



## NE 335 Macromolecular Science

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Nanotechnology Engineering

DEPARTMENT OF CHEMISTRY

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## 1. Introduction

### *Objective*

The main objective of this experiment is to perform the emulsion polymerization of styrene and to study the effects of surfactant concentration on the polymerization and yield. The rate of polymerization is compared at different surfactant concentrations and explained with kinetic theory. Also, the particle size will be monitored over time and assessed by conversion levels. GPC measurements of molecular weights of the polymer are then taken and finally, each of these parameters is used to explain the kinetics of emulsion polymerization.

### *Background*

An emulsion is defined as a discontinuous phase dispersed throughout another continuous liquid phase [1]. Emulsion polymerization takes advantage of the effects of colloidal suspension of two immiscible liquids that is stabilized by an emulsifier, or a surfactant. Generally, the monomers involved in emulsion polymerization are oil-like substances with minimal water solubility, and these monomers are dispersed in a continuous water phase, forming the emulsion. The four main ingredients in emulsion polymerization are as follows:

*Dispersant:* The dispersant is the continuous phase of the emulsion and is the liquid in which all other components are dispersed. Usually, this phase is water.

*Monomer:* For systems where water is the dispersant, the oil-like monomers have limited water solubility, and they are also minimally soluble in their polymer form. Some common monomers include vinyl monomers such as styrene, acrylonitrile, vinyl acetate, isoprene, and 1,3-butadiene [2].

*Emulsifier:* The emulsifier is also known as the surfactant, or soap of the emulsion system. A surfactant is a molecule that possesses both a hydrophilic head and a hydrophobic tail. When mixed in water, surfactant molecules form micelles upon exceeding the “critical micelle concentration”. In solution, surfactants stabilize monomer droplets either by electrostatic or steric means [2]. The concentration of surfactants is very important in determining reaction kinetics in emulsion polymerization.

*Initiator:* As with any other type of polymerization, an initiator is required to kick start the reaction. In emulsion polymerization, the initiator is a water-soluble compound, such as peroxides or persulfates.

Emulsion polymerization occurs in three phases, or intervals. In interval I, there is an excess of monomer droplets in the solution as the polymerization has just started. Polymer particles are formed from the decomposition of the water soluble initiator, and

radical polymerization occurs with monomers to create short oligomeric radicals that act as reaction sites for further polymerization. In this interval, the oligomers are captured by surfactants, which in turn create micelles around the short polymer chains. This behaviour stabilizes the oligomers, and a latex particle is formed which then promotes rapid growth of the oligomeric radical. Interval II of the polymerization involves particle growth by existing oligomeric radicals formed in interval I. In this interval, capture efficiency of the monomer into the micelles is very high due to the number and surface area of particles. Hence, the polymer particles grow as monomers diffuse into the micelles, and depletion of monomers occur as monomers are used up. In the final phase, interval III, the solution is almost entirely free of monomers. Effectively, the rate of polymerization also starts to decrease, causing local viscosity to increase inside the particles due to slower movement of the polymer particles. Termination also slows down, leading to an effect called “autoacceleration” [2].

There are many advantages of emulsion polymerization over other forms of polymerization. For example, when water is used as the continuous phase in the emulsion, it acts as an effective agent for heat removal due to the exothermic nature of polymerizations. Also, another key advantage of emulsion polymerization over homogenous radical polymerization is that increasing the rate of reaction will not yield polymers with lower molecular weights. This is the case in homogenous radical polymerization, and is an obstacle for commercialization. The kinetics of emulsion polymerization effectively allows polymerization to occur faster while at the same time yielding polymers with a high molecular weight.

## 2. Experimental

All procedures were followed exactly as specified in the NE 335 lab manual [2]. The following minor changes were made:

- A gravity funnel was used instead of a Buchner funnel. This is done to minimize yield error due to the pressure that is applied in the Buchner funnel.
- In Step 14, 2.6 g of  $\text{Al}_2(\text{SO}_4)_3$  was added in 100 mL  $\text{H}_2\text{O}$ . The concentration was kept the same but the volume required was increased.

