



High throughput kinetic analysis of photopolymer conversion using composition and exposure time gradients

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Abstract

In this work, monomer composition and exposure time gradients were produced, allowing for rapid, parallel measurements of conversion as a function of composition and exposure time using Fourier transform infrared (FT-IR) spectroscopy. A more comprehensive understanding of how composition affects photopolymerization kinetics is needed due to the complexity of current industrial formulations. In nearly all cases, these applications use multiple monomers, fillers, initiators, and other components to achieve the required properties. The developed technique allows for photopolymerization kinetics to be analyzed rapidly over a large range of compositions, giving a unique insight into the role composition contributes to polymerization kinetics and ultimate conversion within complex formulations. This work analyzed three varied two-component systems, each showing different effects from composition on polymerization kinetics due to formulation changes in functionality, viscosity, and reactivity.

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1. Introduction

Photopolymers have a wide range of applications in dental restoratives, solvent resistant coatings, contact lenses, and numerous other areas. In nearly all industrial applications multiple monomers and reactive oligomers are used to form a polymer network. Other additives such as initiators, fillers, chain transfer agents, and accelerators are added to alter formulation properties and tailor polymerization rates. This complexity provides a wide range of tunable properties that are counterbalanced by the time required to analyze the requisite properties and assess their dependence on composition. Because there are an enormous variety of potential compositions and conditions available, the speed with which polymer property analysis is

performed must be improved if the optimal formulation is to be found for each application.

Parallel evaluation using gradient techniques would alleviate this material characterization bottleneck by producing multiple conditions on a single substrate sample. The production of composition or property gradients was first applied in the material science field to increase the speed of analysis, searching hundreds of unique metallic semiconductors within a short time frame [1–4]. This research spurred interest with polymer researchers, and polymer gradients were produced as discrete or continuous composition gradients [5]. Composition gradients and property gradients have been used for quantification of various polymer properties, appropriate for several fundamental and applied aspects of polymer science. Composition gradients are now used to study degradation profiles, perform parallel synthesis, and test adhesive properties [6–9]. In conjunction with a temperature gradient, phase behavior and surface energy combinatorial studies allow for optimization of the desired network structure [5,8,10]. Systems using thickness, conversion, and catalyst gradients have also been explored [11–13].

Therefore, we focus on the development of a high

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throughput means of evaluating photopolymerization kinetic behavior, which is highly dependent on monomer chemistry, functionality, and composition, while being notoriously difficult to analyze or model due to the complexity of most industrial formulations. Uniquely, a number of novel monomers with rapid polymerization kinetics have recently been found, but the cause for this increased rate is not well understood [14,15]. Dipole effects, hydrogen bonding, and other chemical properties have been proposed as having contributing effects to this high reactivity [16–20]. The use of gradient techniques allows for interactions between these novel monomers and traditional acrylates to be analyzed rapidly in co-polymerizations, where these monomers are likely to be used. This assessment allows for a more complete picture of the advantages these monomers bring to industrial applications and leads to a better understanding of the dominant mechanisms responsible for that behavior.

This study evaluated a technique to analyze polymer conversion as a function of time and composition in a parallel manner, improving the ability to evaluate comonomer formulations systematically and rapidly. Current traditional serial testing uses one composition per sample, monitored in situ with FT-IR [21,22] or calorimetry. To cover a complete range, multiple samples, each with a different composition, are needed to produce a composition axis. There is a limited amount of work available that has done comprehensive studies based on variations in composition, mainly in the area of biomaterials [11,23,24]. In the present study, both serial and parallel methods will be used to obtain similar results, and then additional parallel systems are presented to demonstrate the wide application range and different effects this novel technique enables.

2. Experimental section

2.1. Materials

Hexanediol diacrylate (HDDA, **1**), hexyl acrylate (HA, **2**), and tetrahydrofurfuryl acrylate (THFFA, **4**) were obtained from Aldrich (Milwaukee, WI) and used as received. The photoinitiator dimethoxyphenylacetophenone (DMPA) was obtained from Ciba-Geigy (Hawthorn, NY). Benzyl carbamate acrylate (BCA, **3**) cyclic carbamate acrylate (CCA, **5**) and were synthesized in a manner described in detail elsewhere [19]. Bisphenol-A glycidyl dimethacrylate (BisGMA, **6**) was obtained from Cook composites and polymers (Kansas City, MO). All purchased reagents were used without further purification, and the monomer structures are given in Fig. 1.

