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Kinetics of Polymerization Reaction in Miniemulsions

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KINETICS OF POLYMERIZATION REACTION IN MINIEMULSIONS

A Major Qualifying Project Report:
submitted to the Faculty
of the
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science

by

Allison Elder

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Date: April 8, 2008

Approved:

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ABSTRACT

Miniemulsions are an important part of drug delivery and cosmetics research. In this MQP, the kinetics of the polymerization of methyl methacrylate (MMA) was followed to try and understand more about this reaction. The droplet sizes of the polymerized miniemulsions were also examined. In this project it was found that the polymerization of MMA was successful at 75°C and that increasing the amount of surfactant decreased the droplet size of the miniemulsion and increased the polymer conversion.

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AUTHORSHIP

Both Allison Elder and Katie Hudon contributed equally to this MQP.

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CHAPTER 1: INTRODUCTION

The use of miniemulsions in industry is widespread and is continually expanding as companies create new uses for them. Specifically, polymer miniemulsions are very important in the fields of drug delivery and cosmetics. Polymer miniemulsions can be used to target a specific drug delivery site in the body and enhance the stability of the drug. In cosmetics, polymer miniemulsions can be used to create a homogenous texture between two immiscible ingredients such as in lotions and shampoos.

The main objective of this MQP was to follow the reaction kinetics of the polymerization reaction of MMA in miniemulsions. This was done by carrying out MMA miniemulsion polymerization reactions and taking samples at different times. The percent polymer was calculated once the samples were freeze-dried, which removed the monomer and left only the polymer. Our hypothesis was that the kinetics of the polymerization of MMA would be affected by temperature and amount of surfactant.

In order to characterize the quality of the miniemulsions, droplet size was determined using dynamic light scattering. By varying the surfactant amount, it was expected that the droplet size would also change. We found a statistically significant difference between the extremes of the surfactant amount range. This could have been due to use of Lutensol as the surfactant, as it is known to not provide a significant variation in droplet size in miniemulsions.

It was found that only runs conducted at 75°C achieved polymer conversion of more than 90%. When the same experiments were run at lower temperatures (60°C, 50°C, 40°C) high conversion was not obtained. Many parameters of the experiment were tested to see if they were the cause of the inconsistencies, including time range over which the reactions were carried out, the amount of surfactant, the type of initiator, and purification of the monomer.

CHAPTER 2: BACKGROUND

2.1 *Polymers*

Polymer research is a continuously growing field because of the range of applications related to their variation in size and type. Polymers consist of monomers linked together by covalent bonds to form long chains that usually have highly desirable physical characteristics. The spatial arrangement, orientation, and connection of the polymer are the major factors in determining the physical properties. These factors can be changed by varying several parameters of the molecule including the monomer itself or the specialized chemical groups appended to the monomer. The conditions at which the polymerization is conducted in, such as temperature, pH, and pressure, can also affect the macroscopic properties of the polymer. There seem to be infinite applications of polymers in both biological and technological sectors.¹

The arrangement and orientation of the polymer molecules have a large effect on the physical properties of the polymer as a whole. A polymer can be formed into one of three main types of connections including linear, branched, and cross-linked. Linear polymers form long straight chains of monomers. These long straight chains tend to lead to stronger and tougher polymers because of their increased length. The increased length allows for more intermolecular forces which enhances the strength of the polymer. Branched polymers, in contrast, can either become more or less stable when branches are added. If the branches that are added are long in length then it has a similar affect as long linear chains. The long branches increase the intermolecular forces and entanglements which makes the polymer more resilient. But, if the branches that are attached are short, then it can decrease the strength of the polymer because it may interfere with the organization of the polymer without adding the strength of the intermolecular forces of a long chain. Still, a polymer that has a lot of shorter branches is more

flexible, which also has its advantages. Usually, the strongest polymers are the ones that are cross-linked, which is formed when two strands are attached together by a branch from one to the other. This adds extra stabilization to the polymer and therefore adds strength to the materials it can form.² A visual representation of the three main types of polymer structure is shown in *Figure 1*.

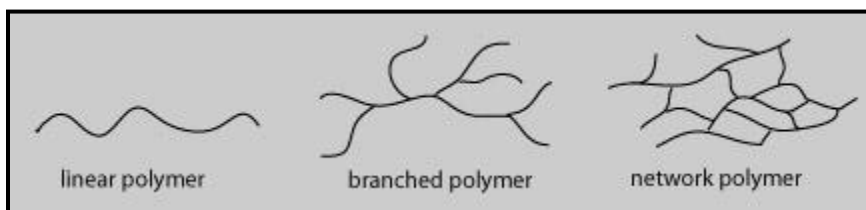


Figure 1: Types of Polymer Structures³

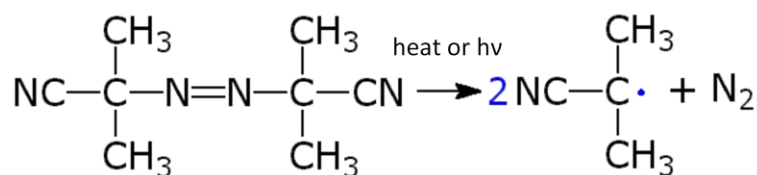
Many parameters can be varied in order to change which type of arrangement is present in a polymer. The conditions at the time of the polymerization reaction can be changed, which would affect the movement and energy of the molecules, and would vary the optimal reaction mechanism and product. The temperature, pressure, and pH of the reactants and their environment can be used to vary the final structure of the polymer. Temperature changes ultimately change both the energy available to the molecules (activation energy barrier) and the viscosity of the solution. Pressure also contributes to the viscosity of the polymer solution.⁴ Viscosity is crucial to the polymer because it affects its structure and the movement of any other surrounding substances, for example tracking molecules, pigments, or pharmaceutical drugs. The pH of the solution can also be a factor that affects the polarity and partial charges of the monomers. Another parameter that can be changed is the monomer or its substituents. Different monomers have different properties; polarity, size, and charge all affect the intermolecular attractions and repulsions which will change the structure of the polymer and therefore its

physical properties. The ability to create the specific characteristics desired for the polymer allows it to be used in numerous applications.

There are endless possibilities for polymers to be used in everyday life and specialty areas. When one thinks of polymers, most of the time plastics come to mind. There are many different types of plastics which all differ in function because of their different composition and structure. One example of a plastic is polyvinyl chloride (PVC), which is very popular in plumbing because of its strength. As for flexible plastic, polyethylene (PE) is the material used for the plastic shopping bags, which are extensively used in modern society. Polymers can also be used in household items such as the Teflon® lining on cooking pans. Basically, most products manufactured today have some sort of plastic used either in its manufacturing or as an integral part of the product.⁵ However, for this project, the main focus is in the applications of polymers in the cosmetic industry and drug delivery systems for the human body. Polymers can be used in these types of chemistry to carry a pigment or medicine to a part of the body and provide an optimal time release for the contents. The ability to control the administration of these chemicals would be able to improve the efficiency of these products.

Polymers are synthesized by polymerization reactions. These are reactions in which single units are bonded together to make a long chain. There are many types of polymerization reactions including condensation and free radical reactions. Condensation polymerization occurs when the monomers are added to the chain with a condensation reaction (releasing a water molecule). Polypeptides, which are the primary structure of proteins, are created using condensation polymerization of amino acids. A very common type of polymerization reaction is known as free radical polymerization. In the initiation step, this reaction requires a free radical to be present to donate its unstable unpaired electron to bond to a stable atom of the monomer,

causing the monomer to radicalize. The next step is to propagate the polymerization, where the monomer radical bonds to another monomer, which forms another radical in the form of a dimer chain. Then, the radical dimer does the same thing to another monomer. This process is repeated many times to form a polymer chain. The polymerization is finally terminated when one radical reacts with another to create a stable molecule. *Figure 2* displays a schematic of the free radical polymerization of methyl methacrylate and the activation of the initiator, Azobisisobutyronitrile (AIBN), which was the reaction carried out for this project.



Activation of AIBN

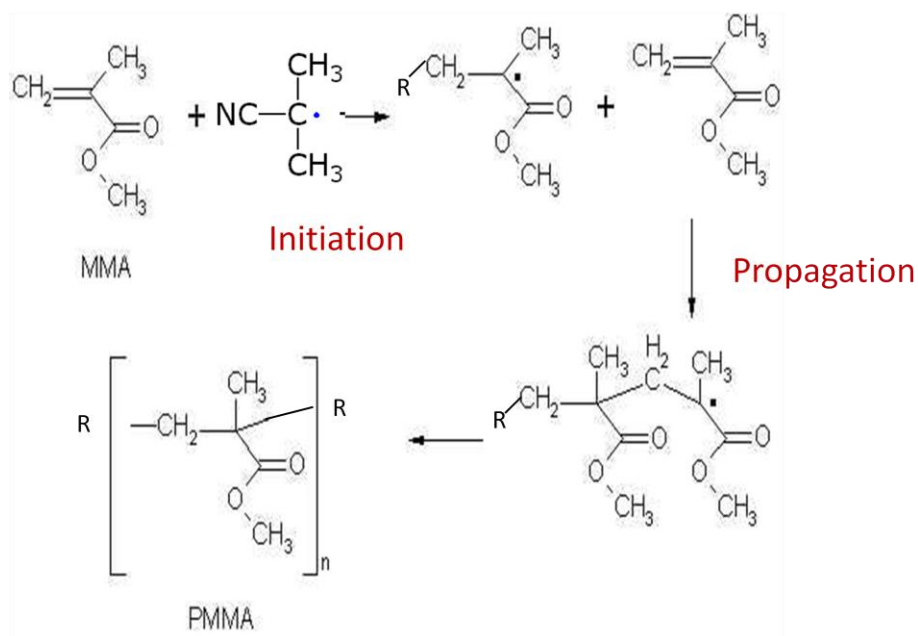


Figure 2: Free Radical Polymerization of Methyl methacrylate⁶

Unfortunately, not all monomers will be able to polymerize and join the long branched chain of the polymer, so the percent polymerization of the monomer is an important characteristic to know when completing a polymerization reaction. Like any other chemical reaction, there comes a point when it is not favorable to continue it. This is when equilibrium is reached. Similar to their structures, percent polymerization can be affected by temperature, pressure, and pH. The lower the temperature, higher the pressure, or higher the amounts of monomer added to the polymer, the more viscous the substance becomes, which further slows down the polymerization because it impedes the diffusion of monomers. Following the conversion of the polymerization reaction is very important in studying a novel technique in controlling polymerization reactions.

2.2 Fluorescence

In order to follow the conversion of polymer, fluorescence is commonly used as a tracer. The intensity of fluorescence is dependent on the ability of the molecules to move about, creating excited states and then returning back to the ground state. Fluorescence is the emission of a photon as an excited electron returns to its ground state after being excited. The excitation wavelength required is always different, shorter, and has more energy than the emission wavelength of the fluorescence. It always loses energy when it fluoresces because the electron will first move around the multiple vibrational states at the excited energy level. *Figure 3* shows a diagram of what occurs during absorption of the excitation light, loss of vibrational energy, and emission of fluorescent light.⁷ The intensity of the fluorescence increases as the concentration of the excited states increase so more of them can then emit the photon at the fluorescence wavelength. Therefore, the fluorescence intensity can be used to determine the amount of fluorescing material present, which is correlated to the amount of the examined substance.

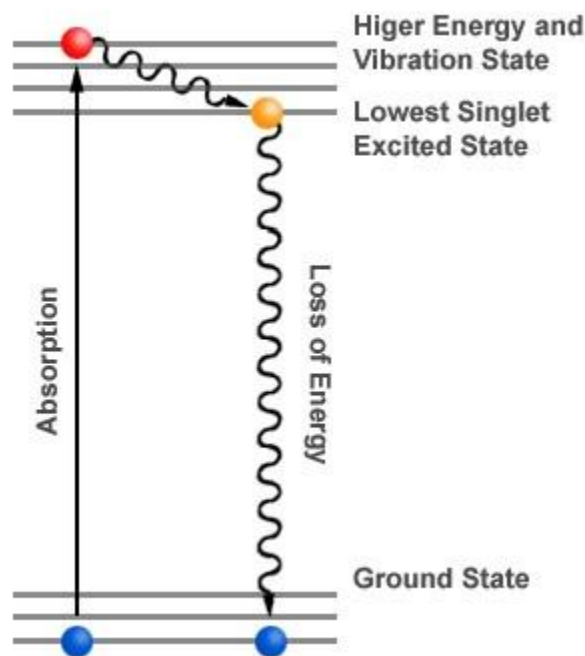


Figure 3: Diagram of Fluorescence⁸

Fluorescence can be very useful not only as a technique to follow polymerization reactions, but also as a tracer for organic synthesis. There are several functional groups that fluoresce under certain conditions that allow scientists to understand both the kinetics and mechanism of the synthesis. In polymerization, the increase in viscosity as more and more polymer is created restricts the movements of the fluorescing compound. The slow diffusion rates lower the collision rates of the fluorescing species which also slows down the emission of the photons. Therefore, it is possible to follow the polymerization reaction using a fluorescing compound within the same encapsulation of the starting materials.⁹ An example of these encapsulations is miniemulsions, which are very useful and a popular area of study for both pharmaceutical and cosmetic scientists.

2.3 Miniemulsions

An emulsion can be described as a dispersion system of two immiscible liquids. In this system, one liquid is dispersed in the other liquid in the form of droplets which are stabilized by the addition of a surfactant and a cosurfactant. The use of a surfactant stabilizes the emulsions by reducing the interfacial tension created between the surface of the droplet and continuous liquid, which prevents the droplets from coagulating. As the droplet size of the emulsions decreases, the amount of surfactant needed increases because the droplets undergo more collisions and need more surface coverage to prevent coalescence.¹⁰ The cosurfactant is added to stabilize the droplet from diffusing and breaking down, which is also known as Ostwald Ripening. In the case of an oil in water emulsion, the cosurfactant is a hydrophobe which increases the osmotic pressure of the trapped species in the droplets which counteracts the Laplace pressure of the droplets.¹¹ An oil in water emulsion stabilized by a surfactant, represented by the black amphiphiles, is depicted in *Figure 4*.

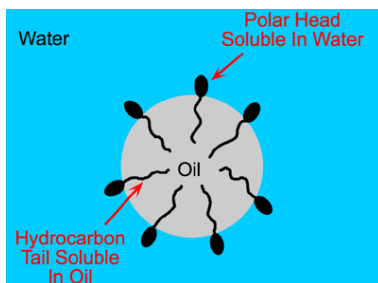


Figure 4: Oil in Water Emulsion¹²

Miniemulsions are emulsions with droplet sizes of about 100-500nm in diameter. The cosurfactants that are commonly used in miniemulsions are long chain alkanes or alcohols, but polymeric hydrophobes have also recently been used. Although the use of surfactants and

cosurfactants allow the droplets to stabilize, they are not stable for long periods of time. Most emulsions seem to be stable for a few hours, but can have a shelf life greater than three months if 2% hexadecane is used as the cosurfactant.¹³ Degradation rates largely depend on the temperature at which the emulsion is kept and the effectiveness of the cosurfactant. The diffusion of emulsions is faster at higher temperatures¹⁴ and is also faster as the cosurfactants' water solubility decreases because for oil in water emulsions a more hydrophobic agent is more effective.¹¹

In order to prepare an oil in water miniemulsion, it is first necessary to dissolve the surfactant in water and to dissolve the cosurfactant (costabilizer) in the monomer. These two solutions are then mixed through stirring to create emulsions and undergo high efficient homogenization in order to form the miniemulsions. A flowchart for the preparation of miniemulsions is shown in *Figure 5*.

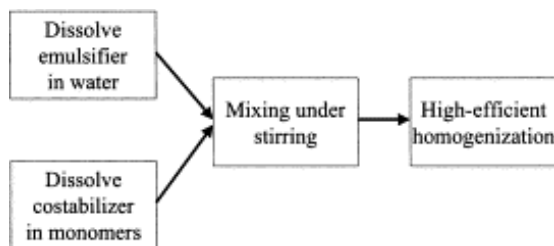


Figure 5: Preparation method for monomer in miniemulsions¹⁴

There are three main types of systems which can be used for miniemulsification which are known as rotor-stator systems, sonicator, and high-pressure homogenizers. A rotor-stator system, which is displayed in *Figure 6* creates miniemulsions through the use of turbulence and shearing while a sonicator, displayed in *Figure 7*, uses ultrasound. In rotor-stator systems, the size of the miniemulsion droplet is related to the rotation speed of the system and the shape of the system. In sonicators, the size of the droplet decreases with sonification time.

