

# Photopolymerization of Acid Containing Monomers: Real-Time Monitoring of Polymerization Rates

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**ABSTRACT:** The relationship between the polymerization rate of various acrylates and methacrylates containing acid groups and their ability to hydrogen bond has been investigated by real-time infrared spectroscopy. The polymerization rate dependence on temperature of the acid-based acrylates and methacrylates is reduced compared to traditional (meth)acrylates with no groups capable of hydrogen bonding. For two of the acid containing monomers, polymerization rates actually decreased with an increase in temperature.

## Introduction

Acrylates and methacrylates have been widely used in radiation curable resins due to their propensity to undergo free-radical photopolymerization at very rapid rates. The relationship between monomer structure and reactivity was investigated extensively in the late 1980s and 1990s by Decker et al.<sup>1–5</sup> using several model monofunctional acrylates with various pendant groups ranging from cyclic carbonates and oxazolidones to dioxolanes and oxetanes. Each of these modified acrylates exhibited much greater polymerization rates than observed for conventional alkyl acrylates. Recently, more extensive research has been performed on a wide variety of acrylate monomers by Jansen et al.<sup>6</sup> and Bowman et al.<sup>7,8</sup> Jansen et al.<sup>6</sup> found that acrylates with urethane and amide side groups capable of hydrogen bonding exhibited very fast polymerization rates at room temperature. However, at high temperatures the rates decreased along with a reduction in the extent of hydrogen bonding measured by infrared analysis. More recently, the polymerization of hydroxyalkyl acrylates has been investigated by examining the extent of hydrogen bonding before and during polymerization.<sup>9</sup> It was concluded that extensive hydrogen bonding leads to dimeric-type species which function as “pseudo diacrylates” accompanied by an enhanced polymerization rate as a result of a heterogeneous polymerization process and the resultant reduced termination rate. In the present study, we extend our previous investigation of hydroxyl acrylates to analysis of the polymerization rate of several acrylates containing acid groups and their ability to hydrogen bond. Since acid containing acrylates and methacrylates are used in a variety of photocurable systems to modify properties and promote adhesion, it is important to attain basic kinetic information about their polymerization in bulk.

## Experimental Section

**Materials.** Acrylic acid (AA), 2-carboxyethyl acrylate ( $\beta$ -CEA), methacrylic acid (MAA), and ethylene glycol methacrylate phos-

phate (EGMAP) were obtained from Aldrich Chemical Co. and used as received. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was obtained from Ciba Specialty Chemical Co.

**Methods.** Real-time infrared (RTIR) spectra were recorded on a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200 W, high-pressure mercury–xenon bulb was channeled through an electric shutter and fiber-optic cable into the sample chamber. Photoreactions were conducted by sandwiching samples between two sodium chloride salt plates at a thickness of  $\sim 20\ \mu\text{m}$ . The salt plate edges were sealed with vacuum grease to suppress monomer evaporation at higher temperatures, and samples were purged for 10 min in dry air before irradiation. Light intensity measurements were made with an IL-1400 calibrated radiometer from International Light. Infrared absorption spectra were obtained under continuous UV irradiation at a scanning rate of 5 scans/s. The unfiltered light intensity at full arc was  $187\ \text{mW}/\text{cm}^2$ . All samples contained 1 wt % photoinitiator [2,2-dimethoxy-2-phenylacetophenone (DMPA)].

The characteristic infrared absorbance bands used to monitor the disappearance of the reactant and monomer during the photoreactions were as follows: acrylic acid ( $1636\ \text{cm}^{-1}$ ), 2-carboxyethyl acrylate ( $1636\ \text{cm}^{-1}$ ), butyl acrylate ( $812\ \text{cm}^{-1}$ ), methacrylic acid ( $1007\ \text{cm}^{-1}$ ), methyl methacrylate ( $1636\ \text{cm}^{-1}$ ), and ethylene glycol methacrylate phosphate ( $817\ \text{cm}^{-1}$ ). The reactant conversions, calculated from the change in the peak area with time, have an approximate error of  $\pm 2\%$ .

