chemical structure of (a) HEA, (b) HPA, (c) HBA, (d) HA, (e) CEA, (f) HEMA, (g) BMA, (h) HDDMA, and (i) GDMA.

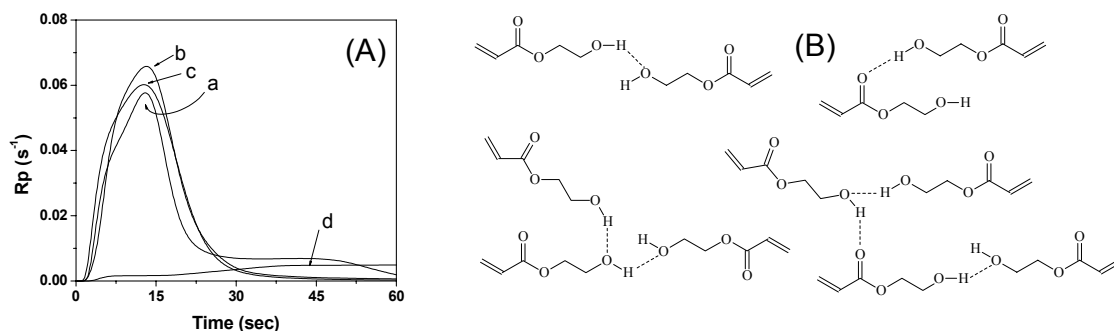
**The degree of hydrogen bonding.** The degree of hydrogen bonding was measured as a function of temperature using FTIR spectroscopy. Each IR spectrum was recorded after equilibrating samples for at least 2 minutes at the desired temperature. The temperature was controlled with an accuracy of  $\pm 1^\circ\text{C}$ . The relative fraction of hydrogen bonded hydroxyl groups was obtained by integrating the total area of the OH stretching peak between  $3100\text{ cm}^{-1}$  and  $3700\text{ cm}^{-1}$ . To calculate the relative fraction of hydrogen bonded carbonyl groups, a least-squares curve fitting procedure was performed using a Gaussian-Lorentzian mixture (50/50) function. Then the carbonyl peaks were deconvoluted to allow assignment of free- and hydrogen bonded peaks with maxima at  $1726$  and  $1704\text{ cm}^{-1}$ , respectively. The ratio of the hydrogen bonded carbonyl peak intensity to the sum of the hydrogen bonded plus the non-hydrogen bonded carbonyl peak intensities is used as a quantitative evaluation of the extent of hydroxyl-carbonyl hydrogen bonding.

**Polymerization kinetics.** The kinetic profiles of the UV-induced polymerizations were studied using real-time FTIR and photo-DSC. Infrared spectra were recorded on a modified Bruker 88 spectrometer designed to allow light to impinge on a horizontal sample using a fiber-optic cable. The real-time FTIR setup has been illustrated elsewhere.<sup>9</sup> Monomer samples with thickness between  $10$  to  $15\ \mu\text{m}$  were placed between two sodium chloride plates. A 200 Watt high pressure mercury xenon lamp (ScienceTech Co.) served as the light source to induce the free-radical polymerization. The infrared absorption spectra were obtained with a MCT detector under continuous UV irradiation using a temperature controlled stage to determine temperature. The concentration of acrylate double bonds during polymerization was monitored at  $812\text{ cm}^{-1}$ . The photo-DSC, used to obtain polymerization exotherms at various temperatures, was based on a Perkin-Elmer DSC7 modified with a shuttered medium-pressure mercury lamp. Sample pans were crimped, and  $2.0\ \mu\text{L}$  samples were placed in the pan to give

film thicknesses of approximately 150~200  $\mu\text{m}$ . The samples were allowed to equilibrate at different temperatures for 3 minutes to get equilibrium sample temperature before irradiation.