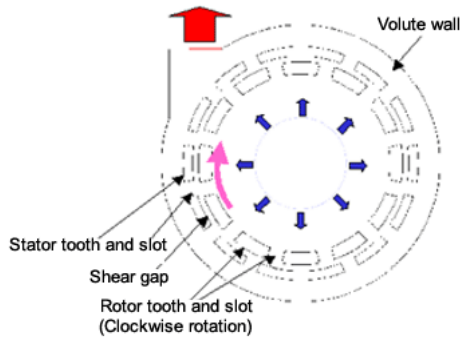


Figure 6: Rotor-stator system¹⁵

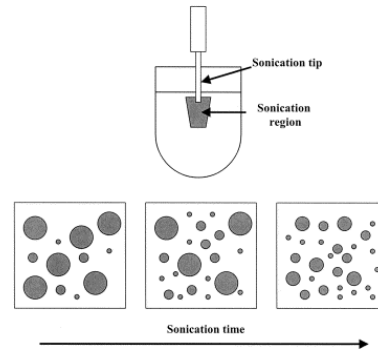


Figure 7: Sonicator¹⁴

High-pressure homogenizers, displayed in *Figure 8*, use pressure to force the dispersed emulsions through a narrow gap at high velocity. The decrease in droplet size is a result of shear, impact, and cavitation forces. The size of the emulsion droplets decreases each time it is passed through the high-pressure homogenizer.¹⁴

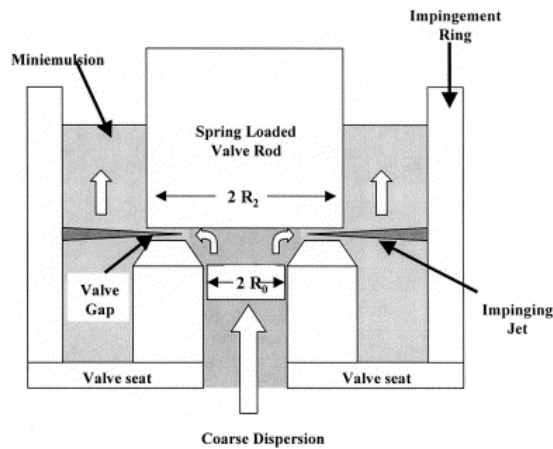


Figure 8: Homogenization valve in a Manton-Gaulin high-pressure homogenizer¹⁴

Once the miniemulsions are created, it is also important to be able to measure the droplet sizes of the miniemulsions. Specifically, droplet size is significant because it affects the miniemulsions' stability as well as factors such as Ostwald Ripening, droplet coagulation, and the polymerization that occurs inside the droplet. Because droplet size affects so many factors, it is imperative to be able to accurately measure the droplet sizes

in order to “understand the mechanisms ruling miniemulsion polymerization.”¹⁴

There are several techniques that can be employed to determine the droplet size of miniemulsions, the most common being dynamic light scattering. Dynamic light scattering measures the Brownian motion of the particles, which can be described as the movement of particles caused by random collisions with the molecules of the surrounding media. This motion can then be correlated with the particles' size. The speed of the Brownian motion is defined by the Stokes-Einstein equation (Eq. 1) in which the size of the particle plays a major role. The diffusion coefficient, D is dependent on temperature, T , viscosity, η , and radius, r . The larger the particle, the smaller the diffusion coefficient, the slower it moves due to Brownian motion.¹⁶

$$D = \frac{kT}{6\pi\eta r} \quad \text{Eq. 1}$$

In dynamic light scattering, a laser is used to illuminate the sample and the fluctuation of the intensity of scattered light is then correlated to give the size of the particles. This is done by using the Stokes-Einstein equation and a digital correlator which, in simple terms, measures the fluctuations of the intensity of the scattered light. The faster the intensity of the light changes, the smaller the particles in the sample. Dynamic light scattering is a very useful technique in the field of miniemulsions; knowing the droplet size of the miniemulsion reveals a lot of information about the miniemulsion and its properties.¹⁶

Emulsions and miniemulsions are important in the fields of cosmetics, food, and for therapeutics.¹⁷ They are also commonly used for plastics, synthetic rubber, and adhesives. One of the main reasons that miniemulsions are so widely used is because they can be coupled with polymerization reactions to create polymer emulsions from

monomer emulsions through the use of an initiator. In an oil and water miniemulsion, the inside of the droplet is the monomer and the initiator is normally water soluble so that it can decompose in the water and form radicals. In simple terms, these radicals will polymerize in the water to form oligoradicals that become increasingly hydrophobic. When their hydrophobicity is large enough, they can enter the droplets and allow the monomer to polymerize through a radical initiated reaction.¹⁴ Oil soluble initiators can also be used, which are added to the initial solution of the organic phase.

2.4 Applications: Drug Delivery and Cosmetics

Two important fields that continually use miniemulsions and polymerization reactions are the cosmetic and pharmaceutical fields. In pharmaceuticals, they are widely used for drug delivery systems and diagnostic tests.¹⁴ In the cosmetics industry, miniemulsion reactions are used in most, if not all of the cosmetic products on the shelves because “it’s the glue that holds it all together.”¹⁸

The use of polymer miniemulsions is very important for drug delivery systems because polymers “can effectively deliver the drug to a target site and thus increase the therapeutic benefit, while minimizing the side effect.” Polymeric nanoparticles can also enhance the stability of drugs and proteins as well as target specific organs and tissues for gene therapy. Peptides, which normally degrade quickly, are now being developed and tested to be used in medicine because they can be encapsulated in nanoparticles, which limits their degradation.¹⁹ These peptide drugs can then be delivered through the body to act as anticancer agents, increase red blood cell production, or help reduce bone breakages from osteoporosis, to name a few.²⁰

In cosmetics, emulsions and polymerization reactions can be used in anything

from mascaras to shampoos to lotions. This is because the use of emulsions and surfactants provide a homogenous texture to these products even though they may use two immiscible ingredients. If emulsions weren't used, cosmetics, which often use polymers and water as their main ingredients, would have an uneven texture.²¹ In moisturizers, the greasiness of the lotion depends on the type of emulsion that is used. In a water in oil emulsion, the product will feel greasier, while an oil in water emulsion will make the lotion feel more moist and creamy.¹⁸ Shampoos and soaps have the ability to clean because of the surfactants in their emulsions. The oily part of the surfactant captures dirt and grime while the water soluble part of the surfactant allows the normally water-insoluble grime to be washed away.²¹ Emulsions also produce the matty feel of cover-up or the gloss and shine of lip-gloss.²² It has been shown that both polymers and miniemulsions are essential to many industries and the study of these topics will have a positive impact on the future of these products.

CHAPTER 3: METHODOLOGY

3.1 Polymerization of MMA Monomer in Miniemulsions

3.1.1 Preparation of Solution for Sonication

To prepare a solution that could be used to create miniemulsions, it was first necessary to create a water based solution and an organic solution. The water based solution was made by adding 250mg of powder Lutensol® AT 50 (BASF Chemical Company) and 18g of MilliQ water to a vial. This solution was allowed to stir by magnetic stirring. While the first solution stirred, an organic based solution was made by adding 50mg of 98% 2,2'-Azobis(2-methylpropionitrile) powder (also known as AIBN) from Acros Organics, 125mg of 99% hexadecane from Aldrich, and 2g MMA (Methyl methacrylate) distilled monomer to a different vial. The organic solution was then added to the water based solution and the two phases were left stir by magnetic stirring for at least one hour at room temperature. While the solutions were stirred, ten empty labeled test tubes were weighed and an oil bath was heated to 75 °C. The oil bath was simultaneously stirred by magnetic stirring.

3.1.2 Sonication and Polymerization

To create miniemulsions from the combination of water and organic phases a Bioblock Scientific Vibra-Cell sonicator was used. The solution was put into the sonicator in an ice bath to inhibit polymerization from starting during the sonication process. It was sonicated for 120 seconds at a 50% cycle (one second on, one second off); also it was made certain that the sonicator probe was not touching any sides of the

vial. After the sonication was over, the probe was cleaned immediately to ensure that there would be no cross-contamination. The solution, now a miniemulsion, was transferred to a round bottom flask and placed inside the 75 °C oil bath with a magnetic stirrer; at this instant the stopwatch was started. At predetermined time intervals, 5, 10, 15, 20, 30, 45, 60, 90, 120, and 150 minutes a sample was taken and put into the corresponding plastic test tube. It was immediately placed in a beaker with liquid nitrogen inside the liquid nitrogen bath very cautiously, when the tube entered the liquid nitrogen bath the time was recorded because this is when the polymerization reaction was stopped. After the last sample was taken, all the test tubes were removed from the liquid nitrogen bath and were allowed to come to room temperature so the condensation on the outside of the tubes could evaporate. When the tubes were rid of the excess condensation, they were weighed again.

3.1.3 Freeze-Drying

The ten labeled test tubes were wrapped together with a rubber band and placed directly in the nitrogen bath for 2-3 minutes. They were then placed in a container specific to the freeze dryer along with paper towels to stabilize the tubes. The freeze dryer container was covered with the specialized lid. Using a VirTis Sentry Benchtop 3L freeze dryer, the samples were left to dry for a period of about three days, or until the samples were room temperature. When the samples were at room temperature it meant that the evaporation of the monomer was complete and the samples were considered to be dry. Then, the samples were weighed a final time.

3.2 Calculations

Once the samples were freeze dried and weighed a final time, the total amount of formed polymer and the percent of polymer formed were calculated for each time that a sample was taken from the heating mixture. The total amount of polymer formed at each time period was calculated by the equation:

$$\text{Polymer} = \left(\frac{\text{weight after freeze drying} - \text{weight of tube}}{\text{weight after cooling} - \text{weight of tube}} \right) \times (\text{Total weight of reactants})$$

The percent of polymer formed at each time period was then calculated by the equation:

$$\text{Formed percent} = \frac{\text{Formed polymer}}{\text{grams of MMA}} \times 100$$

The formed percent of polymer was then plotted with the formed percent of polymer on the y-axis and time in seconds on the x-axis.

3.3 Characterization of Miniemulsions by Particle Size

In order to characterize the miniemulsions, the most useful parameter is the particle size of the droplets. The droplet sizes of the miniemulsion were determined for each of the solutions using the High Performance Particle Sizer, Dynamic Light Scattering (Malvern Instruments). This was done by adding a few droplets of solution to a disposable cuvette and adding MilliQ water. If the liquid in the cuvette was not clear enough, the solution was further diluted with MilliQ water until transparent. The cuvette was then placed in the particle sizer and the droplet size was determined by the machine.

3.4 Continuation of the Polymerization Reactions

The aforementioned methods from preparation of the solution for sonication through freeze drying and calculations were repeated for a total of 32 runs with a few minor changes. Because there was almost not enough solution left at the end of the 2.5 hours for test tube 10, the amount of solution made was scaled up by 1.5 for the remainder of the runs (which made the amount of Lutensol used equal to 375mg). The second run was conducted under the same conditions as the first run in order to solidify the trend (but was scaled up by 1.5 as previously stated). Runs 3 and 4 were also conducted at 75°C, but were carried out with a lower concentration of Lutensol (150mg to 18g water, but when scaled was equal to 225mg to 27g water).

The succeeding runs were carried out at 60°C, 50°C, and 40°C, respectively. Initially, four runs were carried out at 60°C and four were carried out at 50°C. Two of the runs at each temperature were conducted using the higher amount of Lutensol (375mg) while the other two used the lesser amount of Lutensol (225mg). When the results were obtained for the runs at 60°C and 50°C, it was found that the monomer had polymerized with 17% polymer conversion. In order to determine whether the monomer could actually polymerize at 60°C, two miniemulsion solutions containing 75mg of Lutensol were heated over the weekend and tested for percent polymer the following week. Both solutions had a conversion of over 90%. Therefore, polymerization could take place at 60°C, but it took more time. To reflect this conclusion, the runs at 60°C, 50°C, and 40°C were to be tested over a longer time period.

The new runs at 60°C and 50°C were done over a time period of about 23 hours. Samples were taken throughout the day for 7 hours with samples done at 30, 60, 120,

180, 300, and 420 minutes. A final sample was then taken from the solution the next morning after it was left to heat and stir overnight. For both 60°C and 50°C, six runs were conducted, which corresponded to the use of three different amounts of Lutensol. Two runs at each temperature were for solutions with 50, 250, and 450 mg of Lutensol per 18g of water, not including the 1.5 scale up of the experiment.

Unfortunately, the runs that spanned 23 hours at 60°C and 50°C still failed to polymerize correctly, so these runs were repeated using the initial techniques over a period of 2.5 hours for 60°C (with samples taken at the same intervals as the first run) and 5 hours for 50°C and 40°C, with samples taken at 10, 20, 30, 45, 60, 90, 120, 180, 240, and 300 minutes using only 250mg Lutensol per 18g water. However, instead of using AIBN as the initiator, an equal amount of another type of initiator, potassium persulfate (KPS), was used. Because KPS is water soluble, it was not added to either of the solutions before sonication. Instead, it was dissolved in about a gram of water and added by pipette to the already heating miniemulsion solution. The timer was started once the KPS was added because polymerization cannot take place without the initiator. Then, the experiment was continued as before with the immediate cooling of the sample with liquid nitrogen and the weighing of the samples, followed by the freeze drying.

When the experiments with KPS as the initiator failed to work, it was thought that there might have been a problem with the monomer, MMA. Therefore, the monomer was redistilled using a Rotovap at 50°C. Two runs were then carried out using the newly distilled MMA and AIBN as the initiator. These runs were performed like runs 5 and 6 at 60°C, with 250mg of Lutensol and samples taken over the course of 2.5 hours.

CHAPTER 4: RESULTS & DISCUSSION

The major goal in this MQP was to determine the kinetics of the polymerization of MMA in an oil-in-water miniemulsion with respect to the quantitative polymer conversion. By taking samples at different times and calculating the amount of polymer conversion at those times, a polymer conversion curve was able to be created. It was also necessary to measure the droplet sizes in the miniemulsions because droplet size can give insight into many other properties of the miniemulsion.

4.1 Droplet Size of Miniemulsions

An important characteristic of a miniemulsion is its droplet size because it can affect the droplets' stability as well as the polymerization that takes place inside the droplet. The amount of surfactant is the major contributor to the droplet size. It is expected that increased surfactant concentrations used in the miniemulsions will result in smaller droplets in the miniemulsion. This is because the smaller the miniemulsion particle is, the more surface area the particles have in contact with the opposing liquid phase. As a result, smaller emulsion particles need more surfactant to coat the miniemulsions and reduce their interactions with the continuous liquid.

