Microemulsion Polymerization: An Undergraduate Experiment in the Synthesis of Nanosized Polystyrene Particles

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Received October 9, 2000. Accepted December 1, 2000

Abstract: The synthesis of polystyrene nanoparticles through microemulsion polymerization is presented as an undergraduate advanced organic laboratory exercise. The resultant polymer's molecular weight and particle size are studied as a function of monomer and initiator concentration. A comparison of cationic vs. anionic surfactants, and their effects on the polymer produced through microemulsion polymerization are also investigated. A direct relationship is observed between molecular weight and monomer concentration. A direct relationship is also found for the particle size of the latex produced. An inverse relationship is observed for molecular weight and particle size as the initiator concentration was raised. Comparison of molecular weight and latex size for cationic and anionic surfactants demonstrates that the anionic surfactant produces both a higher molecular weight and a larger latex size over the entire monomer and initiator concentration ranges.

Introduction

Solution and emulsion polymerization are the two main methods of polymerization [1]. Solution polymerization is one of the earliest methods of polymerization. Adhesives, thickeners, and water treatment additives are a small representative group of applications. Solution polymerization uses a solvent in which both the monomer and the resultant polymer are soluble. Solution polymerization has its advantages and disadvantages. For example, solution polymerization allows for higher temperatures and easier mixing due to lower viscosities; it also negates the need for surfactants or other costly additives used in other methods of polymerization [2]. However, removal of solvent and possible chain transfer are among the major obstacles in solution polymerization.

Emulsion polymerization takes place with a mixture of two immiscible liquids. The bulk phase is typically aqueous, and the oil phase comprises the monomer; a surfactant is added to reduce the surface tension between the two phases. The concentration of the surfactant is typically under 10% of the bulk phase. The concentration is designed to be only a few percent above the critical micellular concentration (CMC) of the surfactant, to have both monomer-swollen micelles and monomer droplets present in solution. These two structures are on the order of 10 nm to 10 μm, respectively, making the mixture thermodynamically unstable; therefore, without mechanical force, the emulsion will separate into two phases. After the polymerization is complete, the latex particles formed are on the order of 100–400 nm, giving the emulsion an appearance of an opaque, white mixture. Emulsions, through their colloidal composition, allow for greater control of the polymerization, and the latex produced can be used without further processing. The method of emulsion polymerization also permits the alteration of the molecular weight of the polymer by changing initiator and monomer concentrations without changing the kinetics of the process. Though surfactants are required, the concentrations needed are lower than in other polymerization applications.

Microemulsion polymerization is the latest in the family of polymerization techniques. Discovered in 1943 by Hoar and Schulman [3], microemulsions are clear and thermodynamically stable dispersions. The surfactant concentration is set well above its CMC, so that there are only monomer-swollen micelles present. The sole presence of micelles gives the microemulsion its stability. The latex particles that are produced from a microemulsion typically range from 10–50 nm [4–7]. Microemulsion polymerization is the only polymerization technique that can produce particles of this size range. The need for high surfactant concentrations, which can become costly, is a disadvantage of microemulsion polymerization. There have been recent attempts to reduce the amount of surfactant to a few percent.

In a microemulsion there are generally four components: the continuous phase, a surfactant, an initiator, and the monomer. The bulk phase is typically water, though inverse microemulsions exist. These are systems in which the oil is the bulk phase and aqueous phase is encapsulated within the micelle [8]. The surfactant, used to create the micelles that retain the oil soluble monomer, can be ionic or nonionic. The surfactant's charge can be altered, with cationic, anionic and nonionic surfactants available; these can also be mixed to alter intrinsic characteristics of the specific surfactants in solution [9–13]. Surfactant concentration also has a strong effect on the polymer produced [5, 14].

In microemulsion polymerization, radical initiators are the most common. The position of radical initiators within the system can be strategically placed. For example, initiators can be soluble in the continuous phase, inside the micelle, and also at the micelle interface itself [4, 15–16]. Different monomers of varying solubility and functionality also can be used [10]. Other chemicals can be added to the microemulsion to alter the characteristics of the microemulsion or the properties of the polymerized product, such as salts or cosurfactants [17–18].

