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Synthesis of Microgel Polymers as Catalysts

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Synthesis of Microgel Polymers as Catalysts

An Honors Thesis submitted in partial fulfillment of the
requirements for Honors Studies in Chemistry

By:

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Spring 2016

Chemistry

J. William Fulbright College of Arts and Sciences

The University of Arkansas

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Abstract:

New developments in organic synthesis show promise in achieving the best catalytic properties for the hydrolysis of glycosidic bonds through microgel polymers and transition metal complexes. A monomer mix of ethylene glycol dimethacrylate, butyl acrylate, and styrene form miniemulsion polymers after sonication and exposure to UV light. Gravimetric analysis is used to determine the most suitable polymerization conditions by performing experiments at varying pH values, temperatures, monomer amounts, initiator amounts, and lamp heights. The final data show that the best polymerization conditions are a pH of 10.500 at 0°C with a high monomer ratio, 20% initiator amount, and a lamp height of 8 cm. The studies form the basis for improved polymers that will eventually serve as macromolecular catalysts.

I: Introduction

The studies for improved macromolecular catalysts have demanded particular attention in the world of science today. More specifically, research focusing on organic polymer support for catalyst immobilization has drawn much interest (Lu 2009). With this goal in mind, the method of achievement might pair the selectivity of a polymer-ligand system with the catalytic success of transition metal complexes in order to most efficiently perform a particular reaction. The reaction in mind here is the hydrolysis of glycosidic bonds. The mechanism is shown in Figure 1 below.

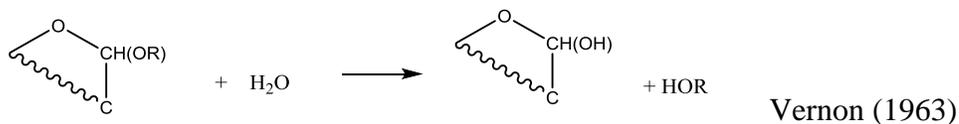


Figure 1: Hydrolysis of Glycosides reaction

Considering the above reaction, the long term goal would be to compare a selective polymer matrix with a transition metal in order to form a catalyst that would aid in the hydrolysis of glycosides, selectively prohibiting activation steps of carbohydrates (Barnett, 2012). Some carbohydrates, such as oligosaccharides, are found on the cell membrane surface and aid in cell to cell recognition (Bertozzi 2001). If this cell recognition was able to be disrupted, it would then be applicable to detect and halt replication of cells in diseases such as the Human Immunodeficiency Virus or cancerous cells in a tumor. This would provide a solid basis for markers and future medicinal treatment of the aforementioned diseases.

For this experiment, the focus was strictly on the polymer complex system of the future catalyst. The work that follows sought to find the best conditions to produce a polymer system with the highest percent polymerization, or the greatest cross-linking outcome. Microgel polymers are easy to prepare in the way that they can be cross-linked and confined in a spherical shape with a very small diameter (Shashoua 1958). The foundation of the microgel polymer system was formed by cross-linking polyacrylates by photo-induced polymerization using a UV-lamp. Photo-induced polymerization with the absorption of UV light involves a free-radical mechanism of the organic cross-linking species in the polymer (Weiss 2009). Photo-induced polymerization also offers advantages in its methods such that it has a quick reaction time, in-situ gelation, and fairly mild reaction conditions (Yagci 2010). The mechanism here is divided into four steps involving a photosensitizer, or initiator, monomer, and free-radical polymer component as shown in Figure 2 below.



Where S = photosensitizer; M = monomer, R• = free radical or polymer fragment

Weiss (2009)

Figure 2: Photo-initiation of polymer chain mechanism

During the trials, many factors were considered in order to achieve the best polymerization results, including temperature, pH of buffer, monomer ratio amounts, percent initiator, and lamp height for the reaction. The polymerization of the polyacrylates yields a heteropolymer which is composed of several repeating units (Sawyer, 2008).

Initially, the polymerization was run at ambient temperature in order to get a good template with minimal error. However, the final result was a successful polymerization of a polyacrylate-styrene system at 0°C and a pH of 10.50. These conditions will better incorporate the proposed ligand and amidine for the future of the catalyst system. From this work, it can then be analyzed through methods such as transmission electron microscopy, gel permeation chromatography, and ability to perform catalytic hydrolysis using transition metal catalysts and glycopyranosides (Striegler 2012). This success will then finalize the search for an improved macromolecular catalyst for the desired hydrolysis reaction.

II: Discussion

The basis of the microgel polymers formed in the following experiments was a crosslinking of ethylene glycol dimethacrylate and butyl acrylate. Styrene served as a stand-in for the future ligand. Sodium dodecyl sulfate was the emulsifier for the mixture.

All polymer components and structures are shown in Table 1 below.