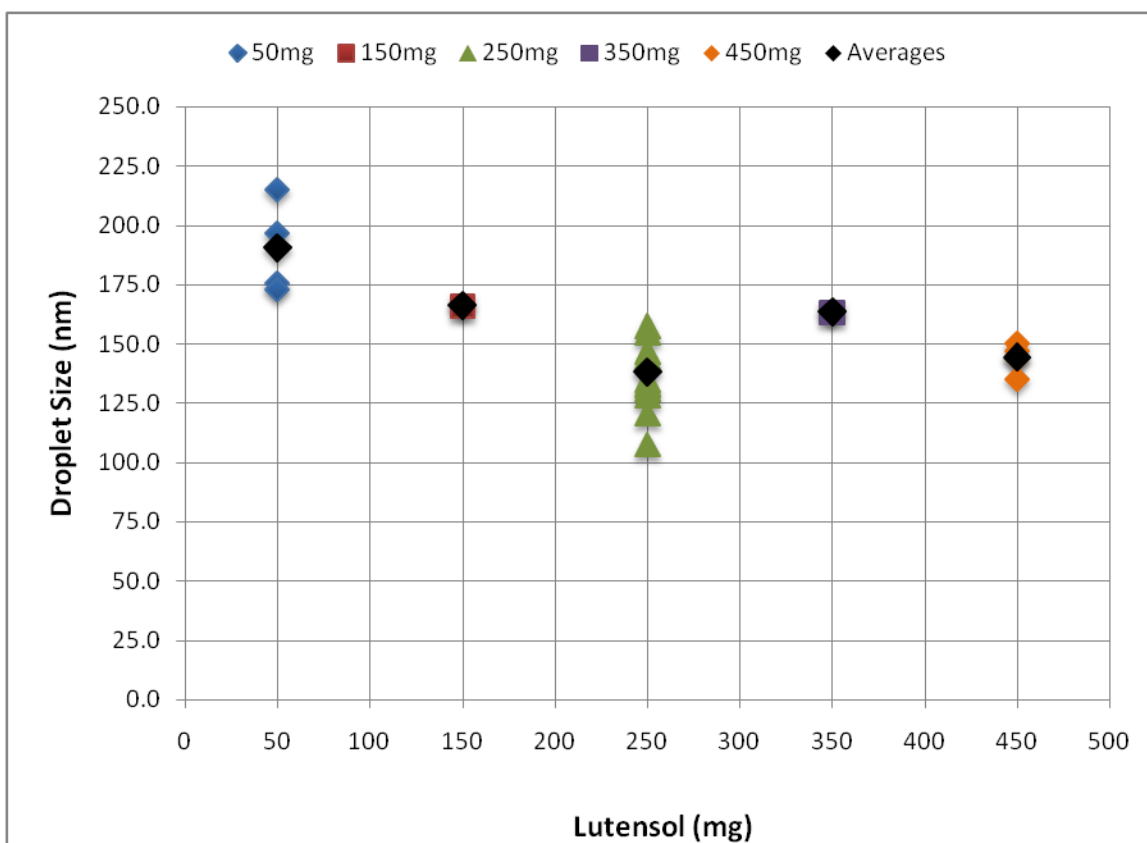


Figure 9: Droplet Size of Miniemulsions

Figure 9 displays the data collected on the droplet size of the miniemulsions as a function of amount of surfactant, Lutensol. Therefore, as the amount of Lutensol used in the miniemulsion increased, the miniemulsion droplet size was expected to decrease. By performing an ANOVA test on the droplet size data obtained for experiments performed with varying amounts of Lutensol ranging from 50mg to 450mg, it could be concluded that the miniemulsion droplet sizes for 50mg and 450mg of Lutensol are statistically different enough ($p=0.004$) from each other that they are distinct. Therefore, since the average droplet size for 50mg is 190.2 nm and the average droplet size for 450mg is 144.1 nm, *Table 1* this research found that the droplet size did decrease as the amount of surfactant was increased.

Table 1: Data for the Droplet Size of the Miniemulsions

Date	Sample	Initiator	Lutensol (mg)	Diameter (nm)
6-Feb	WPI-13	AIBN	50	196.9
6-Feb	WPI-14	AIBN	50	175.7
8-Feb	WPI-19	AIBN	50	215.3
12-Feb	WPI-20	AIBN	50	173.1
Average			50	190.2
7-Feb	WPI-17	AIBN	450	135.1
8-Feb	WPI-18	AIBN	450	143.9
12-Feb	WPI-23	AIBN	450	150.1
12-Feb	WPI-24	AIBN	450	147.2
Average			450	144.1

Lutensol is known to not give much variety when it comes to the miniemulsion droplet sizes²³. Lutensol was used because it provides stable miniemulsions without long sonication times. For this project, it was not our objective to create miniemulsions with significantly different droplet size.

4.2 Polymer Conversion

Several variables that could have affected the conversion of the polymer were examined. The temperature at which the polymerization is conducted is considered to be one of the most influential parameters of the polymerization. The amount of surfactant, which in this case was Lutensol, was also important because it impacts the stability, droplet size, and therefore the polymerization reaction characteristics. The type of initiator used can also either hinder or stimulate the polymerization reaction, especially whether it is soluble in the water phase or organic phase.

4.2.1 Effect of Temperature

Many polymerization reactions were conducted at different temperatures in order

to see a trend in the polymer conversion. It was hypothesized that as the temperature was decreased the polymerization would take longer to reach its maximum conversion. This agrees with fundamental concepts because as the temperature is decreased the molecules have less energy, therefore they move slower, and collide less. The fewer collisions, the more time it takes to complete the necessary mechanism steps of the reaction. We expected to get similar maximum polymer conversion with the different temperatures, but that they would require more reaction time as the temperature was decreased.

The set of experiments was started with 75°C and was continued by testing lower temperatures of 60°C, 50°C, and 40°C. *Figure 10* shows the results of the polymer conversion for the reactions conducted at 75°C. This displays the qualities that were desirable for the subsequent runs conducted at lower temperatures. The steep increase of conversion at the beginning of the experiment, the fairly smooth leveling off of the curve at the maximum conversion, and the considerably high final polymer conversion are the main characteristics that were expected from the kinetics of the polymerization reaction.

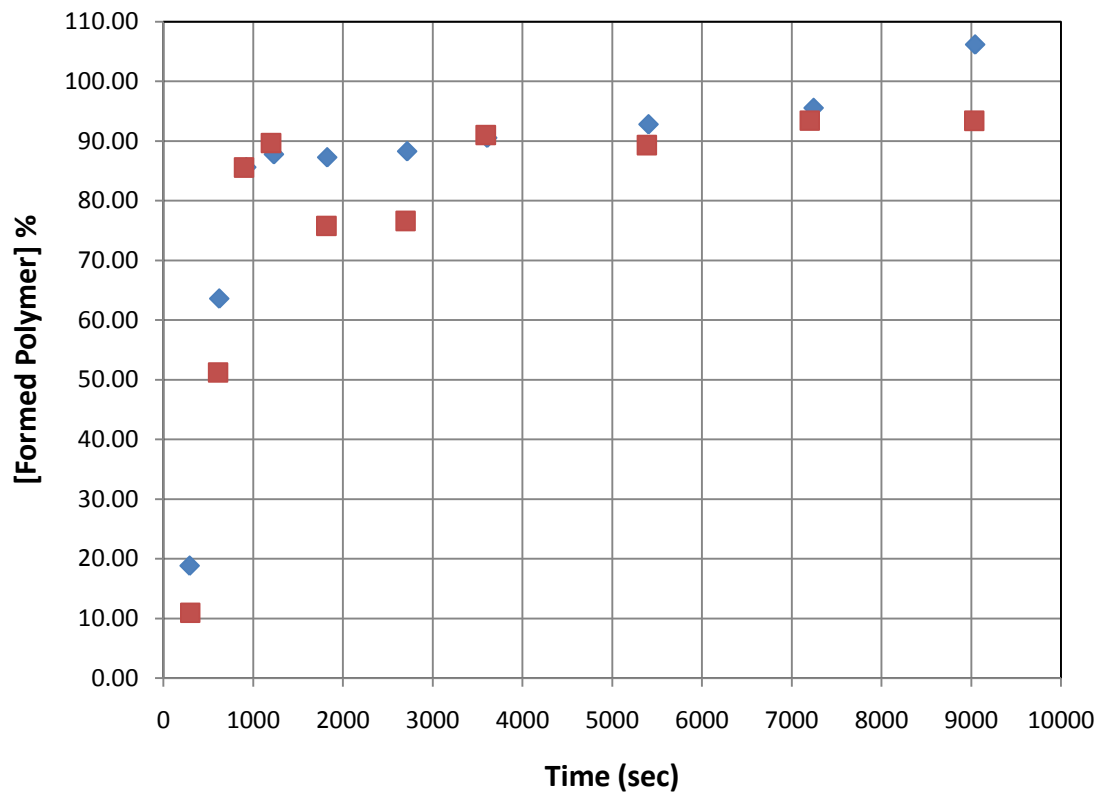


Figure 10: Polymer Conversion at 75°C and 250mg Lutensol

A good maximum conversion of roughly 95% was achieved when the polymerization was performed at 75°C. This set of experiments was continued with the same reaction conditions, except the temperature was decreased to 60°C. *Figure 11* shows the resulting polymer conversion as a function of time at 60°C.

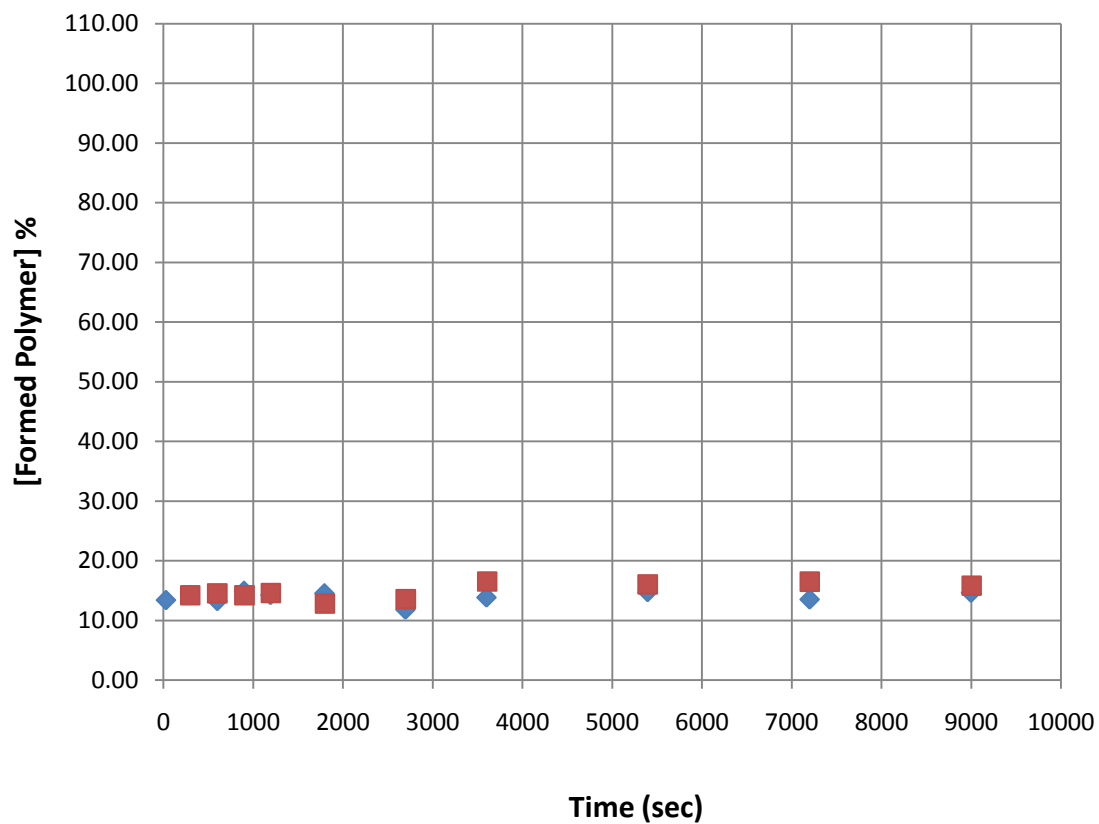


Figure 11: Polymer Conversion at 60°C and 250mg Lutensol

In this case, we did not see any substantial conversion of the monomer to the polymer, only around 15%. A similar result for 50°C (12% conversion) was obtained (*Figure 12*).

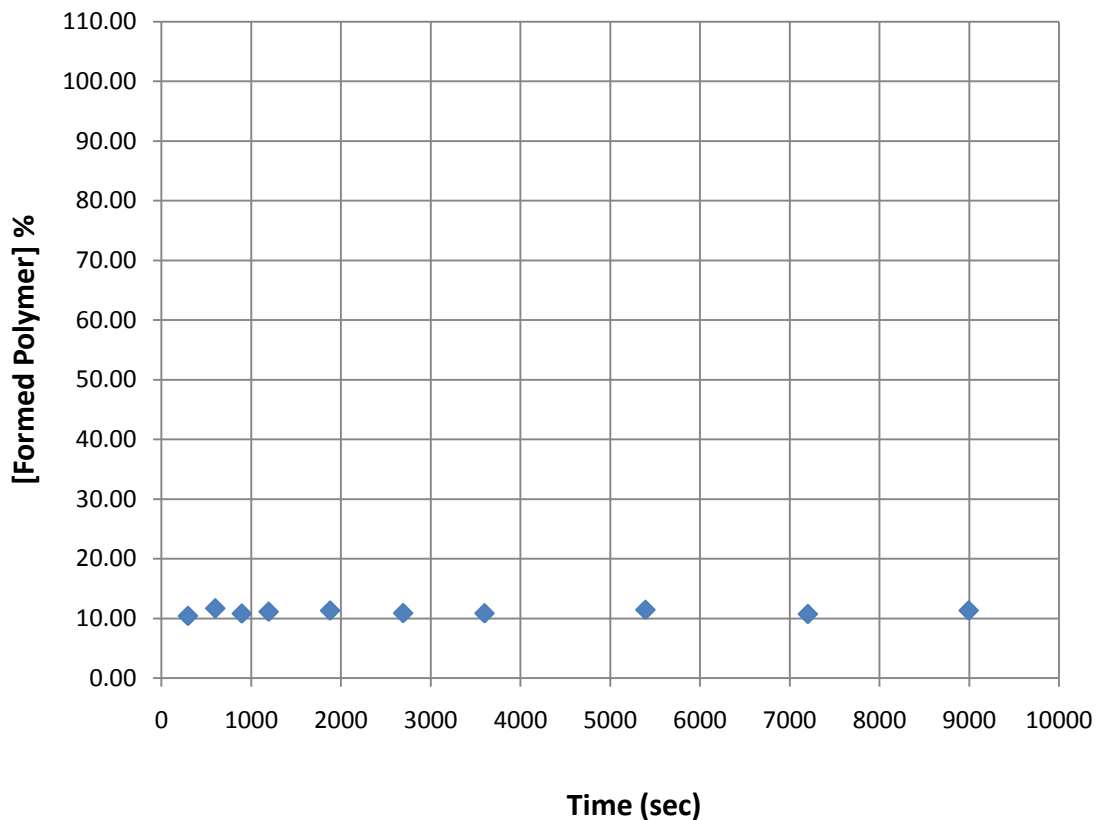


Figure 12: Polymer Conversion at 50°C and 250mg Lutensol

Therefore, the conditions were adjusted to allow more time for the polymerization reaction to achieve higher conversion. We hypothesized that if the polymerization was given ample time, we would be able to see a high conversion then. For the samples taken after the weekend, two methods were used to determine the polymer conversion, oven-dried and freeze-dried. The oven-dried method gave a quick, rough estimate of the conversion. *Table 2* shows the high conversion (93-100%) of the three runs executed this way.

Table 2: Data for Runs 10, 11, and 12: 60°C and 250, 150, and 350mg Lutensol (respectively)

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
2-Feb	WPI-10-1	Overnight	30.65745	3.20559	5.97398	2.76839	3.23991	0.03432	0.38006	12.67715
	WPI-10-2	Over weekend	30.65745	3.13838	5.96820	2.82982	3.43251	0.29413	3.18652	106.28746
	WPI-10-2 O	Overweekend	30.65745	52.63195	xx	1.07527	52.72822	0.09627	2.74479	91.55350
Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
2-Feb	WPI-11-1	Overnight	30.53661	3.18988	5.83447	2.64459	3.20986	0.01998	0.23071	7.64878
	WPI-11-2	Over weekend	30.53661	3.24486	6.44055	3.19569	3.56416	0.31930	3.05109	101.15543
	WPI-11-2 O	Overweekend	30.53661	59.88282	xx	1.05001	59.98340	0.10058	2.92509	96.97798
Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
2-Feb	WPI-12-1	Overnight	30.85547	3.13306	5.70061	2.56755	3.17882	0.04576	0.54992	18.30814
	WPI-12-2	Over weekend	30.85547	3.09921	6.03061	2.93140	3.41849	0.31928	3.36069	111.88547
	WPI-12-2 O	Overweekend	30.85547	59.94193	xx	1.11887	60.05494	0.11301	3.11652	103.75626

To allow the polymerization reactions to reach their maximums, the time range over which the samples were taken was extended to about 24 hours. *Figure 13* shows that of the two trials done, only one had an early steep increase in polymer conversion with a smooth transition to the maximum conversion, but it did not have nearly as high of a maximum conversion (only 60%) that was expected. The other set of data had a very slow, gradual increase in the polymer conversion but a higher polymer conversion at the end (90%).

