SYNTHESIS AND OPTIMIZATION OF EMULSION POLYMERS

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ABSTRACT

Synthesis and Optimization of Emulsion Polymers

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Synthetic latex or resin is perhaps the most important component of any paint formulation. As the binder, it holds all ingredients in a paint together and is responsible for film formation. Various latexes are used in industry though acrylic resins have shown to impart superior paint properties.

This project is concerned with the synthesis of an acrylic latex. Various emulsion polymerization processes were used including semi-batch, starved-feed, and in-situ seeded in the attempt to produce a stable latex that can be used in a broader study concerning the syneresis and rheology mechanisms of latex/thickener systems.

In addition, this project investigates the optimization of the emulsion polymerization teaching lab used in the Polymers and Coatings masters program. Here, a batch emulsion polymerization process was studied and various particle stability aspects altered to produce a stable latex with minimum coagulum.

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1. Introduction

1.1 Project Objectives

Synthetic latex or resin is perhaps the most important component of any paint formulation. As the binder, it holds all ingredients in a paint together and is responsible for film formation. Various latexes are used in industry though acrylic resins have shown to be superior as they impart better stain protection, are water resistant, provide better adhesion, and are resistant to blocking and cracking.

This project is concerned with the synthesis of an acrylic latex primarily composed of two base monomers, methyl methacrylate and n-butyl acrylate. Various emulsion polymerization processes were employed including semi-batch, starved-feed, and in-situ seeded in the attempt to produce a stable latex that can be used in a broader study concerning the syneresis and rheology mechanisms of latex/thickener systems. In addition, this project is also concerned with the optimization of an emulsion polymerization teaching lab used in the Polymers and Coatings program. Here, a batch emulsion polymerization system was studied and various particle stability aspects were investigated in an attempt to produce a stable latex with minimum coagulum content.

1.2 Fundamentals of Polymerization

The development of human civilization has been intertwined with polymeric materials for thousands of years, far before inquisitive scientists began probing the structure of materials that exhibited behavior different from metals

and ceramics. Common natural polymers such as silk and cellulose (i.e. wood products, fiber/linen, etc.) were crucial in the progression of such basic human functions as trade and transportation, but their structures were not fully understood or appreciated until the 1900s. The vast majority of these natural polymers exist in low molecular weight forms and chemists did not believe molecules with high molecular weights were plausible. It wasn't until Hermann Staudinger proposed the structure for rubber that synthetic polymers began to replace natural polymeric materials. It was at this time that the term polymerization was used to explain the chemical combination of small monomeric units to produce large chains or networks called polymers.^{1,2}

Synthetic polymers have since become an integral part of our daily lives and, unlike natural polymers, they can be designed and manipulated to have a wide range of physical, mechanical, and chemical properties making them highly attractive in various industries.

1.2.1 Polymerization Methods

Polymers are synthesized via two major methods: step-growth and chain-growth polymerization. In step-growth, multifunctional monomers react to give dimers, which then combine with other dimers, trimers, or other oligomeric “blocks” of polymer. As seen in **Figure 1**, one example of this is the synthesis of Nylon-6,6 in which adipoyl acid and hexamethylenediamine monomers undergo condensation reactions. At the beginning of the reaction, functional groups of monomers react together to immediately generate a large amount of chains with a low degree of polymerization. As the reaction continues, these short chains

combine to create longer chains, and the process continues until only high molecular weight chains remain. Therefore, high molecular weight is only achieved at high conversion.^{3,4}

Figure 1. Synthesis of Nylon 6,6

The chain-growth mechanism differs mainly in the way that an initiator is used to produce an active site, which can be a free-radical, cation, or anion. Monomers add one at a time to the active site of polymer chains and upon the addition of a monomer, the reactive center will transfer to the new monomer to renew the active site and continue the propagation. This results in a high molecular weight at low conversion of monomer. Typical monomers for radical chain-growth include vinyl molecules such as styrene, methacrylates, and acrylates.^{3,4}

Free-radical polymerization (FRP), a subcategory of chain-growth polymerization, is primarily used for the production of polymers derived from olefinic monomers and is characterized by the fast addition of monomers. Active centers are present in low concentrations (10^{-5} to 10^{-8} mol/L) but chains are able to grow in relatively short times due to a high rate of monomer addition (10^3 to

10^4 monomers/second). Consequently, the length and composition of a chain is determined in seconds.^{3,4,5}

FRP can be divided into three stages: initiation, propagation, and termination. Initiation can be further divided into two stages as seen in **Figure 2**. First, initiator molecules decompose (with decomposition rate coefficient, k_d) at an elevated temperature to most often produce two radicals. Initiator radicals ($R \cdot$) then homolytically react with monomers (with rate coefficient, k_i) to produce a new and larger free-radical ($RM \cdot$). One typical initiator used for FRP is ammonium persulfate, which thermally decomposes into two radical anions. In addition to thermal decomposition, radicals can be produced electrochemically and via photo-initiation and radiation.^{3,4,5}

Figure 2. FRP Initiation

During propagation, chains grow (with propagation rate coefficient, k_p) by the repetitive addition of monomers where each addition creates a new radical that is identical but larger in size than the previous radical, as seen in **Figure 3**. After some time, chains stop growing and terminate via combination or disproportionation. Most chains are terminated via combination where two radicals react with each other to yield a larger chain. Disproportionation occurs when a radical from one chain abstracts a hydrogen from another chain to yield one saturated and one unsaturated chain.^{3,4,5}

Figure 3. FRP Propagation

1.2.2 Polymerization Techniques

There are four main types of polymerization techniques including: bulk, solution, suspension, and emulsion polymerization. Bulk polymerization is the simplest of all polymerization techniques because it requires the fewest ingredients and is used primarily for the polymerization of liquid monomers such as styrene and methyl methacrylate. In bulk polymerization, liquid monomers and initiator are added to a reactor and polymerization is carried out under constant agitation and at elevated temperatures. Bulk polymerization is not only simple, but it also allows the production of a pure polymer. Regardless, bulk polymerization is not commonly used because free-radical polymerizations are highly exothermic, which can lead to auto-acceleration, resulting in highly viscous products with broad molecular weight distributions at best, and charred, burned, or otherwise ruined product or an exploding reaction vessel at worst. The disadvantages of this technique are circumvented with solution polymerization.^{3,4}

In solution polymerization, monomers and initiator are dissolved in a solvent where the polymer forms. Like bulk polymerization, this polymerization is carried out under constant agitation and at elevated temperatures. Once polymerization is complete, the polymer is often used as a solution or can be isolated via evaporation of the solvent. The addition of a solvent in this technique

prevents a significant increase in viscosity because the solvent behaves as a diluent and allows easy stirring.^{3,4}

To overcome the high cost of solvents, suspension polymerization is often used where lipophilic monomers and initiator are suspended in water. Since the initiator is monomer soluble, the polymer is polymerized in monomer droplets that are maintained by continuous agitation. Each droplet is analogous to a bulk reactor and the pearl-like polymer that forms is insoluble in water. Stabilizers can also be added to prevent the coalescing of droplets prior to polymerization. Like solution polymerization; the viscosity increase is negligible and temperature is more readily controlled, but unlike solution polymerization, product isolation is quite simple since the polymer is insoluble in water. Despite these advantages, suspension polymerization can only be used with water insoluble monomers, does not allow the control of particle size, and polymer purity is low due to added stabilizers. In addition, elastomers cannot be synthesized using this method since tacky elastomer particles tend to agglomerate. As a result, commercial plastics and elastomers are largely produced via another technique called emulsion polymerization that accounts for these limitations.^{3,4}

