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# Photopolymerization of HEMA/DEGDMA hydrogels in solution

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**Abstract**

Photopolymerization is a widely used technique to synthesize polymers and hydrogels. The commonly used ultraviolet (UV)-curable mono-, di- or multifunctional vinylated monomers are often volatile, causing difficulty in kinetics analysis such as photo-differential scanning calorimetry (PhotoDSC). In this work, the DSC sample pan is chemically and physically modified such that the resin can be placed uniformly in the sample pan with minimum sample weight loss during measurement. This approach substantially improved experimental accuracy, which in turn provides a better understanding of the reaction kinetics of UV-curable polymers. Kinetic experiments were carried out for poly(2-hydroxyethyl methacrylate) (HEMA)-based hydrogels. The effects of light intensity and water concentration on the reaction kinetics and rheological change was investigated. It was found that increasing the light intensity enhances the polymerization, but too high an intensity slows down the reaction at the later stage. The addition of solvent and high light intensity facilitates the cyclization, delaying macrogelation. The viscosity rise of the resin system and the formed polymer size were also measured using a photorheometer and a particle size analyzer, respectively. The measured gel time, gel conversion and polymer size distribution agree with the kinetic analysis.


*Keywords:* Free radical photopolymerization; Photo-differential scanning calorimetry; Photo-rheometer

## 1. Introduction

Hydrogels are hydrophilic and crosslinking polymeric materials capable of absorbing a large amount of water while maintaining a three-dimensional network structure. Their strong water absorbance and rubbery nature resemble natural tissues, and they have good biocompatibility and biological inertness. Because of those characteristics, hydrogels have been extensively used in the biomedical and pharmaceutical industries for making contact lenses, biosensors, membranes, artificial organs, and carriers for controlled drug delivery [1]. The most commonly used monomers for synthesis of hydrogels are mono- and multifunctional (meth)acrylates and their derivatives. Many comonomers are added to adjust the crosslinking density, thus modifying the swell and mechanical properties of hydrogels. For instance, diethylene glycol dimethacylate (DEGDMA) is usually mixed with 2-hydroxyethyl methacrylate (HEMA) for preparing poly(HEMA) hydrogels, while triethylene glycol dimethacrylate (TEGDMA) is used with methacrylic acid (MAA) for making poly(MAA-*g*-EG) hydrogels [2].

Hydrogels may be synthesized via various polymerization techniques, such as thermal [3], oxidation–reduction (redox) [4] and UV irradiant methods [5–7]. UV-cure is the most commonly applied method due to its distinct advantages of rapid cure, low curing temperature, in-line production, and low energy requirement. A large amount of research has been carried out on the free radical photopolymerization of UV-curable materials with the use of PhotoDSC, in which the hydrogel matrix is usually loaded into an open aluminum pan and then exposed to UV irradiation. The drawback of using an open pan lies in the inevitable sample loss due to the volatility of testing materials, especially for highly volatile monomers like MAA. Some researchers used the sample weight after the reaction to correct the measurement [8]. Such correction is doubtful because sample loss during the reaction is a time-dependent process. When preparing the carriers for drug delivery, solvents like water and ethanol are often used to control the hydrogel structure. However, evaporation of highly volatile solvents like ethanol makes it impossible to use the open DSC pans for kinetic studies of such hydrogel systems. In this study, we chemically and physically modified the DSC sample pan. The advantages of such modifications are demonstrated through the kinetic study of two different

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hydrogel matrices with a PhotoDSC calorimeter. The two hydrogels are a commonly used neutral hydrogel (i.e. poly(HEMA)) and a pH-sensitive one (i.e. poly(MAA-*g*-EG)). The effects of light intensity and solvent content on the reaction kinetics and rheological change of photocurable hydrogels are investigated.

## 2. Experimental

### 2.1. Materials

Monomers used in poly(HEMA) hydrogels were HEMA and the crosslinking agent DEGDMA. The molar ratio of HEMA/DEGDMA was set at 100/1. Monomer MAA and a crosslinking agent TEGDMA with the same molar ratio of 100/1 were used in preparing poly(MAA-*g*-EG) hydrogels. A photoinitiator (PI), 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651), was applied with a concentration of 1 wt% of the monomer mixture for both hydrogels. All chemicals were obtained from Aldrich and used as received. To insure that the hydrogels have a good balance between high mechanical strength and high swelling response to pH stimulus, normally 40–60 wt% water is used for poly(HEMA) hydrogels [9]. The monomer mixture, HEMA/DEGDMA/PI, was dissolved in distilled water to form solutions with 0, 20, 40 or 60% water by weight in this study. The cured resin is optically transparent when the water content is less than 60%. An MAA/TEGDMA mixture diluted in a 50/50 water/ethanol solvent was also used to verify the applicability of modified DSC sample pans.