2.2. Serial testing

Serial testing was done with real-time FT-IR spectroscopy (Nicolet 760 Magna series II FT-IR, Nicolet,

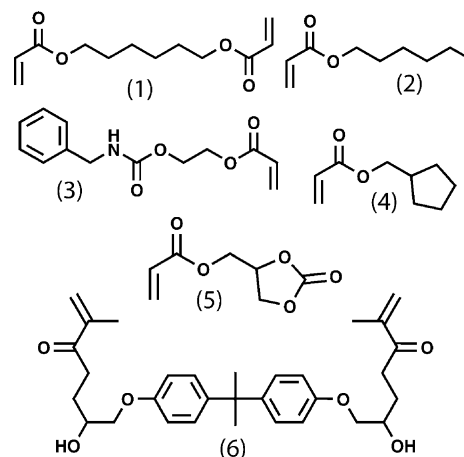


Fig. 1. Chemical structures of monomers used in this study.

Madison, WI) to monitor polymerization kinetics [25]. A horizontal transmission accessory was used to allow horizontal mounting of samples for FT-IR measurements [26]. A MCT/B-XT KBr detector-beam splitter combination was used to obtain a temporal resolution of 0.4 s per scan to monitor these polymerizations. FT-IR spectra were measured with 4 cm^{-1} resolution at two scans per sample. An ultraviolet light source (Novacure, 100 W Hg short-arc lamp, EXFO, Mississauga, Ont., Canada) was equipped with a liquid light guide and band-pass filter (320–500 nm, EXFO, Mississauga, Ont., Canada) and used to irradiate the co-monomer mixtures. The internal aperture of the UV light source was used to control the incident light intensity. Sample thickness was 15–20 μm , and monomer formulations were prepared immediately prior to use. IR spectra collection for serial samples was measured from a single spot on the sample, with multiple samples per composition. The carbon–carbon double bond ($\text{C}=\text{C}$) peaks ($1580\text{--}1660\text{ cm}^{-1}$) were integrated and used to determine conversion after polymerization had completed. Irradiation and conversion measurement were continuous and simultaneous under these conditions unless it is noted that the initiating light source was extinguished at some point during the polymerization.

2.3. Preparation of composition gradients

The gradient mixing procedure is described in detail elsewhere [5], but briefly, a pump is used to introduce a monomer to a rapidly stirred mixer with an initial monomer composition. While the monomer pump runs, a syringe pump extracts solution from the mixer, producing a gradient within the syringe. The gradient solution is dispensed lengthwise onto the 15 by 30 mm sodium chloride (NaCl) crystal substrate then spread orthogonally (widthwise) to the composition gradient using a flat blade. Another NaCl crystal is placed on top of the sample to form a sandwich that yields a more uniform film thickness. The top crystal also prevents oxygen diffusion, limiting oxygen inhibition

to that dissolved in the original mixture. FT-IR spectra were measured with an IR microscope (Nicolet Continuum, Nicolet, Madison, WI) attached to the FT-IR spectrometer (Nicolet 760 Magna series II FT-IR, Nicolet, Madison, WI).

Unexposed monomer samples of known composition were used to produce normalization parameters and calibration profiles for composition. Standard uncertainty of 4 wt% was measured by calibration of peaks in the C–H stretch regime ($2700\text{--}3100\text{ cm}^{-1}$) for the HA/HDDA system. Compositions for the BisGMA/CCA and BCA/THFFA system were measured with a standard uncertainty of 4 wt% by calibration of peaks in the O–H and C–H stretch regimes. More composition points were used for the HA/HDDA system, since the other systems had multiple peaks to use for calibration. Samples with only a composition gradient were produced and analyzed with IR to determine whether the composition was constant along the width of the sample. These samples showed no statistically significant change in composition across the width of the sample.

