

Photopolymerization of Acid Containing Monomers: Real Time Monitoring of Polymerization Rate and Hydrogen Bonding

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Abstract: *The relationship between the polymerization rate of various acrylates and methacrylates containing acid group and their ability to hydrogen bond has been investigated by 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 increasing temperature.*

Introduction

Acrylates and methacrylates have been widely used as 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. ¹⁻⁵ Recently, more extensive research has been performed on a wide variety of acrylate monomers by Jansen et al. ⁶ and Bowman et al ^{7,8}. Jansen et al. ⁶ 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. They concluded that the hydrogen bonding leads to “organization” of the monomer units, although the nature of the “organization” was not specified. The change of hydrogen bonding as the monomer was converted to polymer was not determined as a function of temperature. The polymerization of hydroxyalkyl acrylates has been investigated by examining the extent of hydrogen bonding before and during polymerization in previous work. ⁹ In this study, the relationship between the polymerization rate of various acrylates containing acid group and their ability to hydrogen bond has been studied by real-time FTIR. Since acid containing acrylates and methacrylates are used in a variety of photocurable industrial formulations to promote adhesion, it is important to attain basic information about the polymerization of their polymerization in bulk.

Experimental

Acrylic acid, 2-carboxyethyl acrylate, methacrylic acid and ethylene glycol methacrylate phosphate were obtained from Aldrich Chemical Company and used as received.

Real-time infrared (RTIR) spectra were recorded on a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200W, high-pressure mercury-xenon bulb channeled through an electric shutter and fiber optic cable in the sample chamber. Photoreactions were conducted by sandwiching samples between two sodium chloride salt plates at a thickness of approximately 20 μm . 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 at full arc is 187mW/cm². Light intensity measurements were collected 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 per second. All samples contained 1 wt % photoinitiator [2,2-dimethoxy-2-phenylacetophenone (DMPA)].

The characteristic infrared absorbance band used to monitor the disappearance of the reactant and monomer during the photoreactions were as follows: acrylates (1636, 1618, and/or 812 cm^{-1}), methacrylates (1636 and/or 1007 cm^{-1}), and ethylene glycol methacrylate phosphate (817 cm^{-1}). The reactant conversions, calculated from the change in the peak area over time, have an approximate error of $\pm 2\%$.

Results and Discussion

The four acid based acrylates and methacrylates used in this study are shown in Chart 1. Two, acrylic acid and methacrylic acid, have acid groups alpha to a conjugated carbon-carbon double bond, while the other two are attached to saturated aliphatic structures.

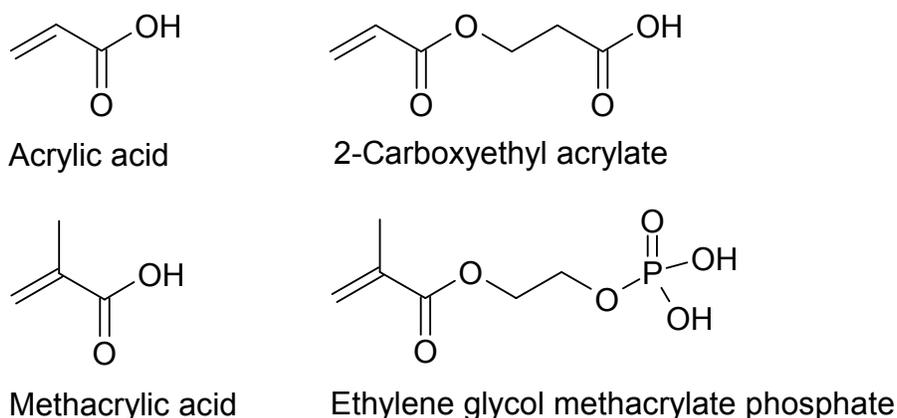


Chart 1. Monomer structures.

Hydrogen bonding is an important parameter that can affect system mobility, organization, and monomer conformation. It is certainly expected that these factors, in turn, can affect polymerization

processes and polymerization rates. As observed in Figure 1a, as temperature increases, the infrared peak at 1704 cm^{-1} (hydrogen bonded C=O) decreases continuously. It is well known that increasing temperature leads to the dissociation of hydrogen bonds, resulting in stronger valence bonding.¹⁰ In Figure 1b, although it is obviously seen that both peaks at 1698 cm^{-1} (hydrogen bonded C=O) and 1733 cm^{-1} (free C=O) increase as temperature increases, the ratio of hydrogen bonded and free C=O actually decreases. From a simple analysis of Figure 1a and 1b, it is thus reasonable to conclude that monomer association resulting from hydrogen bonding decreases with increasing temperature.