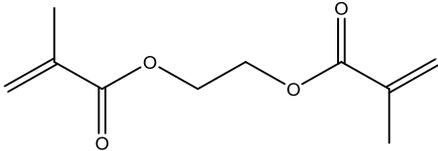
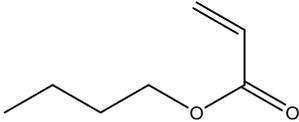
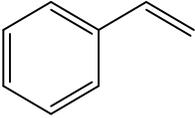
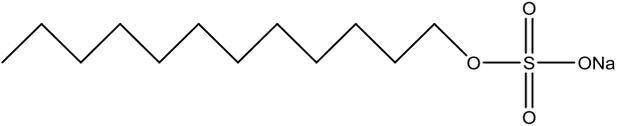
ethylene glycol dimethacrylate (EGDMA)	
butyl acrylate (BA)	
styrene (S)	
Sodium dodecyl sulfate (SDS)	
decane	

Table 1: Names and structures of miniemulsion polymer components.

In order to perform the experiments at different pH levels, the buffers CAPS and TAPS were used. The initiator of the polymerization reaction was 2,2-Dimethoxyphenyl-acetophenone. An inhibitor, pyrochatechol, was also utilized for the aliquots taken over time during the polymerization reaction. All these structures are shown in Table 2 below.

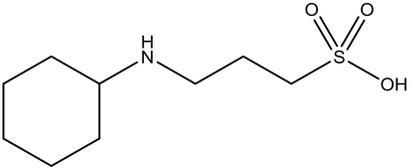
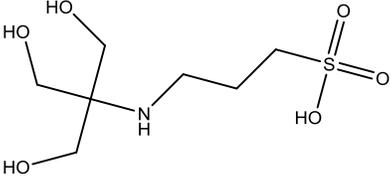
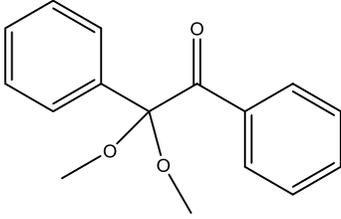
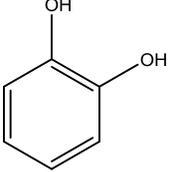
CAPS – pH 10.50	
TAPS – pH 9.00	
2,2-Dimethoxyphenyl-acetophenone (initiator)	
pyrochatechol (inhibitor)	

Table 2: Names and structures of buffers, initiator, and inhibitor for polymerization reaction.

Preparation of EGDMA-BA-S Polymers:

Purification was performed of ethylene glycol dimethacrylate (EGDMA), butyl acrylate (BA), and styrene (S) with Al_2O_3 .

Ambient Temperature: 5 mM CAPS buffer was prepared and adjusted to pH 10.50 with NaOH solution. 5 mM TAPS buffer was prepared and adjusted to pH 9.00 with NaOH solution. A monomer solution was made in the ratio decided with EGDMA-BA-S and

monomer mixes were prepared from it along with sodium dodecyl sulfate (SDS), buffer of choice, and decane. The mixes were left to stir on magnetic stirrer 24-48 hours.

At 0°C: 5 mM CAPS buffer was prepared and adjusted to pH 10.50 with NaOH solution.

5 mM TAPS buffer was prepared and adjusted to pH 9.00 with NaOH solution. A monomer solution was made in the ratio decided with EGDMA-BA-S and monomer mixes were prepared from it along with SDS, buffer of choice, and decane. The mixes were left to stir on magnetic stirrer 24-48 hours.

Sonication of Polymer Mixes:

After stirring 24-48 hours, the mixes were sonicated before polymerization. Each mix was sonicated for 2 minutes in ice at 50 % amplitude and on pulse mode (5 seconds on, 2 seconds off). The sonicator nozzle was also cleaned between each mix to prevent cross-contamination.

Photo-Induced Polymerization:

A UV lamp cooled with water flow was used to polymerize the exposed mixes.

Ambient Temperature: Since regular glass beakers will not allow UV light to pass through, quartz vials were used to hold mixes and set to mix on either side of the lamp on magnetic stirrers. The polymer mixes were exposed to light for 25 minutes with aliquots taken at 5, 7, 9, 12, 25, 20, and 25 minutes.

At 0°C: Mixtures were left to cool to 0°C after sonication and before polymerization.

Glass beakers with open tops were used for polymerization with the UV lamp positioned above the mixes. The polymerization was also done in ice to maintain the established low temperature. The polymers were exposed for 50 minutes with aliquots taken every 5 minutes for 30 minutes, then taken at 40 and 50 minutes.

Before exposure, the initiator 2,2-dimethoxyphenyl-acetophenone was dissolved in MeOH and this solution was injected into each mixture. Also previous to polymerization, each aliquot vessel was filled with an inhibitor solution of pyrochatechol and deionized water. The microgel polymers were left to dry in the heat block at 60°C for 48 hours post polymerization.