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  $150\text{--}200\ \mu\text{m}$ . 1 wt % photoinitiator (DMPA) was used in all samples. The light intensity used was  $0.73\ \text{mW}/\text{cm}^2$ . The calculation method for polymerization rate has been described elsewhere.<sup>10</sup>

The degree of hydrogen bonding of the acrylic acid and methacrylic acid (AA and MAA) was measured as a function of temperature using FTIR spectroscopy. The temperature was controlled with an accuracy of  $\pm 1\ ^\circ\text{C}$ . Each IR spectrum was recorded after equilibrating for at least 2 min at the desired temperature. To calculate the relative fraction of hydrogen-bonded carbonyl groups, a multipeak curve fitting procedure was performed using a Lorentzian function in Origin software. Then the carbonyl peaks were deconvoluted to allow assignment of free and hydrogen-bonded peaks with maxima at  $1733$  and  $1704\ \text{cm}^{-1}$ , respectively (shown in Figure 1).

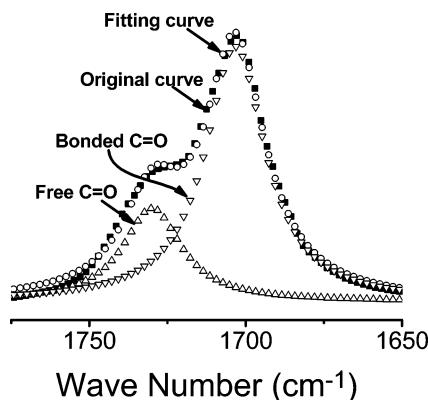
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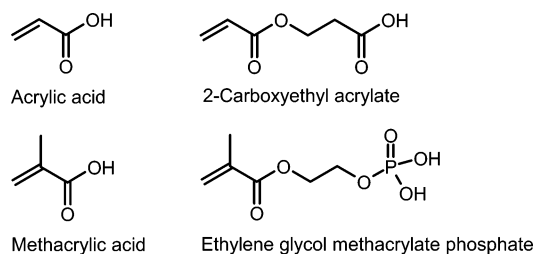
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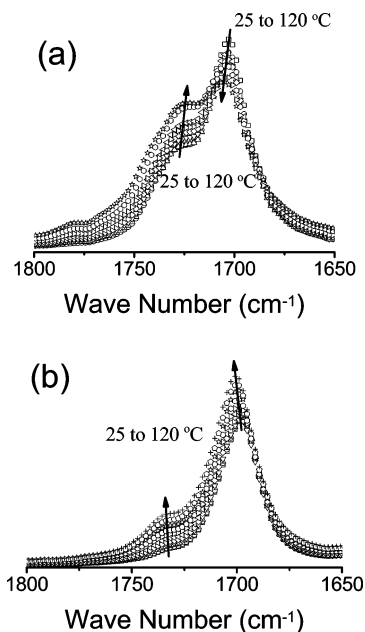
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**Figure 1.** Deconvolution of carbonyl group: (■) original curve, (○) fitting curve, (Δ) free carbonyl, (▽) bonded carbonyl.



**Figure 2.** Chemical structure of monomers.

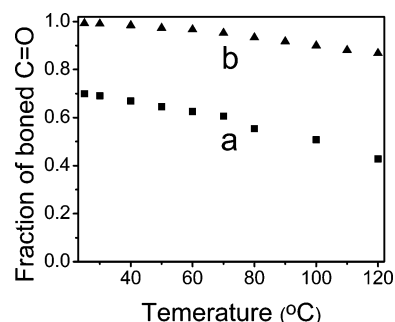


**Figure 3.** FTIR spectra change of carbonyl stretching regions of (a) acrylic acid and (b) methacrylic acid as a function of temperature.

## Results and Discussion

The four acid based acrylates and methacrylates used in this study are shown in Figure 2. Two, acrylic acid and methacrylic acid, have acid groups alpha to a conjugated carbon-carbon double bond, while the other two acid groups are attached to saturated aliphatic structures.