Unlike suspension polymerization, emulsion polymerization uses a water-soluble initiator. Thus, this polymerization is differentiated because it initiates and propagates in water as opposed to the monomer droplets. In order for this to occur, emulsion polymerization necessitates the addition of surfactant to stabilize the monomer droplets and propagating polymer chains. This polymerization mechanism is discussed in great detail in Section 1.3.2. This method allows a

wide selection of monomer species and better control over particle size to achieve more elaborate polymer products; however the inclusion of solvent and surfactant in the reaction vessel largely reduces the product purity, much like suspension polymerization.^{3,4}

1.3 Emulsion Polymerization

The first emulsion polymer, a synthetic rubber composed of 1,3-butadiene and styrene, was synthesized during World War II when Japanese forces restricted American access to the Southeast Asia's natural-rubber sources. Since then, the use of emulsion polymerization has greatly expanded and is now the primary process for the commercial polymerization of various monomers including vinyl acetate, chloroprene, methacrylates and acrylates. The product of emulsion polymerization is a colloidal dispersion of polymer particles in water called a latex. In general, latexes contain 20-70 wt.% solids and particles range 50-1000 nm in diameter. Each particle is typically composed of 1-10000 polymers and each polymer is composed of 10^2 - 10^6 monomeric units. A latex is often used without further separation and can be applied in the production of a wide range of products including rubbers, plastics, paints, adhesives, polishes, paper coatings, and sealants.^{1,2,4,5}

1.3.1 Components of Emulsion Polymerization

There are various components required in formulating latexes: synthetic ingredients such as monomer(s), surfactants, and initiator and post-synthesis ingredients such as biocides added to serve a specific purpose. In addition, the

number of ingredients added to a formulation depends on the type and scale. For example, a laboratory scale recipe contains significantly fewer ingredients than a more complex commercial emulsion polymerization that can have well over 20 different ingredients. Regardless, ingredients affect both the rate at which latex particles are synthesized and the composition and characteristics of the final product.^{5,6,7,8}

1.3.1.1 Continuous Medium

The continuous medium in an emulsion polymerization is water due to its excellent ability to conduct heat, which enables fast polymerization rates while preventing auto-acceleration by maintaining the viscosity of the reaction close to that of water. Water hardness can differ depending on the source and can influence particle size, nucleation, and particle stability. Therefore, deionized water is most typically used. In addition, oxygen content of the water used should be low because oxygen is a free-radical scavenger that can quench initiator radicals, often delaying the start of polymerization. To prevent this initiation delay, water is often deoxygenated by purging with nitrogen gas prior to polymerization.^{5,6,7,8}

1.3.1.2 Surfactants

Surface active agents or surfactants, compounds that alter the surface tension of a liquid, are vital in emulsion polymerization for several reasons: (1) they stabilize monomer droplets; (2) they generate micelles that can serve as nucleation sites, (3) they solubilize monomers and latex polymers; and (4) they

stabilize growing particles by preventing aggregation, resulting in a stable end product. Surfactants are typically included at 1-6 wt.% of monomer, with lower concentration for anionic surfactants and higher concentrations for nonionic surfactants.^{5,6,7,8}

Surfactants are amphiphilic and tend to align themselves at interfaces due to the presence of hydrophobic and hydrophilic segments. At low concentrations, surfactant molecules dissolve according to their solubility. However, at a certain concentration (critical micelle concentration or CMC), the solution becomes saturated and surfactant molecules (50-150) begin to aggregate to form a micelle (about 2-10 nm in diameter) with the polar ends pointing outwards and the nonpolar chains pointed inwards to form a hydrophobic pocket. Micelles repel each other in water due to the presence of polar heads, which have like charges and therefore repel each other in solution. The number and size of micelles depend on both the amount and identity of the surfactant; for instance, larger amounts of surfactant yield smaller-sized micelles. Most micelles are spherical in shape, but depending on the surfactant and the concentration, micelles can also be rodlike.^{5,6,7,8}

1.3.1.2.1 Surfactant Classification

Surfactants fall into one of four categories according to the nature of the hydrophilic segment: anionic, cationic, amphoteric, or non-ionic. Anionic and non-ionic surfactants are most commonly used in emulsion polymerization due to their higher compatibility with negatively charged latex particles.^{5,6,7,8}

Anionic surfactants ionize to produce a negative charge on the molecule's polar head. Sodium dodecyl sulfate (SDS), is one of the most commonly used anionic surfactants in emulsion polymerization. In water, SDS ionizes as seen in **Figure 4**.

Figure 4. Structure of SDS

Cationic surfactants ionize in solution to produce a positive charge on the molecule's polar head. These surfactants are rarely used in emulsion polymerization due to their incompatibility with anionic surfactants and latex particles. Examples include the salts of long chain amines, polyamines, and quaternary ammonium salts.^{5,6,7,8}

Amphoteric or zwitterionic surfactants also ionize to produce a charge; at high pH a negative charge is produced (anionic properties) and at low pH a positive charge is produced (cationic properties). Examples include imidazoline carboxylates and amine oxides.^{5,6,7,8}

Unlike the other three, non-ionic surfactants do not dissociate in solution to yield a charge. Instead, the hydrophilic part is a non-ionic component such as a polyol, sugar derivative, or chain of ethylene oxide. Examples include polyoxyethylenated alkylphenols, polyoxyethylenated straight-chain alcohols, and long-chain carboxylic acid esters.^{5,6,7,8}

1.3.1.2.2 Surfactant Selection

The Hydrophile-Lipophile Balance (HLB) system, is often used when selecting a surfactant. This system looks at the balance between polar and non-polar components in a surfactant to predict properties such as emulsification power, detergency, foaming, and solubilization. For example, surfactants with a low HLB value (<6 or 7) are good water-in-oil emulsifiers, while surfactants with a high HLB value (>8) are good oil-in-water emulsifiers. Since emulsion polymerization is an oil-in-water system, an HLB value of greater than 8 is needed. While this system is useful in selecting preliminary surfactants, trial and error is still required to select the most appropriate surfactant.^{5,6,7,8}

1.3.1.3 Monomers

Monomers constitute the oil phase in emulsion polymerization and are the building blocks of latex particles. Base monomers such as styrene and ethylene make up the majority or 95% of the polymer latex composition. Functional monomers such as methacrylic acid and acrylamide are also included in a formulation to provide stability, improve adhesion, modify polymer solubility, and provide sites for cross-linking.^{5,6,7,8}

In general, monomers have limited solubility in water and therefore over 95% are found in monomer droplets (1-100 microns in diameter) that are stabilized by absorbed surfactant molecules. Monomers can also be found in the hydrophobic pocket of micelles or in the aqueous phase. If the solubility of monomers is too high, particles may not form and instead the monomers will polymerize via solution polymerization. In addition, monomer solubility will also

determine copolymerization kinetics: monomers with a higher solubility will be mostly found in the continuous phase and will not get incorporated in the latex particles as much as a less water soluble monomer.^{5,6,7,8}