Gravimetric Analysis:

This type of analysis is solely based on the mass of a certain analyte within a particular sample. Each component that goes into the polymer mixes was weighed and recorded. The vials were weighed empty, after the aliquot was taken, and after the polymer was dried. With these raw data, Equation 1 below was used to calculate the polymer formation in weight percent polymerization at a certain time.

$$P[\%] = \frac{m_{solid}}{m_{Monomer} + m_{Emulsifier}} \times \frac{m_{all}}{m_{aliquot}} \times 100 \text{ (Gichinga 2010).}$$

Equation 1: Percent polymerization calculation

The first goal of this project was to perform the polymerization with the EGDMA-BA-S system at ambient temperature to determine the best pH conditions for the experiment. The monomer to styrene ratio was chosen for the future ligand to be 1.00% in monomer. CAPS and TAPS buffers were used for the polymerization with a pH of 10.50 and 9.00, respectively. The experiment was repeated many times under these conditions in order to minimize error. Experiment HNM009 yielded the best results from the first semester of work. These can be seen in Figures 3-5 below.

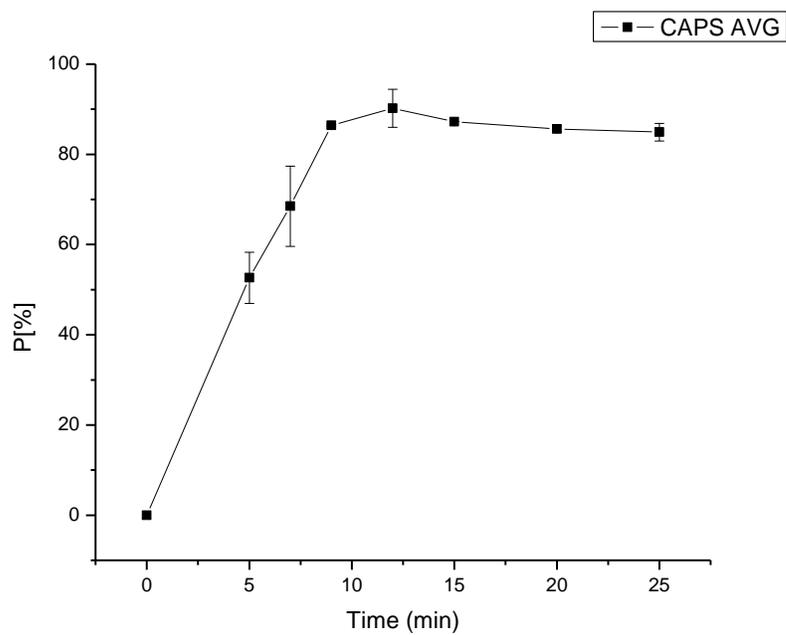


Figure 3: Results and error of experiment HNM009 showing polymerization at ambient temperature with mixes of CAPS buffer at pH 10.50

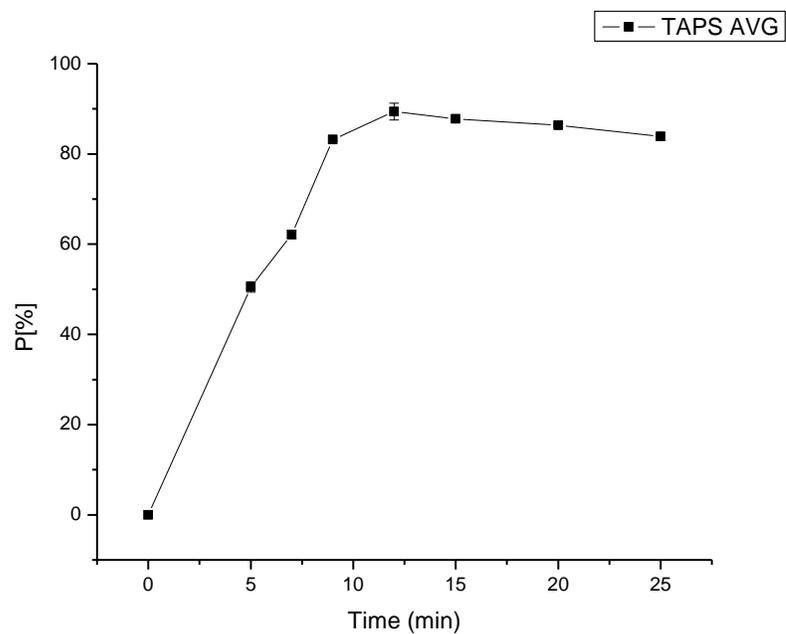


Figure 4: Results and error of experiment HNM009 showing polymerization at ambient temperature with mixes of TAPS buffer at pH 9.00.