2.4. Exposure time gradients

A cover plate attached to a programmable linear motion stage was used to control the exposure time gradient. The exposure time gradient process is presented in Fig. 2. To produce a gradient, the sample is aligned with the edge of the cover plate and advanced 3 mm over the sample, allowing for an unexposed section to determine baseline values for composition as a function of position. An ultraviolet light source (Novacure, 100 W Hg short-arc lamp, EXFO, Mississauga, Ont., Canada) was equipped with a liquid light guide and band-pass filter (320–500 nm filter, EXFO, Mississauga, Ont., Canada) and positioned 20 cm above the sample. Light intensity was controlled through an internal aperture and centering of the light guide,

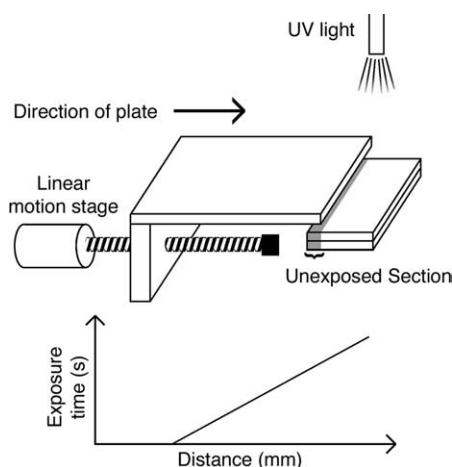


Fig. 2. Exposure time gradient setup with a representative exposure time versus distance plot. As the cover plate moves in the direction of the arrow, more of the sample is blocked from the UV as denoted by the shaded section.

which is constant over the exposed area. The intensity was measured with a radiometer (Model IL1400A with SEL005/WBS320/TD detector, International Light Inc., Newburyport, MA) placed to the sample position. When the UV light is turned on, the cover plate that masks the light moves across the sample at a set speed. As the plate moves across the sample, the UV light is blocked from reaching the sample under the plate. The exposure time is dependent on both the initial position and the speed of the cover plate. For these samples, the edge of the cover plate started at 3 mm (exposure time = 0 s) and moved across the sample for 12 mm at a constant speed. The plate speed is used to calculate an exposure time for each point between 3 and 15 mm. Once the entire sample is covered, the light is turned off, and the sample is arranged for analysis in the IR microscope. Experiments in which the composition gradient direction was rotated relative to the light showed no significant difference in conversion as a function of composition or placement, demonstrating the uniformity of the light over this area.

Samples with only exposure time gradients were analyzed to test the exposure time gradient for repeatability and constant irradiation intensity. IR spectra were compared from three different exposure time gradient samples with constant composition. The average standard uncertainty for conversion at a single exposure time point was 3.0%. Conversion data collected at the same exposure time on a single sample showed no exposure time deviation due to position. Conversion data from one of these samples with 5 mm spacing between runs is shown in Fig. 3. Each of the four runs has the same conversion profile because the light intensity on the sample is constant over the entire area. Average standard uncertainty for conversion when collecting from the same substrate was 1.6%, and no significant difference was found when comparing conversion profiles,

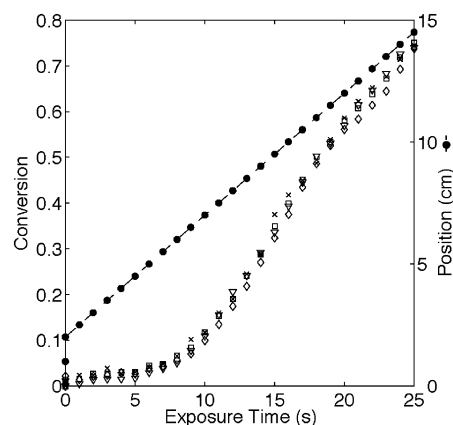


Fig. 3. Conversion as a function of time for a set mixture of HA and HDDA at four positions spaced 5 mm apart on an exposure time gradient sample under a constant light intensity. The distance from the unexposed edge of the salt crystal is given by the black circles (right axis). Samples were polymerized with 365 nm light at 5.0 mW/cm^2 with 0.5 wt% DMPA at $21\text{ }^\circ\text{C}$.

further confirming a constant light intensity profile is produced.

2.5. Parallel testing—FT-IR analysis

FT-IR spectra were measured at 4 cm^{-1} resolution at four scans per point using the IR microscope. A rectangular grid of points is placed on the sample, which are sampled sequentially by the microscope autonomously. A grid of 208 points takes 40 min to complete. This analysis corresponds to eight compositional rows with a step size of 2.5 mm and 26 exposure time columns with a step size of 0.5 mm. The microscope aperture is $100\text{ }\mu\text{m}$ square, with an aperture variation of 0.1 s in the time gradient and a maximum of 0.2 wt% in the composition gradient. The positions of the sample edges and each grid point are known, allowing for exposure time to be calculated for each IR data point taken. Composition is determined with the calibration profiles for each sample point taken, with a maximum standard uncertainty of 4 wt% for each calibration. Only the unexposed sample points are used to determine the composition of that line of data, since C–H stretch peaks shift slightly with carbon–carbon double bond conversion.