S1430-4171(01)02460-8, Published on Web 02/02/2001, 10.1007/s00897010460a, 620104yl.pdf

The formation of radicals in aqueous solution requires that molecular oxygen must be purged from the reaction vessel with an inert gas, such as nitrogen. Oxygen has been shown to be effective in the consumption of radicals [5, 19], therefore, the removal of oxygen from solution immediately prior to initiation prolongs the lifetime of the radicals.

This laboratory explores in detail the effect on the final product when the charge of the surfactant is changed from cationic to anionic while using the same initiator. Varied monomer and initiator concentrations are also investigated. The resultant polymer's molecular weight is determined with gel permeation chromatography (GPC), and the latex formed is analyzed with dynamic light scattering (DLS) to determine particle size.

In a typical laboratory setting, undergraduate students have virtually no exposure to microemulsions, nor experience in the technique of microemulsion polymerization. In this laboratory, students are given the opportunity to learn of these systems and to produce unique polymer particles. Students are also expected to hypothesize the particle size and molecular weight (MW) trends based upon the interactions between the initiator and the varying surfactants, as well as effects of increasing the concentrations of the monomer and initiator. The students then support these predictions by synthesizing these polymers. The students also learn the principles and operation of gel permeation chromatography (GPC) and dynamic light scattering (DLS) instruments.

Experimental

Laboratory Considerations. Due to the relatively large number of microemulsions to be made, we suggest students work in pairs. The synthetic laboratory will need roughly four 3-hour periods. The instrumental analysis time exceeds this allotted laboratory time; other opportunities are therefore needed for adequate instrument time. The number of samples is too many to permit students to run their samples individually, so the instructor can show the students the instruments, while allowing an assistant to complete the data collection. If an assistant completes the GPC and DLS measurements outside of the allotted laboratory time, the raw data can be given to the students for interpretation once the instrumental analysis is complete. Due to the large number of samples created in this laboratory, an autosampler on the GPC instrument is essential. If both GPC and DLS instrumentation are not available, either one of these methods can be used independently.

General. The bulk phase of the reaction is deionized water. The initiator, potassium persulfate (KPS), was purchased from Aldrich and used without purification. **Caution:** potassium persulfate is a strong oxidizer and should be handled with due care.

Both surfactants, sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) were purchased from Aldrich and used without purification. The monomer, styrene, was purchased from Aldrich, and washed with 10% NaOH to deactivate the inhibitor, and then allowed to dry over anhydrous sodium sulfate for 16–24 hours. It was then distilled under reduced pressure, and stored below 4 °C when not in use. A Hewlett Packard series 1050 chromatograph with a variable-wavelength detector was used for the GPC analysis. A Lexel model 85 ion laser with Brookhaven Instruments software (version 2.15) provided the DLS data. Polystyrene standards (e.g., 10^5–10^6g/mol) were purchased from Phenomenex, as was the GPC column: a Phenogel 5 linear 300- x 7.80-mm, 5-µm column. HPLC grade tetrahydrofuran (THF) and water were purchased from VWR.

Polymerization: A. Variation of Monomer Concentration and Surfactant. Prepare a 200 mL of a 15% DTAB solution and allow it to stir for 45min. Using this stock solution, make 100 mL of a 1 mM aqueous solution of KPS; allow stirring for 30 min. In 20-mL scintillation vials, make two series of 10-mL microemulsions composed of 2, 4, 6, and 8% styrene with the DTAB/KPS stock solution. Individually purge each microemulsion with N_2 for 15min, and then place in a 70 °C oil bath for 45 min. From the blue lattice formed, place 5 drops from a disposable pipet in 5 mL HPLC water. Pour the remaining liquid into 150 mL 95% ethanol. Gravimetrically filter the precipitated polymer, and wash with 100 mL of a 50:50 ethanol:water mixture. Let the polymer air dry until the next laboratory period. Repeat the procedure with 200 mL of a 15% SDS solution.

B. Variation of Initiator Concentration. Make 100 mL of a 15 wt% DTAB solution. Use this solution to make 20 mL of 8, 6, 4 and 2 mM KPS solutions. Follow the procedure above, and polymerize each with 4% styrene by combining styrene with the KPS and DTAB solutions in the proper ratio to make a 10-g microemulsion.