As already pointed out in the Introduction, hydrogen bonding is an important parameter that can affect system mobility and organization during polymerization resulting in enhanced rates due to formation of dimer like species. As observed in Figure 3a for acrylic acid, as temperature increases, the infrared peak at 1704  $\text{cm}^{-1}$  (hydrogen bonded C=O) decreases continuously. It is well-known that increasing temperature leads to the

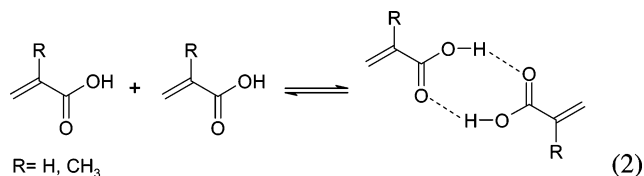


**Figure 4.** Bonded carbonyl fraction for (a) acrylic acid and (b) methacrylic acid as a function of temperature.

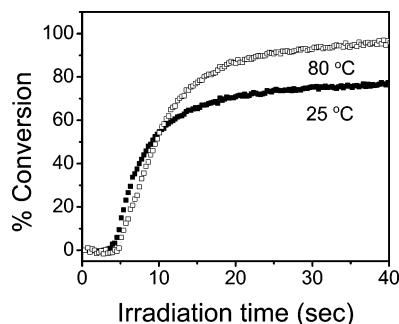
dissociation of hydrogen bonds, resulting in stronger valence bonding.<sup>11</sup> In Figure 3b, although it is obvious that both peaks at 1698  $\text{cm}^{-1}$  (hydrogen bonded C=O) and 1733  $\text{cm}^{-1}$  (free C=O) increase as temperature increases, the ratio of hydrogen-bonded to free C=O in methacrylic acid actually decreases. From a simple analysis of Figure 3a,b, it is thus reasonable to conclude that monomer association resulting from hydrogen bonding decreases with increasing temperature. A more quantitative assessment is obtained by calculating the fraction of hydrogen bonding in each system as follows. In a system where hydrogen bonding occurs between two molecules of the same species, the fraction of hydrogen bonding is given by eq 1.<sup>12,13</sup>

$$X_{\text{bonded C=O}} = \frac{1}{1 + 1.2(A_{\text{free C=O}}/A_{\text{bonded C=O}})} \quad (1)$$

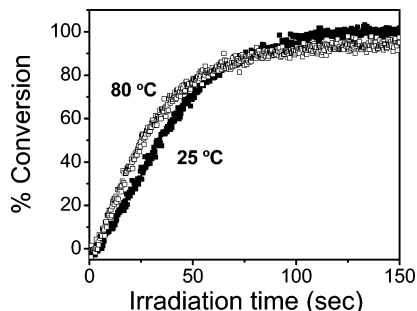
where  $A_{\text{free C=O}}$  and  $A_{\text{bonded C=O}}$  are respectively the absorbance of free and hydrogen-bonded carbonyl groups (C=O). Applying eq 1 to an analysis of the spectra in Figure 3, the fraction of hydrogen-bonded carbonyl groups as a function of temperature is obtained. As seen in Figure 4, at 25 °C, about 70% of the carbonyl groups are hydrogen-bonded for acrylic acid while for methacrylic acid almost 100% of the carbonyl groups are hydrogen-bonded. As shown in Figure 4, in both cases as temperature increases hydrogen bonding decreases. Although other hydrogen-bonded species may be present, traditionally<sup>14</sup> hydrogen bonding of carboxylic acids has been primarily attributed to dimer type species, as illustrated for acrylic acid and methacrylic acid in eq 2.



To probe the effect of hydrogen bonding on the polymerization of both acrylic and methacrylic acid, real-time infrared (RTIR) analysis of the infrared peaks of the acrylate/methacrylate bands were followed as a function of exposure time to a high-pressure mercury lamp source. The decrease in the infrared absorption bands with time was used to determine the corresponding percent conversion vs time plots. In Figure 5, it is quite clear that the rate of polymerization of acrylic acid does not increase with an increase in temperature from 25 to 80 °C, and in fact there is actually a modest decrease in rate with temperature (calculated from the maximum slope of the conversion vs time plots) from 13.8 to 10.2  $\text{s}^{-1}$ . For comparison, butyl acrylate, in addition to polymerizing much slower than acrylic acid, experiences a measurable increase in rate (1.6  $\text{s}^{-1}$  at 25 °C to 2.2  $\text{s}^{-1}$  at 80 °C) with temperature as shown in Figure 6.