### 3. Results

#### *Sample Yields with Time*

**Table 1 Group I Percentage Yields with Time**

Time (min)	Vial Weight (g)	Aluminum Pan weight (g)	Vial Weight with Sample (g)	Polymer Weight with Aluminum Pan (g)	Sample Weight	Polymer Weight	% Yield
15	5.9705	1.0043	8.7793	1.0044	2.8088	0.0001	0.0%
25	5.9703	0.9750	8.8876	0.9752	2.9173	0.0002	0.0%
35	5.9373	1.0070	8.6450	1.0097	2.7077	0.0027	0.4%
45	5.9721	1.0179	8.3505	1.0830	2.3784	0.0651	11.8%
60	5.9528	0.9850	8.6246	1.1385	2.6718	0.1535	24.8%
75	5.9548	1.0079	8.6564	1.2816	2.7016	0.2737	43.7%
90	5.9760	0.9945	8.1952	1.2574	2.2192	0.2629	51.1%
105	5.9255	1.0080	8.8097	1.4633	2.8842	0.4553	68.1%
120	5.9256	0.9969	8.6731	1.4938	2.7475	0.4969	78.0%
180	5.9467	0.9933	8.3673	1.4933	2.4206	0.5000	89.1%

**Table 2 Group II Percentage Yields with Time**

Time (min)	Vial Weight (g)	Aluminum Pan weight (g)	Vial Weight with Sample (g)	Polymer Weight with Aluminum Pan (g)	Sample Weight	Polymer Weight	% Yield
15	5.9803	0.9766	8.5502	0.9824	2.5699	0.0058	1.0%
20	5.9741	0.9543	7.7609	0.9709	1.7868	0.0166	4.0%
25	5.9331	0.9582	8.2295	1.0085	2.2964	0.0503	9.5%
30	5.9102	0.9743	7.8943	1.0407	1.9841	0.0664	14.5%
35	5.9744	0.9930	8.0387	1.0912	2.0643	0.0982	20.6%
40	5.9887	0.9885	8.3767	1.1345	2.3880	0.1460	26.4%
50	5.9663	0.9635	8.1758	1.1297	2.2095	0.1662	32.5%
75	5.9674	0.9793	7.9227	1.2009	1.9553	0.2216	49.0%
90	5.9576	1.0055	8.0540	1.2743	2.0964	0.2688	55.5%
120	5.9327	0.9944	8.3903	1.4365	2.4576	0.4421	77.8%
150	5.9533	0.9771	8.2777	1.4544	2.3244	0.4773	88.8%

#### *Sample Yield Calculation*

The following sample calculation illustrates the yield calculation for Sample 3 (25 min):

The mass fraction of styrene is:

$$\begin{aligned}
 f_{sty} &= \frac{\text{Mass of styrene}}{\text{Mass of styrene} + \text{Mass of H}_2\text{O} + \text{Mass of other components}} \\
 &= \frac{30 \text{ mL} \times 0.909 \text{ g / mL}}{(30 \text{ mL} \times 0.909 \text{ g / mL}) + (90 \text{ mL} \times 1 \text{ g / mL}) + 0.0491 \text{ g} + 0.0477 \text{ g} + 0.6032 \text{ g}} \\
 &= 0.23
 \end{aligned}$$

The sample weight taken in the vial is  $(8.2295 \text{ g} - 5.9331 \text{ g}) = 2.2964 \text{ g}$

The polymer weight is  $(1.0085 \text{ g} - 0.9582 \text{ g}) = 0.0503 \text{ g}$

The percent yield is then:

$$\begin{aligned}
 \% \text{ yield} &= \frac{\text{Dried polymer weight}}{(\text{Styrene mass fraction} \times \text{sample weight})} \\
 &= \frac{0.0503 \text{ g}}{0.2311 \times 2.2964 \text{ g}} \times 100\% \\
 &= 9.5\%
 \end{aligned}$$

### ***Particle Sizes with Time***

**Table 3 Group I Particle Diameters**

<b>Time (min)</b>	<b>Particle Diameter (nm)</b>
15	30.3
25	36
35	46.4
45	57
60	69.5
75	82.4
90	87.7
105	94.7
120	95.1
180	103.1

**Table 4 Group II Particle Diameters**

<b>Time (min)</b>	<b>Particle Diameter (nm)</b>
15	36.4
20	41.7
25	49.6
30	53.2
35	58.3
40	60.3
50	64.8
75	74.4
90	74.9
120	80.2
150	82.7

***GPC Results*****Table 5 Group I and II Molecular Weights, PDI, Viscosity and Hydrodynamic Radius**

	<b>Group I</b>	<b>Group II</b>
Mn (Daltons)	1.540e6	2.558e6
Mw	2.549e6	3.792e6
PDI	1.656	1.483
IV - (dl/g)	4.8225	6.6642
Rh - (nm)	4.8225	70.603

## 4. Discussion

### *Plot of Conversion vs. Time*

The data in Table 1 and Table 2 are plotted in Figure 1 below.