Analysis with GPC. Dissolve roughly 4 mg of product in 2 mL of HPLC grade THF. Filter the sample, through a small cotton ball inserted into a disposable pipet, into a GPC vial. Repeat with a set of polystyrene standards.

Run the GPC analysis. In the autosampler tray, place pure THF in the first position. This THF blank should be run at three different points in the sample sequence to ensure baseline stability. These positions are the first sample, after the standards, and at the end of the sequence. After the initial THF injection, the set of polystyrene standards should be run in order of increasing MW. Finally, the remaining samples should consist of the student's synthesized samples.

DLS Analysis. Standardize the DLS instrumentation with the following parameters: solvent: aqueous; sample time: 1 min; samples: 1.00 x 10^3; baseline difference: 0.01%; first delay: 2.0 µs; last delay: 1.0 x 10^3 µs. Pour solution into clean, dry DLS vial. Wipe the outside of the vial clean with a disposable tissue. Place the vial in the instrument, and execute the analysis run.

Results and Discussion

In a typical undergraduate organic laboratory, students' experience with microemulsion polymerization is virtually nonexistent. Microemulsion polymerization is becoming an important industrial process; students should have an understanding of this process of producing a unique latex particle. In this laboratory, students have exposure to this unique method for the synthesis of nanosized polystyrene particles. They gain experience with analytical tools that are essential to the characterization of polymer latex system.

Molecular Weight. The surfactant is added to water to first create the micellular system; followed by the dissolution of the initiator. Then the monomer is combined with the surfactant/initiator solution in concentrations of 2, 4, 6, and 8 weight percent. The system is then purged with N_2 and heated for 45 min at 70 °C, thus producing the polystyrene latex. Five drops of the resultant polymer latex are removed, then diluted with 5 mL HPLC water, and saved for light-scattering measurements. The remaining latex is then poured into ethanol to precipitate the polymer, which is then washed, dried, and analyzed.

Gel permeation chromatography, or size-exclusion chromatography, is used to analyze the synthesized polymers. The stationary phase is constructed of a highly crosslinked polymer, in this case, styrene/divinylbenzene, which has a high degree of porosity. As the sample polymer molecules, dissolved in the eluent, flow through the stationary phase, the smaller molecules interact with these pores, and are subsequently retained longer in the column; whereas the larger

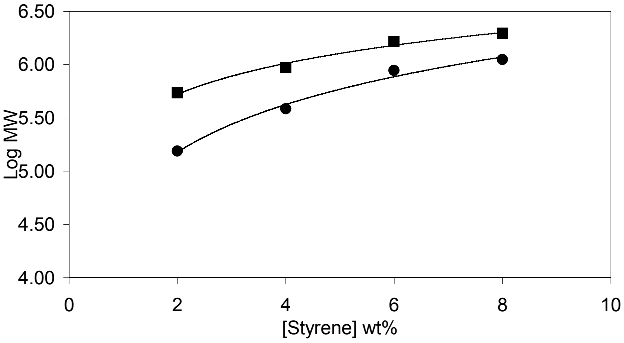
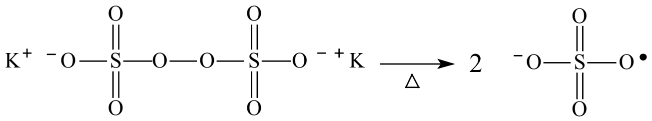
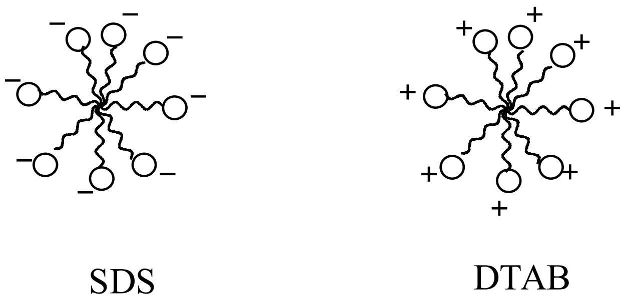


Figure 1. Log MW as a function of styrene concentration for the surfactants SDS (■) and DTAB (●). Conditions for polymerization: both surfactants at 15 wt%; KPS 1 mM.



$$K^+\ {}^-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^{-}\ {}^{+}K \xrightarrow[\Delta]{} 2\ \ {}^-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^{\bullet}$$

Scheme 1. Thermal decomposition of potassium persulfate (KPS).