### 2.2. Modification of DSC pans

A poly(dimethyl siloxane) (PDMS) curing kit (Sylgard®184 silicone kit, Essex Group Inc.) was prepared and dissolved in hexane to form a 0.05 g/ml PDMS solution. About 10 μl PDMS solution was placed in the DSC pan, which quickly spread to the inner corner of the pan by capillary forces. After solvent evaporation, the pan was heated at 60 °C for 4 h to cure the PDMS resin. The cured PDMS formed a thin layer of O-ring-like hydrophobic film inside the pan, as shown in Fig. 1(a). This PDMS ring can prevent the hydrophilic sample from flowing towards the inner corner during sample loading. Through this treatment, the loaded resin sample can form a thin film with uniform thickness, essential for consistent UV irradiation.

To minimize the sample weight loss during measurements, the sample pan was further modified as shown in Fig. 1(b). The PhotoDSC pan was placed face-down and adhered to a layer of photo-safe, double-sided Scotch tape. A small amount of partially-cured HEMA/DEGDMA/PI solution was applied around the outside edge of the pan, which was then completely cured under the UV light. The cured poly(HEMA) formed an edge around the open pan. The Scotch tape above the original pan was removed by a razor, while that on the edge remained. After loading the sample, the pan was covered with a layer of polyethylene (PE) film and sealed by the double-sided Scotch tape along the edge area.

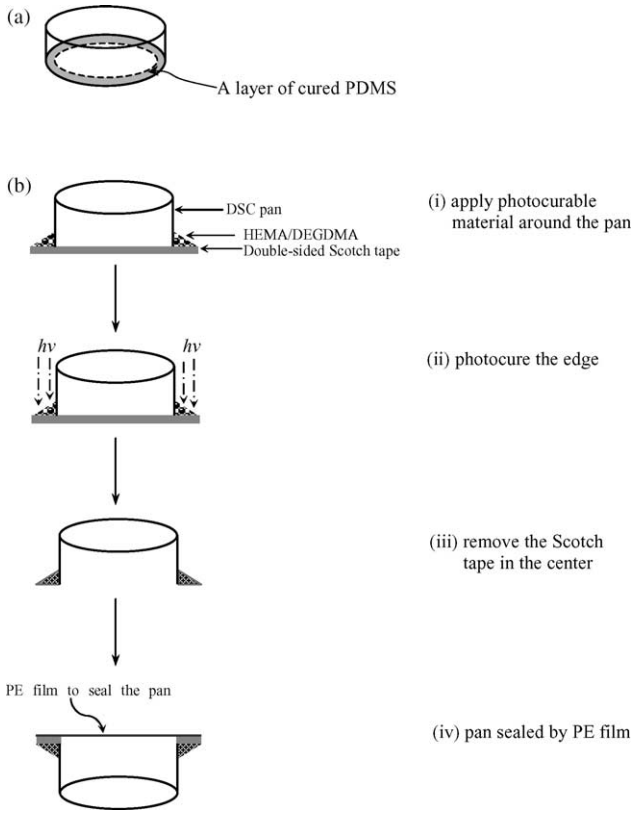


Fig. 1. (a) DSC pan treated with PDMS; (b) Seal of DSC pan.

### 2.3. DSC measurement

The reaction kinetics and the heat of reaction were measured using a PhotoDSC (TA 2920, TA Instruments). UV light (Novacure, 100 W Hg short-arc lamp, EXFO, Mississaugua, Ont., Canada) was used to cure the samples. The reactions were compared in two different aluminum sample pans. One was an unsealed pan covered with a layer of PE film, while the other was a modified pan sealed with a layer of PE film. A micropipette was used for PhotoDSC sampling (5–8 μl), which controlled the sample weight for each test. All measurements were carried out at 30 °C and the light intensity was varied from 0.25 to 40 mW/cm$^2$. Each run was conducted by purging the sample with nitrogen gas until reaching equilibrium, then applying UV irradiation to induce the free radical polymerization.

Reaction exotherm of isothermal photopolymerization was verified by conducting thermal scanning runs on HEMA/-DEGDMA in the presence of 0.2 wt% azobisisobutyronitrile (AIBN) at a heating rate of 2 °C/min from room temperature to 250 °C. A total reaction exotherm of about 463 J/g for HEMA/DEGDMA was obtained, which agrees well with the literature data [3,10].

### 2.4. Rheological measurement

A stress rheometer DCM 300 (Physica) was used to follow the change of viscosity during the isothermal photopolymerization. A UV cell, consisting of a top steel plate with

a diameter of 50 mm and a bottom plate made of quartz glass, was utilized in this test. The UV light source was illuminated from the bottom. The gap between the two plates was set at 1.0 mm and the shear rate used was 0.1 $s^{-1}$. Gel point was assumed when the relative viscosity reached $10^4$.

### 2.5. Particle size analyzer

A Brookhaven 90Plus particle size analyzer was used to detect the polymer size and size distribution during polymerization. Because the formed hydrogel swells more in water than in ethanol, ethanol was used as a solvent to dilute the partially reacted sample for less polymer–polymer interaction. The solution was then filtered with a 0.45 μm filter before measurement. A laser light with a wavelength of 678 nm was used in the particle size analyzer. Measurements were made at 25 °C at an angle of 90°. Sampling time depends on the particle size and the solution concentration. In this test, it was about 10 min per run.

