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Influence of Hydrogen Bonding on Photopolymerization Rate of Hydroxyalkyl Acrylates

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ABSTRACT: The relationship between the photopolymerization rate of hydroxyalkyl acrylates and their structure has been investigated. The polymerization rates of hydroxyalkyl acrylates are significantly higher than those observed for typical monofunctional acrylate monomers and rival those of multifunctional monomers. By polymerizing at several temperatures, it was shown that the enhanced rates are directly proportional to the degree of hydrogen bonding. Apparently, termination rates are greatly reduced by hydrogen bonding, which is present in both the unpolymerized monomer and the final polymer film.

Introduction

Photoinitiated polymerization, a process for producing films with excellent physical properties,[1] has enjoyed rapid industrial growth in coatings, graphic arts, and microelectronics during the past several decades.[2] Because of the importance of speed in photocuring, acrylate monomers have been used due to their high reactivity. In a typical formulation, acrylated multifunctional oligomers and small molecule monofunctional and multifunctional acrylates are used to adjust viscosity, rate of curing, and final film properties. The structures of mono- and multifunctional monomers influence such factors as the structure of the cross-linked network, oxygen inhibition of polymerization, and the ultimate properties of the cured films. In addition, the polymerization rate is directly related to the monomer structure. Extensive research has been performed to assess acrylate monomers which enhance curing speed and optimize physical properties.

The relationship between monomer structure and reactivity was investigated extensively in the late 1980s and 1990s by Decker et al. using several model monofunctional acrylates with various pendant groups ranging from cyclic carbonates and oxazolidones to dioxolanes and oxetanes.[3−7] Each of these modified acrylates exhibited much greater polymerization rates than observed for conventional alkyl acrylates. Andrzejewska et al. reported the effect of heteroatoms including oxygen and sulfur in enhancing the rate of dimethacrylate polymerization in the presence and absence of oxygen as a function of temperature.[8,9] Others have observed rapid photopolymerization in ordered liquid crystalline phases.[10,11] Recently, more extensive research has been performed on various acrylate monomers by Jansen et al.[12−14] and Bowman et al.[15,16] They also concluded that certain pendant groups also enhance profoundly the rate of polymerization. In a particularly interesting report, Jansen et al.[14] found that acrylates with urethane and amide side groups capable of hydrogen bonding exhibited very fast polymerization rates at room temperature: 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, or lack thereof, of hydrogen bonding as the monomer was converted to polymer was not determined as a function of temperature.

Herein, we report polymerization results for hydroxyalkyl acrylates, which are much simpler in structure than the monomers studied previously, and allow for continuous monitoring of hydrogen bonding during polymerization. As in the case reported in ref 14, the relative degree of initial monomer hydrogen bonding is determined by the sample temperature. Concomitant effects on polymerization rate and initial monomer hydrogen bonding are examined as a function of temperature.

Experimental Section

Materials. Hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), hydroxylbutyl acrylate (HBA), hexyl acrylate (HA), lauryl acrylate (LA), and ethyl acrylate (EA) were purchased from Aldrich Chemical Co. and used without further purification. 1,6-Hexanediol diacrylate (HDDA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were obtained from UCB Chemicals and Ciba Specialty Chemicals, respectively. The chemical structures and corresponding acronyms of the monomers used in this study are given in Figure 1.

Methods. 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. A modified horizontal transmission unit was designed to prevent sample flow. The real-time FTIR setup has been illustrated elsewhere.[17] Monomer samples with thickness between 10 and 15 μm were placed between two sodium chloride plates. A 200 W 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 using a temperature controlled stage to determine temperature. The concentration of acrylate double bonds during polymerization was monitored at 812 cm^{-1}.

The photo-DSC, used to obtain polymerization exotherms at various temperatures, was based on a Perkin-Elmer DSC7

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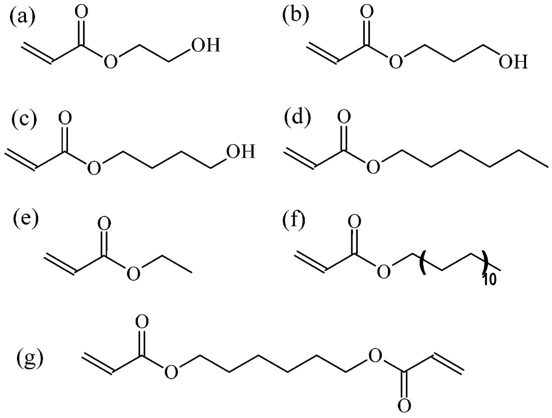

Figure 1. Chemical structure of (a) hydroxyethyl acrylate (HEA), (b) hydroxypropyl acrylate (HPA), (c) hydroxybutyl acrylate (HBA), (d) hexyl acrylate (HA), (e) ethyl acrylate (EA), (f) lauryl acrylate (LA), and (g) 1,6-hexanediol diacrylate (HDDA).

modified with a shuttered medium-pressure mercury lamp. Sample pans were crimped, and 2.0 μL samples were placed in the pan to give film thicknesses of approximately 150−200 μm. The photoinitiator DMPA (1 wt %) was used in all samples. The calculation method for polymerization rate has been described elsewhere.[18]