1.3.1.3.1 Monomer Selection

Monomer selection involves several considerations. They are selected to satisfy a purpose and will dictate the basic physical, chemical, and thermal properties of the latex. The glass transition temperature (T_g) of latex particles greatly influences monomer selection. The T_g of a polymer is the temperature at which the polymer transitions from a hard, brittle, glass-like state to a soft, flexible, rubbery state. To yield continuous films, target particle polymer T_g must be well below ambient temperature. This allows sufficient polymer mobility for the interdiffusion of particle chains during film formation. In addition, the degree of stiffness and strength of a film varies with the concentration of monomer used.^{5,6,7,8}

Desired properties are rarely achieved with the use of one monomer, and instead, a balance of multiple monomers is often considered to yield a copolymer with the desired properties. Rubbery polymers will contribute to flexibility, adhesion, and tackiness while glassy polymers contribute to hardness, strength, and clarity. The glass transition temperature (T_g) of a copolymer is estimated by the Fox equation (equation 1) to establish the weight fractions (W) of each monomer required. W_{mi} describes the weight fraction of monomer i with glass transition temperature T_{gmi} . Desired T_g values range for various product applications. For example, latexes that are used in many architectural coatings

have a desired T_g range of 0-37°C while latexes used in floor polishes have a desired T_g range of 50-75 °C.^{5,6,7,8}

$$\frac{1}{T_g} = \frac{W_{m1}}{T_{g\ m1}} + \frac{W_{m2}}{T_{g\ m2}} + \frac{W_{m3}}{T_{g\ m3}} \dots \quad (1)$$

The compatibility of latex particles must also be taken into account. For example, if the latex will be used in paint, latex particles must be compatible with paint components such as pigments and fillers.

Inclusion of functional monomers is another important consideration. Carboxyl functional monomers, such as acrylic and methacrylic acids, are often included in small quantities (typically 1-3%) to enhance the colloidal stability of the particles. Other functional monomers that can be used include those with hydroxyl, sulfate, or sulfonate groups. Functional monomers also give particles the ability to hydrogen bond or crosslink ionically or covalently. Crosslinking enables the production of gels, influences application performance and enhances properties such as adhesion and strength.^{5,6,7,8}

1.3.1.3.2 Monomer End-Use Applications

Typically, blends of copolymers are used in industry to satisfy desired bulk properties. Styrene-butadiene copolymers are used in applications such as carpet backing, paper coatings, and paint. Styrene-butadiene copolymers along with poly(butadiene) are used primarily for the production of synthetic rubber. Polyethylene-based copolymers are used for adhesives and paint. Polyacrylate copolymers derived from acrylic and methacrylic acids are heavily used in paints

and pigment binders. Lastly, fluoro-containing polymers are used for water repellency.^{5,6,7,8}

1.3.1.4 Initiator

Free-radical initiators used in emulsion polymerization are water-soluble and can be produced via thermal decomposition, redox reactions, or by gamma radiation. The method chosen to generate free-radicals depends on the type of latex being synthesized and hence the reaction temperature. For example, when synthesizing high molecular weight latexes, which have to be synthesized at lower temperatures to prevent auto acceleration, radicals are generated via redox reactions. Unlike redox initiators that are not limited by temperature; thermal initiators do not produce a significant amount of free-radicals below 50 °C.^{5,6,7,8}

The majority of emulsion polymerizations are carried out at 75-90 °C to maximize the polymerization rate and therefore thermal initiators are more commonly used. Thermal initiators include peroxydisulfate salts such as ammonium persulfate and potassium persulfate that decompose homolytically to yield sulfate radical anions.^{5,6,7,8}

1.3.1.5 Other Additives

Other ingredients found in emulsion polymerization serve specific purposes and can be added during latex synthesis or post-synthesis. Chain transfer agents, such as chloroform and carbon tetrachloride can be added to regulate the molar mass and molar mass distribution of latex polymers. Chain

transfer agents are introduced into the reaction mixture during the monomer phase.^{5,6,7,8}

An example of a post-synthetic additive is ammonium hydroxide, which is often added to adjust the pH of the final dispersion. When carboxyl functional groups are used in emulsion polymerization, an increase in the pH of the system deprotonates these functional monomers to yield negative charges that help stabilize latex particles.^{5,6,7,8}

Biocides and fungicides are also added post-synthesis to prevent microbial contamination and deterioration. These additives are particularly important when there's little residual monomer or for latexes that are particularly vulnerable such as styrene-butadiene copolymer latexes. Examples include pentachlorophenol and tetrachloroisophthalonitrile.^{5,6,7,8}

In addition to microbial degradation, latex polymers are also susceptible to UV radiation. UV light absorbers are therefore often included to absorb damaging low-wavelength radiation.^{5,6,7,8}

1.3.2 Emulsion Polymerization Mechanism

The mechanisms by which emulsion polymers are synthesized vary from system to system. The following is a general overview of proposed theories.

The location of the key ingredients (monomers, surfactant, and initiator) is dictated by their solubility in the aqueous medium. Monomers are only slightly soluble in water and therefore aggregate to form monomer droplets (stabilized by both agitation and surfactants) that range 5-20 microns in diameter. Surfactants are amphiphilic in nature and can be found as free-floating molecules and

beyond their CMC they are found as micelles that are either empty or swollen with monomer.

Initiator molecules are primarily found in the aqueous phase where the initiating radicals are produced. Initiation does not occur in monomer droplets because initiators used in emulsion polymerization are oil-insoluble. This differentiates emulsion polymerization from suspension polymerization where initiation occurs in monomer droplets. A common initiator used in emulsion polymerization is ammonium persulfate (APS), which specifically decomposes thermally into two disulfate anionic radicals as seen in **Figure 5**. After the decomposition of the initiator, emulsion polymerization can be divided into 3 stages: stage I (particle nucleation), stage II (particle growth), and stage III.^{5,6,7,8}

Figure 5. Decomposition of APS

1.3.2.1 Particle Nucleation (Stage I)

The exact mechanism of particle nucleation has been widely debated in literature with little consensus due to the fact that different types of species may be present in a system. This includes dissolved surfactant molecules, surfactant micelles, monomer swollen surfactant micelles, surface-active oligomers formed during initiation in the aqueous phase, mixed micelles composed of surfactant and oligomers, and both macro and micro monomer droplets.^{5,6,7,8,9}

One of the earliest proposed mechanisms is micellar (heterogeneous) nucleation where nucleation occurs exclusively in micelles and polymer particles. As seen in **Figure 6**, micellar nucleation begins with the entry of an oil-insoluble initiator radical into a monomer filled micelle. Inside the micelle it reacts with a monomer to form a monomer radical or an actively growing latex particle.