## 3. Results

To demonstrate the advantage of modified DSC pans, the photopolymerization of the HEMA/DEGDMA solution (40 wt% water) was carried out under a light intensity of 0.25 mW/$cm^2$ in both sealed and a unsealed pan. The heat flow was measured, as shown in Fig. 2(a). With a sealed sample pan, an equilibrium state was reached in about 1–2 min, and the measurement was able to start and end at a level close to the 'zero' heat flux. On the other hand, with an unsealed pan covered with a layer of PE film, there was a continuous endotherm due to the evaporation of monomers and solvents. A longer time was needed to reach equilibrium, which would inevitably cause more weight loss. In addition, the measurement started below the 'zero' heat flux level because of the endotherm resulting from sample evaporation. The sample evaporation competed with the reaction during the entire measurement, resulting in a change in the reaction rate profile, a drift of the baseline, and a smaller reaction exotherm. The sample weight before and after the test showed that there was less than a 5% weight loss using a sealed pan, compared to about a 40% loss using an unsealed pan. For samples composed of highly volatile monomers or solvents, i.e. MAA/TEGDMA in water/ethanol, a more severe experimental error was observed, as shown in Fig. 2(b). Since MAA evaporated faster than HEMA due to its high volatility, stronger competition occurred between sample evaporation and chemical reaction for MAA monomers. Consequently, a complete change in the reaction rate profile was observed with the use of an unsealed DSC pan for such systems. Based on these results, we conclude that it is impossible to use the open aluminum pan (even covered with a layer of PE film to minimize the weight loss) for the kinetic analysis of volatile monomers.

Using the modified pan, the effects of solvent concentration and UV irradiation intensity on the reaction kinetics of poly(HEMA) hydrogels were investigated. Fig. 3(a) shows the polymerization rate versus conversion for HEMA/DEGDMA (100/1 mol%) with 20, 40 or 60 wt% water cured at a light intensity of 2.5 mW/$cm^2$. As expected, increasing the solvent content diluted the reactant concentration, hence slowing down the polymerization rate. Shoulder occurred at the very early stage of polymerization (conversion < 10%). Regardless of water concentration, the reaction rate vs. conversion profile followed nearly the same path to the shoulder. In other words, changing the water content had little influence on the early reaction. The solvent started to affect the reaction kinetics thereafter. Fig. 3(b) compares the bulk and solution (40 wt% water) polymerizations of HEMA/DEGDMA (100/1 mol%) under various light intensities, i.e. 0.25, 4.0 and 40 mW/$cm^2$. Clearly, the addition of solvent significantly reduced the reaction rate, in particular the peak. However, it allowed the polymerization to achieve a higher final conversion as compared to the bulk condition (conversion ~80%, see Fig. 3(b)). Similar effects can be found in the reaction rate verse conversion profiles at different light intensities; that is, varying the water content did not affect the reaction kinetics at the early stage.

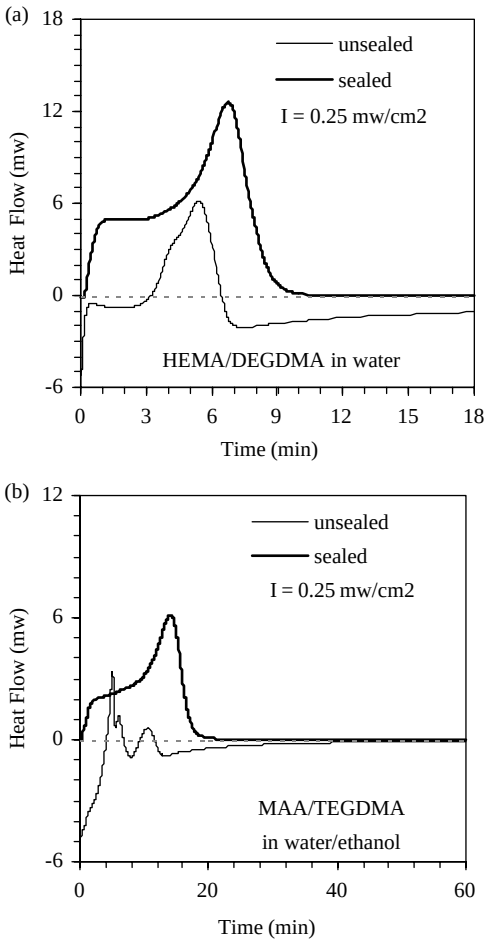


Fig. 2. Comparison of PhotoDSC measurements by using a sealed and an unsealed pan at a light intensity of 0.25 mW/$cm^2$ (a) HEMA/DEGDMA (in 40% water), (b) MAA/TEGDMA (in 50% water/ethanol (50/50)).