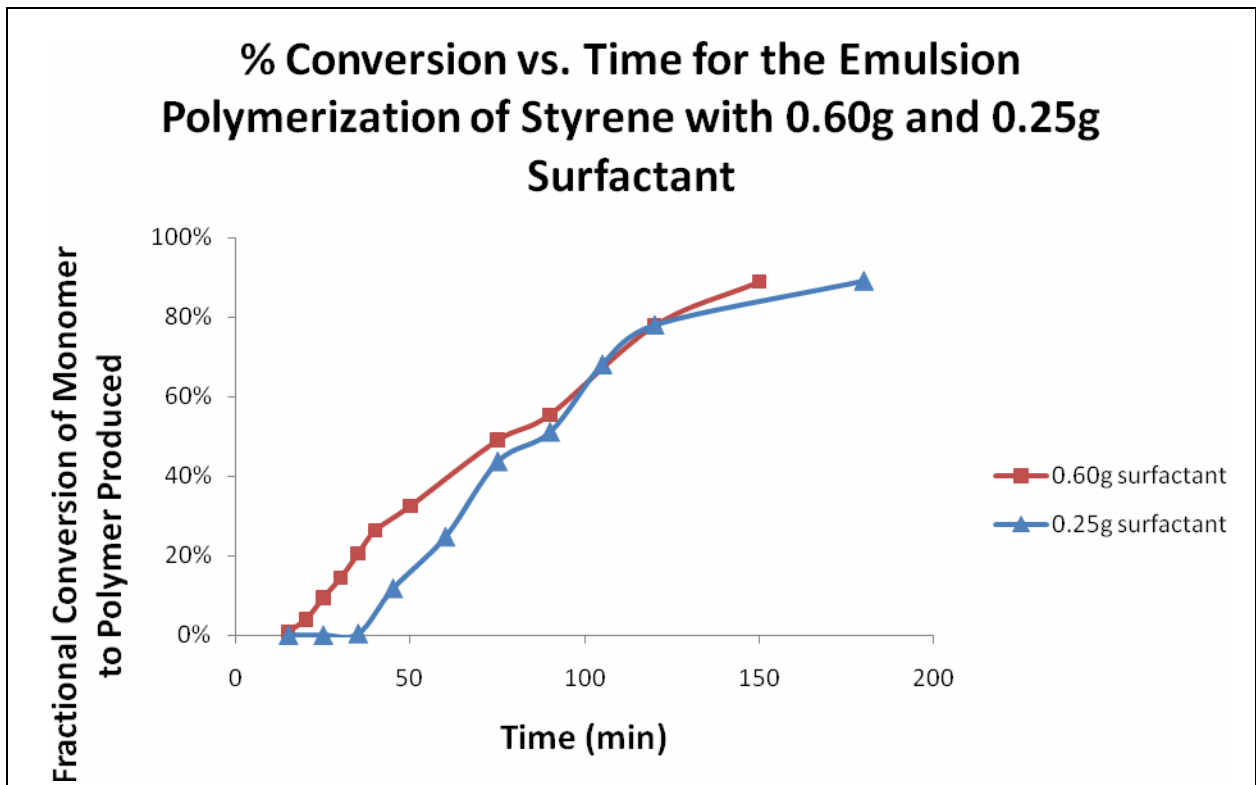


Figure 1 % Conversion vs. time for the emulsion polymerization of styrene with 0.25g (Group I) and 0.60g (Group II) surfactant weights



### Particle Sizes with Time

The data in Table 3 and Table 4 are plotted in Figure 2 below.