Scheme 2. Depiction of the surface charge on the SDS and DTAB micelles, respectively.

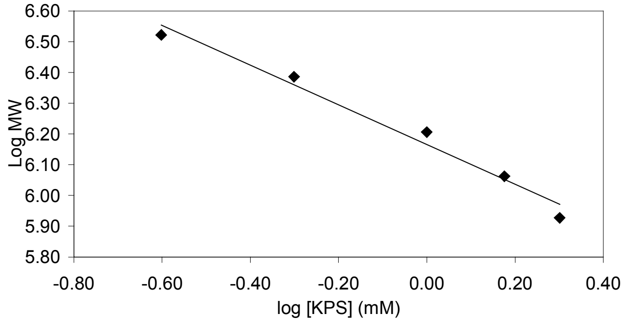


Figure 2. Plot shows the trend associated with initiator concentration variation. Conditions for polymerization: surfactant: SDS (15 wt%), styrene (4 wt%).

molecules are too big to interact with the pores, and their flow through the column is uninhibited [20].

First, a calibration curve, which relates column retention time to molecular weight, is constructed. Polystyrene standards of known molecular weight, which have a well-defined elution time, are used to create the calibration curve. The molecular weight of synthesized samples can then be interpolated. This process is completed for the two surfactants, SDS and DTAB. The data are then tabulated and graphed.

As shown in Figure 1, there exists a direct relationship between styrene concentration and the average molecular weight (MW). The styrene is located almost entirely in the center of the micelles; therefore, as more styrene is added to the system, the larger these micelles will become. As a result of a larger number of monomer units contained in a discrete location, a higher molecular weight is expected due to a higher degree of propagation. This trend is also observed in work reported by Wang and Guo [5, 16].

When KPS is dissolved in water and the temperature is raised, it decomposes to form radical units. For this experiment, the concentration of the initiator is constant at 1 mM, so a relatively constant number of radical units is produced. As more styrene is added to the system, there are more monomer units per radical available; therefore we would expect longer polymer chains and higher molecular weights.

In the case of comparing the two surfactants to each other, the charge generated on the surface of the micelle is the defining element. When SDS is added to water and micelles are formed, the sodium ion disassociates and leaves a negatively charged surface; conversely, when DTAB is in water, the bromide ionizes and leaves the micelle's surface positively charged.

A radical initiator, KPS for example, will decompose to form radical anions. The interaction between the charged micelle surfaces and the negatively charged KPS radical dictates the molecular weight produced. In the case of the SDS/KPS system, the SDS micelle has a negative surface charge; therefore the negative initiator ion would experience charge repulsion. This charge repulsion would decrease the overall flux of radicals entering the micelle. This overall lower concentration of initiating species within the micelle leads to a lower number of initiated polymer chains. The lower number of species initiating polymerization will cause a relatively higher molecular weight. The contrary holds for the DTAB system. The counter ion in DTAB is bromine, leaving the micellular surface with a positive charge. Opposite charges create an attraction between the micellular surface and the initiator anion. This attraction will lead to a larger number of initiated reactions and, consequently, a relatively low molecular weight.

As shown in Figure 2, there is an inverse relationship between log molecular weight and log potassium persulfate concentration. In works by Antonietti et al. [8] and Guo et al. [5], this inverse, linear relationship was also observed.