Figure 6. Micellar Nucleation Mechanism

The second theory of nucleation, homogeneous nucleation, is widely accepted by industrial professionals as the dominant form of nucleation. In this mechanism, as seen in **Figure 7**, the initiator does not enter a micelle but rather

initiates polymerization within the aqueous medium when an initiator radical adds to a monomer. This radical then adds several more monomers until the chain reaches a critical length where the oligomer is no longer soluble in water. At this point, the chain is thermodynamically unstable and collapses on itself or onto dead oligomers found in the aqueous phase to form latex particles. Simultaneously, surfactant molecules adsorb on their surface to impart stability by lowering the interfacial energy. If surfactant is absent, the collapsed chains form coagulum.^{5,6,7,8,9}

Figure 7. Homogenous Nucleation Mechanism

Nucleation does not occur in monomer droplets due to their relatively small surface area when compared to micelles; an initiator molecule is highly

unlikely to enter a droplet as it is more likely to interact with a free-floating monomer before reaching a droplet. Overall, this stage is relatively short and results in stable seed particles that are about 25 nm in diameter. These seeds are expanded in the following stage.^{5,6,7,8,9}

1.3.2.2 Particle Growth (Stage II)

During stage II, monomers from monomer droplets are fed into micellar particles to grow the seeds. Monomers, such as methyl methacrylate and n-butyl acrylate, have limited solubility in water and therefore monomer droplets, monomer-rich micelles, and the aqueous phase are in equilibrium to maintain a constant concentration of free-floating monomers. If the concentration of free-floating monomer decreases, monomers are pulled from droplets (monomer reservoirs) into the aqueous phase via diffusion. Monomers can also react in the aqueous phase to form oligomers or “z-mers” that become insoluble at their critical length. They then move towards the surface of the particles instead of forming new particles as there is not enough soap leftover to accommodate a new stable interface. Particles continue to grow by pulling monomer via diffusion from droplets through the aqueous phase. Stage II terminates when all monomer droplets have been consumed.^{5,6,7,8}

The morphology or microstructure of polymer particles can be controlled during this stage depending on the amount of each monomer, the hydrophobicity and hydrophilicity of monomers used, and the polymerization temperature. Possible morphologies include core/shell, hollow sphere particles or opaque

polymers, multilobe, and internal domain. Branching and crosslinking arms are also introduced during this stage.

1.3.2.3 Stage III

Particle growth is terminated during stage II when monomer droplets are fully consumed and there is no longer a reservoir to re-establish the overall equilibrium of the system. During stage III, only polymer particles exist. During this stage, the concentration of monomer in polymer particles continues to decrease as conversion increases. A polymer colloid will include a number of polymer chains within the particle that can be arranged in a crystalline, amorphous, rubbery or glassy state. Monomer is also retained in the particle and is the solvent of the particles. Particle size is constant by this stage.^{5,6,7,8}

The Tromsdorff effect or auto-acceleration is sometimes observed during this stage. This occurs when the viscosity of the system greatly increases as conversion increases. Since polymer chain radicals cannot move easily in a viscous medium, they cannot find each other to undergo termination and can result in a large rise in temperature and heat generation.^{5,6,7,8}

1.3.3 Emulsion Polymerization Processes

The process and conditions by which an emulsion polymerization is carried out significantly affect the properties of the resulting product. In the simplest process, batch polymerization, all reactants are added to the reaction vessel at the start of the reaction while the more versatile process, semi-batch polymerization, introduces only a portion of the reagents at the start of

polymerization; the remainder is added to the reaction vessel at specific times over the course of the reaction in predetermined amounts. A third process, continuous polymerization, is described by the continuous feed of monomer and removal of product.^{5,6,7,8}

1.3.3.1 Batch

Batch polymerization is the simplest of all emulsion polymerization processes. All ingredients, with the exception of initiator, are charged into the reaction vessel at the beginning of the reaction. The system under constant agitation is equilibrated to a specific temperature then the initiator is added to start the polymerization. Due to the simplicity of the process, only the temperature, type and speed of agitation, and reactor design can be changed to address any problems.^{5,6,7,8}

All three stages described above are present in a batch polymerization. Particle nucleation occurs either through micellar or homogenous nucleation. Particles are then grown by pulling monomers from droplets through the aqueous phase until all droplets are consumed.^{5,6,7,8}

Batch polymerization is primarily used in a laboratory setting to study reaction mechanisms or kinetics of emulsion polymerization. This process is not used in the production of commercial latexes since it has the disadvantage of limited control over particle size and morphology. In addition, the Tromsdorff effect is extremely prevalent in this process, which can cause costly interruptions in a commercial setting.^{5,6,7,8}

1.3.3.2 Semi-Batch

Semi-batch is the most widely used emulsion polymerization process due to its versatility and advantages over a batch process. Unlike batch polymerization, semi-batch is highly reproducible, offers operational flexibility, and control over the size and morphology of particles produced. Semi-batch is characterized by the controlled addition of monomer, surfactant, initiator, or water to a reaction vessel throughout the reaction. Monomer can be introduced as either a pre-emulsion (monomer in water stabilized by surfactants) or as a neat monomer feed (monomer only). In addition, monomer can be added to flood or starve the system. Under monomer-flooded conditions, particle growth occurs via Stage II as described above. The rate of monomer addition is higher than monomer consumption and therefore monomer accumulates as monomer droplets and particles are saturated with monomer. In monomer-starved conditions the rate of monomer addition is significantly lower than the rate of consumption and therefore Stage II is absent. Starved-condition semi-batch often leads to the production of small particle sizes and can be run to high solids.^{5,6,7,8}

1.3.4 In-Situ Seeded Emulsion Polymerization

Seeded emulsion polymerization allows better control of particle size and particle size distribution. In this type of polymerization, typically 5-10% of the total monomer is added at the beginning of the reaction to produce seed particles. The remaining monomer is added directly or as a pre-emulsion over time to enable the seed particles to grow to a desired particle size. Direct addition will result in a larger number of seed particles since all surfactant is added in the

initial seed stage. Pre-emulsion addition has a lower concentration of surfactant in the seed stage and therefore will result in a lower number of seed particles.

5,6,7,8

A secondary nucleation of particles can occur with the addition of the remaining monomers if the concentration of surfactant is too high and/or the concentration of seed particles is too low, resulting in a broad particle size distribution. On the other hand, if not enough surfactant is used, the particle surface charge density would be too low to sufficiently stabilize the suspension which may cause particle coagulation, leading to a reduction in the overall number of particles. 5,6,7,8

Seeded emulsion polymerization is typically run as a semi-batch reaction under monomer-starved conditions, where the monomer is being consumed as fast as it is being added. This ensures that after seed nucleation, the entire polymerization occurs under stage III, in which there are no monomer droplets. In essence, a fixed number of particles are nucleated during stage I and as additional monomer is fed, those particles propagate without nucleating additional particles. Particle size depends on the number of seed particles nucleated: nucleating fewer seed particles results in larger particles while nucleating a large number of seed particles results in smaller particles. 5,6,7,8

1.3.5 Polymer Composition

Polymer architecture describes the distribution of monomer along polymer chains of latex particles and is governed by both the process employed and the reactivity ratios of monomers used. The distribution of monomers becomes

particularly important when the desired latex is a copolymer of various monomeric units. Copolymers can be blocky, alternating, and random. Polymer architecture also relates to the branching and crosslinking of polymer chains.^{7,8}

As described in Section 1.3.1.3.1, the Fox equation can be used to estimate a desired glass transition temperature and to establish the weight fractions of each monomer required. The Fox equation is, however, only accurate for random or alternating copolymers and therefore reactivity ratios of the monomers used must be taken into consideration. Reactivity ratios are used to describe the tendency of a radical to add to itself as opposed to a comonomer. If both reactivity ratios are large, the monomer would rather add to themselves and a copolymer with large homopolymer blocks will form; if they are both close to 1, they have no preference and a random copolymer will form; and if both are small, they would rather add to their comonomer and an alternating copolymer will form.^{3,4,7,8}

For example, consider the reactivity ratios of n-butyl acrylate (BA) and methyl methacrylate (MMA) in **Figure 8**. As proposed by the relative low reactivity ratio of nBA (r_{BA}), BA would rather react with and add methacrylic monomer more than the BA monomer. As seen by the relative high r_{MMA} value, mma would rather add to itself than its comonomer. This is because of the stability of the radicals that form: both are stabilized by ester functionality, but the tertiary radical of methyl methacrylate is more stable than the secondary radical of butyl acrylate. Therefore, both of these monomers would rather add to an

MMA given that it has an additional methyl group that can stabilize the resulting radical.^{3,4,7,8}

Figure 8. Reactivity ratios of nBA and MMA

Since not all reactivity ratios are equal to one, further techniques must be employed to achieve a true random copolymer such as feeding a desired monomer composition under starved conditions. Synthesis under starved conditions allows the monomer feed composition and copolymer composition to be set equal to each other by supplying the monomer feed at a rate slower than propagation consumes the monomers. Through continuous addition of monomers over the course of the polymerization, the ratio of each monomer incorporated into the chain can be precisely controlled.