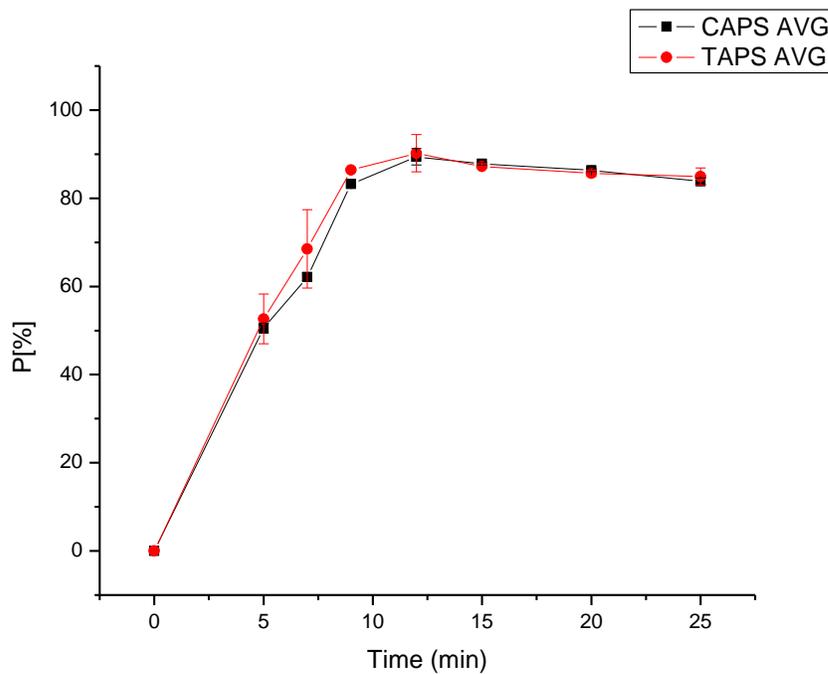


Figure 5: Comparison from experiment HNM009 showing comparison of polymerization between CAPS mixes and TAPS mixes.

From these results, it was hard to conclude whether a CAPS buffer with a pH of 10.50 or a TAPS buffer at a pH of 9.00 would yield a better polymerization at ambient temperature. The next step was to again try to minimize the error within the results for this procedure and also determine if there was any significant difference between the two curves. A few more experiments were performed with the most successful shown below in HNM012. These can be seen in Figures 6-8 below.

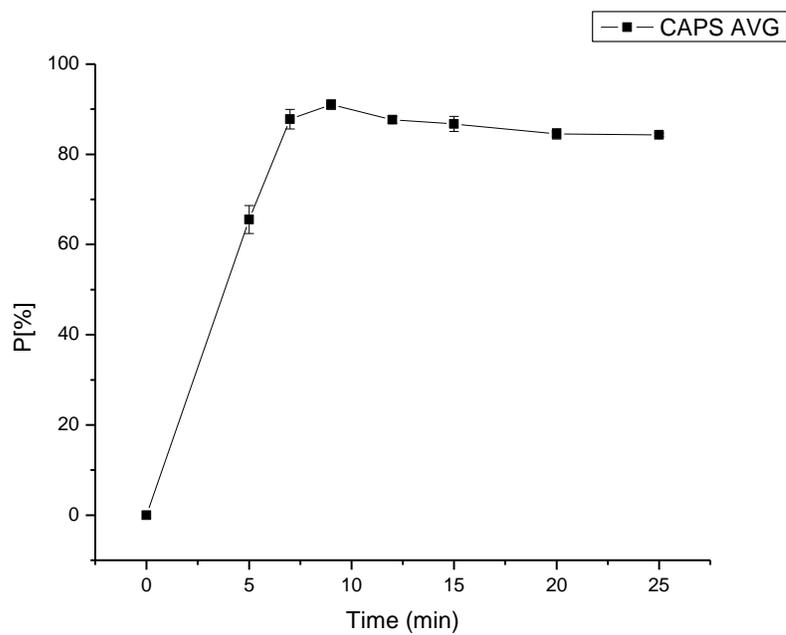


Figure 6: Results and error of experiment HNM012 showing polymerization at ambient temperature with mixes of CAPS buffer at pH 10.50.