To study the effect of light intensity on the reaction kinetics, isothermal reactions were carried out at 30 °C for HEMA/DEGDMA (100/1 mol%) with 40 wt% water. The light

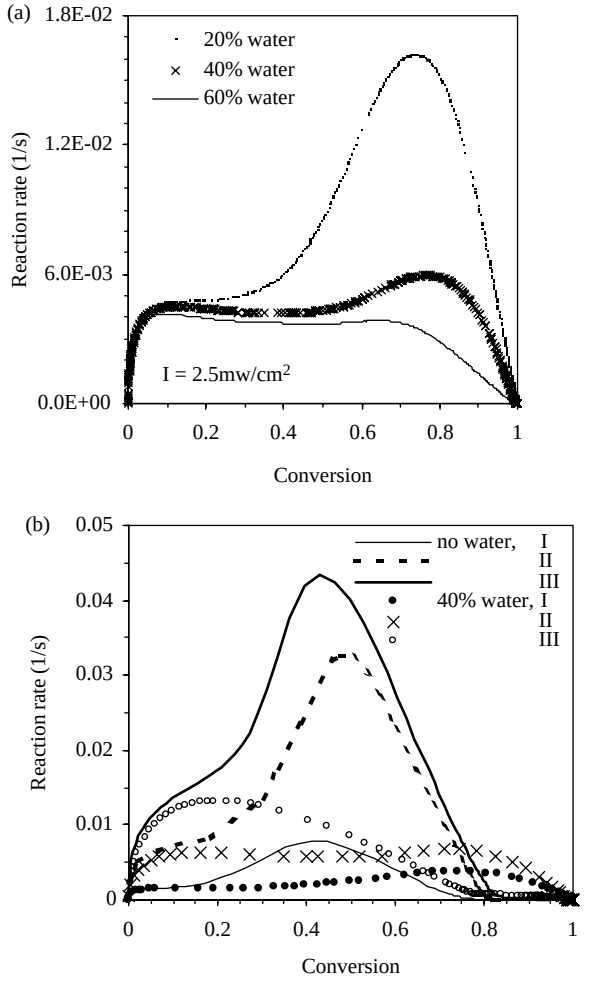


Fig. 3. Reaction rate vs. conversion of HEMA/DEGDMA in the presence of 1% Irgacure 651 (a) with 20, 40 and 60 wt% water content cured under 2.5 mW/cm$^2$; (b) with 0 and 40 wt% water cured under different light intensity (I, II, III: 0.25, 4.9, 40 mW/cm$^2$).

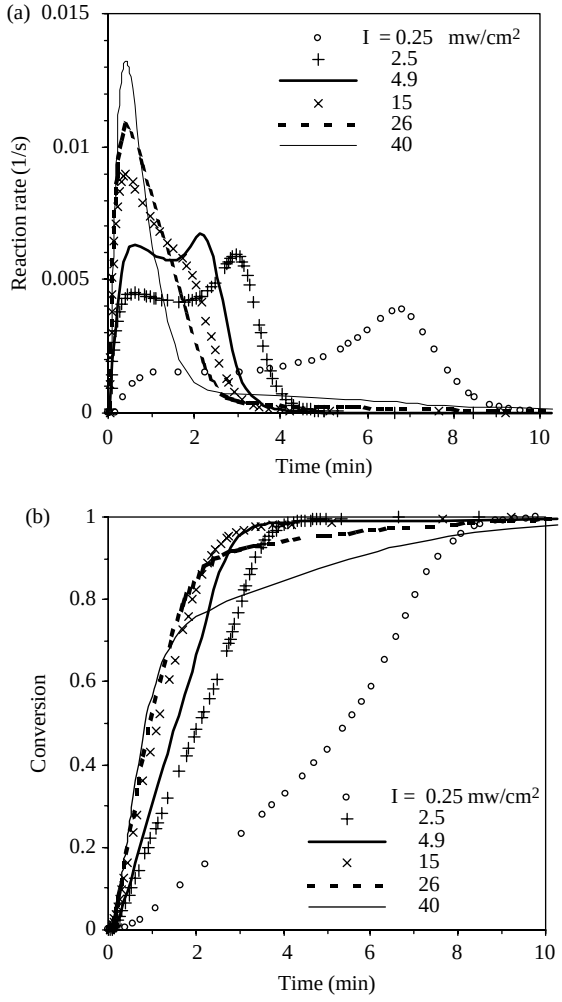


Fig. 4. Effect of light intensity on the polymerization of HEMA/DEGDMA (in water) in the presence of 1% Irgacure 651 (a) reaction rate, (b) conversion.