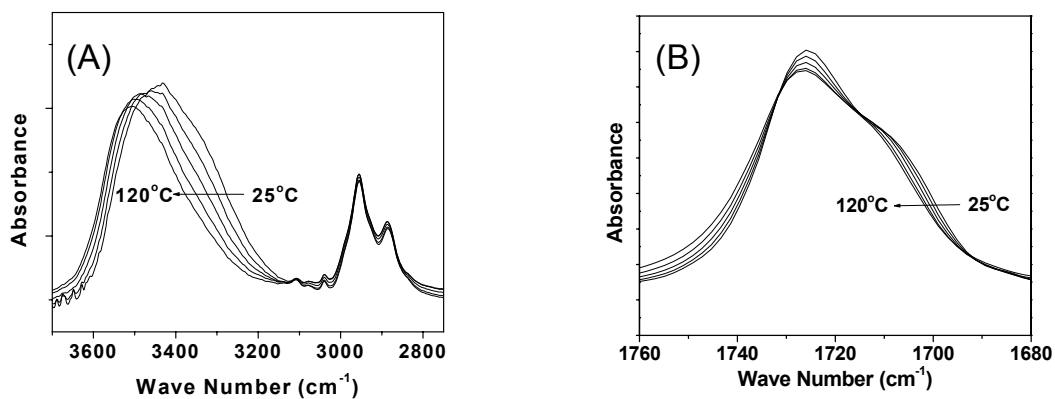
## Results and Discussion

As mentioned in the introduction, some acrylate monomers having certain functional groups show much faster polymerization rates than other acrylates. The acrylate monomers with hydroxyl and acid groups which are capable of forming hydrogen bonding also show abnormally fast polymerization rate. Figure 1 shows polymerization rates of three hydroxylalkyl acrylates along with hexyl acrylate at 25  $^{\circ}\text{C}$ . Even though all of them are monofunctional acrylate monomers, it is quite obvious that the hydroxyalkyl acrylates polymerize much faster than HA. Maximum polymerization rates observed for hydroxyalkyl acrylates are approximately 10 times higher than that of HA. Since the presence of hydroxyl groups does not affect the intrinsic chemical nature of the acrylate double bond, it is reasonable to assume that hydrogen bonding would be responsible for the significantly enhanced polymerization rates. The presence of hydroxyl groups in molecules allows the formation of multimeric aggregated species by hydrogen bonding with the different associations.<sup>10,11</sup> Hydrogen bonds are expected to have bond strengths on the order of 20 kJ/mol.<sup>10,12</sup> The hydrogen bonding in hydroxyalkyl acrylates could occur between hydroxyl groups or between hydroxyl and carbonyl groups as shown in Figure 2(B).



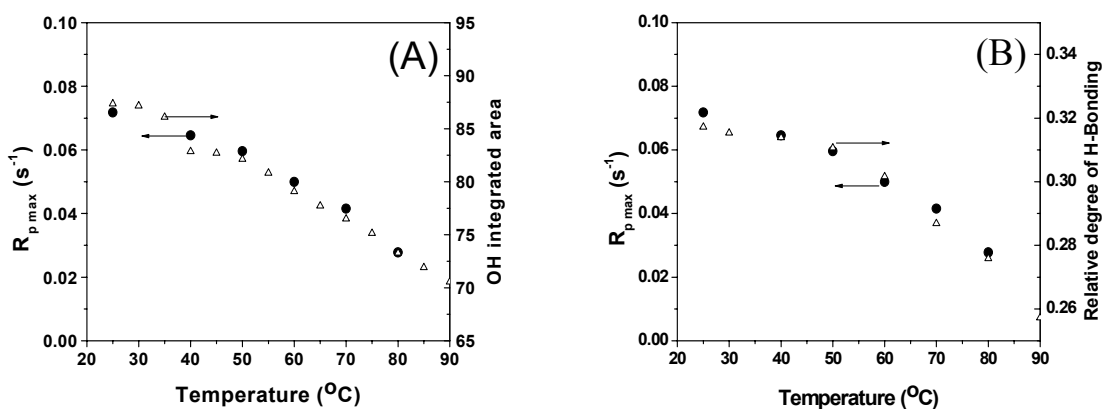
**Figure 2.** (A)  $R_p$  versus time plot for hydroxylalkyl acrylates; (a) HEA, (b) HPA, and (c) HBA, and (d) HA at 25 $^{\circ}\text{C}$  with 1 wt% DMPA. Light intensity is 1.05  $\text{mW}/\text{cm}^2$  and (B) Possible hydrogen bonding in hydroxyalkyl acrylates.

A simple way to study the effect of hydrogen bonding on polymerization rate is investigating relationships between the effect of temperature on hydrogen bonding and the effect of temperature on the polymerization rate. Hydrogen bonding typically decreases with increasing temperature. In Figure 3, the temperature dependence of hydrogen bonding is shown through examination of the infrared spectra of hydroxyl and carbonyl peaks at several temperatures between 25  $^{\circ}\text{C}$  and 120  $^{\circ}\text{C}$ . As the temperature increases, IR spectral bands of the hydroxyl groups change significantly. The OH stretching peak maximum at 3440  $\text{cm}^{-1}$  is shifted to 3510  $\text{cm}^{-1}$  and also, the shoulder observed at 3350  $\text{cm}^{-1}$  disappears at elevated temperatures. In addition, the shoulder peak at 1704-1710  $\text{cm}^{-1}$  due to hydrogen bonded C=O decreases with increasing temperature. From IR spectrum changes in Figure 6, it is obvious that monomer association resulting from hydrogen bonding decreases with increasing temperature.



