

# Efficient synthesis of superabsorbent beads using photopolymerization with a low-cost method

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## SUMMARY

Superabsorbent polymers are widely used in hygiene, agriculture, and contamination removal products. The preparation of superabsorbent beads has been reported in the literature from thermal and photopolymerizations of hydrophilic monomers. The rate of photopolymerization is normally faster than thermal polymerization. Our study aimed to test whether the fast photopolymerization technique would work with cheap, easily accessible monomers, and simple equipment that is affordable to high school students within a typical chemistry lab setting. We also evaluated the water absorbance of polymers prepared from hydrophilic monomers. We chose two hydrophilic monomers, *N,N'*-dimethylacrylamide (DMAA) and *N*-hydroxyethyl acrylamide (HEAA), and employed LED UV/Vis light as the light source to break photoinitiator molecules, with silicone oil as the polymerization medium. We hypothesized that superabsorbent beads could be prepared from DMAA and HEAA using the fast photopolymerization technique at room temperature using silicone oil. Our experiments demonstrated the synthesis of superabsorbent beads from a mixture of DMAA, HEAA, and photoinitiator in 60 seconds at ambient conditions. We also discovered that water absorbance increased with the increase of DMAA when its concentration was equal to or less than 25% by weight in the monomer mixture. Beads were completely soluble in water when the concentration of DMAA was equal to or over 50% by weight. Beads with a 25:75 DMAA: HEAA weight ratio demonstrated the highest efficiency among the six compositions tested. Our research also paves the way for high school students to investigate advanced polymerizations in a very simple way.

## INTRODUCTION

Superabsorbents are substances that can absorb large quantities of liquid relative to their mass (1). Superabsorbent polymers are integrated into many industries and their applications are exponentially increasing (2, 3). These substances are critical for basic cleanliness and hygiene. Such characteristics have propelled them to solve global issues such as agriculture and oil contamination (4). They can be employed in various farming products to help plants retain moisture even in dry seasons (2, 3).

There are two polymerization methods for preparing superabsorbent polymers: thermal and photopolymerization. Hoffman *et al.* recently reported the application of thermally polymerized superabsorbent beads in concentrating microorganisms in water (5, 6). Hoffman constructed a special millifluidic system to prepare the beads with thermal polymerization, in which monomers are polymerized at around 70°C for about 2 hours (5, 6). Zustiak *et al.* prepared polyacrylamide hydrogels with photopolymerization in only one minute (7). Fast photopolymerization was also successfully used to prepare superabsorbent beads from *N,N'*-dimethylacrylamide (DMAA), and 2-hydroxyethylmethacrylate (8).

In the thermal initiation process, free radicals are produced as a result of thermal energy, while in photoinitiation the radicals are produced due to light energy. Thermally-initiated polymerization occurs slowly (in hours) and requires more energy and high cost, in contrast to low-cost photoinitiation where polymerization occurs quickly (in seconds) and at ambient temperatures. In a photopolymerization process, a photo-absorbing molecule (photoinitiator) first absorbs specific wavelengths of light, typically ultraviolet (UV) or visible light. This induces the breakage of a weak bond in the molecule and generates free radicals that initiate the polymerization of many monomers containing weak carbon-carbon pi bonds, including acrylates and acrylamides. It was reported that the rate of UV-initiated crosslinking of methacrylate was three orders of magnitude faster than conventional thermal crosslinking (9). In recent years, significant research efforts have been undertaken toward photopolymerization-based 3D printing technology.

We are particularly interested in photopolymerization because it can potentially be conducted in a high school chemistry lab. Photopolymerization does not require advanced equipment and instrumentation, and an inexpensive LED UV/Vis lamp can be used as the light source to initiate polymerization. Moreover, the impressively faster polymerization rate is easily amendable for students conducting lab experiments in school.

Given this context, our study aimed to test the feasibility of this fast photopolymerization technique with inexpensive, easily accessible hydrophilic monomers, and simple equipment that is affordable to high school students within a typical chemistry lab setting. With this technique, superabsorbent polymers can be prepared more energy

efficiently and sustainably. This is also a good example for high school students to explore and understand some fundamental chemistry concepts such as hydrogen bonding, covalent bonding, pi bonding, and bond polarity.