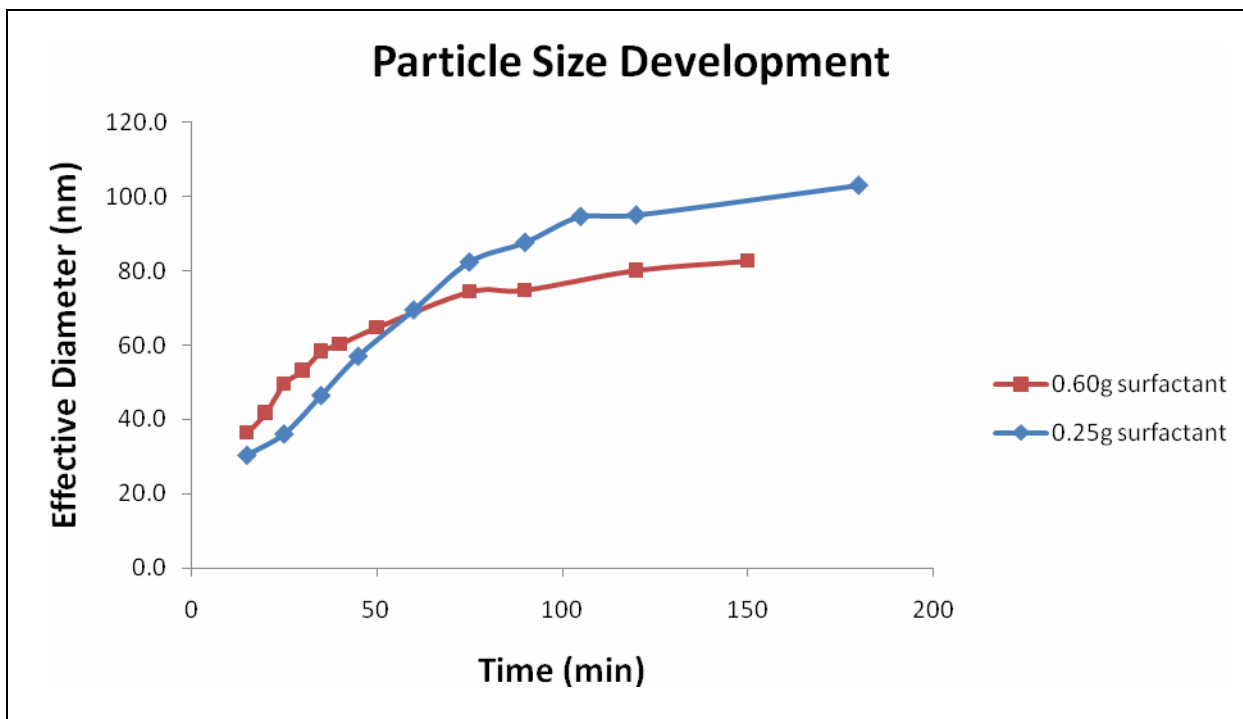


Figure 2 Particle sizes vs. time of two emulsion polymerizations containing 0.60g and 0.25g of surfactant

### Observations and Comparisons

Comparing the conversions plot between groups I and II, it is apparent that both groups follow the same general trend. Clearly, at the beginning of the polymerization ( $t < 30$  minutes), not much yield is observed since not much reaction has happened. The monomers have not had time to form polymer chains, and most of the sample contains monomers instead of polymers, which would have been washed away by methanol during filtering. As more samples are taken over time, the polymer yield increases as emulsion polymerization continues. Monomer droplets begin to enter the micelles formed by surfactant molecules, thereby creating polymer chains more readily. The extracted sample would naturally contain more polymer as time increases, and the yield would increase correspondingly.

Looking at the two plots in Figure 1, it is evident that the reaction with the higher surfactant concentration (0.60 g) yields polymers faster than the reaction with the lower surfactant concentration (0.25 g) at any given time. Polymers grow when the monomer

droplets that are trapped in the micelle become surface active, growing rapidly to form a latex particle [2]. With more surfactant, the emulsion becomes more stable, and more micelles are formed. Since there are more micelles in the solution, there are more sites where polymerization can happen, readily increasing the yield.

In terms of the particle size, it is observed in Figure 2 that at the first half of the polymerization, the reaction with the higher surfactant concentration yields larger particles whereas in the latter half, the reaction with the lower surfactant concentration yields larger particles. This may be attributed once again to the number of micelles present in the emulsion at any given time. With a higher surfactant concentration, more micelles will form, naturally. Since there are more micelles and hence more reaction sites, the monomers in the solution will be more widely dispersed within the large number of micelles. Comparatively, the reaction with the lower surfactant concentration has a lower number of micelles, and all polymerization reactions are forced to occur within these micelles. Hence, all of the monomer must be polymerized in a low number of micelles. In the first case, monomers are “shared” by more micelles, creating more polymers yet ones with smaller particle size. In the second case, monomers are “shared” by fewer micelles, creating larger particle sizes in each micelle, explaining the situation in Figure 2.

According to Smith and Ewart, in interval I of the emulsion polymerization, the number of particles formed from the reaction can be related to various other parameters using the following formula:

$$N = k \left( \frac{R_i}{\mu} \right)^{0.4} (a_s S)^{0.6}$$

In the above equation, N is the number of particles formed,  $R_i$  is the rate of radical initiation,  $\mu$  is the rate of volume growth per particle,  $a_s$  is the surface area occupied by a single surfactant molecule, and S is the surfactant concentration [2]. The equation clearly draws a connection between the surfactant concentration and the number of particles formed, as they are directly correlated. As surfactant concentration increases, so does the number of particles formed, and vice versa. This relationship is consistent with the experimental results. Referring to previous discussions, it was determined that the experiment with the higher surfactant concentration yielded more particles, hence particles with smaller size. This result thus agrees with the expected phenomenon based on the kinetic expression.