**Figure 5.** Conversion vs time as determined via RTIR for acrylic acid at different temperatures. Light intensity:  $18.7 \text{ mW/cm}^2$  with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

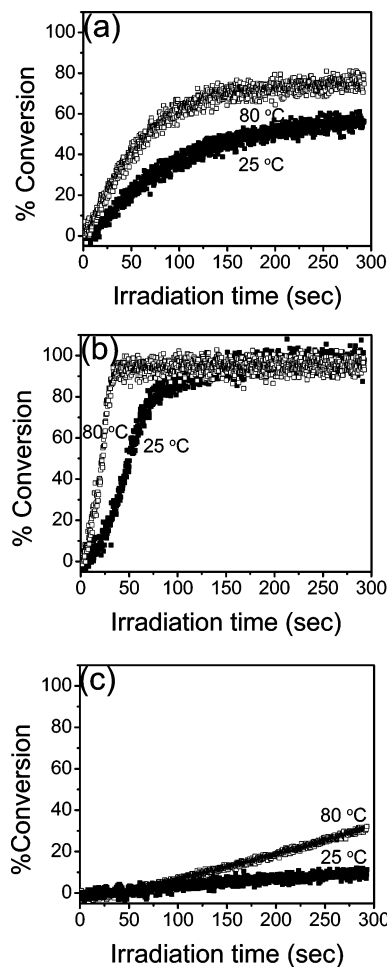


**Figure 6.** Conversion vs time as determined via RTIR for butyl acrylate at different temperatures. Light intensity:  $18.7 \text{ mW/cm}^2$  with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

The decrease in acrylic acid polymerization rate with temperature is in full agreement with the results in Figure 4 for acrylic acid, which indicated a substantial decrease in hydrogen bonding with temperature.

Results obtained for methacrylic acid shown in Figure 7a,b show that although the rates increase with temperature, the increases are nonetheless moderate, from  $0.5 \text{ s}^{-1}$  at  $25^\circ\text{C}$  to  $0.8 \text{ s}^{-1}$  at  $80^\circ\text{C}$  for methacrylic acid and from  $1.6 \text{ s}^{-1}$  at  $25^\circ\text{C}$  to  $3.6 \text{ s}^{-1}$  at  $80^\circ\text{C}$  for ethylene glycol methacrylate phosphate. For comparison, results are shown in Figure 7c for methyl methacrylate at  $25^\circ\text{C}$  and  $80^\circ\text{C}$ . It is obvious that both methacrylic acid and ethylene glycol methacrylate phosphate polymerize much faster than methyl methacrylate. Furthermore, as already stated, the maximum polymerization rate taken from the initial slopes of the plots in Figure 7a,b for methacrylic acid and ethylene glycol methacrylate phosphate increase by factors of 1.7 and 2.2, respectively, upon increasing the temperature from  $25^\circ\text{C}$  to  $80^\circ\text{C}$ , whereas a similar increase in temperature for methyl methacrylate (Figure 7c) leads to an increase in polymerization rate by a factor of 3.2 (from  $0.037 \text{ s}^{-1}$  at  $25^\circ\text{C}$  to  $0.12 \text{ s}^{-1}$  at  $80^\circ\text{C}$ ). The results in Figures 5–7 indicate the role of hydrogen bonding in enhancing polymerization rate and/or ameliorating the inherent increase in rate experienced by non-acid-bearing (meth)acrylates with an increase in temperature.

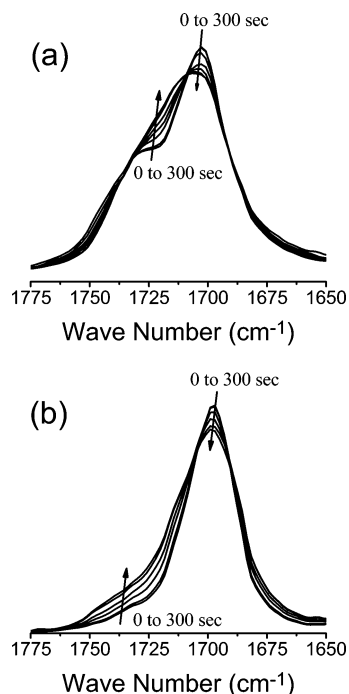
Next, we address the very complicated subject of the changes in hydrogen bonding that occur during the polymerization of acrylic acid and methacrylic acid. Figure 8 shows several 2-dimensional cuts (obtained from 3-dimensional plots) in the carbonyl region of acrylic acid and methacrylic acid during exposure of times up to  $\sim 300 \text{ s}$ . We present these data to be complete, at the same time pointing out that in each case at a given exposure time several types of carbonyl peaks are present involving all possible combinations of hydrogen-bonded species including monomer–monomer, monomer–polymer, and polymer–polymer dimer type carbonyl bonds. As well, the carbonyls of nonbonded monomer acids and polymer side group acids