intensities varied from 0.25 to 40 mW/cm$^2$. Results are shown in Fig. 4(a) and (b). As the light intensity was raised, the initiation rate and hence the polymerization rate increased correspondingly. It was found that when the light intensity changed, the reaction rate profiles (i.e. the size and shape of the exothermic peaks) showed significant variation. Under a low light intensity, the shoulder was small. It gradually became larger and took place at an earlier time with an increased light intensity. However, the occurrence of the peak did not follow the same pattern. When the sample was cured at a light intensity larger than 4.9 mW/cm$^2$, the first peak dominated and the second one became a shoulder. A further increase in the light intensity caused the size of the second peak to become even smaller; for example, a tail was observed at 40 mW/cm$^2$. From the conversion versus time curves presented in Fig. 4(b), one can see that an increase in the light intensity generally reduced the time required to achieve a high conversion. For example, to reach a conversion of 95%, the time required was shortened from 8 to 3.6 min when the light intensity increased from 0.25 to 2.5 mW/cm$^2$. However, if the sample was cured at a light intensity larger than 4.9 mW/cm$^2$, a higher reaction rate was observed at the early stage, but the reaction rate became lower later than that at a low light intensity. Consequently, the time to reach 95% conversion at a light intensity of 40 mW/cm$^2$ was as long as 7.6 min. This indicates that too high a light intensity actually has an adverse effect on the photocure of the resin system. A similar observation was obtained for poly(MAA-*g*-EG) hydrogels as shown in Fig. 5. When MAA/TEGDMA was cured at a light intensity higher than 15 mW/cm$^2$, the reaction rate started to show a significant decreasing trend with an increase in the light intensity as the conversion reached about 40%.

To understand the effect of light intensity and solvent on the structure formation of the polymer, a rheometer equipped with a UV cell was used to follow the viscosity change during the reaction. Fig. 6(a) and (b) display both the relative viscosity and reaction rate as a function of double bond conversion for HEMA/DEGDMA (100/1 mol%) with 40 wt% water cured at 0.25, 2.5, and 40 mW/cm$^2$. One can see that macrogelation occurred at the onset of the second peak under low light intensities (Fig. 6(a)). At a light intensity of 40 mW/cm$^2$, macrogelation occurred near the end of the first peak (Fig. 6(b)). Plotting the gel conversion verse light intensity

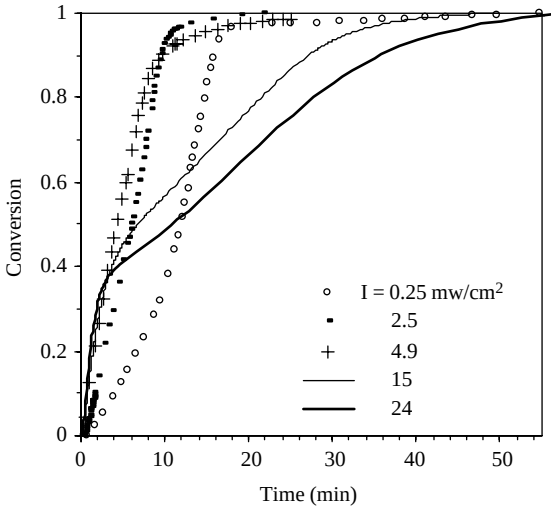


Fig. 5. Isothermal conversion profiles of the polymerization of MAA/-TEGDMA (in 40 wt% of 50/50 water/ethanol) in the presence of 1% Irgacure 651 at 30 °C and different light intensities.

shows that the gel conversion was only 34% if cured at 0.25 mW/cm$^2$, but rose to more than 70% at 4.9 mW/cm$^2$, after which the gel conversion remained nearly the same as shown Fig. 6(c). Fig. 7 shows the relative viscosity change as a function of conversion for HEMA/DEGDMA cured with 0 or 40 wt% water. Both a low (0.25 mW/cm$^2$) and a high (40 mW/cm$^2$) light intensity were used in each case. Gelation was delayed with the addition of solvent. At a low light intensity such as 0.25 mW/cm$^2$, the delay due to the solvent addition was small. However, a significant delay in the gel conversion was observed at 40 mW/cm$^2$.

Fig. 8(a) and (b) compare the size and distribution of polymer formed during the photopolymerization of HEMA/DEGDMA (100/1 mol%) at 0.25 and 40 mW/cm$^2$, respectively. For HEMA/DEGDMA with 40% water and cured at 0.25 mW/cm$^2$, the gel conversion was around 35%. The macromolecules formed in the early reaction were large in size, ranging from 30 to 62 nm at a conversion of 10.5% (Fig. 8(a)). Only one broad distribution peak was observed at this point. As the reaction further proceeded to 20.9% conversion, the molecular size increased significantly. In addition, a bimodal molecular size distribution was observed, which contained small molecules varying from 28 to 37 nm, and larger ones spreading from 105 to 155 nm. When the reaction reached 30% conversion (i.e. approaching the gel point), the size of the large molecules increased to 110–180 nm, while the intensity ratio of smaller molecules to larger ones decreased significantly. Apparently, most small molecules have been converted into much larger clusters. The growth of hydrogels molecules prepared at a light intensity of 40 mW/cm$^2$ is described in Fig. 8(b). Compared to those formed at low light intensities, the molecules formed at high light intensities are much smaller. At a conversion of about 20%, the molecules were so small that the instrument used could not accurately measure their size. When 42% monomers were depleted, a single narrow peak was observed with molecular sizes varying from 14 to 28 nm. The molecular size