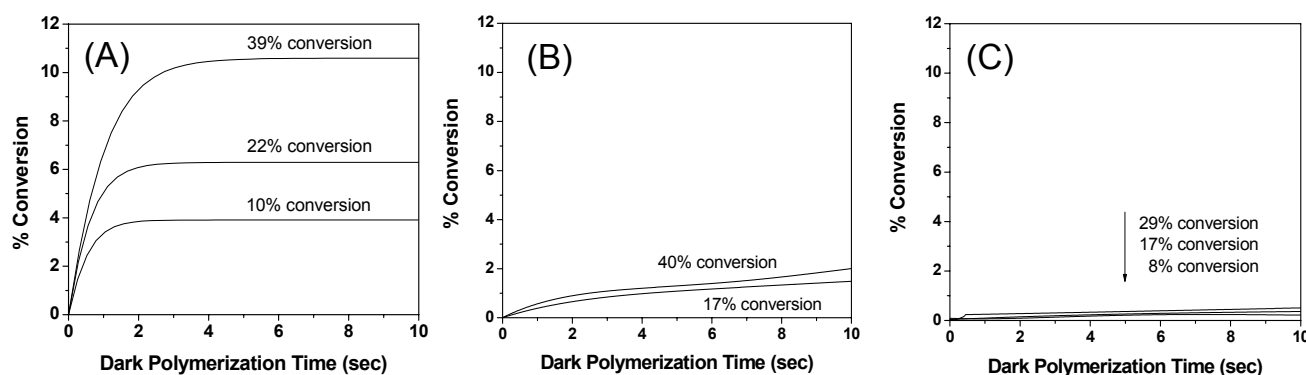
**Figure 3.** IR spectra focusing on the (A) O-H stretch and (B) the carbonyl peak of HEA as a function of temperature.

By obtaining the change of the degree of hydrogen bonding from the results in Figure 3 and comparing with the changes of polymerization rates at different temperatures, it is possible to understand the effect of hydrogen bonding on the polymerization rate. Figure 4 shows a correlation between the relative degree of hydrogen bonding (hydroxyl and carbonyl groups) and the peak maximum polymerization rate ( $R_{p\ max}$ ) as a function of temperature. It is obvious that both polymerization rates and the relative degree of hydrogen bonding decrease simultaneously. It should be noted that the polymerization rates of mono- and multifunctional acrylates such as 1,6-hexanediol diacrylate and HA increase little bit with increasing temperature. Therefore, it is reasonable to conclude that much faster polymerization rates are due to hydrogen bonding from aggregation of monomers. Association of multiple monomers by strong hydrogen bonds could produce pseudo-multifunctional monomers as depicted in Figure 2B. Also, it is expected that strong hydrogen bonds would also form between polymers produced during polymerization process. The hydrogen bonds between monomers as well as polymers result in a polymerization medium with enhanced viscosity. Since covalently bonded multifunctional monomers polymerize much faster than monofunctional monomers from the very initial stages of polymerization due primarily to reduction in termination rate constants,<sup>26-30</sup> it is expected that the hydrogen bonds of hydroxyalkyl acrylate reduce termination rate constants resulting in faster polymerization.



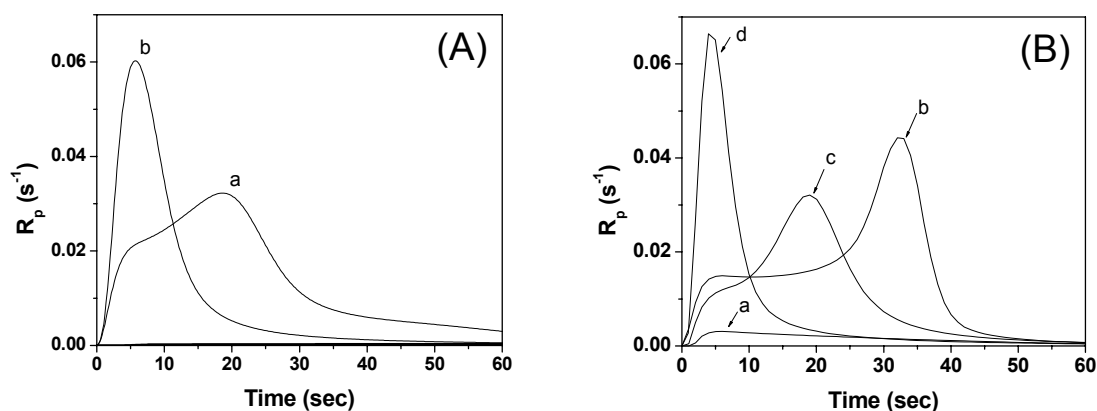
**Figure 4.** Relationships between polymerization rate of HEA and hydrogen bonding of (a) hydroxyl group and (b) carbonyl group and as a function of temperature.