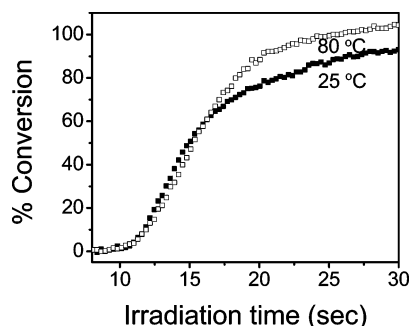
**Figure 7.** Conversion vs time as determined via RTIR for (a) methacrylic acid, (b) ethylene glycol methacrylate phosphate, and (c) methyl methacrylate at different temperatures. Light intensity:  $18.7 \text{ mW/cm}^2$  for all (a), (b), and (c) with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

are also present. On the basis of the predominance in intensity of bands near  $1700 \text{ cm}^{-1}$ , it can be concluded that, although we cannot quantitate the exact contribution of each species, hydrogen bonding to carbonyl groups remains very high throughout the polymerization process and influences the overall monomer conversion rate. Unfortunately, it is not possible to deconvolute the carbonyl peaks and assign quantitative values to each specific hydrogen-bonded species.

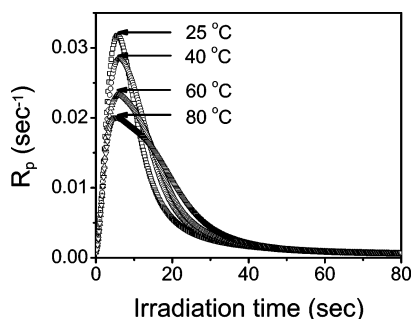
Taking a lead from the results in Figure 7 for ethylene glycol methacrylate phosphate, where a moderate rate increase with temperature occurred similar to the increase for methacrylic acid even though the acid group in ethylene glycol methacrylate phosphate is separated from the methacrylic functionality by an ethylene spacer group, we next evaluate results for 2-carboxyethyl acrylate which has a carboxylic acid appended to an ethyl group at the beta carbon. The results in Figure 9 for 2-carboxyethyl acrylate indicate that the polymerization rate decreases with an increase in temperature, similar to the magnitude of the decrease found for acrylic acid. As already concluded for the other systems, this is indicative of hydrogen bonding being reduced as the temperature increases. The photo-DSC results shown in Figure 10 at several temperatures are in agreement with the RTIR data; i.e., the rate of polymerization decreases moderately as the temperature increases. We have correlated the rate decrease with the decrease in hydrogen bonding by measuring IR spectra of an unpolymerized sample



**Figure 8.** FTIR spectra change of carbonyl stretching regions of (a) acrylic acid and (b) methacrylic acid as a function of UV exposure time. Random slices are given as representative examples. Light intensity is  $18.7 \text{ mW/cm}^2$  with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.



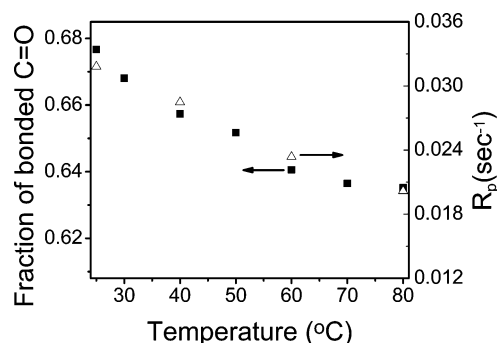
**Figure 9.** Conversion vs time as determined via RTIR for 2-carboxyethyl acrylate at different temperatures. Light intensity is  $1.14 \text{ mW/cm}^2$  with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.