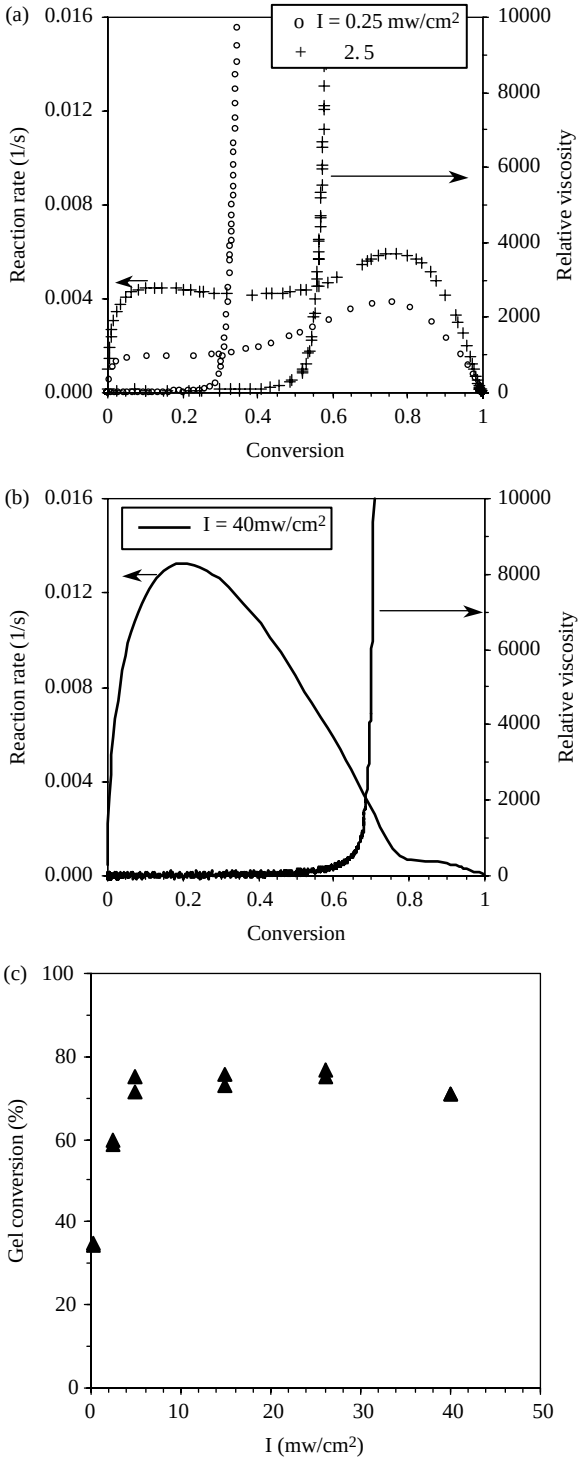


Fig. 6. Reaction rate and viscosity rise as a function of conversion of HEMA/DEGDMA (40 wt% water) cured at (a) low light intensities, (b) a high light intensity; and (c) gel conversion vs. light intensity.

increased only slightly from a conversion of 42 to 61%. Until the reaction approaches macrogelation (conversion ≈ 67%), a bimodal size distribution was observed with the smaller molecules spread from 5 to 11 nm and larger clusters from 35 to 100 nm. Such a bimodal size distribution has also been reported in the photopolymerization of methyl methacrylate and ethylene glycol dimethacrylate in toluene [11,12], and

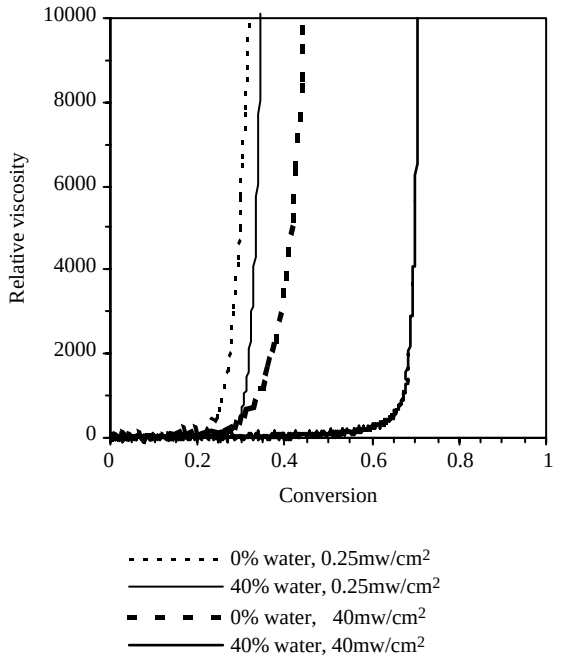


Fig. 7. Relative viscosity change as a function of conversion for HEMA/DEGDMA cured with 0 or 40 wt% water ($I$=0.25 and 40 mW/cm$^2$).