The extent of hydrogen bonding of the hydroxyalkyl acrylates (HEA, HPA, and HBA) was measured as a function of temperature using FTIR spectroscopy. The temperature was controlled with an accuracy of ±1 °C. Each IR spectrum was recorded after equilibrating for at least 2 min at the desired temperature. To facilitate assignment of the hydrogen-bonded OH and C═O groups, the IR spectra of hydroxyalkyl acrylates obtained at 120 °C were subtracted from those obtained at room temperature. The subtracted IR spectra show OH and C═O stretching bands with peak maxima at 3350 and 1704 cm^{-1}, respectively. The relative extent of hydrogen-bonded hydroxyl groups was approximated by integrating peak area between 3100 and 3700 cm^{-1} to obtain an estimate of the relative extent of hydrogen bonding.

The viscosity of hydroxyethyl acrylate and hexyl acrylate were measured using a Brookfield viscometer (model LVTDV-II) at 25 °C.

Results and Discussion

To determine the effect of pendant hydroxyl groups on acrylate polymerization rate, the conversion and polymerization rate of three hydroxylalkyl acrylates (see Figure 1 for structures) along with hexyl acrylate, HA (see Figure 1 for structure), were measured using both real-time FTIR (Figure 2a) and photo-DSC (Figure 2b) at 25 °C. It is quite obvious that the hydroxyalkyl acrylates polymerize much faster than HA even though they all are monofunctional acrylate monomers. Maximum polymerization rates observed for hydroxyalkyl acrylates are approximately 10 times higher than that of HA. For the monomers investigated, the alkyl chain length of the pendant groups in the hydroxylalkyl acrylates does not appear to affect the polymerization rate substantially. Since the presence of hydroxyl groups does not affect the intrinsic chemical nature of the acrylate double bond, it is reasonable to assume that other factors must be responsible for the significantly enhanced polymerization rates of hydroxyalkyl acrylates.

Both chain-transfer reactions and hydrogen bonding have been considered as possible contributors to the enhanced polymerization rate behavior of hydroxyalkyl acrylates.[15,16] These reports suggest that abstracting a hydrogen on the α-carbon next to the hydroxyl group of hydroxyethyl acrylate (HEA) and subsequent reinitiation by the resultant carbon centered radicals may lead to cross-linking, thereby reducing the rate of termination and increasing the polymerization rate.[19] This mechanism could certainly represent one factor contributing to the overall polymerization behavior. However, hydrogen bonding, which was also acknowledged as being a possible factor in influencing the polymerization kinetics,[16] may well be the main driving force behind the rapid polymerization rate. Consider that generally the activation energy for chain-transfer reactions is higher than that for propagation.[19] If a cross-linking reaction caused by chain transfer is the main reason for increased polymerization rates of hydroxyalkyl acrylates, the rate of polymerization should probably increase with increasing temperature. To investigate the effect of temperature on polymerization of hydroxyalkyl acrylates, polymerization rates at various temperatures were measured using photo-DSC and compared to those of lauryl acrylate (LA; see Figure 1 for structure) and 1,6-hexanediol diacrylate (HDDA; see Figure 1 for structure), as shown in Figure 3. The maximum rate of polymerization of HEA decreases drastically with increasing temperature while those of LA and HDDA increase moderately. (Interestingly, the rate of polymerization at room temperature for HEA is almost the same as for the difunctional monomer HDDA.) The maximum polymerization rate of HEA at 25 °C is approximately 2.5 times faster than at 80 °C. On the other hand, LA and HDDA show 10−20% increases in the maximum polymerization rate as the temperature is increased from 25 to 80 °C, the exact

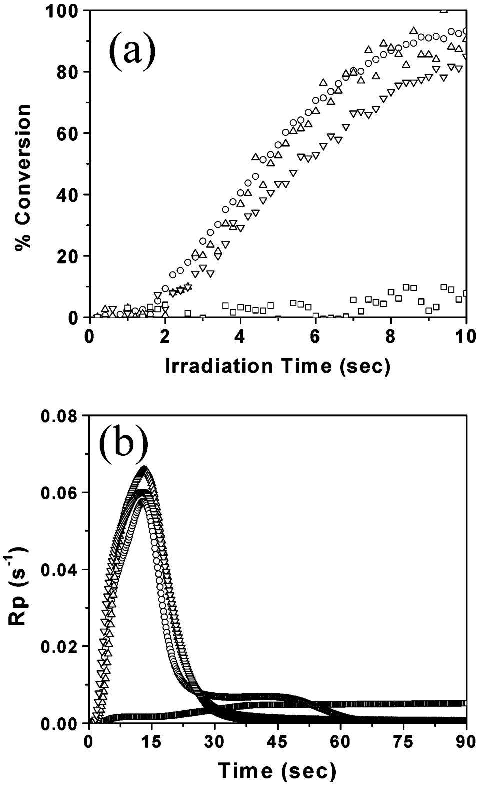

Figure 2. (a) Conversion vs time as determined via RTIR and (b) R_p vs time as determined by photo-DSC for hydroxylalkyl acrylates (○) HEA, (△) HPA, and (▽) HBA and (□) HA at 25 °C. Light intensity is 2 mW/cm^2 for (a) and 1.05 mW/cm^2 for (b) with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