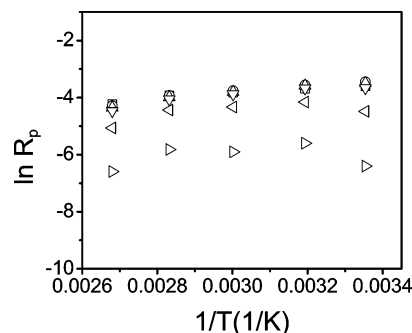
**Figure 10.** Rate of polymerization for  $\beta$ -CEA as a function of time at various temperatures.

as a function of temperature. The results in Figure 11 for both the fraction of hydrogen-bonded carbonyl groups of  $\beta$ -CEA and the exotherm polymerization rate maximum as a function of temperature clearly show that both correspondingly decrease as a function of temperature.

Finally, before concluding, we note that, in general, the dependence of polymerization rate on temperature can also be



**Figure 11.** Hydrogen bonding of carbonyl group (■) and maximum of the  $\beta$ -CEA exotherm polymerization rate in Figure 10 (Δ) as a function of temperature.



**Figure 12.**  $\ln R_p$  plotted vs the inverse of temperature for  $\beta$ -CEA for (□) 5%, (○) 10%, (Δ) 15%, (▽) 20%, (left-pointing Δ) 30%, and (right-pointing Δ) 40% conversion.

described in terms of an activation energy using a simplified Arrhenius relationship as given in eq 3<sup>15</sup>

$$\ln R_p = \text{const} - E_{\text{app}}/RT \quad (3)$$

where  $E_{\text{app}}$ , the apparent activation energy for polymerization, is a very complex function of propagation, termination, backbiting chain transfer (in the case of acrylates), and traditional chain transfer processes. This is further complicated by chain length dependent rate constants and the heterogeneity of the polymerization medium at a given percent of monomer conversion. Using eq 3 simply as a guide, we plotted the polymerization rate data for  $\beta$ -CEA from Figure 10 as a function of temperature. Since eq 3 holds only when the rate ( $R_p$ ) is measured at a given conversion, results at different temperatures must be compared at a constant conversion. Accordingly, plots in Figure 12 for  $\ln R_p$  vs  $1/T$  for  $\beta$ -CEA are given at several different conversions. It is obvious that the slopes of the plots in Figure 12 are near zero or slightly positive, indicating zero or low negative values for  $E_{\text{app}}$ . We suggest that this reflects the effect of hydrogen bonding on termination, with termination increasing disproportionately at elevated temperatures due to an increased concentration of non-hydrogen-bonded  $\beta$ -CEA monomers. Activation energies for acrylic acid, butyl acrylate, methacrylic acid, and methyl methacrylate can also be estimated from the initial slopes in Figure 5 ( $E_{\text{app}} = -1.15 \text{ kcal/mol}$ ), Figure 6 ( $E_{\text{app}} = 1.21 \text{ kcal/mol}$ ), Figure 7a ( $E_{\text{app}} = 1.79 \text{ kcal/mol}$ ), and Figure 7c ( $E_{\text{app}} = 4.48 \text{ kcal/mol}$ ), respectively. In each case the hydrogen-bonded monomer (methacrylic acid or acrylic acid) has a lower  $E_{\text{app}}$  value than the corresponding non-hydrogen-bonded analogue (methyl methacrylate or butyl acrylate). As already stated, we propose that these results are most readily explained by a decrease in hydrogen bonding at elevated temperatures for acid-bearing monomers.

## Conclusions

The photopolymerization of acid containing (meth)acrylates has been investigated using real-time FTIR. The effect of hydrogen bonding on the rate of polymerization is profound compared to monomers containing no acid group. A plausible explanation is that the hydrogen-bonded species behave like conventional diacrylates or dimethacrylates with a concomitant increase in rate due to a reduced termination rate compared to mono(meth)acrylate monomers. As temperature increases, the polymerization rate actually decreases (acrylic acid, 2-carboxyethyl acrylate) or is ameliorated (methacrylic acid, ethylene glycol methacrylate phosphate) with respect to what is found for (meth)acrylates with no acid groups present. The extent of the effect of temperature on polymerization rate is dependent upon the type of the acid group present. Future work will center on evaluation of mixtures of mono- and di(meth)acrylates with varying concentrations of acid-bearing monomers and correlation of polymerization rates and physical/mechanical properties of the cured polymer networks.

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