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Real-Time Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy To Monitor Multiacrylate Polymerization Reactions

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ABSTRACT: Real-time attenuated total reflectance–Fourier transform infrared spectroscopy was used to follow the conversion during acrylate polymerizations by measuring the presence of functional groups at finite depths from the crystal surface. By varying the film thickness, the reactivity of multiacrylates could be spatially resolved. These results were compared to results from differential photocalorimetric studies.

Introduction

Reactions of multifunctional (meth)acrylates have been broadly studied with important applications in information storage systems, various coatings, and dental restorative materials.[1–5] Previous studies of the reaction kinetics of fast diacrylate polymerizations have shown the influence of oxygen, monomer thickness, and temperature on reaction kinetics.[6–8] The techniques developed for monitoring these reactions rely either on the measurement of reaction attributes or on the chemical changes of functional groups during the reaction.

Reaction parameters include the reaction enthalpy and reaction volume changes. Differential photocalorimetry (DPC) uses the heat release of the exothermic polymerization reaction to follow this reaction.[9] Dilatometry follows the loss of volume of the reacting double bonds.[10,11] Both techniques require knowledge of the heat of reaction or of the volume shrinkage as a function of conversion for the reacting system.

Fourier transform infrared (FTIR) spectroscopic techniques have advantages over other methods. For example, they have been used to follow the real-time reaction behavior of the changing functional groups during the reaction.[12–17] Identification of functional groups in the polymerization is favored over following reaction enthalpy or dilatometry since the functional group conversion is independent of delayed volume shrinkage.[18] The above techniques can be used to provide a real-time study of bulk reactivity. The sample thickness that can be tested by FTIR spectroscopy is limited to less than 100 μm due to the saturation of the FTIR signal. Therefore, obvious changes in the reactivity due to thickness changes and the resulting decrease in light intensity are ignored. A method using multiple internal reflectance has been reported, but the sample thicknesses are smaller than 10 μm and are not done in real time.[19]

The method developed here uses real-time attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy to follow the reaction conversion by measuring the presence of functional groups at only a finite depth from the crystal surface. Since the IR signal penetrates only a few angstroms into the sample,[20] the reaction may be examined in only a narrow region at the bottom of the reacting film. By varying the film thickness, the reactivity of the multiacrylates can be spatially resolved. Comparison of the real-time ATR–FTIR and DPC techniques can also be accomplished.

Experimental Part

The monomer used was 1,1,1-trimethylolpropane triacrylate (TrMPTrA; Polysciences, Warrington, PA) which was mixed with 1 wt % 2,2-dimethoxyphenylacetophenone (DMPA; Aldrich, Milwaukee, WI) as a photoinitiator.

A differential photocalorimeter (DPC; Model 930, TA Instruments, Wilmington, DE) was used to monitor the isothermal heat generation during the UV-induced polymerization at 30 °C. The monomer and photoinitiator mixture was stabilized for 15 min in an inert nitrogen atmosphere prior to irradiation. The monomer and photoinitiator mixture weight was con-

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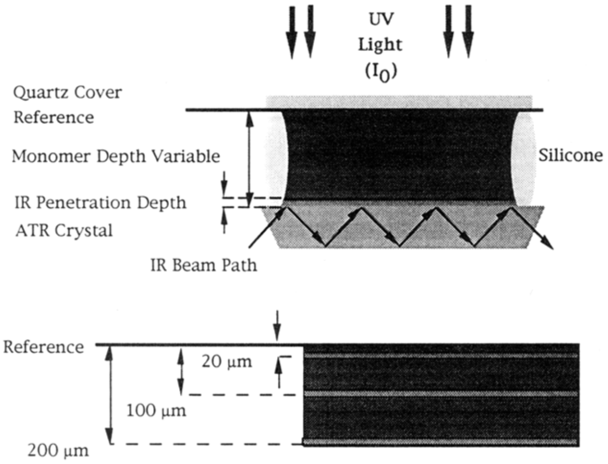

Figure 1. Schematic of real-time ATR–FTIR reaction device. The sample reference is the monomer–quartz crystal interface, with variable monomer sample depths possible.

trolled to between 2.1 and 2.3 mg. An empty pan was used as a reference in the DPC cell. The light intensity used was 1 mW/cm^2 as measured by a radiometer (IL 1350; International Light, Newburyport, MA). The UV light source produced light at 365 nm.