1.3.6 Particle Stability

One of the most important goals of emulsion polymerization is the production of colloiddally stable latex particles that are able to remain dispersed for long periods of time. Particles that are colloiddally unstable form aggregates that can lead to coagulation, which is a costly defect of emulsion polymers. The DLVO theory looks at the balance between two main forces (electrostatic repulsion and Van-der Waals attraction) to explain the stability of colloiddal particles and the formation of coagulum in some systems.

Figure 9. DLVO theory

Consider two latex particles. As seen in **Figure 9**, the dash line represents the resulting energy when both Van-der Waals and repulsive forces between the particles are averaged. If the distance between the two particles decreases, they can enter a flocculated state, which is represented by the secondary minimum in

the plot. If the distance between these two particles decreases further with sufficient energy to overcome the energy barrier, they can enter the aggregated state, which is the lowest energy minimum represented in the plot. It is important to not that both flocculated and aggregated particles retain their particle identity as they are not touching and are only in close proximity of each other. However, under certain conditions, chains can interdiffuse between particles. As a result, particles lose their identity and form a single mass of coagulated polymer; unlike aggregation and flocculation, coagulation is an irreversible process.^{10,11}

Coagulation formation results in an unstable dispersion when the temperature of the system is well above the glass transition temperature of the polymer. At a temperature higher than the T_g , the particles are soft and flexible and interdiffuse with ease. A system with a large T_g , on the other hand, will not coagulate because there is not enough flexibility for chains to interdiffuse and therefore, aggregated particles will retain their particle identity.^{8,10,11}

Rubber, for example, is produced by coagulating an alkaline dispersion. Acid is first added to neutralize electrostatic charges and particles aggregate. Rubber has a glass transition temperature of $-70\text{ }^{\circ}\text{C}$ and therefore, at room temperature, aggregated particles will have enough flexibility that chains can interdiffuse between particles.

Emulsion polymers are prepared as colloids, which are thermodynamically unstable by nature and therefore need to be stabilized to prevent the formation of coagulum. Stability varies on the recipe and reaction conditions used, including the agitation speed, reaction temperature, water-monomer ratio, the solubility of

the monomer in water, surfactant type and concentration, initiator type and concentration, and total electrolyte concentration.

One of the simplest ways to stabilize particles is through the incorporation of a functional monomer such as methacrylic or acrylic acid. Having carboxylic acid functional groups on the surface of latex particles allows them to become charged with an increase in pH. Charged surfaces repel each other and prevent the agglomeration of latex particles. Stability supplied by functional monomer is highly sensitive to the electric double layer surrounding latex particles and thus the ionic strength of the aqueous medium. As seen in **Figure 10**, a larger electric double layer (low ionic strength) yields more stable particles because particles experience more negative charge on their surface. Here, the electrostatic repulsion term dominates and the overall interaction energy is positive or repulsive. Having a high concentration of salts essentially shields or compresses the negative charges responsible for particle-particle repulsion and flocculation and aggregation may occur. Here, the electrostatic repulsion decreases and the Van-der Waals attractive term dominates. As a result, the overall interaction energy is negative or attractive. ^{8,10,11}

Figure 10. Particle stability derived from surface charges

Particles can also be stabilized through electrostatic and steric repulsions. An example of electrostatic repulsion is the stability provided by an anionic surfactant, which decreases the interfacial energy of the system by introducing negative charges to particles. Steric repulsion is typically achieved via grafted polymers such as polyvinyl alcohol. Particles with grafted entities cannot come together because the potential energy between the particles would increase significantly. Grafted polymers differ from surfactants in that they do not have a charged head and instead repel through size and steric hindrance.

1.3.6.1 Coagulation

Coagulation can be divided into 3 types: (i) coagulum formed during polymerization that is recovered by filtration, (ii) coagulum deposited on reaction vessel surfaces including walls and agitator, and (iii) coagulum formed in the latex during transportation or storage. Regardless of type, coagulum is an unstable form of latex and can result in an ineffective synthesis as well as a costly waste of reagents.^{8,11}

The texture of coagulum can vary significantly and can range from tiny grains in an otherwise stable latex to a single solid polymer with little to no fluid. Typically it is found as lumps that can be soft and sticky, hard and granular, or hard and friable. Although unusual, latex can coagulate completely in a single rubbery lump often resulting in the agitator to seize. In addition, coagulum can be found as microscopic grains that cannot be removed via filtration or sedimentation and remain dispersed in the latex. This type of coagulum appears as surface roughness upon film casting.

Since every emulsion polymerization is different, each system needs to be considered separately to determine an effective method to decrease or eliminate the formation of coagulum. Generally, coagulation can be reduced through the modification of the reaction vessel, reaction conditions, or by altering the polymerization recipe.

Seeded polymerizations have been shown to reduce coagulation when compared to batch polymerizations. This is due to the absence of monomer droplets that can flocculate when the agitation speed is not optimized. Agitation rate should be at a speed just enough to maintain mixing as high speeds can disrupt micelles and cause particles and droplets to flocculate. Similarly, the monomer/water ratio can be decreased, which in turn would reduce the collision frequency between droplets and particles.^{7,8,11}

Addition of multiple surfactants, for example a combination of sodium dodecyl sulfate (anionic) and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (non-ionic), has also shown to decrease coagulation. Surfactants work better in combination and therefore having a distribution of surfactants provides a superior balance of properties that impart stability.

Coagulation can also be decreased by better controlling the temperature of the reaction vessel. For example, temperature can significantly increase during rapid exotherms of particle nucleation if a batch process is employed. For this reason, efficient heat transfer is especially vital in batch polymerizations.

Other methods to decrease coagulation include limiting the addition of salts to maintain particle surface charges and adding buffers to maintain a system at an alkaline pH.

2 Experimental Methods

Methyl methacrylate (stabilized), nbutyl acrylate (stabilized), and acrylic acid (unstabilized) were obtained from Sigma Aldrich. Ammonium persulfate and sodium dodecyl sulfate were obtained from Fisher Scientific. Triton X-200 (polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether) was obtained from Dow Chemical Company. PolyStep B5 (sodium lauryl sulfate) was obtained from Stepan. Stabilizers from MMA and nBA were removed prior to use and all other chemicals were used as received with no further purification or modification.

2.1 Instrumental Methods and Analysis

Latexes were characterized via solids content, dynamic light scattering (DLS), differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR).