We chose DMAA as one of the two monomers for this study as previous studies have reported its polymerization with thermal and photo processes (5-8). The nitrogen atom in DMAA can form a hydrogen bond with water, making it a good candidate for synthesizing superabsorbent polymers. The HEAA was chosen as the co-monomer in this study, as HEAA has the same acrylamide carbon-carbon double bond as DMAA, and therefore could be considered to be photopolymerizable like DMAA. (5-8) HEAA has a hydroxy group (-OH) that can form two types of hydrogen bonds when it is surrounded by water molecules. (5-8) In the first type, a hydrogen bond is formed between two hydroxy groups, and in the second type, a hydrogen bond forms between the hydroxy group of HEAA and water molecules. (5-8) Besides the hydrogen bond, both monomers have strong polar groups, which makes them hydrophilic and ideal building blocks for preparing superabsorbent beads. We hypothesized that superabsorbent beads could be prepared from hydrophilic HEAA and DMAA with the faster photopolymerization technique at room temperature in silicone oil.

Although there are many commercially available photoinitiators, we selected Bis(2,4,6-trimethylbenzoyl) phenylphosphineoxide (BAPO) due to its strong absorbance at around 400nm, which matched the peak output (around 400nm) of the LED UV/Vis light that was selected for this study (10). In this way, the energy absorbed by the photoinitiator BAPO was maximized.

To determine the best monomer combination for high water absorbance, we photopolymerized six monomer mixtures with different weight ratios of HEAA/DMAA and measured the water absorbance of photopolymerized products (beads). All 6 monomer mixtures successfully photopolymerized at ambient conditions in 1 minute, and the 25:75 ratio of DMAA: HEAA demonstrated the highest water absorbance. Our study has confirmed that superabsorbent beads can be prepared from the faster, low-cost, and environmentally-friendly photopolymerization process. This is particularly important for developing areas where people may not be able to afford and operate expensive and advanced equipment. Our work also demonstrated that high school students can explore functional materials with faster and simpler photopolymerization techniques.

## RESULTS

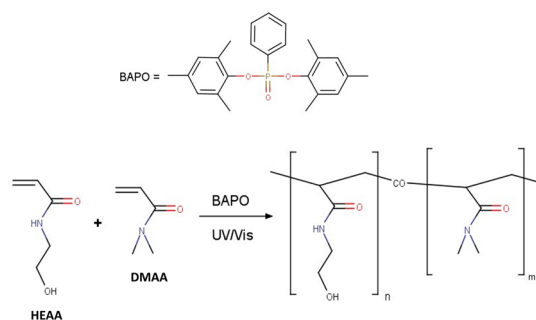
To test our hypothesis, we designed and explored six photopolymerizations with various weight ratios of DMAA and HEAA (Table 1). We photopolymerized monomer solutions with BAPO using LED UV/Vis light to form polymers (Figure 1). For all photopolymerizations, we employed 0.1% of BAPO by weight to the total monomer. A very simple photopolymerization apparatus with a low-cost LED UV/Vis

Polymers	DMAA (g) <sup>a</sup>	HEAA (g) <sup>b</sup>	%DMAA <sup>c</sup>	WA <sup>d</sup>	Std. Dev. <sup>e</sup>
A	0.57	1.71	25	90	11
B	1.02	1.02	50	WS	NT
C	1.55	0.52	75	WS	NT
D	0.43	1.72	20	89	18
E	0.21	1.89	10	56	2.9
F	0.04	1.96	2	43	1.0