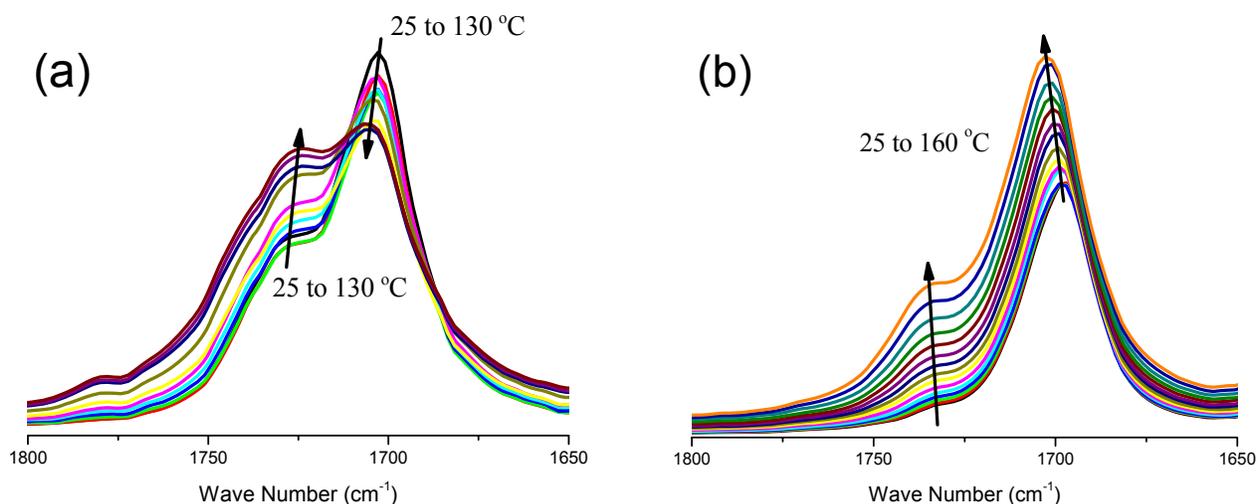


Figure 1. FTIR spectra change of carbonyl stretching regions of (a) acrylic acid and (b) methacrylic acid as a function of temperature.

As already suggested hydrogen bonding leads to the formation of multifunctional structures held together by loose bonding as well as an initial viscosity increase. This should restrict termination, leading to a buildup in radical concentration and a higher polymerization rate. As already indicated, Jansen et al⁶ reported that acrylates with urethane and amide groups capable of forming hydrogen bonds exhibit higher polymerization rates at room temperature than at higher temperatures since at higher temperatures there is a reduction in hydrogen bond.

In order to probe the effect of hydrogen bonding on the polymerization of both acrylic and methacrylic acid, real-time infrared analysis of the infrared peaks of the acrylate/methacrylate bands near 1636 and 810 cm^{-1} are both followed as a function of exposure time to a high pressure mercury lamp source. The decrease in the infrared absorption bands with time were used to determine the corresponding percent conversion versus time plots. In Figure 2, it is quite clear that the rate of polymerization of acrylic acid does not increase with an increase in temperature from 25 °C to 80 °C (there appears to be a modest decrease in rate with temperature). For comparison we mention that butyl acrylate experiences a measurable increase in rate with temperature over the same range. Results obtained for methacrylic acid and ethylene glycol methacrylate phosphate shown in Figure 3 show that although the rates are higher at the higher temperature, the rate increase with temperature is nonetheless moderate (e.g., the maximum polymerization rate taken from the initial slope of the plot in Figure 3a for methacrylic increases by a factor of ~ 1.8 upon increasing the temperature from 25 °C to 80 °C whereas a similar increase in temperature for methyl methacrylate leads to an increase in polymerization rate of a

factor of 3.4). The results in Figures 2 and 3 indicate the role of hydrogen bonding in ameliorating the inherent increase in rate experienced by non-acid bearing (meth)acrylates with an increase in temperature. Finally, we note that the results for ethylene glycol methacrylate phosphate also indicate only a moderate increase in rate with temperature similar to the increase experience for methacrylic acid, even though the acid group in ethylene glycol methacrylate phosphate is separated from the methacrylic functionality by an ethylene spacer group.

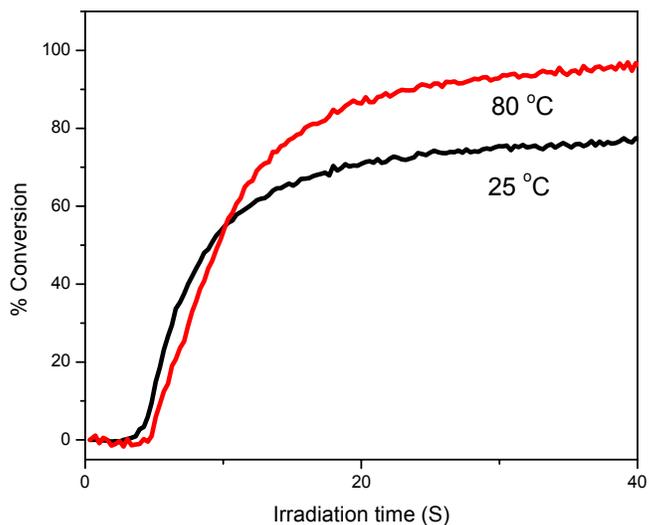


Figure 2. Conversion vs time as determined via RTIR for acrylic acid at different temperatures. Light intensity: 18.7 mW/cm^{-2} with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