2.1.1 Solids Content

The weight of three 58 mm aluminum dishes and paperclips were obtained and recorded. Without taring, about 300 mg of latex was added to each pan and overall mass was recorded. About 3 mL of DI water was added to each pan to evenly spread the latex using the paperclip. The pans were placed in the oven at 110 °C for exactly an hour. The pans were allowed to equilibrate to room temperature then weighed. The non-volatile fraction was determined using equation 2.

$$\text{Solids fraction} = \frac{(\text{mass after oven} - \text{mass of pan and paperclip})}{\text{mass of sample}} \quad (2)$$

2.1.2 DLS

A very dilute sample of latex in nanopure water was prepared for DLS analysis. About 10 microliters of the sample were added to a disposable cuvette, which was then placed in the sample holder of a DynaPro NanoStar instrument to measure the average latex particle size.

2.1.3 DSC

DSC analysis was conducted using a DSC Q1000 instrument and TA Universal Analysis software. A latex film sample of about 500 mg was prepared in a DSC pan. The temperature was first ramped up from ambient to 200 °C at 20 °C/min, then ramped down to -50 °C at 20 °C/min, and then ramped up to 200 °C at 20 °C/min. Each step was marked to end the cycle.

2.1.4 NMR

To determine the copolymer composition, NMR analysis was performed using a Bruker 300 MHz. A piece of latex film was dissolved in deuterated chloroform and the %MMA and %nBA of the copolymer were determined by equations 3 and 4.

$$\%MMA = \frac{\frac{\text{Area of MMA peak}}{\# \text{ of MMA hydrogens}}}{\frac{\text{Area of MMA peak}}{\# \text{ of MMA hydrogens}} + \frac{\text{Area of nBA peak}}{\# \text{ of nBA hydrogens}}} \quad (3)$$

$$\%nBA = \frac{\frac{\text{Area of nBA peak}}{\# \text{ of nBA hydrogens}}}{\frac{\text{Area of MMA peak}}{\# \text{ of MMA hydrogens}} + \frac{\text{Area of nBA peak}}{\# \text{ of nBA hydrogens}}} \quad (4)$$

2.2 Acrylic Latex Synthesis

Three processes, semi-batch, starved-feed, and in-situ seeded, were used to synthesize an acrylic latex with the following target properties: 40-50 wt.% solids, particle diameter range from 50-200nm, and glass transition temperature range between 15-17°C. **Table 1** summarizes the molecular weight, polymer glass transition temperature, and density of the monomers (methyl methacrylate (MMA), n-butyl acrylate (nBA), acrylic acid (AA)) used. Synthetic methods are described below.

Table 1. Literature values of monomer properties

Monomer	MW (g/mol)	T _g (°C)	Density (g/mL)
MMA	100.12	105	0.94
nBA	128.17	-54	0.875
AA	72.06	105	1.05

Table 2. Synthetic reagents and amounts for Latexes 1 and 2

Monomer Feed	Mass (g)
MMA	63.75
nBA	53.75
AA	7.5
Triton X-200	4
DI Water	127.5
Initiator Reactor Charge	Mass (g)
Ammonium persulfate	0.75
DI Water	9.0
Post-neutralization	Mass (g)
Ammonium hydroxide	1.4
DI Water	1.4

2.2.1 Semi-batch Polymerization (Latex 1)

A monomer feed (pre-emulsion), initiator reactor charge, and post neutralization were prepared by combining the components outlined in **Table 2**. Pre-emulsion and initiator charge were prepared in an Erlenmeyer flask and 25mL scintillation vial, respectively. Both were capped with rubber septa and purged for 15 minutes under nitrogen gas. Glassware was assembled according to **Figure 11**, capped, and vacuum back-filled with nitrogen gas. A 25% quantity of the pre-emulsion was added using a purged syringe to the 3-neck, 500mL round bottom flask (RBF) equipped with magnetic stir bar. The RBF was heated to 70°C then 25% of the initiator charge was added to start polymerization. The rest of the pre-emulsion and initiator charge were added in 25% additions at 15, 30, and 45-minute marks. After 60 minutes, the temperature was increased to 85 °C for an additional hour to consume residual monomers. The reaction mixture was cooled to 30-35 °C, neutralized with ammonium hydroxide, and then filtered through cheesecloth. A drawdown of Latex 1 was prepared and allowed to dry overnight.¹²

Figure 11. Semi-batch polymerization synthetic setup for Latex 1

2.2.2 Starved-feed Polymerization (Latexes 2-3)

A monomer feed (pre-emulsion), initiator reactor charge, and post neutralization were prepared by combining the components outlined in **Table 2**. **Figure 12** summarizes the synthetic setup used for the starved-feed polymerization of Latex 2. Pre-emulsion and initiator charge were prepared in an Erlenmeyer flask and 25mL scintillation vial, respectively and were purged for 15 minutes under nitrogen gas. Pre-emulsion was placed under vigorous mixing to emulsify. A syringe pump attached to a needle was used to deliver the purged APS initiator solution into one neck while a peristaltic pump delivered the purged pre-emulsion from the Erlenmeyer flask into the reaction vessel. The reaction

was maintained at 70 °C with vigorous stirring as initiator solution and pre-emulsion were continuously fed over 5 hours. The syringe pump and peristaltic pump were programmed to deliver 2.75 mL/hr and 53.3 mL/hr, respectively. After 5 hours, the reaction was heated to 85 °C to digest any unreacted monomer. The reaction vessel was allowed to cool to room temperature, neutralized, and then filtered through cheesecloth. A drawdown was prepared and allowed to dry overnight.

Figure 12. Starved-feed polymerization synthetic setup for Latexes 2-3

The same process was used to synthesize Latex 3 with 4wt.% acrylic acid. Synthetic reagents and amounts are outlined in **Table 3**.

Table 3. Synthetic reagents and amounts for Latex 3

Monomer Feed	Mass (g)
MMA	66.25
nBA	53.75
AA	5
Triton X-200	4
DI Water	127.5
Initiator Reactor Charge	Mass (g)
Ammonium persulfate	0.75
DI Water	9.0
Post-neutralization	Mass (g)
Ammonium hydroxide	1.4
DI Water	1.4

2.2.3 In-situ Seeded Polymerization (Latexes 4-6)

The reactor charge, monomer feed, initiator reactor charge, and post-neutralization solution reagents and amounts for the synthesis of Latexes 4-6 are outlined in **Table 4**. The reactor charge and a stir bar were added to a 500 mL round bottom flask (RBF), which was then clamped, submerged in an oil bath and heated to 80-85 °C. A condenser was attached to the RBF with two rubber septa in the remaining necks, as shown in **Figure 13**. The monomer feed and initiator reactor charge were prepared by adding the reagents in the order listed to an Erlenmeyer flask and 25 mL scintillation vial, respectively. After the reaction flask reached 80-85 °C, X% (X=5 for Latex 4 and X=3 for Latex 5,) of the monomer feed was added into the RBF followed by the initiator reactor charge to initiate the seed reaction. The reaction was held for 10 to 15 minutes at 80-85 °C until the exotherm was completed and temperature returned to this temperature

range. The remainder of the monomer feed was added to the RBF over 3 hours at a rate of 0.90 g/min for Latex 4 and a rate of 0.80 g/min for Latex 5. The temperature was maintained at 80-85 °C 30 minutes past starvation of the monomer feed to ensure all residual monomer was consumed. The reaction flask was then cooled below 40 °C and the post-neutralization solution was added. Finally, the latex was filtered through cheesecloth and stored in a glass bottle. A drawdown was prepared for each latex and allowed to dry overnight.