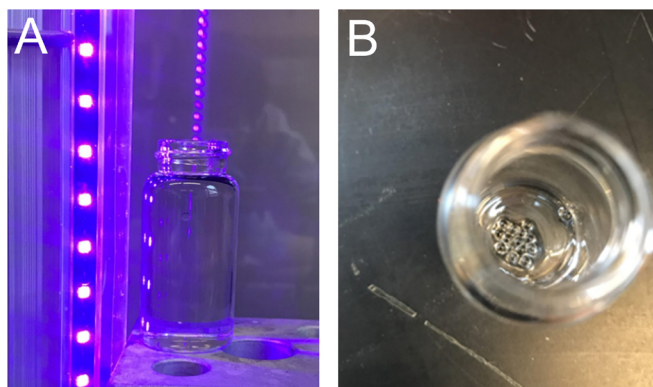
**Table 1: Polymers Prepared from Different Compositions of DMAA and HEAA.** All photopolymerization was conducted at 0.1% by weight of BAPO. a) Grams of DMAA in monomer mixture; b) grams of HEAA in monomer mixture; c) weight percentage of DMAA in monomer mixture; d) water absorbance after 96 hours at ambient conditions; e) standard deviation of water absorbance at the 96-hour point. NT: Not tested; WS: water soluble.

light purchased online was effective to conduct this research, and this apparatus could be set up at any high school chemistry lab (Figure 2A). The total photopolymerization time was only 60 seconds. In this process, the liquid monomer droplet turned into a solid bead at the bottom of the vial. After washing off the residue of silicone oil on the surface of the beads and vacuum-drying, the solid beads were successfully obtained from all six photopolymerizations (Figure 2B). This supported our hypothesis that polymer beads could be prepared from hydrophilic DMAA and HEAA using the fast photopolymerization technique at room temperature in silicone oil. All the beads prepared from gauge 18 needle size, needed in this study, had a diameter of about 2.5 millimeters.

Further, to test whether these photopolymerized beads were superabsorbent, we measured the water absorbance of these beads. We prepared three samples for each composition and determined the average water absorbance and standard deviation for compositions A (25 AM: 75HEAA), D (20 AM: 80 HEAA), E (10 AM: 90 HEAA), and F (2 AM: 98 HEAA) (Figure 3). Co-polymers A, D, E, and F had higher water absorbance rates in the first 20 hours, and then the rate gradually decreased until the beads reached their peak absorbance, which was typically at 4 days (Figure 3). The



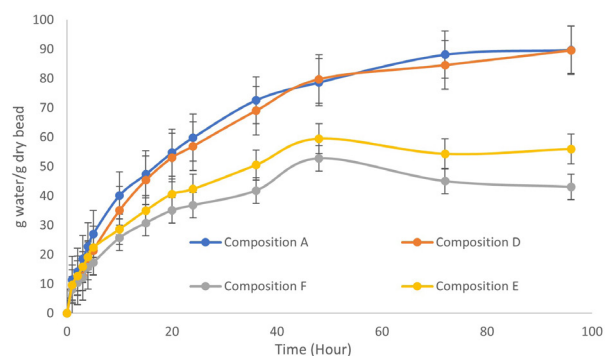
**Figure 1: Photopolymerization of DMAA and HEAA with UV/Vis light using BAPO as the photoinitiator.** Hydrogen bonding occurs with the -OH groups. "n" and "m" values represent variables for a number of monomers within the polymer chain.



**Figure 2: Process of preparing superabsorbent needs and final dry products.** (A) Monomer droplets polymerized sinking. (B) Photopolymerized beads after being washed by hexanes and dried in a vacuum oven.

size of the beads increased substantially after water was absorbed but remained insoluble in water even after four days (Figure 4). After being stored in water at ambient conditions for 4 days, beads with compositions of A, D, E, and F absorbed  $90 \pm 11$ ,  $89 \pm 18$ ,  $56 \pm 3$ , and  $43 \pm 1$  times their original dry weights worth of water, respectively.