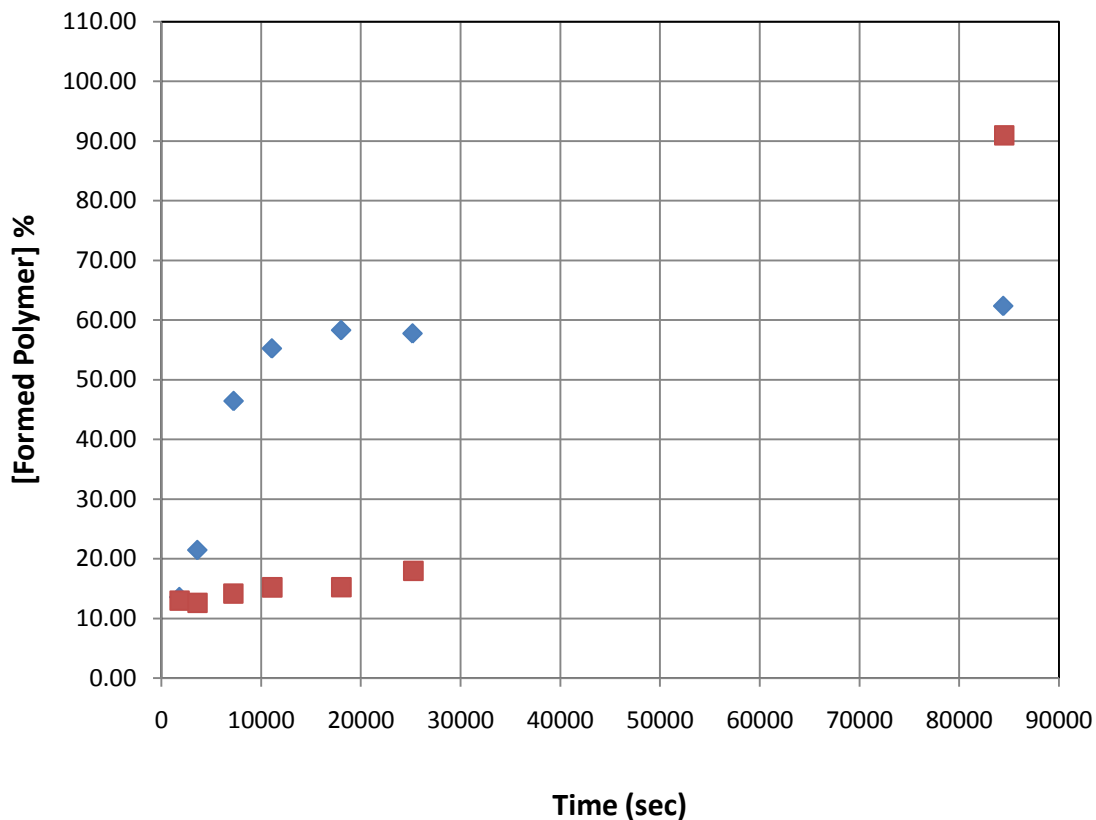


Figure 13: Polymer Conversion at 60°C and 250mg Lutensol (extended time)

The results that were obtained show that more experiments should be conducted in order to determine if a higher polymer conversion could be obtained by varying the temperature of the polymerization reaction.

4.2.2 Effect of Amount of Surfactant

Normally, the more surfactant used, the smaller the droplet size because there is more surfactant available to stabilize the interface between the water and oil phases. Because the miniemulsion droplet size is a major factor that can affect how the polymerization occurs, it was important to test different amounts of surfactant and obtain their percent polymer conversion. Ideally, miniemulsions with higher amounts of surfactant should result in greater polymer conversion because they have smaller droplets

and therefore more nucleation sites for polymerization to occur. As a result, we tested different amounts of surfactant in order to determine whether this would have an effect on the polymerization reaction and the conversion amounts.

For the four trials at 75°C, two different amounts of surfactant were tested. The first amount tested used 250mg of Lutensol while the second amount used was 150mg. For the experiments using 250mg of Lutensol, an average of about 95% conversion of monomer to polymer was recorded (as seen previously in *Figure 10*). For the runs with 150mg of Lutensol, an average of approximately 88.5% polymer conversion was detected, as displayed in *Figure 14*. Therefore, for the runs at 75°C, a larger amount of Lutensol resulted in greater amount of polymer conversion, which was consistent with our expectations.

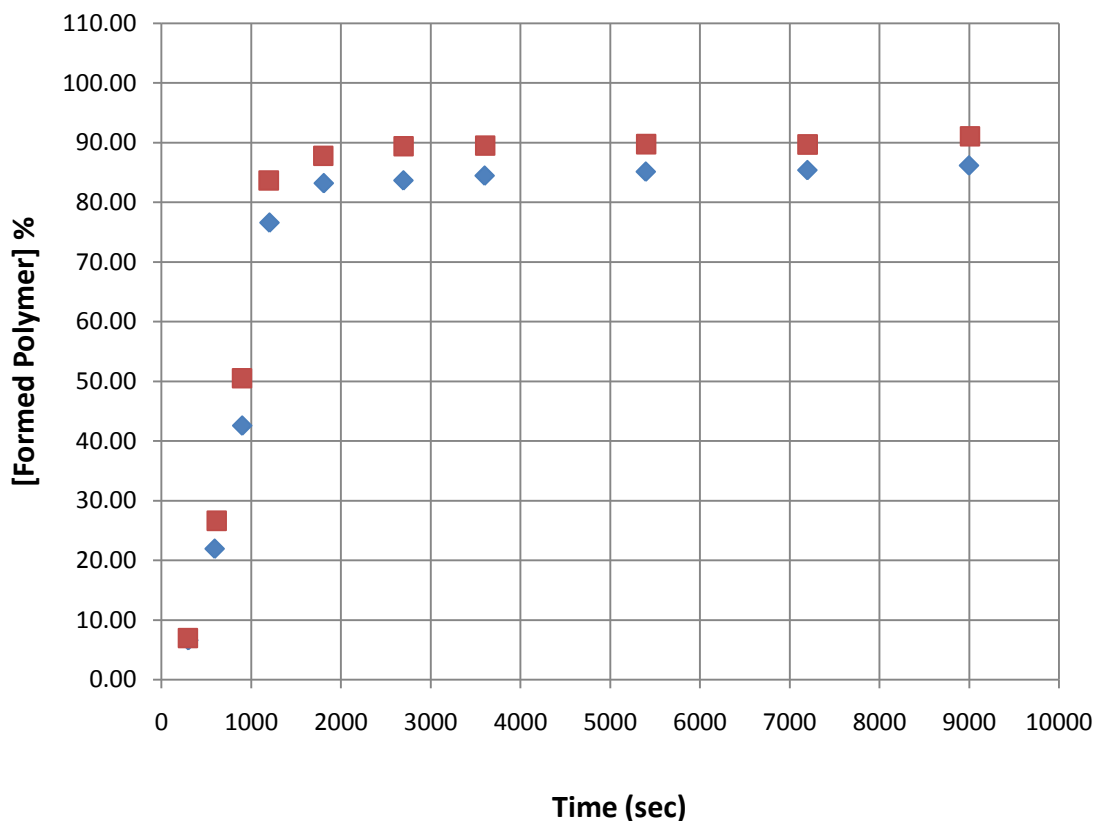


Figure 14: Polymer Conversion at 75°C and 150mg Lutensol

By changing the amount of surfactant, the overall polymer conversion result was also slightly changed. The difference may not be as drastic as desired because the surfactant used, Lutensol, does not usually change the droplet size very much. Therefore, a large difference in maximum polymer conversion would not be expected when using Lutensol as the surfactant.

4.2.3 Effect of Type of Initiator

The type of initiator used for the polymerization reaction can affect polymer conversion. It is very important to the polymerization of the miniemulsion whether the initiator is soluble in the water or organic phase. If it is water soluble then secondary nucleation can occur. Since the polymerization can start outside the droplets, the polymer can coagulate outside the droplet, and therefore would not be as efficient as if it is soluble in the organic phase. When the initiator is soluble in the organic phase, the polymerization is concentrated inside the miniemulsion droplets and takes full advantage of the abundance of nucleation sites created by the miniemulsion.

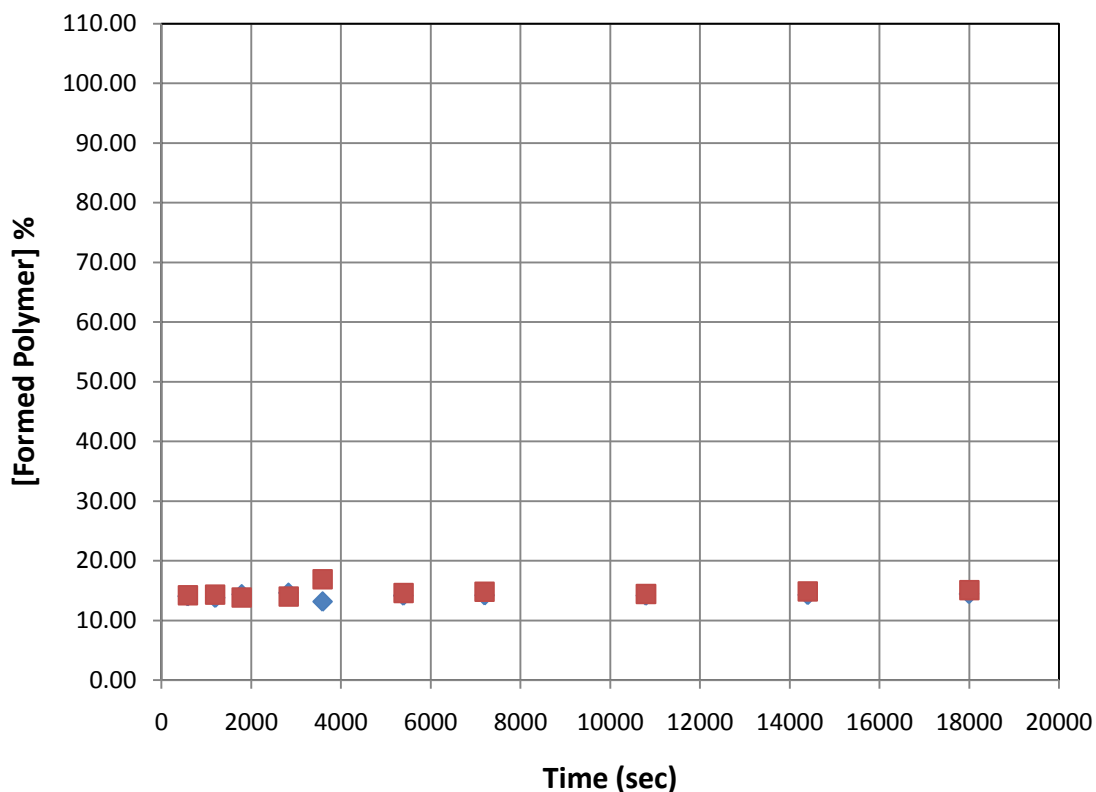


Figure 15: Polymer Conversion at 50°C, 250mg Lutensol, and KPS (initiator)

Figure 15 shows that when the water soluble initiator, KPS, was used in place of the organic soluble, AIBN, there was no change in the polymer conversion as a function of time. KPS was tested in order to determine whether there was a problem with the AIBN that was being used. Since there was no improvement of the quality of the polymer conversion, there is no evidence to show that there were any problems with the purity of the AIBN.

4.3 Possible Correlation to Fluorescence Experiments

As a secondary objective, the correlation of the polymer conversion data with the fluorescence experiments of pyrene located in a miniemulsion similar to the miniemulsions studied in this MQP was examined. However, there were a few

differences that could significantly affect the resulting correlation. The miniemulsions for the MQP didn't contain pyrene and mainly used AIBN for the initiator, whereas the fluorescence experiments used KPS for the initiator and had UV radiation present during the experiments.

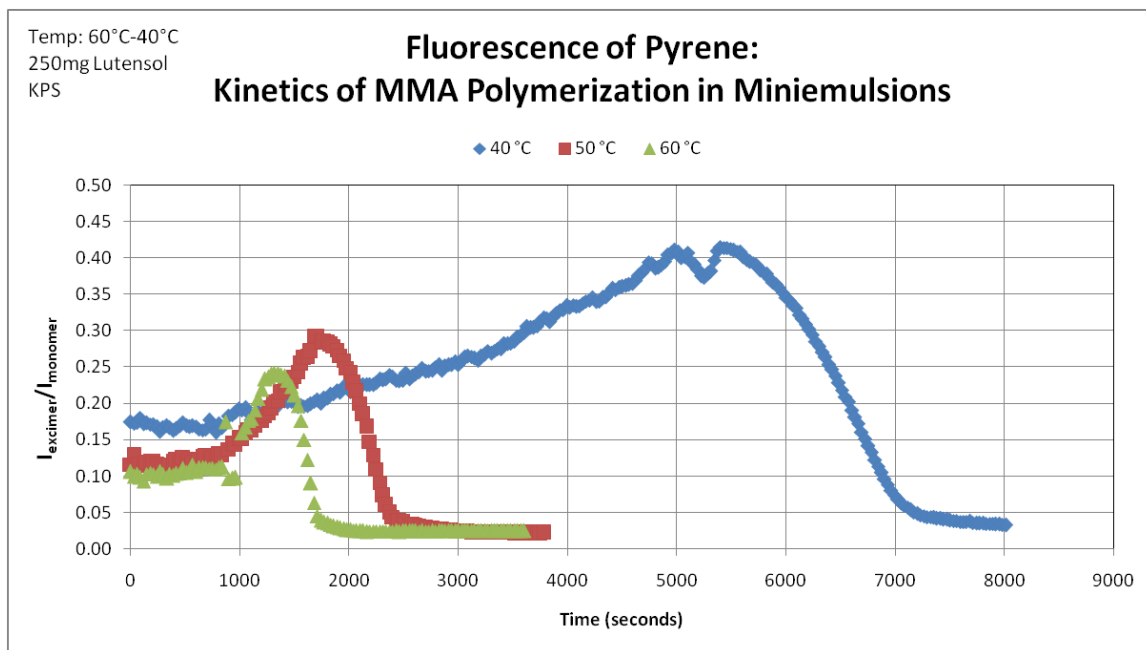


Figure 16: Example of Fluorescence Kinetic Curve²⁴

Figure 16 shows one of the curves generated with the fluorescence of pyrene within the polymerization reaction. It displays the effect of temperature on the polymerization reaction, the lower the temperature the longer the reaction takes. The relative amount of fluorescence from the excimer (trimer) to the fluorescence of the monomer correlates to the viscosity of the sample, the more viscous the less excimer that can be formed. The amount of formed polymer is directly related to the viscosity of the sample, the more polymer the more viscous the solution. This relation between the amount of polymer to the amount of fluorescence from the excimer is a novel method for following the kinetics

of polymerization in miniemulsions. Therefore, because there were so many differences in the conditions of the experiment, it would probably be necessary to perform polymerization kinetics experiments with conditions more similar to the fluorescence experiments.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

Overall, this MQP was successful in following the polymerization of MMA at 75°C. The experiments that succeeded in polymerizing more than 20% of the monomer MMA in a period of 24 hours or less were the trials conducted at 75°C. The experiments conducted at 60°C, 50°C, and 40°C were unable to polymerize more than 20% of the monomer in 24 hours. However, the polymerization reaction at 60°C was able to convert over 80% of the monomer to polymer when it was heated over the weekend from Friday night to Monday morning.

During the polymerization conversion experiments, several features of the experiment were varied to pinpoint the cause for the lack of polymer conversion. The amount of Lutensol was changed to see if a change in droplet size would have an effect on the amount of polymer conversion. A small change was seen in the experiments at 75°C when the amount of Lutensol was changed, but this was one of the few hypotheses that worked came out as expected. The time range over which the polymerization reactions were held was extended to allow for more polymer conversion. Only after letting the reaction go over the weekend, did any significant polymer form. Next, the type of initiator was changed from organically soluble AIBN to water soluble KPS, to see if the bottle of AIBN being used was expired. No difference was seen when a different initiator was used. The final attempt to determine the fault in the experiment was to purify the monomer again, and use it right away in the reaction. Still, none of these attempted solutions showed any significant polymer conversion (13-14%). After all of these experiments, a conclusion as to why the method did not work to determine the polymer conversion has not been reached.

It is possible that these low polymerization conversion trials could have been due to the heat requirements of the initiator, AIBN, not being met. It has been found that AIBN has several conditions that must be present to initiate the polymerization. In order for the AIBN to become a radical it must be excited, either by heat or UV radiation, typically a temperature of 70°C-90°C is required for the activation of AIBN²⁵. Perhaps, this is the reason why the polymerization reaction of MMA did not have a significant conversion at the lower temperatures (60°C, 50°C, and 40°C). Since the fluorescence experiments had UV radiation present during the reaction that could also be why those experiments had significant polymer conversion at the lower temperatures.

However, most of the experiments done at the lower temperatures had a calculated 10-14% polymer conversion. It could be possible that this calculated conversion was actually residual species left in the sample even after freeze drying, such as AIBN, hexadecane, and Lutensol. More experiments testing the use of UV radiation to activate the initiator should be conducted. Performing a control experiment without the monomer present to determine if a residual is actually in the samples would also be beneficial. In addition, experiments including monomer modified with pyrene in the polymerization reaction could provide further insight to the chemical nature of the polymerization reaction.