Table 4. Synthetic reagents and amounts for Latexes 4-6

Reactor Charge	Mass (g)
DI Water	68.75
Sodium dodecyl sulfate	0.038
Monomer Feed	Mass (g)
Methyl methacrylate	59.38
n-Butyl acrylate	59.38
Acrylic acid	3.75
Sodium dodecyl sulfate	2.4
DI Water	37.5
Initiator Reactor Charge	Mass (g)
Ammonium persulfate	0.5
DI Water	2.5
Post-neutralization	Mass (g)
Ammonium hydroxide	2
DI Water	7.5

Figure 13. In-situ seeded polymerization synthetic setup for Latexes 4-6

Latex 6 was synthesized using a 5% seed to probe particle size and nucleation. The above procedure was used with a few modifications. First, only half of the initiator reactor charge was added along the 5% monomer feed to initiate the seed reaction. The remainder of the initiator reactor charge was added throughout the reaction by adding aliquots throughout the synthesis using a syringe. This was done to ensure the concentration of initiator radicals was maintained at a constant concentration. Second, after the monomer feed was completely fed, the reaction was held at 80-85 °C for an hour instead of half an hour to consume residual monomers.

Samples were removed with a disposable pipet after the completion of the seed reaction and every 30 minutes until the entire monomer feed was

completely fed. To stop the samples from reacting further, they were cooled in an ice bath. The samples were then characterized using DLS.

2.3 Optimization of Emulsion Polymerization Teaching Lab

The following latexes (Latex A-J) were characterized by their latex synthesis efficiency, which was quantified by the mass of coagulum formed during their synthesis.

2.3.1 Original Teaching Lab

The amount of each reagent and synthetic setup for the original emulsion polymerization teaching lab recipe (Latex A) is summarized in **Table 5** and **Figure 14**, respectively. The batch ingredients were combined in a dry 500 mL three-neck round bottom flask equipped with stir bar (set to 350 RPM). Rubber septa were placed over the outer joints with a condenser attached at the center joint. The condenser was capped with a rubber septum and a vent needle. A purge line was established with a stainless steel needle for the inlet nitrogen line and the reaction mixture was purged for 15 minutes. Then the reactor flask was heated to 70°C in an oil bath.

The initiator reactor charge was prepared in a scintillation vial, capped, and purged with nitrogen. The solution was added to the reaction flask using a purged syringe in 3 mL aliquots at increments of 0, 20, and 40 minutes. After one hour, the reaction vessel was removed from the oil bath, neutralized, and filtered through a Gordon filter.

Table 5. Synthetic reagents and amounts for Latexes A-C

Batch Charge	Mass (g)
MMA	60
nBA	60
AA	2.5
Triton X-200	4.0
DI Water	130
Initiator Reactor Charge	Mass (g)
Ammonium persulfate	0.75
DI Water	9.0
Post-neutralization	Mass (g)
Ammonium hydroxide	1.4
DI Water	1.4

Figure 14. Synthetic setup for Latexes A and G-J

2.3.2 Modification of Synthetic Batch Setup

Figure 15 summarizes the synthetic setup used for the batch synthesis of Latexes B-F. This setup differs from **Figure 14** in that an overhead stirrer was used in place of a stir-bar to maintain agitation even during the heavy formation of coagulum.

Latex B was synthesized using the same reagents and amounts as Latex A (refer to **Table 5**) but was synthesized using the modified synthetic batch setup (**Figure 15**). Agitation speed of overhead stirrer was set to about 252 RPM.

Latex C was synthesized in a similar manner to Latex B but the initiator reactor charge was added in 1.5 mL aliquots at intervals of 0, 10, 20, 30 and 40 minutes. Agitation speed was decreased to about 198 RPM.

Figure 15. Modified batch synthetic setup for Latexes B-F

2.3.3 Change of Surfactant to SDS

Latexes D-H were synthesized using surfactant sodium dodecyl sulfate (SDS) instead of Triton X-200. Reagents and amounts for the batch charge are outlined in **Table 6**. Initiator reactor charge and post-neutralization reagents and amounts (see **Table 5**) remained the same for the synthesis of Latexes D-F however amounts were halved for the synthesis of Latexes G-H. Latexes D-F were synthesized using the setup outlined in **Figure 15** and Latexes G-J were synthesized using the setup outlined in **Figure 14**. The agitation speed for Latexes D-F was set to about 198 RPM while the agitation speed for Latexes G-J

was set to 290 RPM. A water bath instead of oil bath was used for Latexes E-J to better control the amount of heat generated during exotherms.

Table 6. Synthetic reagents and amounts for Latexes D-H

	Latex D	Latex E	Latex F	Latex G1	Latex G2	Latex H
Batch Charge	Mass (g)	Mass (g)	Mass (g)	Mass (g)	Mass (g)	Mass (g)
MMA	60	60	60	30	30	30
nBA	60	60	60	30	30	30
AA	2.5	5.66	18.72	9.46	9.46	2.93
SDS	1.0	1.40	1.40	1.55	0.70	0.73
DI Water	130	146	162	80	80	76
Bicarbonate	-	-	-	-	1.50	1.50

2.3.4 Change of Surfactant to SLS

Latex J1 and J2 was synthesized using sodium lauryl sulfate (Polystep-B5); the reagents and amounts are outlined in **Table 7**. Synthetic setup outlined in **Figure 14** was used with an agitation speed of 290 RPM, a reaction temperature of 80 °C, and a water bath.

Table 7. Synthetic reagents and amounts for Latexes J1-J2

	Latex J1	Latex J2
Batch Charge	Mass (g)	Mass (g)
Methyl methacrylate	30	30
n-Butyl acrylate	30	30
Acrylic acid	2.93	2.93
Polystep-B5	2.6	2.6
DI Water	76	76
Bicarbonate	0	1.5
Initiator Reactor Charge	Mass (g)	Mass (g)
Ammonium persulfate	0.38	0.38
DI Water	4.5	4.5
Post-neutralization	Mass (g)	Mass (g)
Ammonium hydroxide	0.7	0.7
DI Water	0.7	0.7

3 Results and Discussion

3.1 Acrylic Latex Synthesis

Although emulsion polymerization is well established in industry, it is a rather difficult synthesis to accomplish in a laboratory setting, as there are various variables that can impact the outcome. Therefore, part of the purpose of this study is to gain that expertise to produce latexes that can then be used in further studies.

Prior work within Cal Poly's Polymers and Coatings program was conducted using commercial latexes to study the syneresis and rheological properties of latex/thickener systems. The major problem with using commercial products is that properties of the latex (e.g. molecular weight), the synthetic recipe (e.g. identity of additives used), and methods used are often not disclosed. In addition, commercial latexes can vary significantly from batch to batch resulting in data that is not very reproducible.¹³

To address this problem, acrylic latexes composed of base monomers methyl methacrylate and n-butyl acrylate were synthesized using various methods. Due to the thermodynamically unstable nature of latex dispersions, a functional monomer, acrylic acid was incorporated into the copolymer. Latex particles were further stabilized by the addition of a surfactant, three of which were studied here: Triton X-200, SDS, and SLS.

Latexes 1-6 were synthesized as copolymers with the target values outlined in **Table 8**. Target values, such as glass transition temperature and particle size, were driven by commercial values. Here, a glass transition

temperature below room temperature was targeted to allow for film formation. The average particle diameter for commercial latexes is around 148 and therefore this value was targeted for the synthesis of Latexes 4-6 (in-situ seeded polymerization). The synthesis of Latexes 1-3 was more exploratory and therefore no particle size was targeted. **Table 9** summarizes the latexes synthesized and their names; latexes were named according to their synthetic method, followed by their acrylic content, and finally the wt.% of seed used. Latex 6 (ISS3-3%AA-5%Seed) was synthesized to probe particle size and nucleation and therefore will be discussed separately from Latexes 1-5.