An FTIR spectrophotometer (Model 800, Nicolet, Madison, WI) with a mercury–cadmium–teluride (MCT) detector and an ATR accessory (variable-angle specular reflectance accessory, Spectra-Tech, Stamford, CT) was modified to isolate the monomer from the oxygen in the dry air purge inside the FTIR spectrophotometer using a quartz crystal (CO-IR, transparent to UV but absorbing IR, Esco Products, Oak Ridge, NJ) on top of the monomer. Inert silicone grease was used to seal the sides around the crystal as shown in Figure 1. A UV light source (Ultracure 100, EFOS, Mississaugua, Ontario, Canada) with a fiber-optic cable irradiated the ATR crystal perpendicularly at 365 nm. A modified outer window for the FTIR was made using neutral density filters (Melles Griot, Irvine, CA) that allowed adjustment of the incident UV radiation to 1.0 mW/cm^2 at the monomer surface and minimized the potential interference between the UV light and the IR path. The temperature in the FTIR was measured between 27 and 30 °C. The reaction was isothermal due to the small sample size and the air flow through the text cell.

A background spectrum with the silicone grease on the ATR crystal was obtained by allowing the crystal center to remain completely clean. The monomer was transferred to the clean portion of the ATR crystal surface with a micropipette. The monomer and photoinitiator mixture was also exposed to a nitrogen purge prior to the experiment. The quartz crystal was then placed on top of the monomer so that the silicone grease completely sealed the system. The final thickness of the monomer layer between the Ge and quartz crystals was recorded.

The reaction was initiated by using a remote control to simultaneously open the shutter for the UV source as the data collection began. All experiments used a scanning frequency of 4 scans/s with a resolution of 8 cm^{-1} in the forward sweep only mode.

Results and Discussion

Using ATR–FTIR spectroscopy, the monomer TrMPTrA was observed to rapidly react, forming a glassy polymer. The interferogram data gathered from the reaction were Fourier-processed to generate the spectra which were then converted from transmission to absorbance based on the background from the Ge crystal and the silicone, which has a very low absorbance of IR and did not hinder the integration process. The resulting absorbance spectrum of the TrMPTrA monomer can been seen in Figure 2. The baseline was adjusted so that the end points for the absorbance peak for C=C (from 1653 to 1600 cm^{-1}) were set to zero.

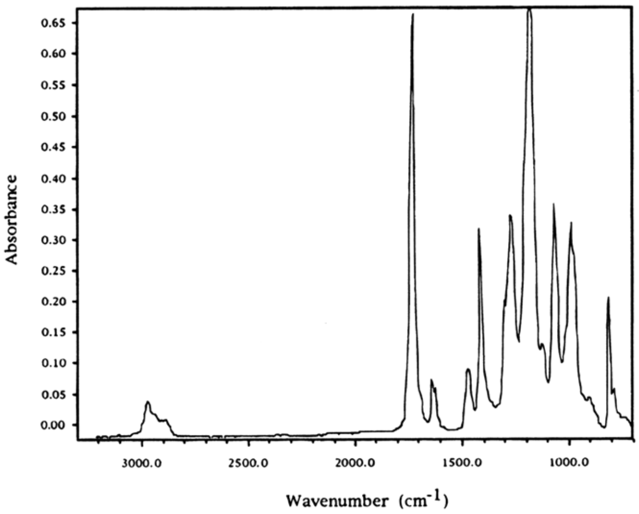

Figure 2. IR spectrum of TrMPTrA.

For the unreacted monomer, the area of the peak was integrated to give a value of A_m or the initial C=C concentration. The integrated C=C peaks for the spectra were normalized to the inactive $-CH_3$ absorbance from the monomer spectrum at 2961 cm^{-1} to adjust for gain differences. From the integrated spectra and the previously established baseline and normalization, the value of A_t can be calculated. Equation 1 was used to determine the fractional conversion, X_t, as a function of time for each spectrum.

$$X_t = \frac{A_m - A_t}{A_m} \tag{1}$$

Here, A_m is the area of the 1630 cm^{-1} peak of the monomer, and A_t is the corrected area of the unreacted C=C peak at time *t*.

The penetration depth of the IR beam can be controlled by the selection of crystal, the incident IR beam angle, and the face angle of the crystal.[20] The penetration depth, d_p, is given by the following equation:

$$d_p = \frac{\lambda}{\left[4\pi n_c\left[\left(\sin^2\theta - \left(\frac{n_p}{n_c}\right)^2\right)\right]\right]^{0.5}} \tag{2}$$

where

$$\theta = \beta - \sin^{-1}\left[\frac{\sin(\beta - \psi)}{n_c}\right] \tag{3}$$

Here, λ is the infrared wavelength, n_p and n_c are the indices of refraction of the polymer and crystal, respectively, θ is the incident light angle of the beam, β is the end-face angle, and ψ is the optical angle of the beam. By changing the ATR crystal or end-face or incident light angles, the penetration depth could be adjusted.