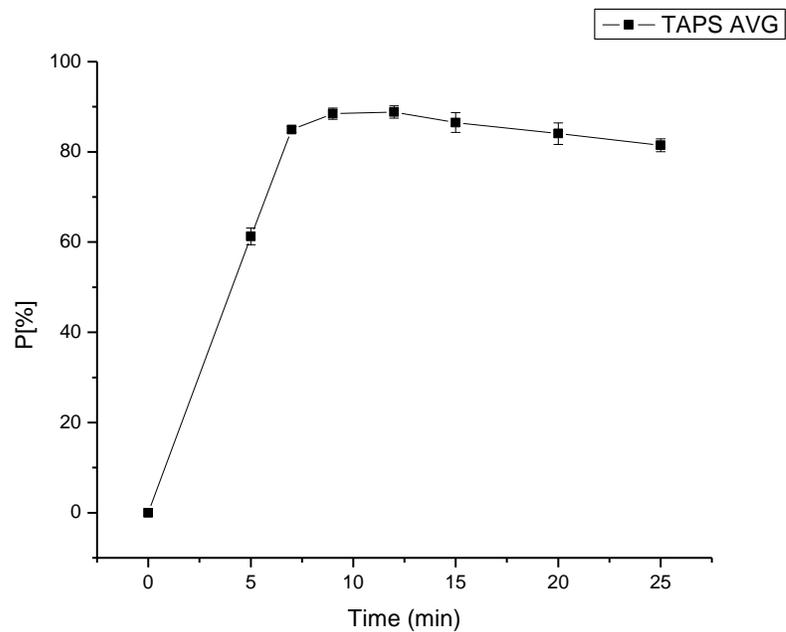


Figure 7: Results and error of experiment HNM012 showing polymerization at ambient temperature with mixes of TAPS buffer at pH 9.00

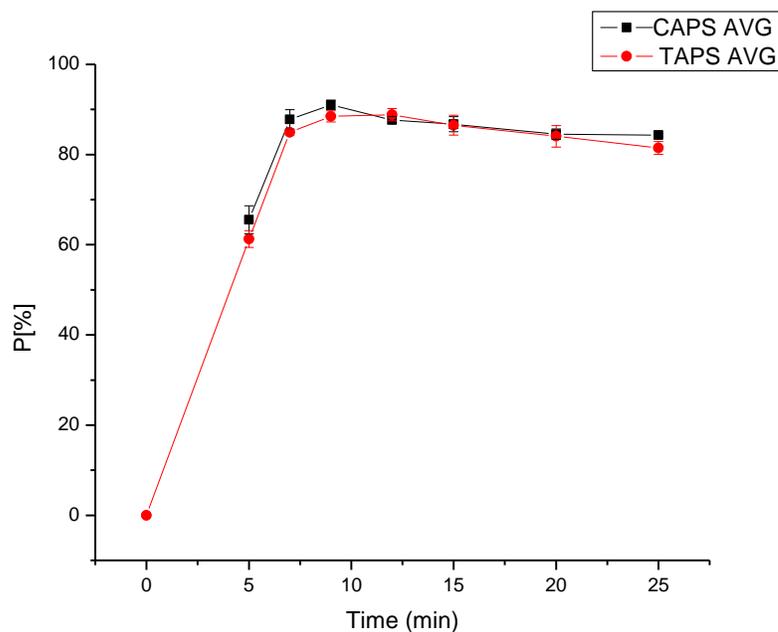


Figure 8: Comparison from experiment HNM012 showing comparison of polymerization between CAPS mixes and TAPS mixes.

These results came out with about the same amount of error with CAPS peaking only slightly over TAPS at the peak of polymerization (9-10 minutes). There was not enough significant difference to determine which pH runs a better polymerization reaction at ambient temperature

To continue on, the experiment was performed at 0°C with the CAPS buffer to imitate the conditions that will be later used when all components are incorporated in the system. This took many repetitions of the polymerization along with changing elements such as cross linking amounts of the monomers, mole percent initiator, and lamp height. All polymerizations were unsuccessful until the lamp height was lowered a significant amount in the second part of experiment HNM025, shown in Figure 9 below.

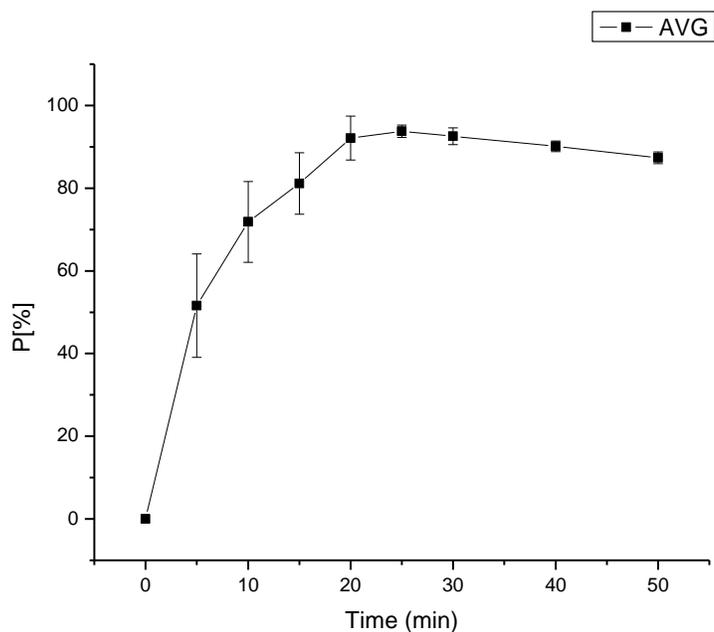


Figure 9: 2nd polymerization and error of experiment HNM025 at 0°C with CAPS buffer at pH 10.50, cross-linking amount of 0.75-1.0-0.035 mmol, 20% initiator, and lamp height of 8cm.