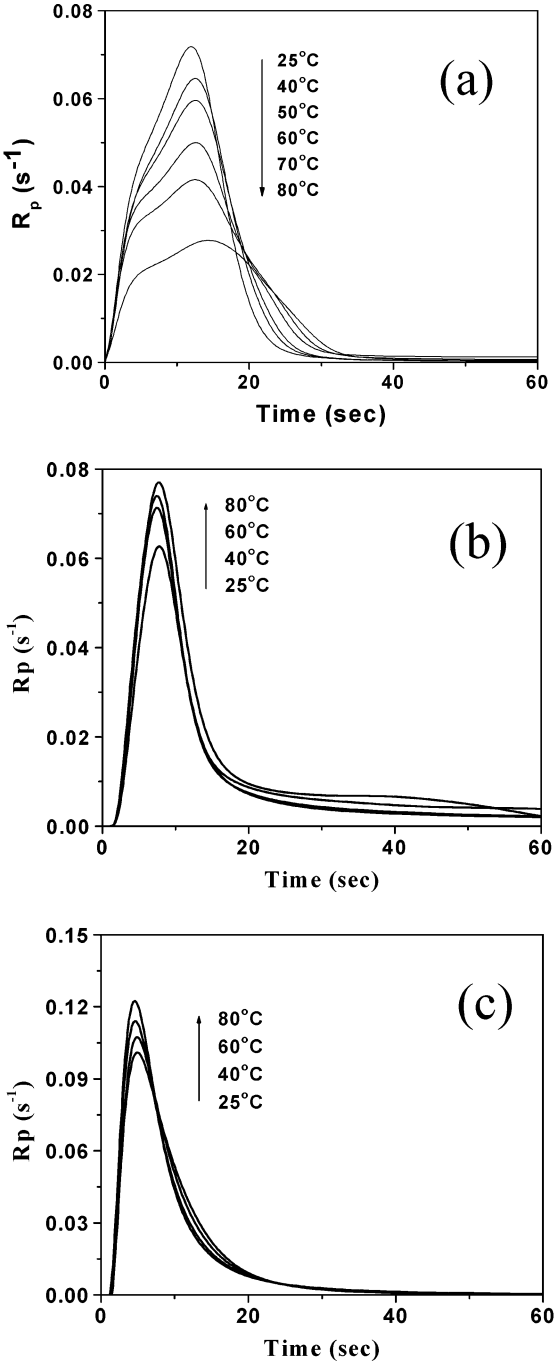

Figure 3. Rate of polymerization as a function of time at various temperatures for (a) HEA, (b) HDDA, and (c) LA as determined by photo-DSC. Light intensity is 0.93 mW/cm^2 for (a) and (b) and 78.8 mW/cm^2 for (c) with 1 wt % DMPA as a photoinitiator.

opposite of the behavior observed for HEA. The temperature effect for HEA suggests that chain transfer does not account for the high polymerization rate. Additionally, when the hydroxyalkyl acrylates are polymerized, the resulting polymers are totally soluble at conversions below 80%, further indicating that chain-transfer reactions are minimal and not the primary reason for the increase in the rate of polymerization, although they may play a limited role.

Inspired by Jansen's work,[14] we propose that hydrogen bonding is primarily responsible for the enhanced polymerization rates. The presence of hydroxyl groups in molecules can lead to formation of multimeric aggregated species dictated by the extent of associations.[20,23,24] It is reasonable to assume that hydroxyalkyl acrylate monomers and polymers could exist with numerous types of hydrogen bonds. Certainly, the major molecular association of hydroxyalkyl acrylates should be hydrogen bonding between hydroxyl groups (Figure 4a) or between hydroxyl and carbonyl groups (Figure 4b): such hydrogen bonds are expected to have bond strengths on the order of 20 kJ/mol.[20−22] Also, it is possible that the hydroxyl group can form multiple hydrogen bonds, as shown in Figure 4c,d. It is logical, as suggested by Jansen's work for the acrylates with urethane and amide side groups,[14] that the association of hydroxyalkyl acrylate monomers (and the polymers produced) can affect the rate of polymerization.