When the initiator concentration is increased, there are more radicals available per monomer unit. As the number of radical units increases, the number of initiated polymer chains increases. When this occurs as the monomer concentration is held constant, the shorter each polymer chain will become, yielding a lower average molecular weight. Another explanation is that a higher number of radicals are in solution. As the overall initiator concentration increases, the radicals produced through the initiator's decomposing increases, though this is not a simple linear relationship. Therefore, as a polymer chain is initiated, there is a greater chance that there will be termination through radical recombination. Radicals will recombine for a number of reasons; the most prominent process, due to the sheer number radicals present, is free

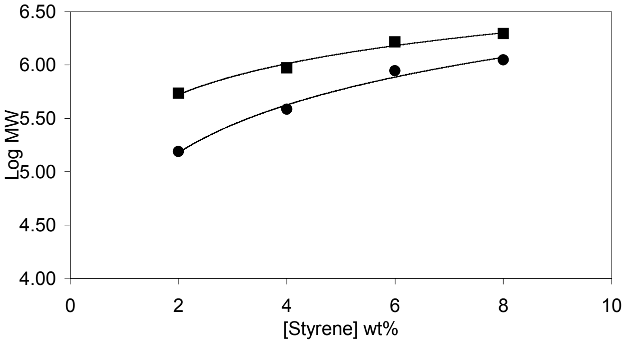


Figure 3. Monomer concentration effect and the relative latex-size comparison between SDS (■) and DTAB (•).

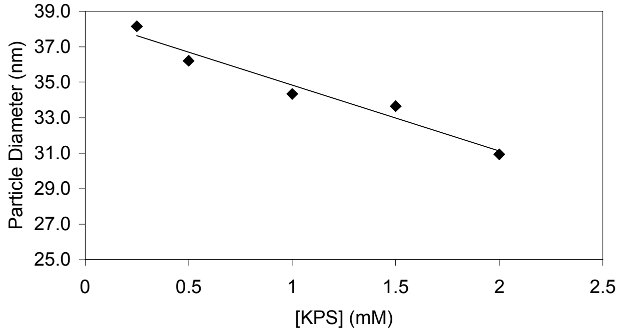


Figure 4. Latex diameter as a function of initiator concentration. Surfactant: SDS (15 wt%); styrene (4 wt%).

radical-radical termination. The solvent cage effect is also a contributing factor [21].

Particle Size. The unique characteristic of latexes produced through microemulsion polymerization is their nanometer range particle size. One of the most popular methods for evaluating particle size, and the one employed in this laboratory exercise is dynamic light scattering. DLS is a method of particle-size determination based upon the scattering of photons as they interact with the electrons of the molecule. According to semiclassical light scattering theory [22], when light impinges on matter, the electric field of the light induces an oscillating polarization of electrons in the molecules. The molecules then serve as secondary sources of light, and subsequently scatter light. By measuring the intensity of the scattered light at different angles, the particle size of the sample can be determined.

To prepare DLS samples, roughly 1 mL of the polymer lattice is diluted to 10 mL with HPLC water.

As shown in Figure 3, the monomer concentration and the relative surfactant effects follow roughly the same relationship as their molecular weight counterpart. The polymer produced from the increased monomer concentration has a larger particle size.

The charge interaction accounts for the comparatively larger size associated with the SDS system than with the DTAB. The repulsion between the negatively charged KPS radical and the negative SDS micelle allows for fewer radicals to initiate polymerization. The fewer radicals present to start polymerization, the longer each chain will be, making the molecular weight and particle size larger.

The particle diameter has been found to be inversely proportional to the concentration of initiator. In Figure 4, an inverse, linear relationship exists between particle diameter and initiator concentration. In this case, as the concentration of the initiator is raised, there are more radicals produced in the thermal decomposition. In a controlled system, as there are more radicals present, the polymer produced will have a lower molecular weight, as well as a smaller particle size. In works by Wang et al. [16] and Puing et al. [21], similar behavior was reported.

Conclusion

The effects of monomer concentration, initiator concentration, and varying surfactant structure are examined. Each of these variations has a predictable and recognizable trend relative to the molecular weight of the final polymer, and particle size of lattice formed. Molecular weight and particle size increase as the monomer concentration is raised, and decrease as the initiator concentration is raised. When the two surfactants are compared, there is a higher molecular weight and particle size for the SDS system as compared to the DTAB system. This is due to the charge interaction between the micelles formed by these two surfactants and the ionic form of the radical initiator.

Upon completion of this laboratory, students will have had exposure to the synthesis of some unique polymer nanoparticles. Students will gain knowledge in predicting differing results when process parameters are altered, and experience with two useful analytical techniques.

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