Figure 3 shows penetration depth variations with IR wavelength obtained from possible combinations of crystals (ZnSe, Ge, and Si) with varying incident light and end-face angles (30°, 45°, and 60°). Penetration depths could be obtained between 95 and 340 nm for the C=C peak at 1600 cm^{-1} of interest in the TrMPTrA photopolymerization. With the 45° end-face and inci-

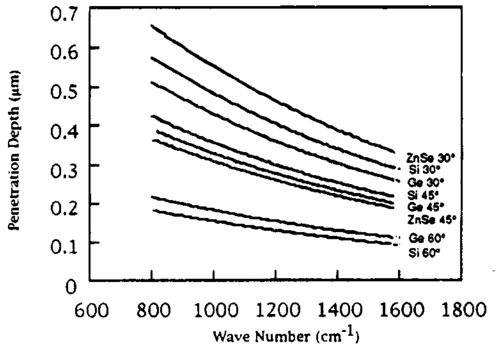

Figure 3. Penetration depth into the reacting monomer with variations in wavelength of interest in sample, crystal materials (germanium, silicone, and zinc selinide) and the angles of incident IR light and crystal end face of 30°, 45°, and 60°.

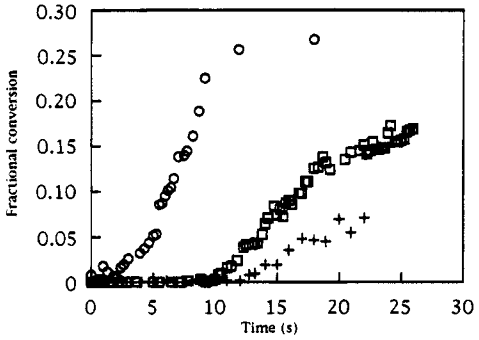

Figure 4. Conversions as a function of time as measured from the lowest 0.2 μm depth with polymer layer thicknesses of 16 (□), 130 (○), and 560 μm (+) as determined by ATR–FTIR.

dent light angle on a germanium crystal, if the C=C peak is followed at 1600 cm^{-1}, the penetration depth is 200 nm.

The monomer thickness between the quartz and the Ge crystals was varied to allow the reaction to be followed at different depths from the monomer–quartz crystal surface which was used as the plane of reference. Figure 4 shows the reaction data for monomer layer thicknesses of 16, 130, and 560 μm. As expected, the sample with a thickness of 16 μm reacted much faster than the thicker samples due to the reduced light intensity at the crystal surface with the thicker monomer layers. The local conversion at the crystal surface can be seen to increase with decreasing monomer layer thickness. The induction time, defined again as the time required for 1% conversion, increased with increasing monomer layer thickness, from 1.5, 10, and 12 s for thicknesses of 16, 130, and 560 μm, respectively.

The ATR–FTIR experiments were repeated with a number of polymerizing monomer samples of varied monomer thickness. The local conversions were compared at 90 s after UV irradiation, as shown in Figure 5. The reaction time of 90 s was preferred because it is approximately an order of magnitude larger than the induction time; this is important because the reaction enthalpy can be a function of conversion and the deviation is greatest toward the end of the reaction.[21] For the ATR-FTIR experiments, the local conversion decreased with increasing thickness of the monomer samples, this is again attributed to the reduction in light intensity with monomer thickness.

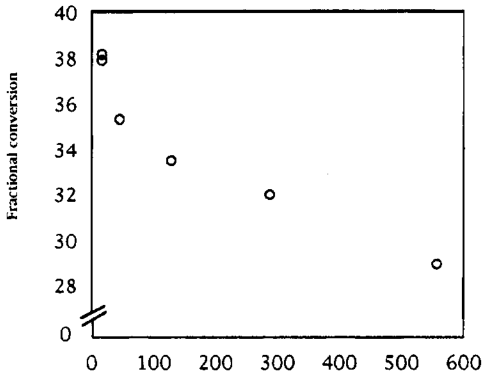

Figure 5. Conversion by ATR–FTIR determined after 90 of UV irradiation as a function of various monomer layer thicknesses.