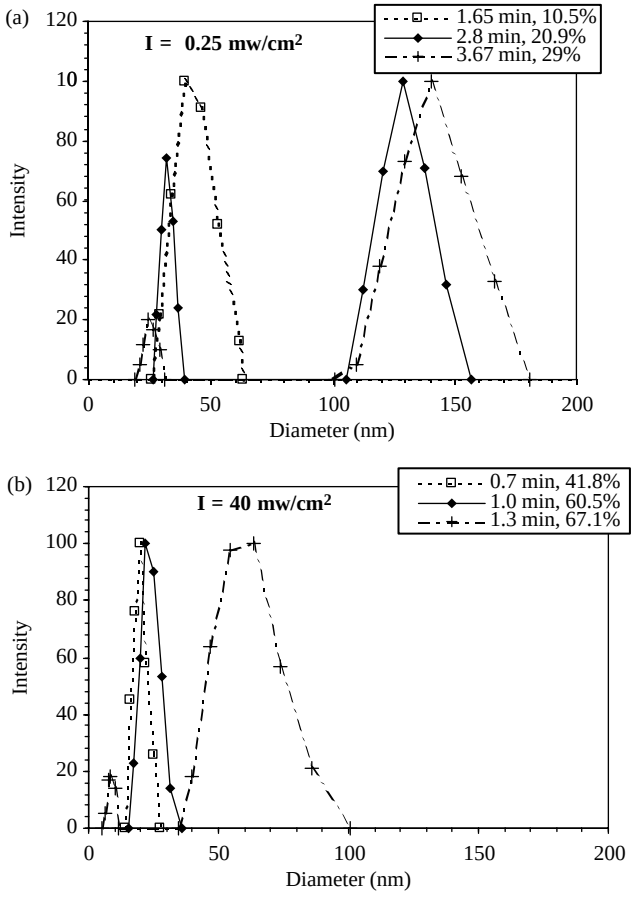


Fig. 8. The molecular size distribution of HEMA/DEGDMA hydrogels (40 wt% water) cured at (a) 0.25 mW/cm$^2$, (b) 40 mW/cm$^2$.

the copolymerization between styrene and dimethylacrylates in toluene [13,14].

## 4. Discussions

The multiple peaks observed in the free radical crosslinking polymerization have been reported for several mono- and divinyl monomers [8,15–18]. Horie and coworkers [15] studied the EGDM/MMA system and found double maxima in the reaction rate curves. They postulated that the two peaks were caused by microgel formation. The first one was attributed to the Trommsdorff effect for the bulk material when the resin mixture was homogeneous, while the second one was due to the Trommsdorff rate acceleration in the microgels. They assumed that the reactivity of a radical with a pendant vinyl group in EGDM is approximately 1/10 of that with the vinyl groups on unreacted EGDM and MMA vinyl groups. As a result, the concentration of the pendant vinyl groups increases steadily through the reaction as the concentration of the vinyl groups on the free monomer is depleted. When the pendant vinyls start to react, the high concentration of pendant vinyls causes dense local crosslinking, leading to microgel formation and a second autoacceleration in the reaction rate. Such postulation has also been used to interpret the occurrence of multiple reaction peaks in the acrylic acid (and *N*-vinylpyrrolidone) copolymerization with TEGDMA [8], in the photopolymerization of a series of oligo(methylene) oxide and oligo (ethylene oxide) dimethacrylates [16], and in the reaction between multifunctional methacrylate and acrylate monomers [17].

Based on our experimental results, a significant delay in the gelation was observed for the photopolymerization of HEMA/DEGDMA hydrogels in the presence of solvent and cured at high light intensities. For the chain crosslinking polymerizations, the existence of multifunctional monomers leads to the formation of pendant double bonds on the growing macroradicals. The pendant double bonds can react with propagation radicals through intramolecular reactions to form cycles (cyclization). Cyclization does not substantially contribute to the increase of molecular weight and the degree of crosslinking of polymer chains. Instead, they form so-called ‘microgels’. The pendant double bonds may also react through intermolecular reactions to form network structures. Therefore, network formation may coexist with the microgel formation during polymerization. The relative rates of intra- and intermolecular reactions are controlled by the initial monomer composition as well as other external curing conditions, such as the solvent content and light intensity.

With little or no solvent, the growing macroradicals are surrounded by adjacent monomers, making it easy for the radicals to add monomers, and leaving less time and chance for the radicals to interact with pendant vinyls for cyclization. The addition of solvent dilutes the monomer concentration, thus increasing the distance between radicals and free vinyls (monomers) or pendant vinyls on polymer chains. This results in a lower rate of adding monomers onto the growing macroradicals, while allowing more time and chance for