Carbon–carbon double bond conversion is determined through a normalization procedure. The same C=C peaks from the serial testing are used. The area of these peaks is integrated and then normalized by the peak area of the carbonyl (C–O) peak at 1730 cm^{-1} . Since, each composition will have an initial ratio of carbonyl to C=C bonds, this normalization removes any changes in the spectra area due to thickness changes or crystal defects that would reduce the beam intensity. The carbonyl peak does change with conversion, but most of the change occurs in peak width, not peak area. Carbonyl peak area increases 3% on average, which correlates with the increased conversion in the system. When using this normalization, the maximum conversion error produced by the normalization is less than 0.5%.

When a constant composition map was sampled, this normalized carbon–carbon peak area is constant across the entire mapped area, even with thickness changes. The standard error of the normalized peak area for this sample was 0.9%. With the conversion, composition, and exposure time known for each data point, a 2D color map is produced for a sample with axes of exposure time and composition. Multiple maps with different composition ranges are combined to produce the entire map. After the IR analysis is completed, the polymer samples are available for additional data collection of different compositions or finer time spacing if needed.

The serial color map was produced similarly, using the same time range as the parallel technique to enable appropriate comparisons. Normalization was not done within the serial samples, since only a single area is sampled throughout the irradiation. The serial technique provides information that does not incorporate any dark

polymerization, whereas the parallel, high-throughput technique includes effectively all of the dark polymerization that occurs at a given exposure time.

3. Results and discussion

3.1. HA/HDDA serial and parallel comparison

HA and HDDA were used to compare the novel parallel technique with the more standard serial technique for measuring polymerization kinetics. These monomers have a similar backbone structure but differ in the number of reactive acrylate functional groups. This co-monomer system was used as a comparative test between the two techniques to ascertain the value of the parallel technique. The only difference in the infrared (IR) spectra of these two monomers is caused by the methyl end group on hexyl acrylate. This makes the composition calibration possible by using the shape of the C–H stretching absorptions. The calibration was performed using five standard compositions, and maps of known compositions were taken to ensure the calibration would be valid over the entire region sampled. For the serial procedure, the mass of each sample is known and used to determine the uniform composition.

Serial and parallel procedures used a light intensity of 5.0 mW/cm^2 for irradiation with 0.5 wt% DMPA as the initiator, and the maximum exposure time was 24 s. The error due to the gradients in the sampled aperture area was 0.1 s in the exposure time axis and a maximum of 0.3 wt% in the composition axis. The results for the serial sampling are shown in Fig. 4, and the conversion color map obtained from gradient testing is shown in Fig. 5. These figures were produced in Matlab R13 with the pcolor function, using interpolated shading and a grayscale color map. Figures produced show composition on the Y-axis and the time scale on the X-axis. Colors on the figure relate to the conversion at

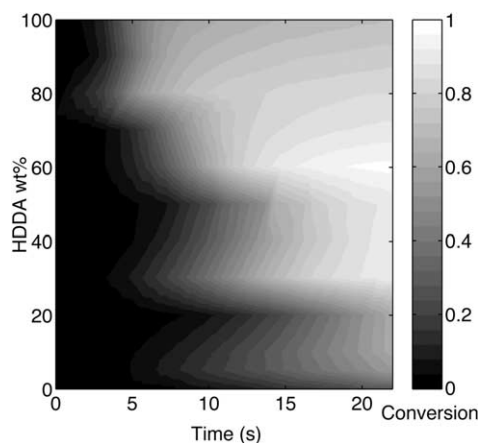


Fig. 4. HA/HDDA serial results with a time spacing of 0.6 s and 12 distinct composition results. The color bar scale to the right of the color map denotes the conversion. Samples were polymerized at 5.0 mW/cm^2 with 0.5 wt% DMPA at $21\text{ }^\circ\text{C}$.