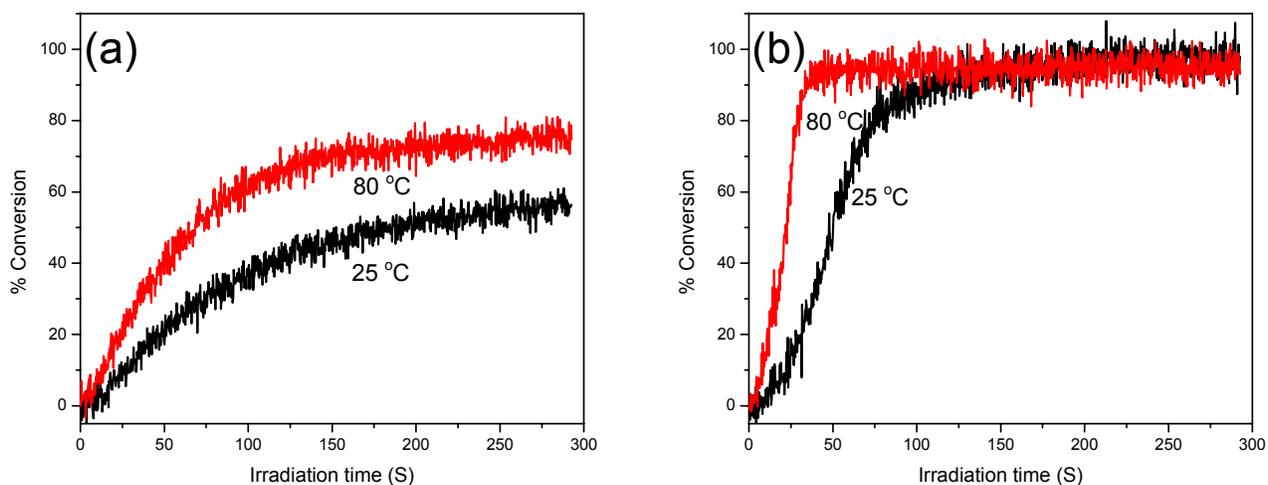


Figure 3. Conversion vs time as determined via RTIR for (a) methacrylic acid and (b) ethylene glycol methacrylate phosphate at different temperatures. Light intensity: 18.7 mW/cm^{-2} for both (a) and (b) with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

The results in Figure 4 for 2-carboxyethyl acrylate indicates 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 the hydrogen bonding being reduced as the temperature increases. Indeed, we have correlated the rate decrease with the decrease in hydrogen bonding by measuring IR spectra of an unpolymerized sample as a function of temperature.

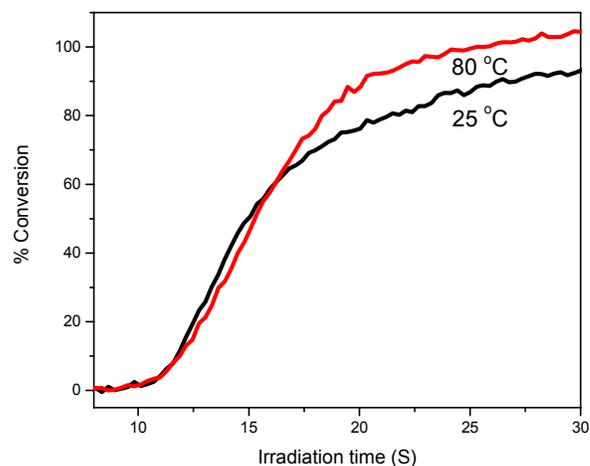


Figure 4. Conversion vs time as determined via RTIR for 2-carboxyethyl acrylate at different temperatures. Light intensity is 1.14 mW/cm^2 with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

Conclusions

The photopolymerization of acid containing (meth)acrylates has been investigated using real-time FTIR. The effects of hydrogen bonding on the rate of polymerization is profound compared to monomers containing no acid group, and the extent of the effect of temperature on polymerization rate is dependent upon the type of the acid group present. The role of hydrogen bonding on both polymerization rates and film formation of photocurable systems containing monomers with acid functional groups will be highlighted in the presentation, and the corresponding change of hydrogen bonding during polymerization will be presented.

Acknowledgements

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