If indeed hydrogen bonding is operative in HEA polymerization, then there should be a correlation between the effect of temperature on hydrogen bonding and the effect of temperature on the polymerization rate, as seen in Figure 3a. Therefore, we recorded the IR spectra of HEA as a function of temperature, paying particular attention to the spectral regions that are associated with hydrogen bonding. The IR spectra of HEA at temperatures from 25 to 120 °C are shown in Figures 5 and 6. In Figure 5, the broad O−H peak from 3700 to 3100 cm^{-1} results from free OH stretching and hydrogen-bonded OH stretching due to varying structures and geometries. Upon increasing the temperature, the OH stretching peak maximum at 3440 cm^{-1} shifts to 3510 cm^{-1}. Also, the shoulder observed at 3350 cm^{-1} disappears at elevated temperatures. The results in Figure 6 for HEA clearly show two carbonyl peak maxima at approximately 1704 cm^{-1} attributable to a hydrogen-bonded carbonyl and 1728 cm^{-1} attributable to a free carbonyl stretching band. As observed in Figure 6, as the temperature increases, the shoulder peak at 1704 cm^{-1} (hydrogen-bonded C=O) decreases continuously. It is well-known that increasing temperature leads to dissociation of hydrogen bonds, resulting in stronger valence bonding.[20,25] From the results in Figures 5 and 6, it is reasonable to conclude that monomer association resulting from hydrogen bonding decreases with increasing temperature.

A more quantitative description of hydrogen-bonding changes as a function of temperature can be determined by careful analysis of the IR spectra in the OH and carbonyl regions. Unfortunately, separation of the O−H stretching bands in the region between 3100 and 3700 cm^{-1} into its different hydrogen-bonding and free OH stretching vibrations by deconvolution as well as assigning molar extinction coefficients of the respective OH stretching bands is virtually impossible to accomplish with any degree of accuracy. Li and Brisson[25] have shown that a reasonable assessment of overall hydrogen-bonding (hydroxy−hydroxy and carbonyl−hydroxyl) changes with temperature in the O−H region involves calculating the total intergrated area between 3100 and 3700 cm^{-1}. As shown in Figure 7a, the change in the integrated area of the OH stretching with temperature correlates to the decrease in polymerization rate maximum ($R_{p,max}$) with temperature. The change in the hydrogen-bonded carbonyl peak height at the 1704 cm^{-1} vs temperature (Figure 7b) also follows the decrease in $R_{p,max}$ with temperature. Borrowing from the description of hydrogen-bonded monomer association proposed in ref 14, it is certainly justified to assert that association of HEA molecules by strong hydrogen bonds

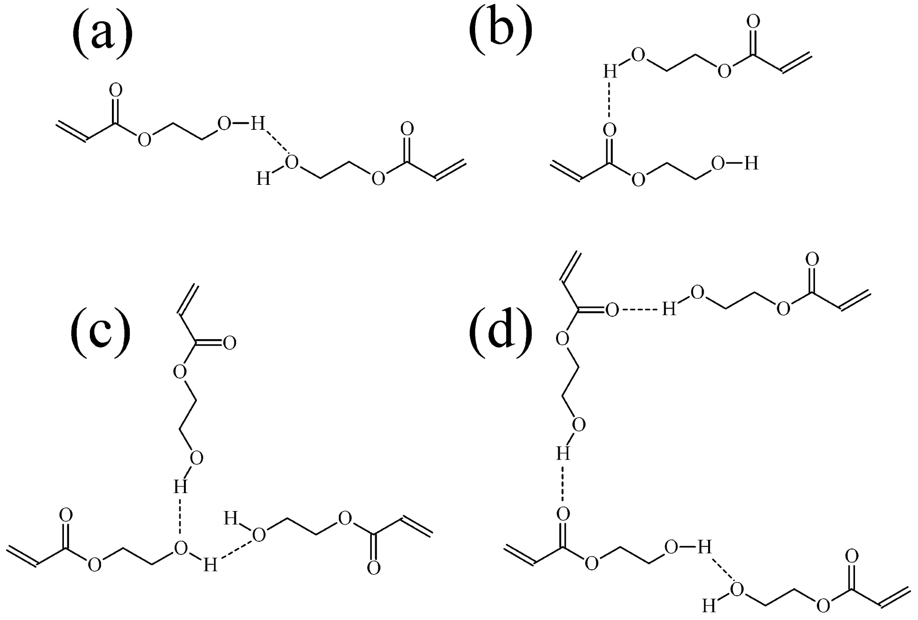

Figure 4. Possible hydrogen bonding in hydroxyalkyl acrylates.

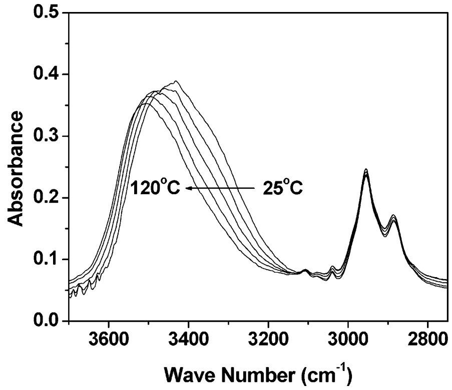

Figure 5. IR spectra focusing on the O−H stretching of HEA as a function of temperature.

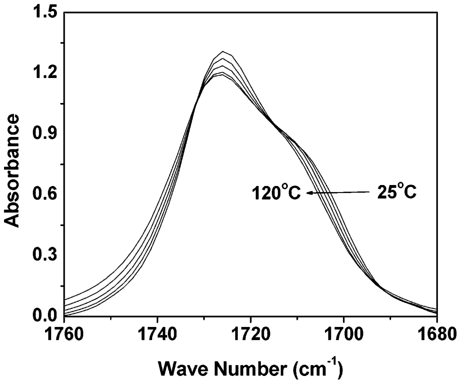

Figure 6. IR spectra focusing on the carbonyl stretching of HEA as a function of temperature.