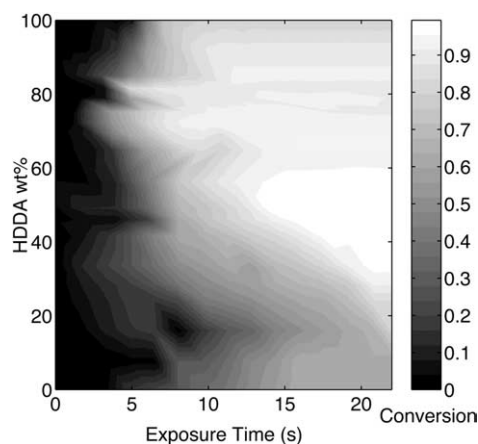


Fig. 5. HA/HDDA parallel conversion results with a time spacing of 1 s and 19 distinct compositions assessed by the IR microscope. The color bar scale to the right of the color map denotes the conversion. Samples were polymerized at 5.0 mW/cm^2 with 0.5 wt% DMPA at 21°C .

that corresponding time and composition, with a color bar legend for conversion supplied for each distinct system. For example, in Fig. 4 at 15 s and 80 wt% HDDA, the color at that point corresponds to conversion between 0.80 and 0.84.

A comparison of the serial and parallel results shows similar trends in the conversion as a function of exposure time and composition. The highest conversion occurs in the same area for each sample, near 60 wt% HDDA. The fastest photopolymerization appears near 80 wt% HDDA in both serial and parallel samples. The standard uncertainty for conversion is 4% in both the serial and the parallel samples, giving each method comparable error.

The principal differences in the conversion between parallel and serial samples arise from the difference in the exposure measurement protocol. In general, parallel samples appear to have faster kinetics overall than the serial sampling. Serial sampling is an in situ method, measuring conversion with real time monitoring using FT-IR. In the parallel method, the samples are analyzed following the exposure and a post-cure period, which allows for additional dark polymerization to occur prior to sample analysis. This dark polymerization effect varies depending on the termination kinetics and the conversion at each sample point. In situ kinetics for the parallel technique cannot be readily determined without extensive modeling, since dark polymerization occurs in all sampled points. There is a possibility for non-isothermal effects; however, heat transfer to the salt crystal and the use of thin films mitigates these effects.

For industrial applications dark polymerization and temperature effects are advantageous as a frequent goal is to optimize the polymerization conditions for a high ultimate conversion while preserving a short exposure time, implying that the described parallel approach is advantageous and well suited for this type of comprehensive polymerization evaluation. This parallel system allows for automated operation of the IR spectra collection, which

frees operator time and limits sample preparation time to production of the parallel sample and microscope setup. The serial technique requires the changing of samples after every photopolymerization and sample mixing for each composition, requiring significantly more time. Time is also saved in evaluation speed by using the parallel technique; however, it comes with the loss of in situ kinetics.

3.2. CCA/BisGMA results

Parallel tests were also conducted on the co-monomer system of CCA and BisGMA. This system is an effective test for this technique since it spans a wide range of viscosities and the kinetics of the individual monomers are widely different. In addition, this system is a unique combination of monomers including both an acrylate and dimethacrylate. The compositions evaluated ranged from 0 to 50 wt% BisGMA as higher amounts of BisGMA are not miscible due to the high viscosity of the mixture. Samples were polymerized at a light intensity of 4.0 mW/cm^2 with 0.5 wt% DMPA as the initiator, and results from this system are shown in Fig. 6.

Fig. 6 shows a non-linear effect in conversion behavior as the weight percent of BisGMA is increased. There are two primary effects occurring as BisGMA is added to the mixture. The first is the increase in viscosity and ultimate cross-linking density of the polymer, which leads to earlier autoacceleration and vitrification, as caused by dramatically reduced radical mobility. Secondly, a relatively slowly polymerizing dimethacrylate is being added in ever increasing amounts that slows polymerization kinetics due to reactivity. With this co-monomer system the novel monomer exhibits very rapid kinetics all of the way to completion that are not affected by the BisGMA monomer addition until after 10 wt% BisGMA is added. Additional BisGMA reduces the double bond concentration within the mixture, which should also slow down the

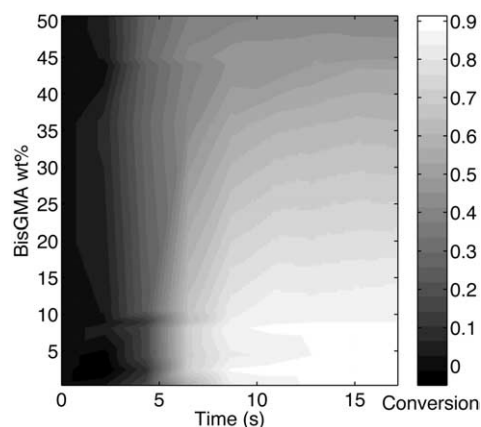


Fig. 6. BisGMA/CCA conversion results with a time spacing of 1 s and 11 distinct compositions. The color bar scale to the right of the color map denotes the conversion. Samples were polymerized at 4.0 mW/cm^2 with 0.5 wt% DMPA at 21°C .

photopolymerization kinetics. The post-cure polymerization of pure CCA is significantly greater than pure BisGMA, which also accounts for the reduced polymerization as BisGMA concentrations increases.