As for the miniemulsion droplet sizes, they did follow the expected trend of decreasing in size as the amount of surfactant was increased. They were all relatively close in size (100-200nm range) however, a statistically significant trend was found. Because Lutensol is said to not have much range for miniemulsion droplet sizes, this could be remedied for future studies that want greater differences and better trends in

droplet size by using a different surfactant. Differences in droplet sizes could also be expanded by sonicating for longer or shorter periods of time. Additional experiments should be conducted to explore the effect of sonication time on miniemulsion particle size.

From this project, it was found that this method to determine the polymer conversion was effective at 75°C for the polymerization of MMA. Perhaps more aspects of the experiment could be tested to verify that everything is scientifically sound. Overall, it seems that several conditions, such as activating the initiator with UV radiation, performing control experiments to determine any residual species, and modifying the monomer to include pyrene should be adjusted in order to compare it to the fluorescence experiments.

APPENDIX

In this section we have included our supplemental data tables and graphs. The tables are grouped to have two runs each; both runs were conducted at the same conditions. These pairings of runs were also plotted together.

Table 3: Data for Runs 1 and 2: 75°C and 250mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
17-Jan	WPI-1	291	20.56291	3.24156	5.63032	2.38876	3.28806	0.04650	0.40028	18.81984
	WPI-2	621	20.56291	3.24476	5.93686	2.69210	3.42180	0.17704	1.35227	63.57929
	WPI-3	922	20.56291	3.19617	5.68740	2.49123	3.41671	0.22054	1.82036	85.58724
	WPI-4	1230	20.56291	3.22700	5.59024	2.36324	3.44151	0.21451	1.86648	87.75567
	WPI-5	1824	20.56291	3.15552	5.26652	2.11100	3.34602	0.19050	1.85563	87.24533
	WPI-6	2715	20.56291	3.15870	4.95442	1.79572	3.32262	0.16392	1.87706	88.25286
	WPI-7	3607	20.56291	3.23682	5.00466	1.76784	3.40233	0.16551	1.92516	90.51421
	WPI-8	5405	20.56291	3.13339	4.85617	1.72278	3.29871	0.16532	1.97324	92.77502
	WPI-9	7245	20.56291	3.17849	4.16716	0.98867	3.27617	0.09768	2.03160	95.51900
	WPI-10	9045	20.56291	3.21521	3.59302	0.37781	3.25669	0.04148	2.25761	106.14530
18-Jan	WPI-2-1	300	30.67992	3.20917	5.89594	2.68677	3.23790	0.02873	0.32806	10.93640
	WPI-2-2	609	30.67992	3.23796	5.97025	2.73229	3.37468	0.13672	1.53518	51.17695
	WPI-2-3	898	30.67992	3.08720	5.75331	2.66611	3.31016	0.22296	2.56568	85.52992
	WPI-2-4	1200	30.67992	3.22657	6.06835	2.84178	3.47564	0.24907	2.68897	89.63965
	WPI-2-5	1817	30.67992	3.13655	5.95442	2.81787	3.34530	0.20875	2.27279	75.76606
	WPI-2-6	2698	30.67992	3.13850	5.97380	2.83530	3.35078	0.21228	2.29702	76.57363
	WPI-2-7	3592	30.67992	3.24255	5.89818	2.65563	3.47877	0.23622	2.72900	90.97420
	WPI-2-8	5388	30.67992	3.13873	5.95698	2.81825	3.38475	0.24602	2.67821	89.28121
	WPI-2-9	7201	30.67992	3.19749	5.98818	2.79069	3.45229	0.25480	2.80119	93.38067
	WPI-2-10	9034	30.67992	3.20794	6.43468	3.22674	3.50251	0.29457	2.80078	93.36706

Table 4: Data for Runs 3 and 4: 75°C and 150mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
21-Jan	WPI-3-1	299	30.52301	3.14366	5.77269	2.62903	3.16099	0.01733	0.20120	6.63133
	WPI-3-2	593	30.52389	3.14448	5.83377	2.68929	3.20319	0.05871	0.66637	21.96263
	WPI-3-3	900	30.52389	3.13807	5.81585	2.67778	3.25142	0.11335	1.29207	42.58500
	WPI-3-4	1204	30.52389	3.18200	5.91751	2.73551	3.39026	0.20826	2.32385	76.59097
	WPI-3-5	1809	30.52389	3.21189	5.94244	2.73055	3.43771	0.22582	2.52436	83.19980
	WPI-3-6	2697	30.52389	3.23487	6.06275	2.82788	3.47004	0.23517	2.53840	83.66252
	WPI-3-7	3602	30.52389	3.19396	6.19873	3.00477	3.44621	0.25225	2.56248	84.45589
	WPI-3-8	5398	30.52389	3.22730	6.13951	2.91221	3.47373	0.24643	2.58292	85.12966
	WPI-3-9	7199	30.52389	3.23276	5.96816	2.73540	3.46493	0.23217	2.59075	85.38769
	WPI-3-10	9000	30.52389	3.15787	6.15061	2.99274	3.41419	0.25632	2.61429	86.16353
22-Jan	WPI-4-1	297	30.49533	3.20747	6.01668	2.80921	3.22676	0.01929	0.20940	6.97287
	WPI-4-2	617	30.49533	3.15115	6.00397	2.85282	3.22589	0.07474	0.79894	26.60371
	WPI-4-3	899	30.49533	3.24815	5.94385	2.69570	3.38216	0.13401	1.51600	50.48114
	WPI-4-4	1197	30.49533	3.15244	5.95437	2.80193	3.38318	0.23074	2.51130	83.62366
	WPI-4-5	1804	30.49533	3.26030	6.07742	2.81712	3.50380	0.24350	2.63589	87.77224
	WPI-4-6	2699	30.49533	3.12773	6.16170	3.03397	3.39472	0.26699	2.68360	89.36084
	WPI-4-7	3609	30.49533	3.23703	6.12180	2.88477	3.49118	0.25415	2.68666	89.46280
	WPI-4-8	5400	30.49533	3.23533	6.14593	2.91060	3.49250	0.25717	2.69446	89.72249
	WPI-4-9	7200	30.49533	3.19140	6.00792	2.81652	3.44010	0.24870	2.69275	89.66573
	WPI-4-10	9008	30.49533	3.24917	6.29561	3.04644	3.52223	0.27306	2.73337	91.01836

Table 5: Data for Runs 5 and 6: 60°C and 250mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
25-Jan	WPI-5-1	28	30.67979	3.14559	5.89163	2.74604	3.18163	0.03604	0.40265	13.41263
	WPI-5-2	600	30.67979	3.17975	5.84547	2.66572	3.21433	0.03458	0.39798	13.25703
	WPI-5-3	898	30.67979	3.14288	5.83955	2.69667	3.18234	0.03946	0.44893	14.95427
	WPI-5-4	1193	30.67979	3.24253	6.08973	2.84720	3.28229	0.03976	0.42843	14.27133
	WPI-5-5	1794	30.67979	3.16212	5.70775	2.54563	3.19832	0.03620	0.43628	14.53280
	WPI-5-6	2697	30.67979	3.20062	5.85952	2.65890	3.23139	0.03077	0.35504	11.82664
	WPI-5-7	3600	30.67979	3.20135	5.84558	2.64423	3.23720	0.03585	0.41595	13.85562
	WPI-5-8	5396	30.67979	3.13673	5.86639	2.72966	3.17612	0.03939	0.44272	14.74733
	WPI-5-9	7202	30.67979	3.09176	5.90423	2.81247	3.12898	0.03722	0.40601	13.52460
	WPI-5-10	9000	30.67979	3.23513	5.96570	2.73057	3.27425	0.03912	0.43954	14.64136
25-Jan	WPI-6-1	298	30.69792	3.14532	5.99232	2.84700	3.18520	0.03988	0.43001	14.22243
	WPI-6-2	599	30.69792	3.23640	5.91966	2.68326	3.27482	0.03842	0.43955	14.53787
	WPI-6-3	902	30.69792	3.16294	5.87391	2.71097	3.20087	0.03793	0.42950	14.20575
	WPI-6-4	1195	30.69792	3.22745	6.02499	2.79754	3.26764	0.04019	0.44101	14.58639
	WPI-6-5	1798	30.69792	3.13066	5.98584	2.85518	3.16673	0.03607	0.38781	12.82681
	WPI-6-6	2699	30.69792	3.17915	5.93591	2.75676	3.21603	0.03688	0.41068	13.58308
	WPI-6-7	3606	30.69792	3.21790	5.94818	2.73028	3.26236	0.04446	0.49989	16.53364
	WPI-6-8	5395	30.69792	3.23921	6.07499	2.83578	3.28400	0.04479	0.48486	16.03669
	WPI-6-9	7200	30.69792	3.24494	5.94645	2.70151	3.28886	0.04392	0.49907	16.50676
	WPI-6-10	9004	30.69792	3.20780	6.08717	2.87937	3.25265	0.04485	0.47816	15.81507

Table 6: Data for Runs 7 and 8: 60°C and 150mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
28-Jan	WPI-7-1	304	30.50359	3.24332	5.95674	2.71342	3.25406	0.01074	0.12074	4.03594
	WPI-7-2	598	30.50359	3.26029	6.03447	2.77418	3.25974	-0.00055	-0.00605	-0.20216
	WPI-7-3	899	30.50359	3.14346	5.88056	2.73710	3.16190	0.01844	0.20550	6.86954
	WPI-7-4	1201	30.50359	3.18540	6.00553	2.82013	3.20473	0.01933	0.20908	6.98908
	WPI-7-5	1800	30.50359	3.17445	6.02322	2.84877	3.18154	0.00709	0.07592	2.53774
	WPI-7-6	2696	30.50359	3.14589	6.04473	2.89884	3.16803	0.02214	0.23297	7.78773
	WPI-7-7	3604	30.50359	3.17593	5.94885	2.77292	3.19408	0.01815	0.19966	6.67416
	WPI-7-8	5400	30.50359	3.23772	6.16982	2.93210	3.26084	0.02312	0.24052	8.04020
	WPI-7-9	7199	30.50359	3.20942	6.08038	2.87096	3.23237	0.02295	0.24384	8.15104
	WPI-7-10	8999	30.50359	3.19189	6.25025	3.05836	3.21681	0.02492	0.24855	8.30839
28-Jan	WPI-8-1	299	30.48969	3.25921	6.01925	2.76004	3.26139	0.00218	0.02408	0.80433
	WPI-8-2	589	30.48969	3.20001	5.98507	2.78506	3.20725	0.00724	0.07926	2.64728
	WPI-8-3	898	30.48969	3.18421	5.85425	2.67004	3.20083	0.01662	0.18979	6.33882
	WPI-8-4	1197	30.48969	3.16668	5.90228	2.73560	3.17663	0.00995	0.11090	3.70396
	WPI-8-5	1799	30.48969	3.23307	5.95076	2.71769	3.23727	0.00420	0.04712	1.57378
	WPI-8-6	2693	30.48969	3.14300	5.99404	2.85104	3.15749	0.01449	0.15496	5.17560
	WPI-8-7	3606	30.48969	3.19325	6.03286	2.83961	3.21225	0.01900	0.20401	6.81381
	WPI-8-8	5392	30.48969	3.21335	5.81237	2.59902	3.22829	0.01494	0.17526	5.85378
	WPI-8-9	7197	30.48969	3.25308	6.18925	2.93617	3.25775	0.00467	0.04849	1.61969
	WPI-8-10	8998	30.48969	3.22949	6.05366	2.82417	3.24614	0.01665	0.17975	6.00370

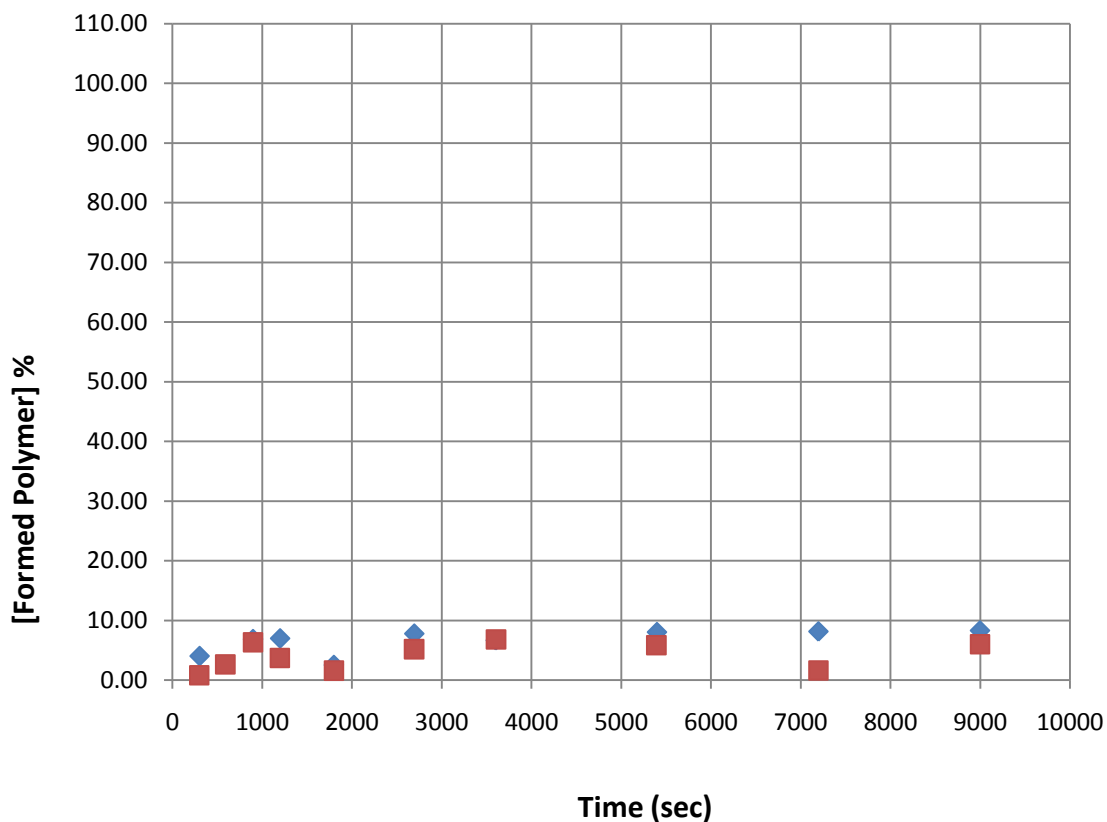


Figure 17: Polymer Conversion at 60°C and 150mg Lutensol

Table 7: Data for Run 9: 50°C and 250mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
29-Jan	WPI-9-1	296	30.68442	3.24302	6.00069	2.75767	3.27119	0.02817	0.31345	10.40978
	WPI-9-2	600	30.68442	3.18803	5.98161	2.79358	3.22006	0.03203	0.35181	11.68404
	WPI-9-3	896	30.68442	3.17597	5.86655	2.69058	3.20451	0.02854	0.32548	10.80949
	WPI-9-4	1195	30.68442	3.14866	5.99093	2.84227	3.17967	0.03101	0.33478	11.11817
	WPI-9-5	1880	30.68442	3.14189	5.86433	2.72244	3.17211	0.03022	0.34061	11.31184
	WPI-9-6	2694	30.68442	3.17278	5.91725	2.74447	3.20209	0.02931	0.32770	10.88314
	WPI-9-7	3601	30.68442	3.13843	5.84909	2.71066	3.16730	0.02887	0.32681	10.85347
	WPI-9-8	5394	30.68442	3.10167	5.84207	2.74040	3.13242	0.03075	0.34431	11.43479
	WPI-9-9	7204	30.68442	3.21036	6.07663	2.86627	3.24054	0.03018	0.32309	10.72999
	WPI-9-10	8996	30.68442	3.23367	6.00818	2.77451	3.26449	0.03082	0.34085	11.31992

Table 8: Data for Runs 13 and 14: 60°C and 50mg Lutensol (overnight)