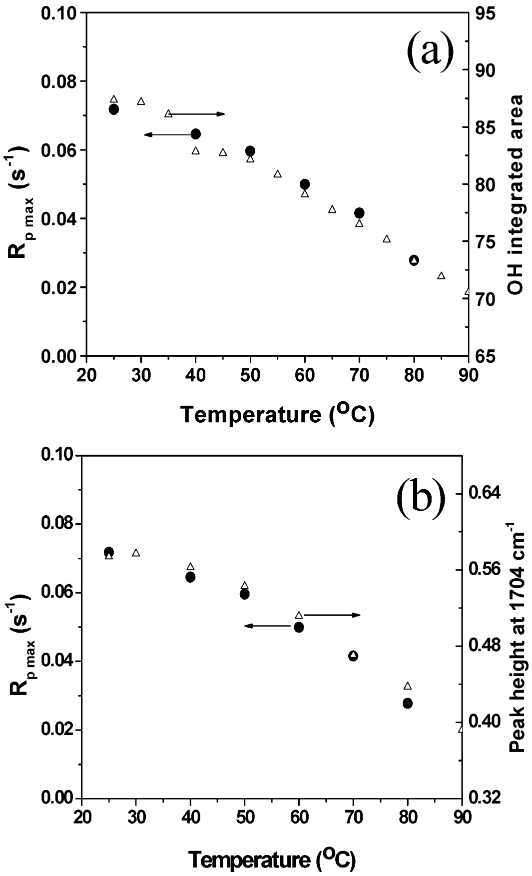

Figure 7. Relationship between hydrogen bonding of (a) hydroxyl group and (b) carbonyl group and polymerization rate of HEA as a function of temperature.

could produce pseudo-multifunctional monomers (as depicted in Figure 4). The association of HEA monomers by hydrogen bonding leads to a higher viscosity (6.05 mPa s) and density (1.12 g/mL) for HEA compared to those for HA (1.85 mPa s and 0.888 g/mL) which does not have hydrogen bonding between monomers. Since covalently bonded multifunctional monomers polymerize much faster than monofunctional monomers due primarily to a reduction in the termination rate,[26−30] it would be expected that the hydrogen-bonded "multifunctional" monomers also exhibit rapid polymerization rates, due to a reduced termination rate, compared to monofunctional monomers. Also, hydrogen bonding to the carbonyl could alter the electron density of the acrylate double bond and enhance the rate constant for propagation as was recently shown to occur for butyl methacrylate.[31] Having provided critical information correlating changes in polymerization rate and hydrogen bonding with temperature, additional consideration will

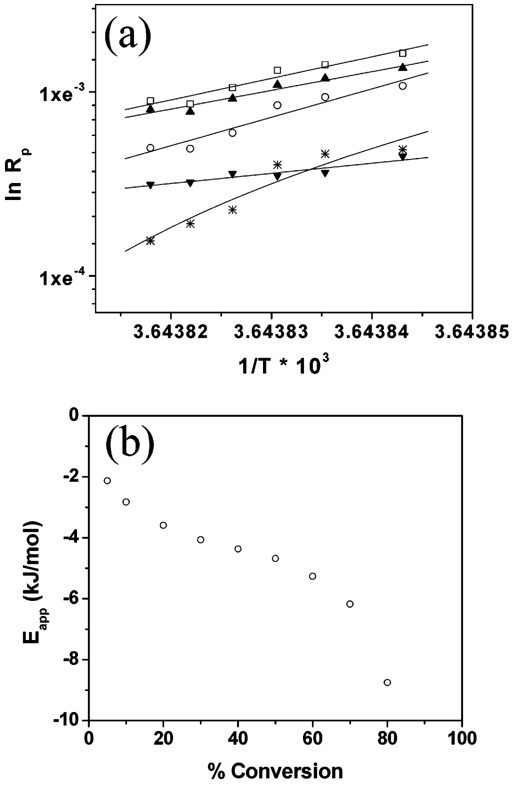

Figure 8. (a) ln R_p plotted vs the inverse of temperature for (▼) 5%, (▲) 30%, (□) 50%, (○) 70%, and (*) 80% conversion. (b) Apparent activation energy (E_a) as a function of HBA conversion.