This procedure was repeated with the same conditions once more in order to be sure of the success rate and with more mixes to try and lower the overall error in HNM026.

Results are shown in Figure 10 below.

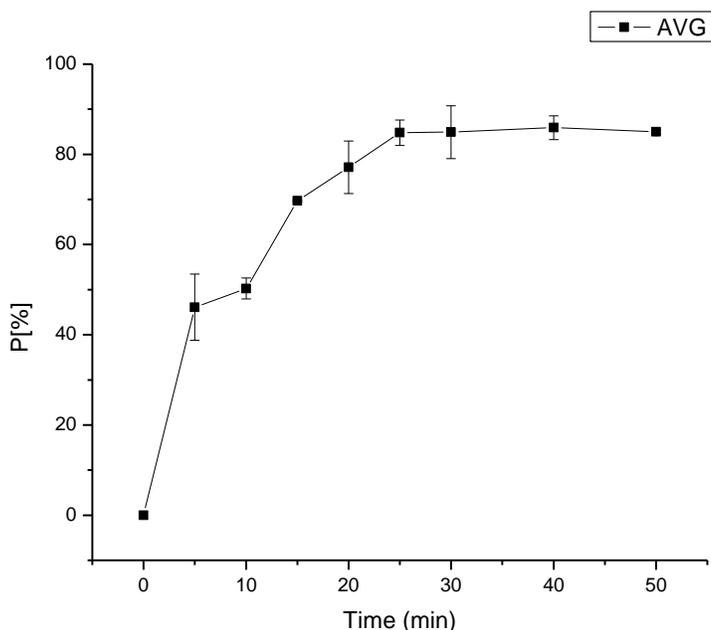


Figure 10: Polymerization and error of experiment HNM026 at 0°C with CAPS buffer at pH 10.50, cross-linking amount of 0.75-1.0-0.035 mmol, 20% initiator, and lamp height of 8cm.

This attempt was unsuccessful to improve error, however it did assure of the success rate.

III: Summary of Results

Initially, ten experiments were completed that primarily worked towards deciding what pH level and temperature the polymerization performed best. After correcting aspects of the procedure such as aliquot time-intervals and data analysis, it was clear the polymerization worked well at ambient temperature (around 25°C), but would not be best to later incorporate the ligand. Ultimately, the results led to pursuing the polymerization at a pH of 10.50 and a temperature of 0°C. These conditions should be optimal for the future components of the system added in later to test the catalytic ability for the hydrolysis of glycosides reaction.

The next goal was to try and determine how to get the polymerization to work at a lower temperature. Unfortunately, when the temperature of the experiment is lowered, the polymerization is much harder to control and does not work with the same system as at 25°C. Many factors were varied to try and minimize this instability and error such as, stirring speed, monomer ratio amounts, initiator amount, and lamp height. A few experiments were performed at a lamp height of 13 cm with varying cross-linking amount and initiator amount. The only combination that partially worked was EGDMA-BA-S (0.75-1.0-0.035 mmol) and a 20 mol % initiator amount compared to the monomer amount. After this, the lamp height was varied at the same conditions, until a lowered lamp at 8cm proved successful in the polymerization at 0°C.

The same experiment with EGDMA-BA-S (0.75-1.0-0.035 mmol), 20 mol % initiator, and 8 cm lamp height was repeated with more monomer mixes to try and achieve a better average between mixes. The experiment again proved successful at these conditions, but the error was still high. This could be due to the fact that at such a low lamp height, it is hard to equally distribute the light between more than two mixes. The last experiment attempted kept the same lamp height of 8 cm, but used the initial conditions of cross-linking amount and initiator amount (EGDMA-BA-S = 0.25-1.5-0.035 mmol and 5 mol % initiator). The experiment involving these conditions with a lower lamp height proved unsuccessful overall.

For the future, the template of polymerization conditions at 0°C that has been determined here could be used to continue to decrease the error margin with more mixes. The polymer then could be made with a ligand instead of styrene in the system, and then

finally, tested for catalytic ability for the hydrolysis of glycosides when linked to a transition metal complex.

All in all, the system determined at zero degrees should serve as a step in the right direction for the future creation of an improved macromolecular catalyst for the hydrolysis of glycosides. With a ligand inserted in the polymer system, the idea would be to immobilize a transition metal complex made from others in the lab. Combining the selectivity and strength of the polymers with the catalytic successes of the metal complexes will help developing carbohydrate-binding agents in the hydrolysis of glycosides.