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
5-Feb	WPI-13-1	918	30.38528	3.23498	5.89044	2.65546	3.24622	0.01124	0.12861	4.27254
	WPI-13-2	1797	30.38528	3.23877	6.00212	2.76335	3.25700	0.01823	0.20045	6.65902
	WPI-13-3	3579	30.38528	3.14376	5.88592	2.74216	3.16678	0.02302	0.25508	8.47367
	WPI-13-4	7258	30.38528	3.28435	6.09975	2.81540	3.32528	0.04093	0.44174	14.67442
	WPI-13-5	10980	30.38528	3.17166	5.90512	2.73346	3.21872	0.04706	0.52312	17.37795
	WPI-13-6	17982	30.38528	3.23436	6.09084	2.85648	3.46420	0.22984	2.44488	81.21826
	WPI-13-7	25211	30.38528	3.17070	6.09279	2.92209	3.42201	0.25131	2.61324	86.81113
	WPI-13-8	85568	30.38528	3.14041	6.05899	2.91858	3.34732	0.20691	2.15414	71.55980
5-Feb	WPI-14-1	914	30.38594	3.22376	5.89747	2.67371	3.23419	0.01043	0.11853	3.95079
	WPI-14-2	1789	30.38594	3.14630	5.68932	2.54302	3.15848	0.01218	0.14554	4.85078
	WPI-14-3	3572	30.38594	3.14237	5.78440	2.64203	3.15748	0.01511	0.17378	5.79216
	WPI-14-4	7256	30.38594	3.26319	5.71898	2.45579	3.28135	0.01816	0.22470	7.48925
	WPI-14-5	10970	30.38594	3.14595	5.73091	2.58496	3.16824	0.02229	0.26202	8.73313
	WPI-14-6	17989	30.38594	3.16388	5.88608	2.72220	3.19119	0.02731	0.30484	10.16051
	WPI-14-7	25218	30.38594	3.17224	5.52173	2.34949	3.19657	0.02433	0.31466	10.48775
	WPI-14-8	85563	30.38594	3.20016	4.89380	1.69364	3.22180	0.02164	0.38825	12.94047

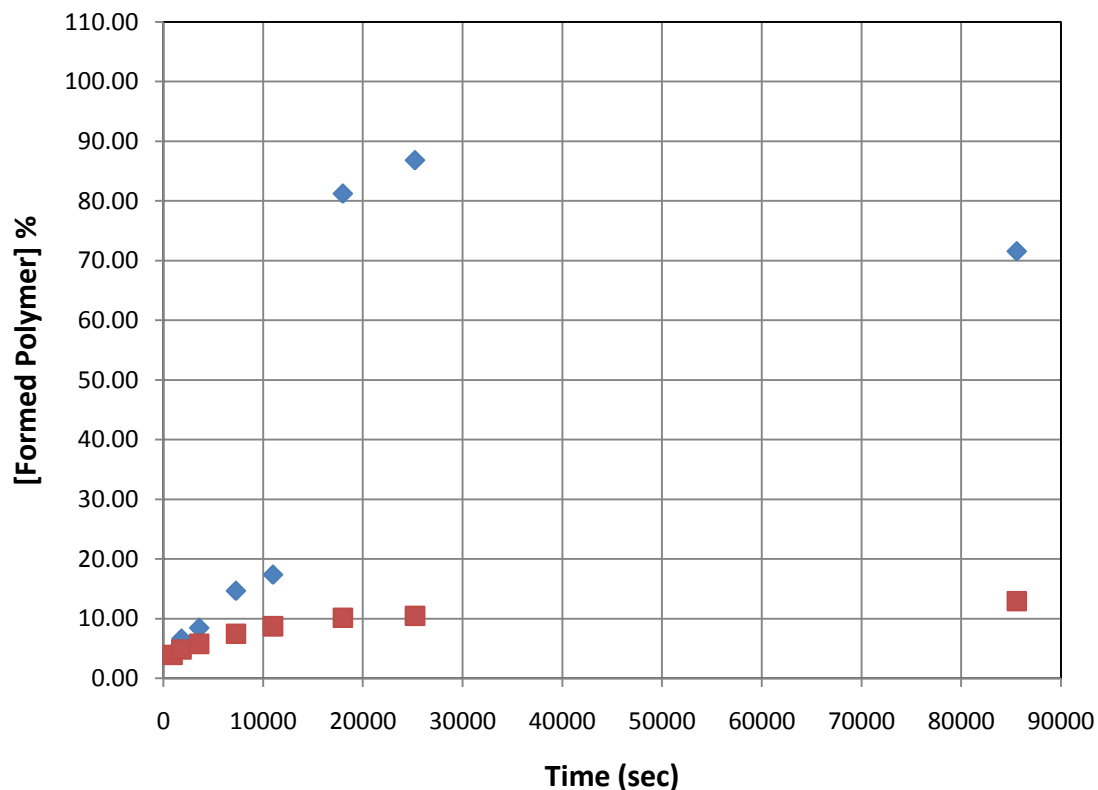


Figure 18: Polymer Conversion at 60°C and 50mg Lutensol

Table 9: Data for Runs 15 and 16: 60°C and 250mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
6-Feb	WPI-15-1	1803	30.65949	3.15297	5.85516	2.70219	3.18905	0.03608	0.40937	13.59756
	WPI-15-2	3606	30.65949	3.14381	6.01355	2.86974	3.20433	0.06052	0.64658	21.47666
	WPI-15-3	7244	30.65949	3.23831	6.01589	2.77758	3.36496	0.12665	1.39799	46.43538
	WPI-15-4	11082	30.65949	3.20746	5.88894	2.68148	3.35291	0.14545	1.66305	55.23948
	WPI-15-5	18028	30.65949	3.14772	5.79706	2.64934	3.29940	0.15168	1.75532	58.30436
	WPI-15-6	25189	30.65949	3.23119	5.77839	2.54720	3.37563	0.14444	1.73856	57.74772
	WPI-15-7	84424	30.65949	3.20871	6.22237	3.01366	3.39323	0.18452	1.87722	62.35333
6-Feb	WPI-16-1	1822	30.67210	3.19517	5.89172	2.69655	3.22959	0.03442	0.39151	12.96340
	WPI-16-2	3619	30.67210	3.20169	6.04895	2.84726	3.23699	0.03530	0.38027	12.59111
	WPI-16-3	7218	30.67210	3.22082	6.02289	2.80207	3.25984	0.03902	0.42712	14.14245
	WPI-16-4	11112	30.67210	3.22952	6.00703	2.77751	3.27104	0.04152	0.45851	15.18162
	WPI-16-5	18040	30.67210	3.20461	5.98421	2.77960	3.24621	0.04160	0.45904	15.19944
	WPI-16-6	25261	30.67210	3.19244	6.18101	2.98857	3.24526	0.05282	0.54210	17.94946
	WPI-16-7	84509	30.67210	3.18758	6.07808	2.89050	3.44646	0.25888	2.74707	90.95822

Table 10: Data for Runs 17 and 18: 60°C and 450mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
8-Feb	WPI-17-1	1803	30.97414	3.19206	5.97034	2.77828	3.25624	0.06418	0.71552	23.82976
	WPI-17-2	3583	30.97414	3.18658	5.89936	2.71278	3.25072	0.06414	0.73234	24.38992
	WPI-17-3	7179	30.97414	3.19378	5.97649	2.78271	3.25324	0.05946	0.66184	22.04210
	WPI-17-4	11147	30.97414	3.20676	5.93008	2.72332	3.27015	0.06339	0.72098	24.01143
	WPI-17-5	18040	30.97414	3.22017	5.92792	2.70775	3.29117	0.07100	0.81217	27.04866
	WPI-17-6	25210	30.97414	3.18269	6.06187	2.87918	3.25786	0.07517	0.80868	26.93219
	WPI-17-7	84593	30.97414	3.18537	6.09250	2.90713	3.29634	0.11097	1.18233	39.37650
8-Feb	WPI-18-1	1805	30.35491	3.22988	5.92742	2.69754	3.29186	0.06198	0.69745	23.21534
	WPI-18-2	3588	30.35491	3.19124	6.15403	2.96279	3.26122	0.06998	0.71697	23.86517
	WPI-18-3	7205	30.35491	3.13513	6.00816	2.87303	3.20596	0.07083	0.74835	24.90970
	WPI-18-4	11122	30.35491	3.18987	5.90283	2.71296	3.25690	0.06703	0.74999	24.96418
	WPI-18-5	18063	30.35491	3.15498	5.83418	2.67920	3.22654	0.07156	0.81076	26.98712
	WPI-18-6	25223	30.35491	3.18483	6.19915	3.01432	3.26601	0.08118	0.81750	27.21141
	WPI-18-7	85142	30.35491	3.16109	6.19466	3.03357	3.47755	0.31646	3.16660	105.40379

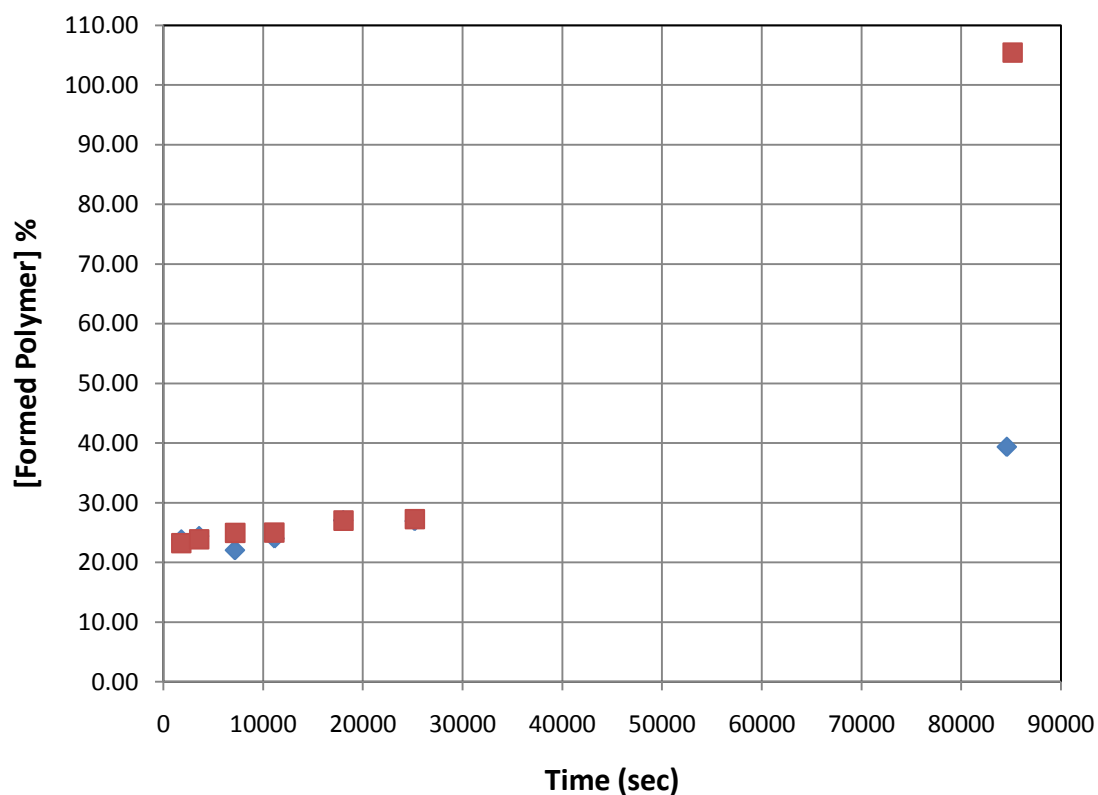


Figure 19: Polymer Conversion at 60°C and 450mg Lutensol

Table 11: Data for Runs 19 and 20: 50°C and 50mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
11-Feb	WPI-19-1	1807	30.36334	3.14222	6.02633	2.88411	3.15480	0.01258	0.13244	4.41413
	WPI-19-2	3594	30.36334	3.17423	6.04776	2.87353	3.11043	-0.06380	-0.67415	-22.46886
	WPI-19-3	7207	30.36334	3.13866	6.07728	2.93862	3.14735	0.00869	0.08979	2.99263
	WPI-19-4	11125	30.36334	3.22502	6.04344	2.81842	3.23787	0.01285	0.13844	4.61396
	WPI-19-5	17987	30.36334	3.13272	6.00956	2.87684	3.14452	0.01180	0.12454	4.15090
	WPI-19-6	25184	30.36334	3.13663	6.06458	2.92795	3.14802	0.01139	0.11812	3.93674
	WPI-19-7	85146	30.36334	3.20010	6.13086	2.93076	3.22284	0.02274	0.23559	7.85211
11-Feb	WPI-20-1	1749	30.36053	3.13738	6.13008	2.99270	3.15165	0.01427	0.14477	4.81665
	WPI-20-2	3546	30.36053	3.19555	5.76410	2.56855	3.21083	0.01528	0.18061	6.00924
	WPI-20-3	7126	30.36053	3.17559	6.17930	3.00371	3.18805	0.01246	0.12594	4.19029
	WPI-20-4	11183	30.36053	3.19238	6.02636	2.83398	3.20658	0.01420	0.15213	5.06146
	WPI-20-5	18123	30.36053	3.23558	6.07517	2.83959	3.24883	0.01325	0.14167	4.71351
	WPI-20-6	25516	30.36053	3.14058	6.05058	2.91000	3.15885	0.01827	0.19061	6.34205
	WPI-20-7	84417	30.36053	3.18551	6.03686	2.85135	3.19898	0.01347	0.14343	4.77201

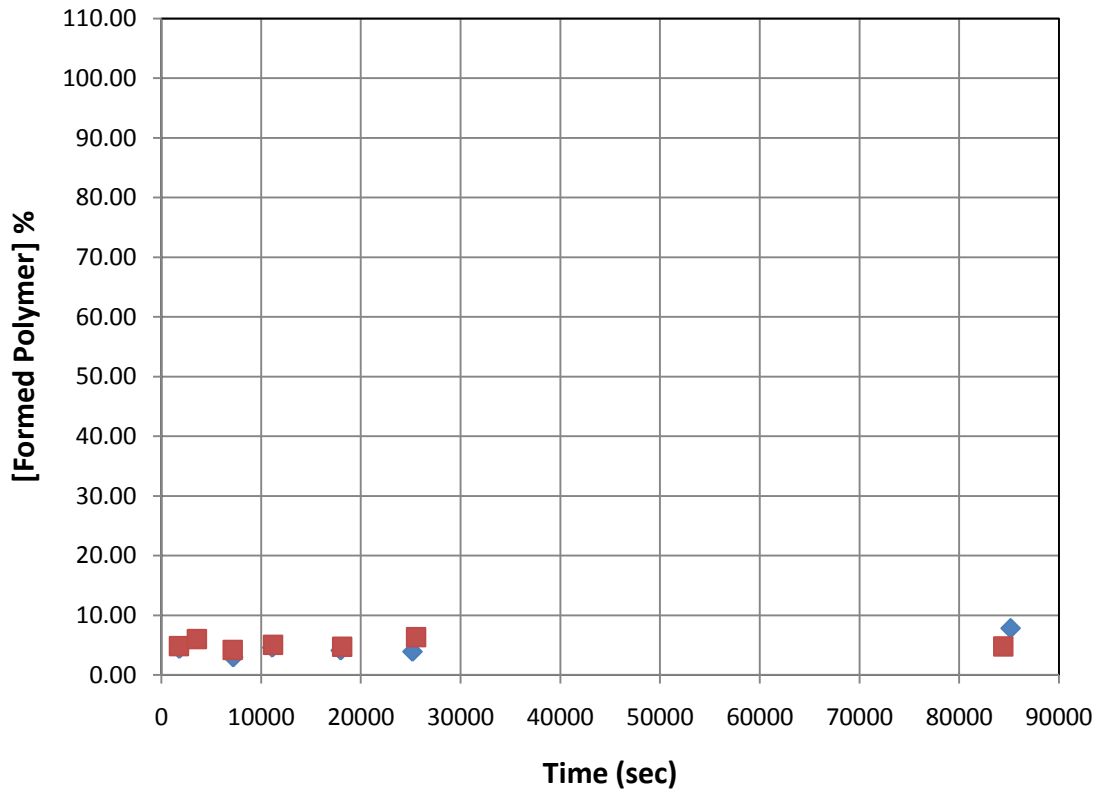


Figure 20: Polymer Conversion at 50°C and 50mg Lutensol

Table 12: Data for Runs 21 and 22: 50°C and 250mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
12-Feb	WPI-21-1	1818	30.67520	3.22827	6.27581	3.04754	3.26841	0.04014	0.40403	13.43052
	WPI-21-2	3608	30.67520	3.17527	6.06376	2.88849	3.21742	0.04215	0.44762	14.87961
	WPI-21-3	7195	30.67520	3.14744	5.93200	2.78456	3.18598	0.03854	0.42456	14.11302
	WPI-21-4	11157	30.67520	3.23967	6.00446	2.76479	3.27947	0.03980	0.44158	14.67864
	WPI-21-5	18052	30.67520	3.14151	5.99110	2.84959	3.17945	0.03794	0.40842	13.57625
	WPI-21-6	25490	30.67520	3.19294	6.05798	2.86504	3.23776	0.04482	0.47988	15.95166
	WPI-21-7	84376	30.67520	3.21587	6.06272	2.84685	3.25976	0.04389	0.47292	15.72048
12-Feb	WPI-22-1	1845	30.69356	3.16122	5.87445	2.71323	3.20259	0.04137	0.46800	15.51046
	WPI-22-2	3637	30.69356	3.14459	5.91409	2.76950	3.18757	0.04298	0.47633	15.78668
	WPI-22-3	7226	30.69356	3.18611	5.96540	2.77929	3.22611	0.04000	0.44175	14.64037
	WPI-22-4	11131	30.69356	3.21335	5.93065	2.71730	3.25420	0.04085	0.46143	15.29257
	WPI-22-5	18062	30.69356	3.21048	5.90998	2.69950	3.24306	0.03258	0.37044	12.27704
	WPI-22-6	25269	30.69356	3.22963	6.07999	2.85036	3.27418	0.04455	0.47973	15.89915
	WPI-22-7	84339	30.69356	3.13941	5.88508	2.74567	3.18787	0.04846	0.54173	17.95399