Another equation that relates the kinetics of emulsion polymerization is important in interval II of the reaction. The equation is as follows:

$$R_p = \frac{N \tilde{n} k_p [M]}{N_A}$$

$R_p$  is the rate of polymerization,  $[M]$  is the monomer concentration,  $k_p$  is the rate constant of propagation,  $N$  is the number of particles,  $N_A$  is Avogadro's number, and  $\bar{n}$  is the number of radicals per particle. Comparing experimental results with this equation, it seems that the reaction that yielded a higher number of particles (the one with the higher surfactant concentration) also had a higher rate of polymerization. This relationship agrees with that described in the equation.

Finally, the molecular weights of the samples from Groups I and II are compared. Theory predicts that the molecular weight of samples would increase with time since polymerization would have proceeded further at later times. The data from both Groups I and II exhibit this result, showing that the experiment agrees with the theory. Next, it is observed that the molecular weight obtained in Group II is larger than that of Group I. This result can be explained by the amount of surfactant added. Group II had a higher surfactant concentration than Group I and as such, Group II obtained polymers with a higher chain length and degree of polymerization, which correspond to increased molecular weight.

## 5. Questions

### *Question 1*

***The locus of polymerization is the micelles in emulsion polymerization. Explain why this is the case in the early stages of reaction when the amount of monomer in droplets far exceeds the amounts in micelles.***

In the early stages of emulsion polymerization, there is an excess of monomer droplets. However, micelles at this stage have a greater surface area than the monomer droplets, which effectively contributes to their activity. As such, a growing radical is more likely to react within a micelle rather than with a monomer droplet due to the relative surface area of the two. Consequently, most of the reaction occurs at the micelles, and they can be considered as the locus of polymerization that carries on the reaction.

### *Question 2*

***In an ideal emulsion polymerization the reaction rate in interval II is essentially constant (do your results confirm this?). Explain why this is the case.***

The reaction rate is given by the slope of the plot in Figure 1. As can be seen in this figure for the 0.60g surfactant, the slope of the conversion vs. time plot in the middle of Figure 1 is fairly constant indicating a steady reaction rate in interval II.

Why is this the case? The plot of percent conversion vs. time is fairly logarithmic. This is to say that the reaction starts off fairly slow in the beginning but picks up speed quickly

and reaches a steady maximum, continues to progress at this maximum rate, and then slowly starts to slow down and eventually level off as the reaction approaches completion.

The initial slow phase in the beginning is not seen on the graph in Figure 1 because this interval occurs only for a very brief period and was too quick to be measured. Once the reactants have picked up heat from the surrounding hot water bath, the initiator forms free radicals that it uses to form short strands of monomers known as oligomers. The polymerization then starts to take place at a much faster rate than before causing the reaction rate to accelerate because there is a constant supply of monomer molecules from the monomer droplets for the free radicals to react with. The polymerization continues at this relatively high constant rate seen in the graph as a steeper, linear slope. With time, the monomer droplets begin running out and the polymerization does not have enough of its reactants to keep producing products at this constant supply. As a result, the reaction rate begins decelerating seen by a decrease slope in the graph. Finally, all monomer droplets are exhausted leaving no reactant molecules for the radicals to react with. The slope of the graph, and thus the reaction rate, levels off and reaches zero [3].

### ***Question 3***

***Give two examples of polymers used as rubbers, in general application, which are made by emulsion polymerization.***

Two examples of polymers used as rubbers which are made by emulsion polymerization are:

1. **Polybutadiene:** a rubber most commonly used to manufacture tires for automobiles and airplanes. Polybutadiene is a very tough and elastic rubber that can withstand large amount of friction without undergoing significant wear or tear.
2. **Fluoroelastomers:** These are special purpose synthetic rubbers made by emulsion polymerization. They have wide chemical resistance and superior performance, especially in high temperature application in different media. They are therefore very heat resistant and are used in environments where extreme temperature resistance is needed such as chemical process plants, gaskets, airplanes, etc.

## 6. References

- [1] J.Duhamel, *Nanotechnology Engineering NE 233 Lecture Notes*, University of Waterloo, Waterloo (2007).
- [2] N.McManus, M.Tam, J.Duhamel, *Nanotechnology Engineering NE 335 Lab Manual*, University of Waterloo, Waterloo, pp. 4-1 to 4-14 (2008).
- [3] Odian George, *Principles of Polymerization*, Haboken New Jersey, 2004.