Investigating termination kinetics of hydroxyalkyl acrylates provides further understanding and evidence for the effect of hydrogen bonds on polymerization rate. Termination kinetics can be examined by investigating the dark polymerization, polymerization after shuttering the UV light at various conversions. Conversion during the dark polymerization is closely related to the termination kinetics of the polymerization system. Limited mobility of growing polymer chains by crosslinks and/or molecular interactions results in higher conversion during dark polymerization due to diffusion controlled termination kinetics. Figure 5 shows the dark polymerization behavior of HEA both at 25 °C and 80 °C, along with HA at 25 °C. The dark conversion of HEA at 25°C is much greater than that obtained at 80°C. After about 40% conversion, dark conversion of HEA at 25 °C is approximately 11% while it is only about 2% at 80 °C. This behavior is as would be expected based on the results already discussed. At higher temperature, dissociation of hydrogen bonds results in enhanced termination due mainly to an increase in diffusion. The dark conversion during polymerization of HA which does not form hydrogen bonds is negligible due to fast termination in the absence of hydrogen bonding. Therefore, increased viscosity and limited chain mobility by hydrogen bonds between molecules reduce termination rates resulting in fast polymerization.



**Figure 5.** Dark conversions of HEA and HA after various conversions for HEA at (A) 25 °C and (B) 80°C, and (c) for HA at 25°C.

It is also reasonable to expect that mono- and multifunctional monomers containing functional groups which can form hydrogen bonds and/or strong interactions should show fast polymerization. We have also investigated polymerization of several acrylates and methacrylates with hydroxyl and acid groups including hydroxylalkyl methacrylates and 2-carboxylethyl acrylate. Their polymerization rates are depicted in Figure 6 and compared with other acrylates and methacrylates. CEA polymerizes much faster than HEA as shown in Figure 6A. It is expected that stronger hydrogen bonds between acids group than those between hydroxyl groups<sup>10</sup> causes more strictly hindered mobility of polymer chains resulting in reduced termination. The hydroxyalkyl methacrylates also have significantly enhanced polymerization rates compared to BMA (alkylacrylate) which have no hydrogen bonding. The maximum polymerization rate of HEMA is faster than HDDMA. However, HDDMA shows the maximum polymerization rate earlier than HEMA because HDDMA, difunctional monomer, should form crosslinked microgel at the very initial stage of polymerization upon irradiation compared to HEMA which forms physically crosslinked networks. Interestingly, GDMA, difunctional methacrylate with a hydroxyl group, polymerizes much faster than HDDMA and HEMA probably due to forming both chemically and physically crosslinked networks.



**Figure 6.**  $R_p$  versus time as determined by photo-DSC for (A) acrylates (a: HEA, b: CEA) and (B) methacrylates (a: BMA, b: HEMA, c: HDDMA, and d: GDMA) with 1 wt% DMPA at 25°C. Irradiance is 1.43 mW/cm<sup>2</sup> for (A) and 79 mW/cm<sup>2</sup> for (B).

## Conclusions

The effect of hydrogen bonds on polymerizations of several acrylates and methacrylates have been investigated by correlating the extent of hydrogen bonding with polymerization rates. The degree of hydrogen bonding and the rate of polymerization are directly related. Both hydrogen bonding and the polymerization rate decrease with increasing temperature, unlike conventional acrylate polymerization. Hydrogen bonding significantly influences on the termination process by reducing polymer radical mobility. Dark polymerization results strongly support reduced termination rate in the presence of hydrogen bonds. Stronger hydrogen bonding results in more dramatic effect on polymerization as explained with CEA and GDMA.

## Acknowledgements

The authors acknowledge Fusion UV Systems, Inc. for funding this work.

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