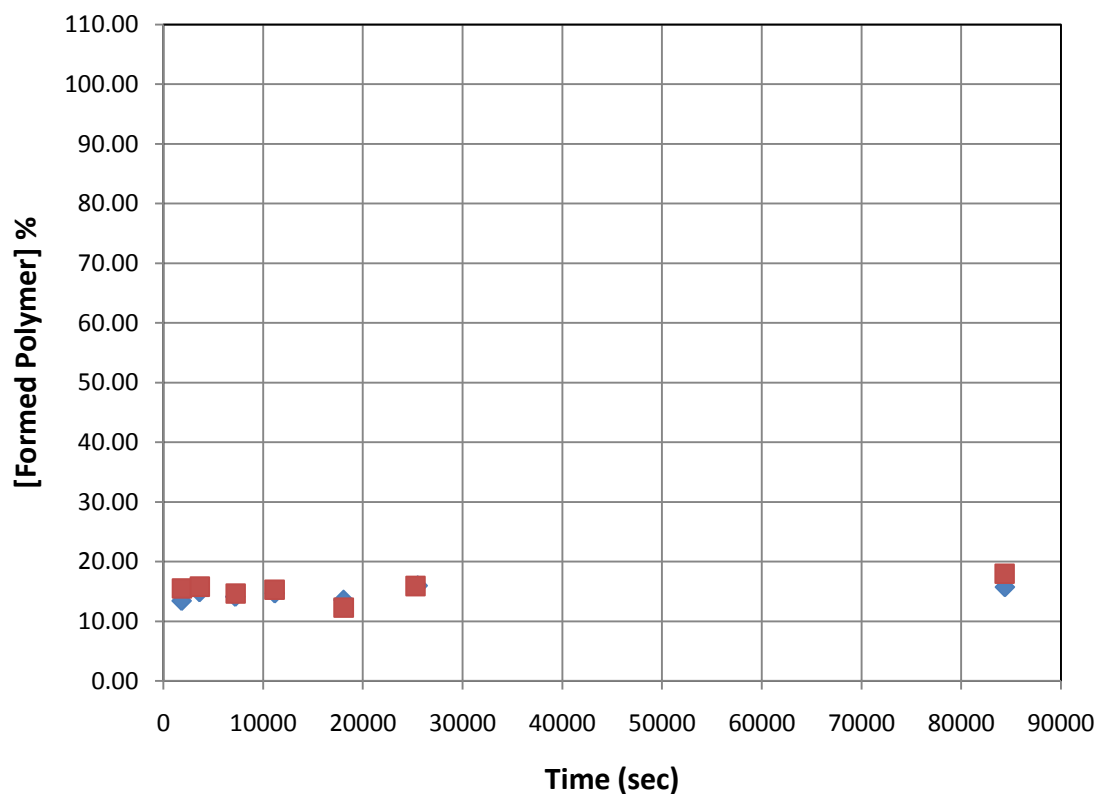


Figure 21: Polymer Conversion at 50°C and 250mg Lutensol

Table 13: Data for Runs 23 and 24: 50°C and 450mg Lutensol

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
14-Feb	WPI-23-1	1793	31.01387	3.21527	5.93347	2.71820	3.28373	0.06846	0.78111	25.54696
	WPI-23-2	3597	31.01387	3.16512	5.89501	2.72989	3.23881	0.07369	0.83718	27.38087
	WPI-23-3	7177	31.01387	3.23731	6.02368	2.78637	3.30397	0.06666	0.74196	24.26668
	WPI-23-4	11095	31.01387	3.19638	6.08419	2.88781	3.27196	0.07558	0.81170	26.54741
	WPI-23-5	18030	31.01387	3.19185	6.03878	2.84693	3.26352	0.07167	0.78076	25.53550
	WPI-23-6	25227	31.01387	3.18899	5.95581	2.76682	3.26126	0.07227	0.81009	26.49482
	WPI-23-7	84300	31.01387	3.19847	6.00373	2.80526	3.27170	0.07323	0.80960	26.47889
14-Feb	WPI-24-1	1747	30.97840	3.23914	6.17566	2.93652	3.41425	0.17511	1.84730	61.29363
	WPI-24-2	3541	30.97840	3.23084	6.06408	2.83324	3.41160	0.18076	1.97641	65.57772
	WPI-24-3	7115	30.97840	3.23876	6.02411	2.78535	3.41949	0.18073	2.01006	66.69416
	WPI-24-4	11057	30.97840	3.21624	6.00421	2.78797	3.38233	0.16609	1.84550	61.23402
	WPI-24-5	17986	30.97840	3.21426	6.32004	3.10578	3.39924	0.18498	1.84507	61.21973
	WPI-24-6	25189	30.97840	3.21733	6.03236	2.81503	3.39964	0.18231	2.00626	66.56789
	WPI-24-7	84270	30.97840	3.13365	6.04796	2.91431	3.30806	0.17441	1.85394	61.51386

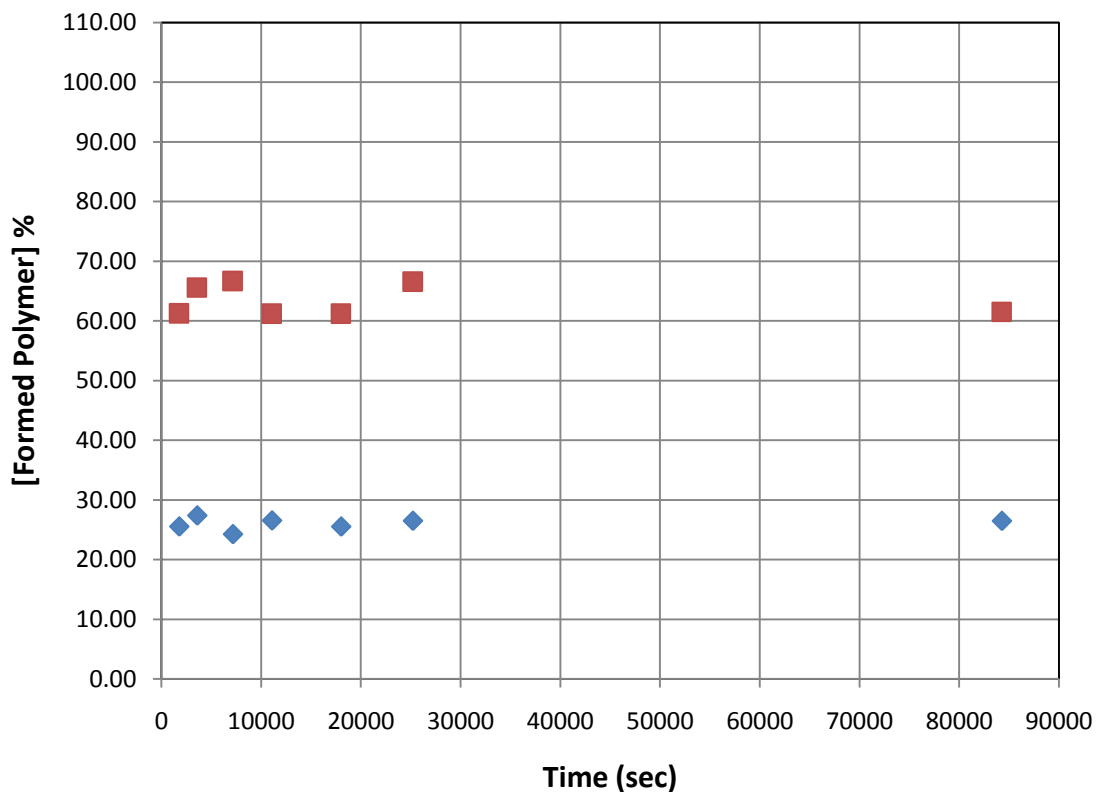


Figure 22: Polymer Conversion at 50°C and 450mg Lutensol

Table 14: Data for Runs 25 and 26: 60°C, 250mg Lutensol, and 75mg KPS

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
13-Feb	WPI-25-1	300	31.69017	3.19997	6.04545	2.84548	3.23643	0.03646	0.40606	13.49565
	WPI-25-2	592	31.69017	3.14692	6.03748	2.89056	3.18445	0.03753	0.41145	13.67506
	WPI-25-3	894	31.69017	3.20264	5.86924	2.66660	3.23723	0.03459	0.41107	13.66235
	WPI-25-4	1194	31.69017	3.16566	5.80302	2.63736	3.19975	0.03409	0.40962	13.61414
	WPI-25-5	1793	31.69017	3.19585	6.03546	2.83961	3.23267	0.03682	0.41091	13.65708
	WPI-25-6	2680	31.69017	3.24324	6.09353	2.85029	3.28037	0.03713	0.41282	13.72046
	WPI-25-7	3600	31.69017	3.14592	5.94137	2.79545	3.18269	0.03677	0.41684	13.85398
	WPI-25-8	5374	31.69017	3.21138	5.99511	2.78373	3.24882	0.03744	0.42622	14.16581
	WPI-25-9	7177	31.69017	3.18865	5.93456	2.74591	3.22723	0.03858	0.44525	14.79819
	WPI-25-10	8976	31.69017	3.15124	5.73340	2.58216	3.18746	0.03622	0.44452	14.77400
13-Feb	WPI-26-1	298	31.67378	3.22910	6.07907	2.84997	3.26618	0.03708	0.41210	13.68502
	WPI-26-2	597	31.67378	3.16129	5.95414	2.79285	3.19842	0.03713	0.42109	13.98374
	WPI-26-3	898	31.67378	3.16063	6.01972	2.85909	3.19790	0.03727	0.41289	13.71126
	WPI-26-4	1223	31.67378	3.09239	5.95856	2.86617	3.12959	0.03720	0.41109	13.65170
	WPI-26-5	1799	31.67378	3.13914	6.06841	2.92927	3.17753	0.03839	0.41511	13.78493
	WPI-26-6	2709	31.67378	3.22572	6.11636	2.89064	3.26410	0.03838	0.42054	13.96551
	WPI-26-7	3596	31.67378	3.15363	6.02978	2.87615	3.19179	0.03816	0.42024	13.95541
	WPI-26-8	5408	31.67378	3.23129	6.02212	2.79083	3.26856	0.03727	0.42299	14.04662
	WPI-26-9	7209	31.67378	3.20825	5.92880	2.72055	3.24673	0.03848	0.44800	14.87730
	WPI-26-10	9021	31.67378	3.15142	6.23695	3.08553	3.19428	0.04286	0.43997	14.61061

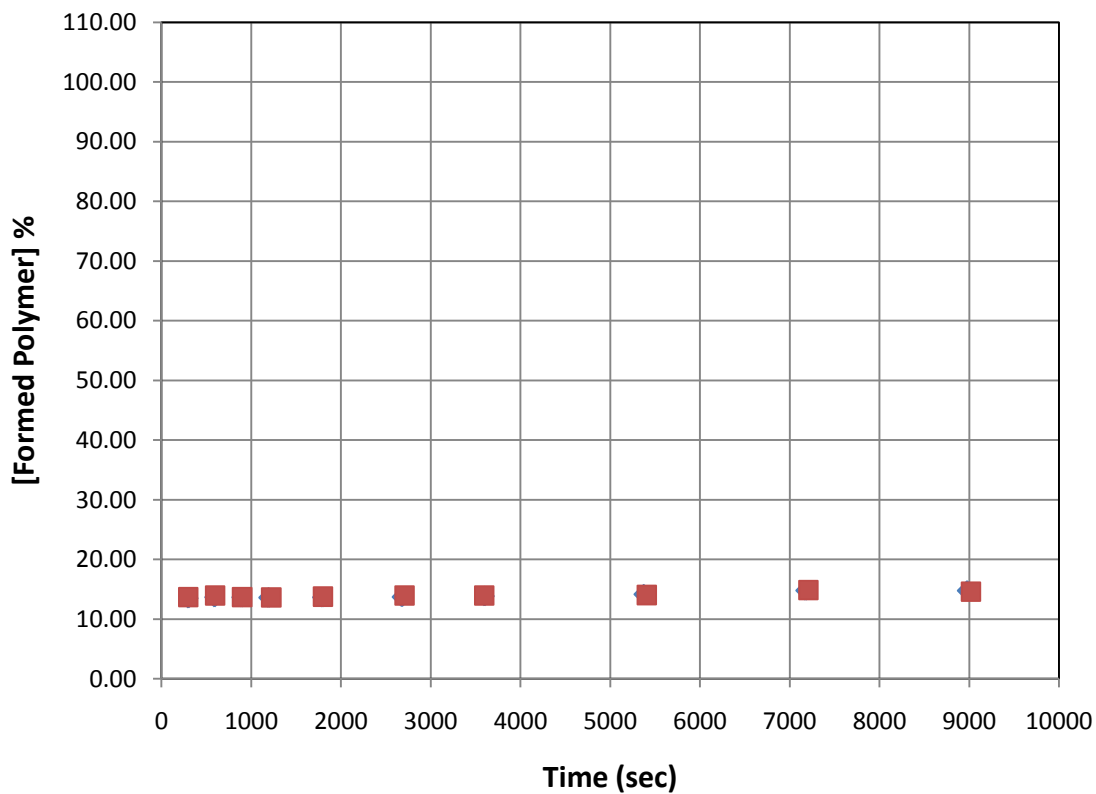


Figure 23: Polymer Conversion at 60°C, 250mg Lutensol, and KPS

Table 15: Data for Runs 27 and 28: 50°C, 250mg Lutensol, and 75mg KPS

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
14-Feb	WPI-27-1	581	31.69509	3.22708	5.95176	2.72468	3.26336	0.03628	0.42203	14.05756
	WPI-27-2	1195	31.69509	3.16123	5.91234	2.75111	3.19719	0.03596	0.41429	13.79971
	WPI-27-3	1786	31.69509	3.23335	6.10737	2.87402	3.27245	0.03910	0.43120	14.36300
	WPI-27-4	2828	31.69509	3.15651	5.99135	2.83484	3.19576	0.03925	0.43884	14.61737
	WPI-27-5	3589	31.69509	3.19668	6.04968	2.85300	3.23225	0.03557	0.39516	13.16256
	WPI-27-6	5388	31.69509	3.17221	5.89159	2.71938	3.20869	0.03648	0.42518	14.16260
	WPI-27-7	7200	31.69509	3.20152	6.08671	2.88519	3.24035	0.03883	0.42656	14.20859
	WPI-27-8	10793	31.69509	3.18551	5.93369	2.74818	3.22239	0.03688	0.42534	14.16785
	WPI-27-9	14402	31.69509	3.28218	6.05732	2.77514	3.31971	0.03753	0.42863	14.27749
	WPI-27-10	17996	31.69509	3.20187	5.97437	2.77250	3.23979	0.03792	0.43350	14.43959
14-Feb	WPI-28-1	589	31.71212	3.18937	6.02653	2.83716	3.22763	0.03826	0.42765	14.21083
	WPI-28-2	1195	31.71212	3.24104	6.09371	2.85267	3.27990	0.03886	0.43199	14.35521
	WPI-28-3	1786	31.71212	3.24222	5.96914	2.72692	3.27809	0.03587	0.41714	13.86173
	WPI-28-4	2832	31.71212	3.15225	5.93617	2.78392	3.18925	0.03700	0.42147	14.00565
	WPI-28-5	3591	31.71212	3.15060	6.01348	2.86288	3.19653	0.04593	0.50877	16.90642
	WPI-28-6	5393	31.71212	3.23567	6.00573	2.77006	3.27410	0.03843	0.43995	14.61974
	WPI-28-7	7198	31.71212	3.15082	5.91879	2.76797	3.18970	0.03888	0.44544	14.80210
	WPI-28-8	10797	31.71212	3.13235	5.84175	2.70940	3.16950	0.03715	0.43482	14.44921
	WPI-28-9	14401	31.71212	3.13331	6.03369	2.90038	3.17420	0.04089	0.44708	14.85664
	WPI-28-10	18002	31.71212	3.21154	5.91457	2.70303	3.25028	0.03874	0.45450	15.10313