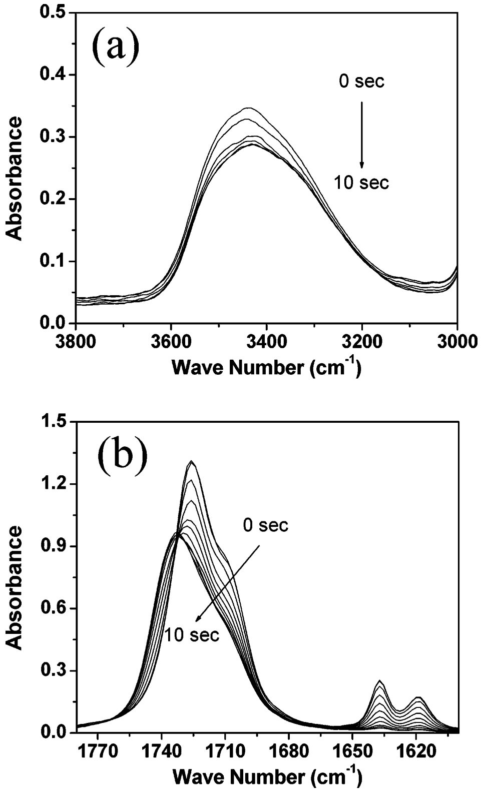

Figure 9. FTIR spectra of (a) hydroxyl and (b) carbonyl stretching regions of HEA as a function of polymerization time at 25 °C.

next be given to the kinetic reason for the decrease in polymerization rate with temperature.

In general, the dependence of polymerization rate on temperature can be described in terms of activation energy using an Arrhenius relationship as given in eq 1[19]

$$\ln R_p = \text{constant} - E_{app}/RT \qquad (1)$$

where E_{app}, the apparent activation energy for polymerization, is equal to $E_p - E_t/2$,[32] E_p is the activation energy of propagation, and E_t is the activation energy for termination. With eq 1 in mind, we measured polymerization rate data for HEA and hydroxybutyl acrylate (HBA) as a function of temperature. Herein, we present results only for HBA as representative of the behavior of all three of the hydroxyalkyl acrylates. Since eq 1 holds only when the rate is measured at a given conversion, results at different temperature must be compared at a constant conversion. Accordingly, plots in Figure 8a for ln R_p vs $1/T$ for HBA are given at several different conversions. It is obvious that E_{app} values for HBA obtained from the slopes of the plots in Figure 8a are negative at all conversions (Figure 8b). The negative values of E_{app} are simply a consequence of E_p being smaller than E_t. This reflects the effect of hydrogen bonding on termination, with termination becoming less hindered at elevated temperatures. Interestingly, E_{app} values become more negative with increasing conversion (see Figure 8b). As conversion increases, it is reasonable to expect that hydrogen bonding involving the polymers (polymer−polymer and monomer−polymer) produced during polymerization results in lower mobility of growing polymeric radicals and a higher activation energy for termination.

Additional information about the effect of hydrogen bonding on polymerization of hydroxyalkyl acrylates can be obtained by following hydrogen bonding during polymerization. Figure 9 shows the IR spectra of HEA photopolymerization indicating changes in hydrogen bonding of hydroxyl (Figure 9a) and carbonyl groups (Figure 9b) as a function of conversion at 25 °C. After 10 s, conversion reaches virtually 100% as indicated by the loss of acrylate carbon−carbon double bond peaks at 1620 and 1637 cm^{-1}(Figure 9b). The overall shape of the absorption in the OH stretching region (3100−3700 cm^{-1}) does not change (Figure 9a) although there is a small overall decrease in the intensity during polymerization. The results in Figure 9b show that the carbonyl peak maximum shifts to higher wavenumbers when monomer is converted to polymer due to a difference between the α,β-unsaturated conjugated carbonyl in acrylate double bonds and the α,β-saturated conjugated carbonyl in the polymer. The isosbestic point indicates a direct conversion from monomer to polymer carbonyl (no intermediate compounds). It is evident from curve-fitting results that the peak maxima of the conjugated and unconjugated carbonyl groups participating in hydrogen bonding have IR absorption bands at 1704 and 1710 cm^{-1}, respectively, and the free conjugated and unconjugated carbonyl groups have bands at 1726 and 1735 cm^{-1}. Examination of Figure 9b shows that the shoulder of the carbonyl peak, indicative of the hydrogen-bonded carbonyl group, decreases only modestly during polymerization, consistent with a low loss in OH hydrogen bonding (Figure 9a). The extent of hydrogen bonding in the cured film is clearly observed via a comparison of the carbonyl region in polymers made by polymerizing HEA and HA (see Figure 1 for structure). It is quite evident that there is extensive hydrogen bonding in poly(hydroxyethyl acryl-

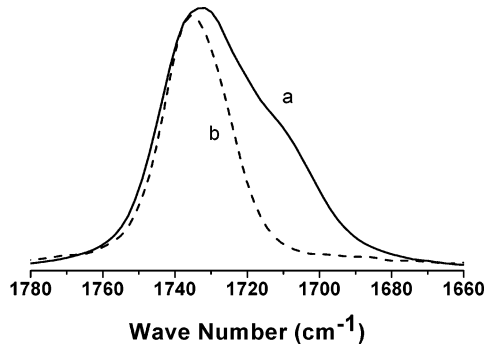

Figure 10. FTIR spectra of carbonyl stretching region of (a) poly(hydroxyethyl acrylate) and (b) poly(hexyl acrylate).