IV: Experimental Methods

Procedure HNM009:

Purification of EGDMA, BA, S was performed with Al_2O_3 (neutral). A 5 mM CAPS buffer was prepared with 0.1112g CAPS per 90 mL of H_2O and then was adjusted to pH 10.48 with NaOH solution. Finally, the buffer was adjusted to 100mL. A 5 mM TAPS buffer was prepared with 0.1214g TAPS per 90 mL of H_2O and then was adjusted to pH 9.04 with NaOH solution. Finally, the buffer was adjusted to 100mL. A monomer stock solution in ratio EGDMA-BA-S (0.25-1.5-0.035 mmol) was made enough for 9 mixes and then dispersed in equal amounts, 245.14 mg, between 8 mixes. 0.25 mmol (72mg) of SDS and 80 mg (about 0.56 mmol) of decane were added to each mix. Four of the mixes were dissolved in 4.8g of 5mM CAPS buffer and the other four mixes were dissolved in 4.8 g of 5mM TAPS buffer. These monomer mixes were left to stir for 24-48 hours. After stirring, the mixes were sonicated for 2 min at 50% amplitude on pulse mode in ice (5s

on, 2s off). An inhibitor mix was made of 82.18 mg of Pyrocatechol per 2mL of H₂O. 10μL of this inhibitor was injected in each aliquot vessel prior to polymerization. Initiator mix for first polymerization set (A1, A2, B1, B2) was made with 126.60 mg of 2,2-Dimethoxyphenyl-acetophenone per 500μL MeOH. 100μL of this initiator solution was injected in each mix. Polymerization by UV light was performed at ambient temperature for 25 minutes with first set of mixes (A1,A2,B1,B2). Aliquots were taken at 5, 7, 9, 12, 15, 20 and 25 minutes. Initiator mix for second polymerization set (A3, A4, B3, B4) was made with 125.51mg of 2,2-Dimethoxyphenyl-acetophenone per 500μL MeOH. 100μL of this initiator solution was injected in each mix. Polymerization by UV light at ambient temperature for 25 minutes was performed for the second set of mixes (A3,A4,B3,B4). Aliquots were taken at 5, 7, 9, 12, 15, 20 and 25 minutes. The aliquots were evaluated gravimetrically by weighing the vial empty, with the aliquot, and with the polymer after dried at least 48 hours at 60°C in heat block.

Procedure HNM012:

Purification of EGDMA, BA, S was performed with Al₂O₃ (neutral). A 5 mM CAPS buffer was prepared with 0.1102g CAPS per 90 mL of H₂O and then was adjusted to pH 10.48 with NaOH solution. Finally, the buffer was adjusted to 100mL. A 5 mM TAPS buffer was prepared with 0.1230g TAPS per 90 mL of H₂O and then was adjusted to pH 9.01 with NaOH solution. Finally, the buffer was adjusted to 100mL. A monomer stock solution in ratio EGDMA-BA-S (0.25-1.5-0.035 mmol) was made enough for 9 mixes and then dispersed in equal amounts, 245.14 mg, between 8 mixes. 0.25 mmol (72mg) of SDS and 80 mg (about 0.56 mmol) of decane were added to each mix. Four of the mixes were dissolved in 4.8g of 5mM CAPS buffer and the other four mixes were dissolved in

4.8 g of 5mM TAPS buffer. These monomer mixes were left to stir for 24-48 hours. After stirring, the mixes were sonicated for 2 min at 50% amplitude on pulse mode in ice (5s on, 2s off). An inhibitor mix was made of 82.18 mg of Pyrocatechol per 2mL of H₂O. 10μL of this inhibitor was injected in each aliquot vessel prior to polymerization. Initiator mix for first polymerization set (A1, A2, B1, B2) was made with 125.89 mg of 2,2-Dimethoxyphenyl-acetophenone per 500μL MeOH. 100μL of this initiator solution was injected in each mix. Polymerization by UV light was performed at ambient temperature for 25 minutes with first set of mixes (A1,A2,B1,B2). Aliquots were taken at 5, 7, 9, 12, 15, 20 and 25 minutes. Initiator mix for second polymerization set (A3, A4, B3, B4) was made with 126.83 mg of 2,2-Dimethoxyphenyl-acetophenone per 500μL MeOH. 100μL of this initiator solution was injected in each mix. Polymerization by UV light at ambient temperature for 25 minutes was performed for the second set of mixes (A3,A4,B3,B4). Aliquots were taken at 5, 7, 9, 12, 15, 20 and 25 minutes. The aliquots were evaluated gravimetrically by weighing the vial empty, with the aliquot, and with the polymer after dried at least 48 hours at 60°C in heat block.