Table 16: Data for Runs 29 and 30: 40°C, 250mg Lutensol, and 75mg KPS

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
14-Feb	WPI-29-1	590	31.82375	3.21814	6.07471	2.85657	3.26097	0.04283	0.47715	15.76671
	WPI-29-2	1198	31.82375	3.23839	6.01513	2.77674	3.27960	0.04121	0.47230	15.60649
	WPI-29-3	1785	31.82375	3.24692	6.16699	2.92007	3.28778	0.04086	0.44530	14.71442
	WPI-29-4	2835	31.82375	3.18688	5.91376	2.72688	3.22643	0.03955	0.46156	15.25171
	WPI-29-5	3588	31.82375	3.14322	6.01598	2.87276	3.18535	0.04213	0.46671	15.42162
	WPI-29-6	5391	31.82375	3.18921	5.67692	2.48771	3.22906	0.03985	0.50978	16.84483
	WPI-29-7	7191	31.82375	3.23019	5.82398	2.59379	3.26872	0.03853	0.47273	15.62076
	WPI-29-8	10791	31.82375	3.21489	6.04115	2.82626	3.25534	0.04045	0.45547	15.05027
	WPI-29-9	14400	31.82375	3.14493	5.89203	2.74710	3.18608	0.04115	0.47670	15.75191
	WPI-29-10	18012	31.82375	3.23664	5.89235	2.65571	3.27708	0.04044	0.48460	16.01284
14-Feb	WPI-30-1	605	31.69081	3.19205	5.99465	2.80260	3.23264	0.04059	0.45898	15.24153
	WPI-30-2	1205	31.69081	3.14291	5.93308	2.79017	3.18230	0.03939	0.44739	14.85682
	WPI-30-3	1789	31.69081	3.21265	6.01473	2.80208	3.25689	0.04424	0.50034	16.61519
	WPI-30-4	2854	31.69081	3.17692	5.65106	2.47414	3.21519	0.03827	0.49019	16.27814
	WPI-30-5	3602	31.69081	3.23800	5.92621	2.68821	3.27677	0.03877	0.45705	15.17761
	WPI-30-6	5400	31.69081	3.15003	5.57058	2.42055	3.18442	0.03439	0.45025	14.95164
	WPI-30-7	7201	31.69081	3.22801	5.63233	2.40432	3.26283	0.03482	0.45895	15.24078
	WPI-30-8	10811	31.69081	3.16383	5.43409	2.27026	3.19633	0.03250	0.45367	15.06532
	WPI-30-9	14404	31.69081	3.12782	5.71378	2.58596	3.16526	0.03744	0.45883	15.23648
	WPI-30-10	18020	31.69081	3.17492	5.76384	2.58892	3.21357	0.03865	0.47311	15.71092

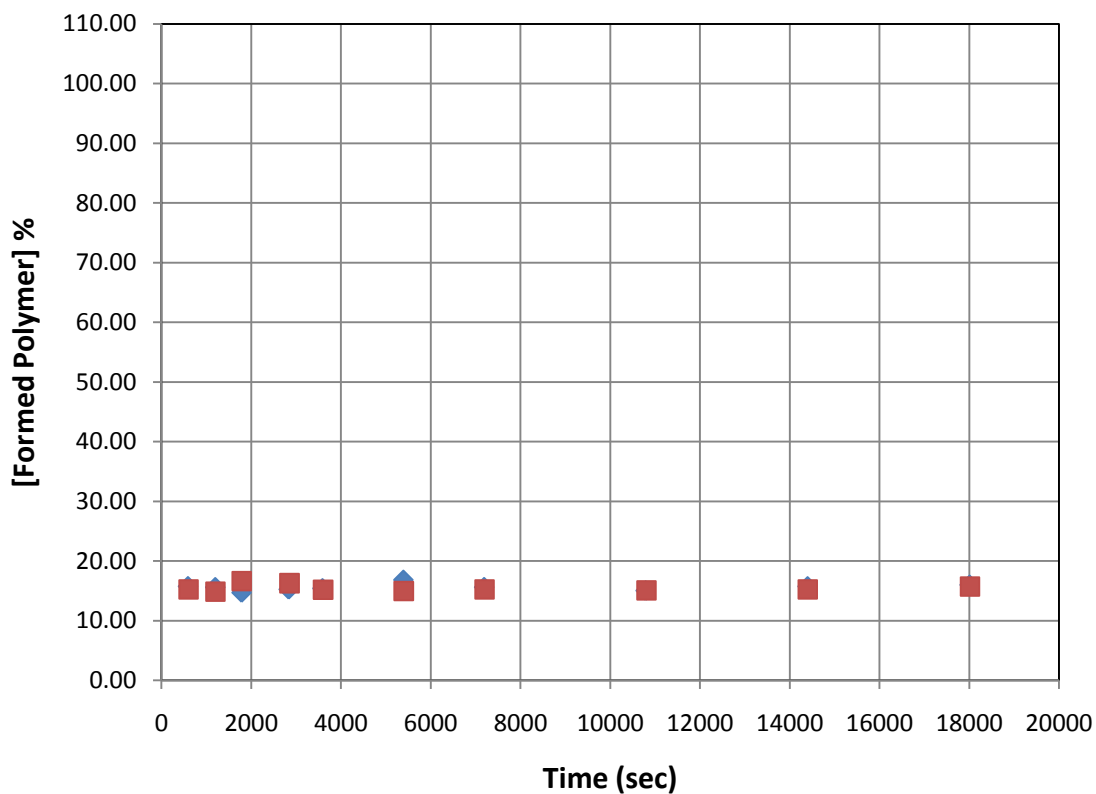


Figure 24: Polymer Conversion at 40°C, 250mg Lutensol, and KPS

Table 17: Data for Runs 31 and 32: 60°C, 250mg Lutensol, AIBN, and new monomer

Date	Run	time	Total	tube	cooled+tube	cooled	dried+tube	dried	Polymer	% Polymer
		sec	g	g	g	g	g	g	g	%
20-Feb	WPI-31-1	297	30.70922	3.24051	5.95653	2.71602	3.27494	0.03443	0.38929	12.90064
	WPI-31-2	594	30.70922	3.13771	5.97776	2.84005	3.17413	0.03642	0.39381	13.05032
	WPI-31-3	896	30.70922	3.15652	5.80440	2.64788	3.18969	0.03317	0.38469	12.74836
	WPI-31-4	1201	30.70922	3.20260	6.00509	2.80249	3.23772	0.03512	0.38484	12.75315
	WPI-31-5	1795	30.70922	3.20135	6.05265	2.85130	3.23938	0.03803	0.40959	13.57346
	WPI-31-6	2710	30.70922	3.21188	6.10989	2.89801	3.24808	0.03620	0.38360	12.71206
	WPI-31-7	3594	30.70922	3.13124	5.96963	2.83839	3.16690	0.03566	0.38581	12.78546
	WPI-31-8	5514	30.70922	3.23396	5.88097	2.64701	3.26766	0.03370	0.39097	12.95631
	WPI-31-9	7193	30.70922	3.16485	5.81612	2.65127	3.20052	0.03567	0.41316	13.69167
	WPI-31-10	9004	30.70922	3.20936	6.14909	2.93973	3.25199	0.04263	0.44532	14.75758
21-Feb	WPI-32-1	301	30.65438	3.21195	6.05236	2.84041	3.24438	0.03243	0.34999	11.66384
	WPI-32-2	600	30.65438	3.15683	6.02468	2.86785	3.19070	0.03387	0.36204	12.06520
	WPI-32-3	902	30.65438	3.21940	6.10557	2.88617	3.25387	0.03447	0.36611	12.20099
	WPI-32-4	1189	30.65438	3.12885	5.99674	2.86789	3.16322	0.03437	0.36737	12.24314
	WPI-32-5	1805	30.65438	3.13750	6.01004	2.87254	3.17125	0.03375	0.36016	12.00282
	WPI-32-6	2713	30.65438	3.09923	5.96617	2.86694	3.13273	0.03350	0.35819	11.93719
	WPI-32-7	3590	30.65438	3.13175	5.61163	2.47988	3.16135	0.02960	0.36589	12.19374
	WPI-32-8	5391	30.65438	3.15198	6.03291	2.88093	3.18694	0.03496	0.37199	12.39694
	WPI-32-9	7251	30.65438	3.15406	5.97586	2.82180	3.18866	0.03460	0.37587	12.52638
	WPI-32-10	9005	30.65438	3.15834	5.72934	2.57100	3.19094	0.03260	0.38869	12.95362

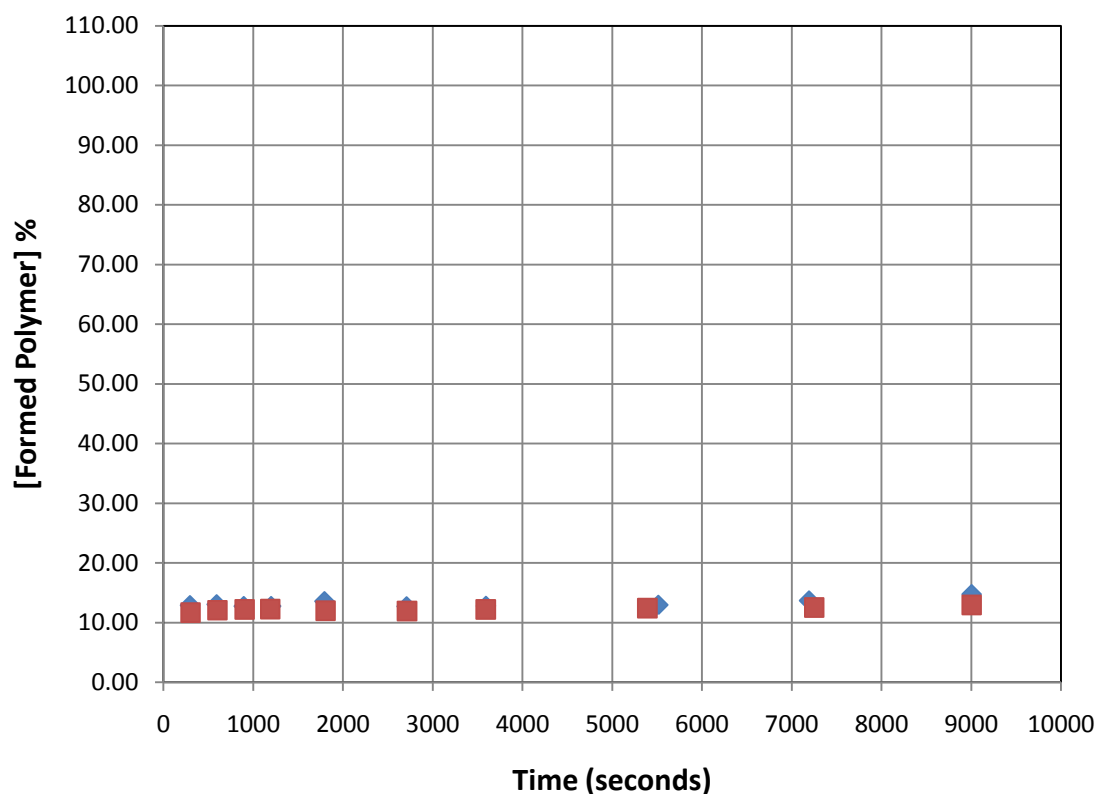


Figure 25: Polymer Conversion at 60°C, 250mg Lutensol, and new Monomer

BIBLIOGRAPHY

- ¹ Painter, P and Coleman, M. Fundamentals of Polymer Science. Woodhead Publishing. 1997.
- ² Brandrup, J. Polymer Handbook 4th Ed. New York. Wiley-Interscience. 1999.
- ³ "Macromolecular Amphiphiles." Wiesner Research Group – Cornell University. 2007. Accessed 14 Jan 2008. <<http://people.ccmr.cornell.edu/~uli/pages/macamp.htm>>.
- ⁴ Buback, M., et al. "Critically Evaluted Termination Rate Coefficients for Free-Radical Polymerization, 1 The Current Situation." *Macromolecular Chemistry and Physics*. 203. 2570-2582. 2002.
- ⁵ Arnold, L. K.: Introduction to Plastics. Iowa State University Press. 1968.
- ⁶ "Polymerization of MMA". Technische Universiteit Eindhoven. Accessed 18 Mar 2008. <http://students.chem.tue.nl/poly05/polymerization_of_mma.htm>.
- ⁷ Mcquarrie, D. Quantum Chemistry. University Science Books. 1983.
- ⁸ "Fluorescence." Mekentosj-Science. 2001. Accessed 16 Jan 2008. <<http://mekentosj.com/science/fret/fluorescence.htmlhtml> >.
- ⁹ Blinder, S.M. Introduction to Quantum Mechanics: in Chemistry, Materials Science, and Biology. Elsevier Science and Technology Books. 2004.
- ¹⁰ Sadtler, Veronique M. et al. "Ostwald Ripening of Oil-in-Water Emulsions Stabilized by Phenoxy-Substituted Dextrans". *Journal of Colloid and Interface Science*. 254. 355-361. 2002.
- ¹¹ Landfester, Katharina. "Polyreactions in Miniemulsions". *Macromolecular Rapid Communication*. 22. 896-936. 2001.
- ¹² Grove, Richard. "Emulsions." Notes on Making Cola. 2005. Accessed 16 Jan. 2008. <<http://sparror.cubecinema.com/cube/cola/chemistry/cola1.htm>>.
- ¹³ Shork, F.J. et al. "Miniemulsion Polymerization" *Colloids and Surfaces A: Physiochemical and Engineering Aspects* 153. 39-35. 1991.
- ¹⁴ Asua, Jose M. "Miniemulsion Polymerization." *Progress in Polymer Science*. 27. 1283-1346. 2002.
- ¹⁵ (Inline Mixing Devices.) Fluent. Accessed 16 Jan. 2008. <<http://www.fluent.com/solutions/examples/x85.htm>>

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- ¹⁶ HPPS Operators Guide. Malvern Instruments Ltd. England. 2001
- ¹⁷ Rotureau, E. et al. "From Polymeric Surfactants to Colloidal Systems (1): Amphiphilic Dextrans for Emulsion Preparation." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 288. 131-137. 2006.
- ¹⁸ Kinnier, Sharon. "Emulsions". All Natural Beauty. Accessed 16 Jan. 2008. <<http://www.allnaturalbeauty.us/emulsions.htm>>.
- ¹⁹ Soppimath, Kumaresh S. et al. "Biodegradable Polymeric Nanoparticles as Drug Delivery Devices". *Journal of Controlled Release*. 70. 1-20. 2001.
- ²⁰ "Peptide Drug Discovery Research Reenergized". *Genetic Engineering and Biotechnology News*. 26. 8. 2006. Accessed 16 Jan. 2008. <<http://www.genengnews.com/articles/chitem.aspx?aid=1564&chid=1>>.
- ²¹ Heard, Daniel. "Putting on a Good Face- The Chemistry of Cosmetics." Australian Academy of Science. 2004. Accessed 16 Jan. 2008. <<http://www.science.org.au/nova/083/083key.htm>>.
- ²² Argawal, Rupish K. et al. "Cosmetic Composition". FreshPatents.com 2006. Accessed 16, January 2008. <<http://www.freshpatents.com/Cosmetic-composition-dt20061207ptan20060275332.php>>.
- ²³ Tiarks, F., Landfester, K., Antonietti, M. "Preparation of Polymeris Nanocapsules by Miniemulsion Polymerization." *Langmuir*. 17. 908-918. 2001.
- ²⁴ Mascherin, Marion. ENSIC-INPL. Nancy, France
- ²⁵ Herrmann, Heinz. Liquid Developer and Copolymer Polarity Control Agent for Use Therewith. United States 4243736. Jan. 6, 1981.