We also conducted t-tests to check if there were significant differences in average water absorbances between compositions A/D and E/F. These particular comparisons were selected due to their close values. Our results indicated that there was no significant difference in water absorbance between the A and D beads ( $p=0.80$ ). There was also no significant difference in water absorbance between beads E and F ( $p=0.45$ ). Overall, the absorbance efficiencies increased with the increase of DMAA in the monomer solution when DMAA's weight percentage to the total monomer was equal to or less than 25%. Sample F had the least DMAA content (2%) in this study, and it absorbed the least water among the four water-insoluble samples (A, D, E, and F). Although the difference in water absorbance between A and D was probably less than the experimental error, composition A with DMAA/HEAA=25/75 by weight was the most effective monomer ratio for water absorbance in this study.

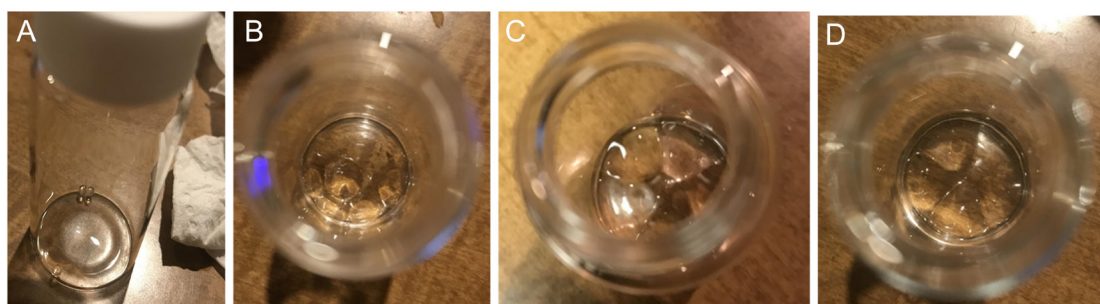


**Figure 3: Average water absorbance and standard deviation of beads prepared from different compositions of DMAA and HEAA at ambient conditions for 96 hours.** Three samples were measured for each composition. The error bars are representative of the standard error of the three samples.

Compositions B and C were not included in Figure 3 because rather than absorbing water, these dissolved after five hours. The water absorbance of beads B and C in the first four hours was plotted in Figure 5. Both beads demonstrated an increase of water absorbance initially, then dropped due to part of the polymer dissolved in water. After five hours, all the beads of compositions B and C completely dissolved in water.

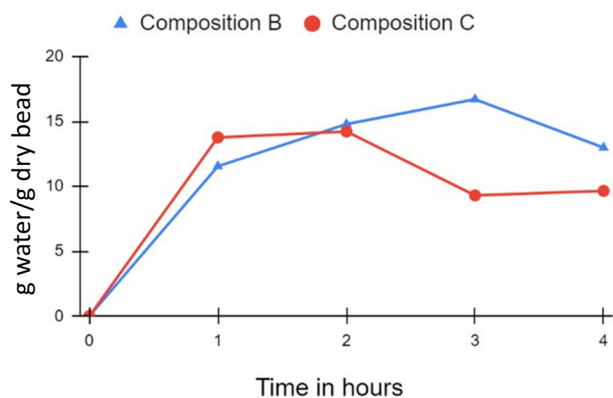
## DISCUSSION

BAPO had good solubility in both monomers, therefore clear liquid mixtures of monomer and photoinitiator BAPO were formed from all six monomer compositions. Small hydrophilic spheres were formed in strong hydrophobic silicone oil and sank naturally due to their higher density. Upon shining of UV/Vis Light, weak bonds in BAPO broke quickly inside the droplets and formed radicals, which initiated co-polymerization of DMAA and HEAA at room temperature (5-8). When polymerization occurred, the weak pi bond in monomers broke, and many monomer units were linked together via strong sigma bonds to form polymers (5-8). The formation of solid beads suggested that higher molecular weight polymers were synthesized. This photopolymerization was also an environmentally-friendly process as it turned



**Figure 4: The size of A beads increased substantially after water absorbance when the beads were kept in dry conditions followed by water for different times.** (a) Dry, (b) 5 hours, (c) 20 hours, and (d) 96 hours.





**Figure 5. Water absorbance changes of compositions B and C at ambient conditions.** The water absorbance of Composition B (blue triangles) increased in the first hour and then dropped. The water absorbance of Composition C (red circles) increased in the first three hours and then dropped.

small liquid molecules into solid polymers without generating any hazardous chemical waste.