Procedure HNM025:

Purification of EGDMA, BA, S was performed with Al₂O₃ (neutral). A 5 mM CAPS buffer was prepared with 0.1159g CAPS per 90 mL of H₂O and then was adjusted to pH 10.08 with NaOH solution, which will be at pH 10.50 when temperature is lowered to 0°C. Finally, the buffer was adjusted to 100mL. A monomer stock solution in ratio EGDMA-BA-S (0.75-1.00-0.035 mmol) was made enough for 5 mixes and then dispersed in equal amounts, 280.14 mg, between 4 mixes. 0.25 mmol (72mg) of SDS and 80 mg (about 0.56 mmol) of decane were added to each mix. These monomer mixes were

left to stir for 24-48 hours. After stirring, the mixes were sonicated for 2 min at 50% amplitude on pulse mode in ice (5s on, 2s off). An inhibitor mix was made of 82.08 mg of Pyrocatechol per 2mL of H₂O. 10μL of this inhibitor was injected in each aliquot vessel prior to polymerization. Each monomer mixed was placed in ice after sonification and the temperature of mixes were measured before polymerization to guarantee they were at 0°C. Initiator mix for first polymerization set (A1, A2) was made with 271.11 mg of 2,2-Dimethoxyphenyl-acetophenone per 300μL MeOH. 100μL of this initiator solution was injected in each mix. The UV lamp was placed about 20 cm above open beakers about 3.5cm in diameter in bowl of ice. Polymerization by UV light was performed at 0°C for 50 minutes with first set of mixes (A1,A2). Aliquots were taken at 5, 10, 15, 20, 25, 30, 40 and 50 minutes. Initiator mix for second polymerization set (A3, A4) was made with 271.57 mg of 2,2-Dimethoxyphenyl-acetophenone per 300μL MeOH. 100μL of this initiator solution was injected in each mix. The UV lamp was placed about 8 cm above open beakers about 3.5 cm in diameter in bowl of ice. Polymerization by UV was performed at 0°C for 50 minutes for the second set of mixes (A3,A4). Aliquots were taken at 5, 10, 15, 20, 25, 30, 40 and 50 minutes. The aliquots were evaluated gravimetrically by weighing the vial empty, with the aliquot, and with the polymer after dried at least 48 hours at 60°C in heat block.

Procedure HNM026:

Purification of EGDMA, BA, S was performed with Al₂O₃ (neutral). A 5 mM CAPS buffer was prepared with 0.1159g CAPS per 90 mL of H₂O and then was adjusted to pH 10.07 with NaOH solution, which will be at pH 10.50 when temperature is lowered to

0°C. Finally, the buffer was adjusted to 100mL. A monomer stock solution in ratio EGDMA-BA-S (0.75-1.00-0.035 mmol) was made enough for 5 mixes and then dispersed in equal amounts, 280.14 mg, between 4 mixes. 0.25 mmol (72mg) of SDS and 80 mg (about 0.56 mmol) of decane were added to each mix. These monomer mixes were left to stir for 24-48 hours. After stirring, the mixes were sonicated for 2 min at 50% amplitude on pulse mode in ice (5s on, 2s off). An inhibitor mix was made of 83.83mg of Pyrocatechol per 2mL of H₂O. 10µL of this inhibitor was injected in each aliquot vessel prior to polymerization. Each monomer mixed was placed in ice after sonification and the temperature of mixes were measured before polymerization to guarantee they were at 0°C. Initiator mix for polymerization was made with 451.05 mg of 2,2-Dimethoxyphenyl-acetophenone per 500 µL MeOH. 100µL of this initiator solution was injected in each mix. The UV lamp was placed about 8 cm above open beakers about 3.5cm in diameter in bowl of ice. Polymerization by UV light was performed at 0°C for 50 minutes for all four mixes. Aliquots were taken at 5, 10, 15, 20, 25, 30, 40 and 50 minutes. The aliquots were evaluated gravimetrically by weighing the vial empty, with the aliquot, and with the polymer after dried at least 48 hours at 60°C in heat block.

Data Analysis:

Vessels the aliquots were taken in were weighed before the reaction. Then, the polymer aliquots taken overtime were weighed after the reaction. The dry polymers were weighed after allowing them to dry to room temperature. The weights of the aliquot and dry polymer were found by subtraction using worksheets in Origin 7 program. Using the equation 1 listed above and software program, the percent polymerization for the reaction was found over time for each mix. The average of percent polymerization for the mixes over time was plotted along with standard deviation.

Instrumentation:

The Beckman ϕ 200 pH Meter was calibrated before use in buffer solutions of 4, 7, and, 10 pH and used to make buffer solution for polymer mixes. The Mettler Toledo Classic analytical balance was used for weighing out polymer components and for gravimetric analysis. The Branson Digital Sonifier 50% amplitude was used for sonicating polymer mixes before reaction. The Heidolph MR Hei-Standard magnetic stirrers were used to stir mixes before and during polymerization reaction. The Simran SMVS-500 power source converter with UV lamp was used for light in radical polymerizations. The VWR Digital heat block was used for drying polymers after reaction.

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