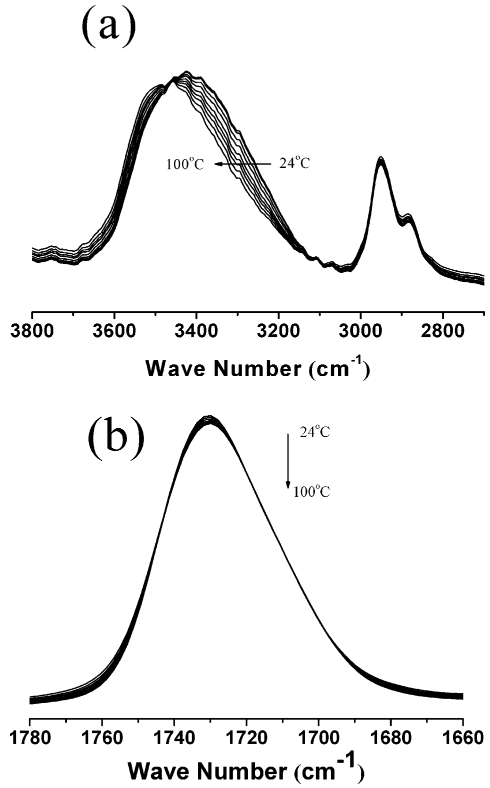

Figure 11. FTIR spectra change of (a) hydroxyl and (b) carbonyl stretching regions of poly(hydroxyethyl acrylate) as a function of temperature.

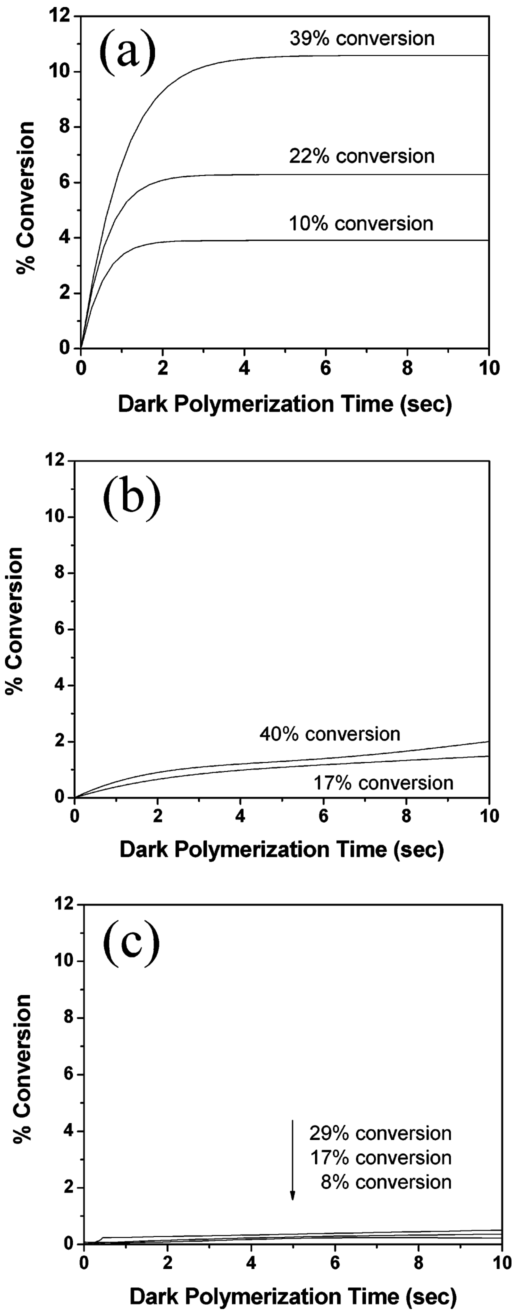

Figure 12. Dark conversion of HEA and HA after various conversions for HEA at (a) 25 °C and (b) 80 °C and (c) for HA at 25 °C.

ate). This can be seen in IR spectra in Figure 10 by comparing the red-shifted carbonyl band in curve a with that in curve b. Next, the poly(hydroxyethyl acrylate-)sample is heated from 24 to 100 °C. The results are shown in Figure 11. We first point out that there is a slight shift in the IR spectrum between 1660 and 1780 cm^{-1} in Figure 11 compared to Figure 10 at 24 °C. There was a 30 min delay in recording the spectra in Figures 9 and 11: the exact origin of the shift is not clear. The small shift could possibly be due to a relaxation of the matrix after polymerization. The small changes in the hydrogen-bonded IR bands between 3100 and 3700 cm^{-1} (OH region) and 1750−1690 cm^{-1} (carbonyl region) in Figure 11 with temperature compared to those in Figures 5 and 6 for the monomer are clearly reflective of stronger hydrogen bonding in the solid poly(hydroxyalkyl acrylate) films. At this point, we stress that the hydrogen bonding of the liquid monomer is not lost upon polymerization. In fact, the hydrogen bonding appears to be more favorable in the film as evidenced by the small change in hydrogen bonding of poly(hydroxyethyl acrylate) with increasing temperature. This suggests that stronger hydrogen bonding (polymer to polymer and by inference monomer to polymer) occurs as the conversion of monomer to polymer proceeds during the polymerization process. Although there are no quantitative results obtainable correlating termination rate constants with hydrogen bonding, it certainly seems reasonable that highly hydrogen-bonded systems would behave much as multifunctional monomers and have low termination rate constants.