Both monomers are capable of forming hydrogen bonds with water, so we expected that co-polymers prepared from both monomers via fast photopolymerization would have high water absorbance. All the beads either dissolved in water or absorbed significant amounts of water (Table 1). The order of DMAA content in water-insoluble beads was A>D>E>F and this order was consistent with the observed water absorbance. This correlation of DMAA content and water absorbance implies that the DMAA repeating unit in the polymer absorbed more water than the HEAA unit. Although HEAA was considered a hydrophilic component, the strong hydrogen bond formed between multiple -OH groups of HEAA would be able to hold the polymer chains from dissolving into water. This trend was further illustrated by the complete dissolution of beads in samples B (50%) and C (75%) with higher DMAA weight percentages. This could be a result of fewer hydrogen bonds formed from -OH groups as HEAA's contents in B and C were less than that in samples of A, D, E, and F. Clearly, the beads prepared from the hydrophilic monomers, in this study, using the fast photopolymerization process absorbed more water than hydrophobic polymers. For example, the reported water absorbance of poly(methyl methacrylate), a common hydrophobic polymer, was only 0.02 (11). The water absorbance of both A (90) and D (89) beads was slightly higher than that of the superabsorbent beads prepared from the thermal polymerization process, which was 80 times their dry weight (6).

Sources of human error could have influenced results. When recording the mass of superabsorbent beads, unabsorbed water could have accounted for mass. Likewise, the use of different scale calibrations could have affected the accuracy of mass measurements.

In conclusion, successful photopolymerization combined with the high water absorbance of the beads demonstrated

that superabsorbent beads could be prepared from DMAA and HEAA using the fast photopolymerization technique, which neither required high reaction temperature nor special equipment. In general, DMAA units in polymer chains appeared to absorb more water than the HEAA units. There was a limit to how much DMAA could be used before the bead completely dissolved in water rather than absorbing it. Further process optimization is necessary to find the best superabsorbent beads, such as tuning the concentration of BAPO and wavelength of the light source. It would be also very interesting to test the performance of beads prepared from other monomer combinations.

## MATERIALS AND METHODS

### Beads Preparation

About two grams of monomer mixtures were prepared by combining two monomers at different weight ratios. The amount of BAPO (97%, Sigma-Aldrich) was measured and added so that all solutions contained 0.1% BAPO by mass. Solutions were magnetically stirred at room temperature to ensure BAPO had completely dissolved. An 18-gauge needle (Amazon) was used to apply the solution dropwise into silicone oil. When the liquid monomer dropped into the silicone oil, it maintained a spherical shape. While the droplet was sinking, the UV/Vis light was turned on. It took about 30 seconds until the bead reached the bottom of the vial and the UV/Vis light was kept on for additional 30 seconds before the bead was transferred to a small vial. This process was repeated until 30 beads were generated, which were then washed 3 times with hexanes. The beads were placed into a vacuum oven for drying for a minimum of 12 hours at 100°C before the water absorbance tests.

### Water Absorbance Measurement

Fifteen dry beads were randomly placed into three 20 mL glass vials, with 5 beads in each vial. The dried mass of all the beads in each of the vials was recorded. Each of these vials was filled with 20 grams of distilled water, sealed, and kept at room temperature. At various time intervals of 1, 2, 3, 4, 5, 10, 15, 20, 24, 30, 36, 42, 48, 72, and 96 hours, the excess water was extracted and the total mass of beads with absorbed water was checked. Water absorbance was calculated with the following equation:

$$\text{Water Absorbance} = \frac{W_{\text{absorbed}} - W_{\text{dry}}}{W_{\text{dry}}}$$

where  $W_{\text{absorbed}}$  is the mass of beads along with absorbed water and  $W_{\text{dry}}$  is the initial mass of the beads (dried).

### Statistical Analysis

T-tests for significance were conducted with Microsoft Excel and Google Sheets. The cutoff for statistical significance was a  $p$ -value of 0.05.

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