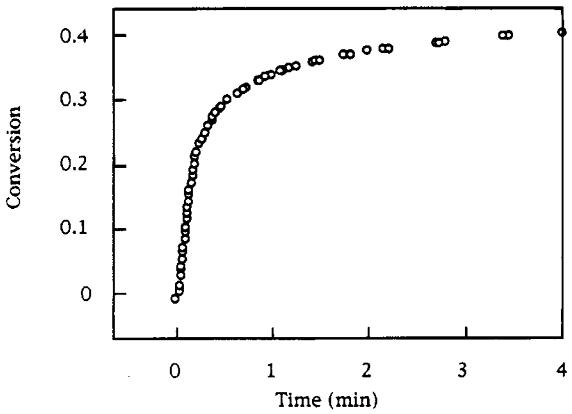

Figure 6. Conversion of TrMPTrA as a function of time, during the UV polymerization by differential photocalorimetry at 1 mW/cm^2.

For comparison and validation purposes, DPC results of these reactions were obtained. DPC analysis gave the instantaneous heat generation from the reaction monomer and photoinitiator mixture. The heat generation rate is proportional to the heat of reaction of the monomer. The theoretical heat of reaction of TrMPTrA was determined to be 872.6 kJ/g. This was calculated from the product of three acrylate double bonds in TrMPTrA and the heat of reaction of the acrylate double bond in lauryl acrylate, known to be[22] 20.6 kJ/mol. Integration of the reaction rate curve and use of the theoretical conversion yielded bulk conversions which with further analysis could be used to directly compare these results to the ATR–FTIR results. Figure 6 shows a typical conversion profile as a function of time for the polymerization of TrMPTrA by DPC. The bulk conversion of TrMPTrA was 35.8 ± 3.1% at 90 s after irradiation using hexaplicates. The induction time, defined as the time to achieve 1% conversion, was determined to be 1.8 ± 0.1 s. The DPC sample thickness, as measured following the reaction, was 0.25 ± 0.03 μm.

Finally to compare the DPC data to the ATR–FTIR data, the data of Figure 5 were curve-fitted using a least-squares program and the resulting equation was integrated over the same monomer thickness as determined in the DPC experiments. A final correction was necessary in the DPC experiments. The small monomer and photoinitiator sample formed a spherical section due to the poor wetting of the monomer on the DPC pan with a maximum thickness of 0.25 ± 0.03 μm. The ATR–FTIR data were collected for narrow depth bands of 0.2 μm. The ATR–FTIR experimental data were compared to DPC data by approximating the shape of the DPC sample to a segment of a sphere and determining the volume fraction of this segment as a function of depth from the surface. The product of this volume fraction and conversion at 90 s with depth, as determined by a curve fit through Figure 5, was integrated with depth to determine an overall conversion for comparison. This value was determined to be 35.2% conversion following 90 s of UV irradiation, which can be compared to 35.8 ± 3.1% in the bulk from the DPC experiments. The calculated conversion from the ATR–FTIR experiments was within the error of the DPC experiments.

Additionally, the heat generation detected was expected to lag behind the actual conversion. The induction time is not easily compared between the testing methods. The local induction times observed by ATR–FTIR are 1.5–12 s, while the DPC bulk induction time is 1.8 s. Due to the indirect method of monitoring the heat of reaction with the DPC, we would expect the measured conversion to lag behind real conversion by 0.1–0.3 s, which is equivalent to the time required for heat conduction through the polymer and the DSC pan.

Conclusion

ATR–FTIR spectroscopy is preferred over DPC in studying kinetics. The former technique monitors the presence of chemical species, whereas DPC monitors the heat release and infers the conversion from the theoretical enthalpy of reaction. Bulk conversion calculated from the DPC studies falls within the range of local conversions calculated from ATR–FTIR spectroscopy at various thicknesses. Integration of the local conversions from ATR–FTIR spectroscopy over the monomer thickness used in the DPC experiments yields comparable values in the bulk, 35.2% by ATR–FTIR and 35.8% by DPC. ATR–FTIR spectroscopy is rapid enough for these reactions and is sensitive to thickness changes without unavoidable bulk averaging in other techniques. The induction time observed in the ATR–FTIR technique is shorter than that in the DPC technique due to the delay of heat transmission through the sample in the DPC experiments.

This is the first attempt to use real-time ATR–FTIR monitoring of these reactions spatially. All other techniques used for kinetics studies of these systems have only monitored the bulk properties. The use of various crystals and incident/end-face angles can alter the penetration depth of the IR beam and the thickness of the polymer layer being studied. With the added ability of altering the monomer thickness above the penetration depth, the reaction of thicker monomer layers can be studied. This cannot be done with other FTIR techniques relying on transmission.

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