pendant double bonds to react with radicals on the same chain to form primary cycles. Thus, the intramolecular reaction becomes a more competitive mechanism when solvent is added. The relative rates of the intra- and intermolecular reactions are also strongly affected by the intensity of incident light. A high light intensity leads to a faster initiation, more radicals and more pendant vinyls in the system. Consequently, cyclization may dominate from the beginning of the reaction. Fig. 7 shows that the addition of solvent does not influence the gelation much at low light intensities, probably because cyclization plays a very weak role there. Thus the molecules formed are large as shown in Fig. 8(a). The kinetics and structure formation at low light intensities show a similar trend to those in the linear polymerization. As seen from Fig. 6(a), the reaction rate was slow at the beginning. At the gel point, the system viscosity went to infinite and the Trommsdorff effect set in, causing a rapid increase in the polymerization rate despite the consumption of monomers. At a still high conversion about 75%, the reaction rate reached the maximum. Finally, the reaction entered the autodeceleration stage until vitrification. In contrast, cyclization can be a dominant mechanism for the system cured at high light intensities. The addition of water also greatly enhanced the intramolecular reaction, resulting in a significant increase in the gel conversion. Several experimental [19–21] and theoretical [17,22] studies showed that the cyclization rate was high at low conversion. The pendant double bonds were consumed predominately to form cycles in the beginning. Therefore, the formed molecules are generally small in size. Macrogelation occurred at a very high conversion. After that the system entered the Trommsdorff effect, at which a small tail was observed.

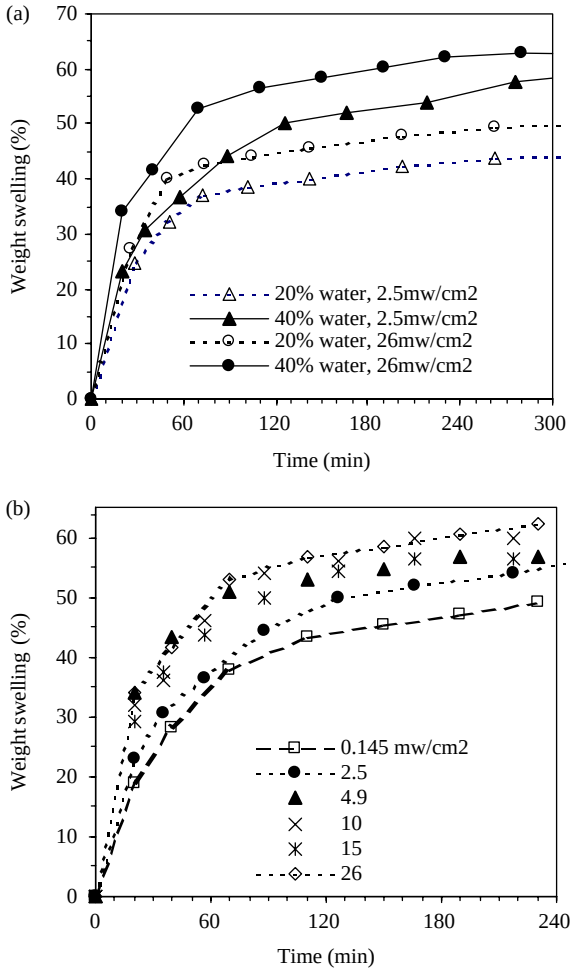


Fig. 9. The weight swelling percentage of HEMA/DEGDMA hydrogels cured (a) with different water concentrations, (b) at different light intensities.

Because of the presence of pendant double bonds, the formed polymer molecules are reactive. They may react with monomers and other polymers to form larger clusters, leading to a bimodal molecular size distribution. Approaching the gel point, most small molecules have converted to the larger clusters and intermolecular reaction among these large clusters finally leads to macrogelation.

Both a high light intensity and the addition of solvent facilitate the cyclization, thus playing a significant role in the overall structure formation during polymerization. One of the most important physical properties featuring the hydrogels is the weight swelling percentage after the dried hydrogel immerses into water or buffer solutions, i.e. ratio of weight of the swollen sample to the initial weight of the dried sample. Fig. 9(a) and (b) shows this property associated with the HEMA/DEGDMA hydrogels cured in the presence of different water concentrations, as well as under various light intensities. When the light intensity increased from 0.145 to 26 mW/cm$^2$, the swelling percentage of cured hydrogels rose from 46% to about 62% after immersing into water for 4 h. Other properties of hydrogels such as tensile and tear strength were also influenced by changing the reaction conditions [23].

## 5. Conclusion

The modified DSC pan can provide uniform sample exposure to UV light and minimize sample loss during reaction, thereby significantly improving the measurement accuracy. The copolymerization of HEMA/DEGDMA was enhanced as the light intensity increased, especially at the low light intensity range and low conversion. At a higher light intensity, an adverse effect was observed. The optimal light intensity for poly(HEMA) hydrogels was about 5 mW/cm$^2$. The addition of water slowed down the reaction, while a higher conversion was attained. Multiple exothermic peaks were observed on the polymerization rate profiles. Varying the solvent concentration and light intensity had a great influence on the reaction rate, as well as on the position and size of the peaks. It was found that the addition of water had a limited affect on the first peak (or shoulder), while the second peaks depended on both light intensity and water concentration.

The addition of water and the use of high light intensity significantly enhanced the cyclization. This resulted in a dramatic delay in the gel point, and a reduction in the polymer size during the polymerization. It also led to an increase in the weight swelling ratio of the cured hydrogels.

## Acknowledgements

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