3.3. BCA/THFFA results

To investigate novel monomer interactions further, the third monomer system used to demonstrate the capability of this unique analysis technique was a co-polymer of two monoacrylate materials, BCA and THFFA. BCA is an acrylic monomer with very rapid polymerization kinetics and strong polar interactions, while THFFA is a typical monoacrylate with much slower polymerization kinetics [20]. This co-polymerization was chosen as a test system to analyze the effects of diluent monomers as additives to novel monomer systems. A lower initiator concentration and larger time step were used for this system to allow for a longer time and conversion profile to be measured, since BCA polymerizes too rapidly at the conditions of the other two systems tested. Samples were polymerized at a light intensity of 5.0 mW/cm² with 0.1 wt% DMPA initiator with results shown in Fig. 7. No perceptible phase separation was seen in any monomer or polymer samples.

Fig. 7 shows a nearly linear decrease in the conversion profile when THFFA is added. At approximately 40 wt% BCA the polymerizing mixture has a large inhibition time and relatively slow polymerization. Compositions below 25 wt% BCA showed no measurable conversion occurring over the time span analyzed. The ultimate conversion is also found to decrease as the amount of BCA is reduced; however, the system reaches nearly complete acrylic conversion when the composition is more than 85 wt% BCA.

Since, both monomers are monoacrylates without any significant viscosity differences, there is a linear relationship that is not seen in the previous two systems and provides

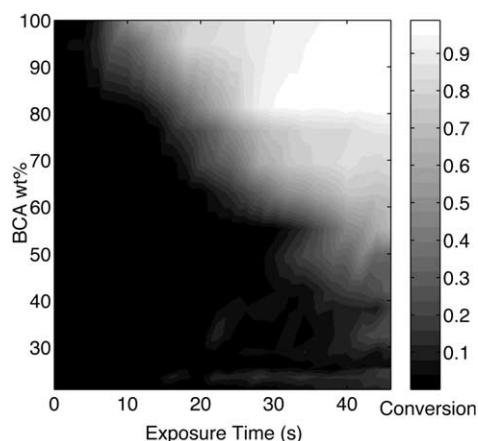


Fig. 7. BCA/THFFA conversion results with 13 distinct compositions assessed and a time spacing of 2 s. The color bar scale to the right of the color map denotes the conversion. Samples were polymerized at 5.0 mW/cm² with 0.1 wt% DMPA at 21 °C.

some insight into the polymerization mechanism of these monomers. There is no change in reactive group functionality in this system, and the kinetics appear to be dominated simply by the concentrations of each acrylate. The proposed mechanisms of novel monomers such as BCA can be evaluated with composition gradients to probe the effects of their inclusion as an additive. At 70 wt% BCA, the conversion of the system reached over 80 percent. This provides evidence that THFFA is incorporated into the matrix, even though the photopolymerization of THFFA by itself is relatively slow. The THFFA delays the polymerization of BCA but does eventually become incorporated into the matrix.

4. Conclusion

The techniques shown here allow for a rapid analysis of conversion as a function of monomer composition and exposure time. As the results show agreement with the traditional serial sampling technique, this method provides a facile route for studying the effects of composition on photopolymer properties. This technique works for a wide range of monomer viscosities and monomer types, allowing for co-polymerizations of many types to be studied. In addition, large differences in kinetics can be captured by controlling the speed and composition range analyzed.

With this technique, the effect of composition on photopolymerization kinetics provides insight into the impact of different monomer properties have on the kinetics of the formulation. For the HA/HDDA sample non-linear changes occur due to changes in both functionality and reactivity, increasing the polymerization rate until cross-linking from the higher functionality monomer eventually limits the overall conversion of the system. In the BisGMA/CCA system, viscosity effects dominate the functionality change, reducing the polymerization rate due to vitrification at relatively low conversion. In the BCA/THFFA system a linear dependence on monomer concentration is found. This technique provides a unique insight into composition effects that can be further explored with different and more complex monomer formulations.

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