The polymerization kinetics of hydroxyalkyl acrylates can be investigated further by recording the polymerization of HEA and HA after shuttering the UV light at several conversions. Figure 12 shows the dark polymerization behavior of HEA both at 25 and 80 °C, along with HA at 25 °C. The extent of the dark conversion for HEA at 25 °C (Figure 12a) is much greater (beginning at the same base conversion) than that obtained at 80 °C (Figure 12b). For example, after about 40% conversion, dark conversion of HEA at 25 °C is approximately 11% while it is only about 2% at 80 °C. This is consistent with the fact that at higher temperature termination is particularly enhanced due most assuredly to an increase in radical diffusion resulting from dissociation of hydrogen bonds. Also, we note that some of the inherent increase in the propagation rate constant with temperature may be mediated by reduction in electron density of the acrylate double bond as pointed out in ref 31. Finally, the dark conversion during polymerization of HA at 25 °C (Figure 12c) is negligible due to fast termination in the absence of hydrogen bonding. Thus, we conclude that hydrogen bonding in HEA dramatically reduces termination rates.

Conclusions

The polymerization of hydroxyalkyl acrylates has been investigated by examining the extent of hydrogen bonding before and during polymerization. The degree of hydrogen bonding and the rate of polymerization of hydroxyalkyl acrylates are directly related. Both hydrogen bonding and the polymerization rate decrease with increasing temperature, unlike conventional acrylates. Presumably, hydrogen bonding greatly impairs the termination process due to reduced polymer radical mobility. For hexyl acrylate (HA) at 25 °C and hydroxyethyl acrylate (HEA) at 80 °C, dark conversions are either negligible or quite small. On the other hand, for HEA at 25 °C, much higher dark conversions indicate that hydrogen bond greatly reduces the termination rate.

References and Notes

(1) Fouassier, J. P. *Photoinitiation Photopolymerization and Photocuring; Fundamentals and Applications*; Hanser Publishers: Munich, 1995.
(2) Pappas, P. *Radiation Curing, Science and Techonology*; Plenum Press: New York, 1992.
(3) Decker, C.; Moussa, K. *Macromolecules* **1989**, *22*, 4455.
(4) Decker, C.; Moussa, K. *Makromol. Chem.* **1991**, *192*, 507.
(5) Moussa, K.; Decker, C. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2197.
(6) Decker, C.; Moussa, K. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 159.
(7) Decker, C.; Moussa, K. *Eur. Polym. J.* **1991**, *27*, 881.
(8) Andrzejewska, E. *Polym. Bull.* **1996**, *37*, 199.
(9) Andrzejewska, E.; Andrzejewski, M. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 665.
(10) Guymon, C. A.; Hoggan, E. N.; Clark, N. A.; Rieker, T. P.; Walba, D. M.; Bowman, C. N. *Science* **1997**, *275*, 57.
(11) Guymon, C. A.; Bowman, C. N. *Macromolecules* **1997**, *30*, 5271.
(12) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2002**, *35*, 7529.
(13) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Polym. Prepr.* **2001**, *42*, 769.
(14) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861.
(15) Berchthold, K. A.; Nie, J.; Elliot, J. E.; Hacioglu, B.; Luo, N.; Trotter, A. J. N.; Stansburry, J. W.; Bowman, C. N. *Proc. Radtech Europe* **2001**, 265.
(16) Beckel, E. R.; Berchthold, K. A.; Nie, J.; Lu, H.; Stansburry, J. W.; Bowman, C. N. *Polym. Prepr.* **2003**, *44*, 31.
(17) Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Kudyakov, I.; Viswanathan, K.; Nason, C.; Guymon, C. A.; Hoyle, C. E. *Polymer* **2003**, *44*, 2859.
(18) Lester, C. L.; Smith, S. M.; Guymon, C. A. *Macromolecules* **2001**, *34*, 8587.
(19) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991.
(20) George, A. J. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
(21) Hadzi, D. *Hydrogen Bonding*; Pergamon Press: New York, 1959.
(22) Lommerse, J. P. M.; Price, S. L.; Taylor, R. *J. Comput. Chem.* **1997**, *18*, 757.
(23) Kuo, S. W.; Chang, F. C. *Macromolecules* **2001** *34*, 5224.
(24) Su, Y.; Kuo, S.; Yei, D.; Xu, H.; Chang, F. *Polymer* **2003**, *44*, 2187.
(25) Li, D.; Brisson, J. *Polymer* **1998**, *39*, 801.
(26) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(27) Anseth, K. S.; Bowman, C. N. *Polym. React. Eng.* **1993**, *1*, 499.
(28) Anseth, K. S.; Bowman, C. N.; Peppas, N. A. *J. Polym. Sci., Polym. Chem.* **1994**, *32*, 139.
(29) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Polymer* **1994**, *35*, 3243.
(30) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* **1994**, *27*, 650.
(31) Beuermann, S. *Macromolecules* **2004**, *37*, 1037.
(32) Tryson, G. R.; Shultz, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2059.

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