First, a semi-batch process was used to synthesize Latex SB1-6%AA. To decrease the influence of reactivity ratios, Latexes SF1-6%AA and SF2-4%AA were synthesized using monomer starving conditions. Here, the monomer was fed at a slow rate over 6 hours to ensure that the monomer was incorporated immediately. The acrylic content was decreased from 6wt% to 4wt.% to minimize the possible synthesis of polyacrylic acid and to produce a latex that more closely resembles commercial products. An in-situ seeded was employed for latexes ISS1-3 to gain control over the final particle size. In addition, this method was used to probe particle size and nucleation.

Table 8. Target monomer compositions and properties for Latexes 1-6

Latex	Wt.% MMA	Wt.% nBA	Wt.% AA	Wt.% Solids	T _g (°C)	Particle size (nm)
1,2	51.0	43.0	6	47.6	18.0	-
3	53.0	43.0	4	47.6	18.0	-
4,5,6	48.5	48.5	3	53.6	10.5	148

Table 9. Names of latexes synthesized

Latex	Method	Wt.% AA	Wt.% Seed	Latex Name
1	Semi-batch	6	-	SB1-6% AA
2	Starved-feed	6	-	SF1-6% AA
3	Starved-feed	4	-	SF2-4% AA
4	In-situ seeded	3	5	ISS1-3% AA-5% Seed
5	In-situ seeded	3	3	ISS2-3% AA-3% Seed
6	In-situ seeded	3	5	ISS3-3% AA-5% Seed

3.1.1 Solids

Experimental solids content values were calculated according to equation 2 of section 2.1.1. All experimental values (summarized in **Table 10**) are in close agreement with target values. The discrepancy between target and experimental values are attributable to the formation of coagulum during the polymerization. The amount of coagulum was not measured for Latexes SB1 and SF1 due to difficulty removing it from the round bottom flask.

Table 10. Solids content data

Latex	Target (Wt.%)	Experimental (Wt.%)	Wt.% Coagulum
SB-1-6% AA	48.2	43.8	-
SF-1-6% AA	48.2	44.1	-
SF-2-4% AA	48.2	40.3	1.3
ISS-1-3% AA-5% Seed	51.8	46.8	1.1
ISS-2-3% AA-3% Seed	51.8	50.9	1.7

3.1.2 Particle Size

All latexes obtained ranged from a milky white to light blue color in appearance. The color of the latex can give insight into the particle size of the latex particles. For example, a latex particle diameter of around 500 will result in

a milky white product, while a latex particle diameter of around 100 will result in a light blue product. Latex color varies by particle diameter because different sized particles will scatter light differently.

Dynamic light scattering does not measure particle size directly and instead directly measures the diffusion coefficient of a sample. Therefore, it is important to note that particle size is technique dependent and that different values will be obtained depending on the characterization method used.

Semi-batch emulsion polymerization does not allow great control over particle size and therefore, no particular particle diameter was targeted. Subsequently, an In-situ seeded polymerization was used and a particle diameter of around 148 (the average particle diameter for commercial latexes) was targeted for the synthesis of Latexes ISS1-2. As seen in **Table 11**, experimental values are comparable to the target diameter.

It is significant to note that varying the seed in an in-situ process is an easy way to control the final particle size of the latex. In theory, decreasing the seed will result in the nucleation of fewer seed particles, and therefore larger final particles will be obtained. On the other hand, if the seed is increased, a larger number of seed particles will be nucleated, and therefore smaller final particles will be obtained.

Table 11. Particle size data

Latex	Particle Size (nm)
SB-1-6% AA	210 +/- 12
SF-1-6% AA	406 +/- 23
SF-2-4% AA	542 +/- 32
ISS-1-3% AA-5% Seed	134 +/- 5
ISS-2-3% AA-3% Seed	143 +/- 3

3.1.3 Glass Transition Temperature

DSC was used to analyze the glass transition temperature of the latexes. As expected, the experimental glass transition temperatures obtained lie between the T_g of the homopolymers. As seen in **Table 12**, after comparing the experimental T_g values obtained for Latexes SB1 and SF1, it is evident that running the synthesis under monomer starving conditions results in a T_g that is closer in agreement with the target value of 15.1 °C.

It is important to keep in mind that all dsc plots gave broad glass transition temperatures and therefore, the numbers provided in **Table 12** are not reliable and do not truly represent the glass transition temperature of the latexes.

Table 12. Glass transition temperature data

Latex	Target T_g (°C)	Experimental T_g (°C)
SB-1-6% AA	15.1	38
SF-1-6% AA	15.1	18
SF-2-4% AA	15.1	9
ISS-1-3% AA-5% Seed	6.6	7
ISS-2-3% AA-3% Seed	6.6	11

3.1.4 Copolymer Composition

Copolymer composition was analyzed using proton NMR. Representative proton peaks were selected for each polymer component: the chemical shift at 3.6 ppm corresponds to the methyl group protons of MMA side chains while the chemical shift at 4.2 ppm corresponds to hydrogens on nBA ($-\text{CH}_2-$ protons near the ester group of nBA side chains). Using equations 3 and 4 of section 2.1.4, the composition of the copolymer was determined for each latex.

It is difficult to analyze the microstructure of the latex particles because kinetic data was not obtained to determine how monomer was consumed or incorporated. In addition, DSC data plots were generally broad and therefore it can only be concluded that statistical copolymers of various distributions were prepared. It is important to note, however, that running a synthesis under starving conditions brought the copolymer composition closer to target values.

The amount of acrylic acid for each latex was not determined for each latex. An internal standard can be included in future analysis to analyze acrylic acid contribution.

Table 13. Copolymer Composition data

Latex	Wt.% MMA		Wt.% nBA	
	Target	Experimental	Target	Experimental
SB1-6% AA	51.0	45	43.0	55
SF1-6% AA	51.0	53	43.0	47
SF2-4% AA	51.0	52	43.0	48
ISS1-3% AA-5% Seed	48.5	68	48.5	32
ISS2-3% AA-3% Seed	48.5	46	48.5	54

3.1.5 Probing Particle Size and Nucleation

Latex ISS3-3%AA-5%Seed was synthesized using a 5% seed to probe particle size and nucleation. Using this data, an estimate of the final particle diameter can be obtained.

A seed diameter of 34 +/- 3 nm was observed via DLS after 5% of the monomer had been fed. Based on this diameter, the volume was calculated to be $2 \times 10^4 \text{ nm}^3$ by modeling the particle after a sphere. After feeding 100% of the monomer, the particle volume should have been 20 times larger ($4 \times 10^5 \text{ nm}^3$), which translates into a final particle diameter of roughly 90 nm. The final particle size was measured by DLS to be 129 +/- 3 nm.⁵

Figure 16. Analysis of particle growth and nucleation

Particle nucleation was analyzed by plotting particle volume as a function of percent monomer added. In an in-situ seeded latex synthesis, a linear function is ideal and is indicative of latex particles growing in a controlled way: seed

particles are exclusively being grown throughout the synthesis (no nucleation of new particles), which results in a narrow distribution of particle size. If the slope of the curve is decreasing as the percent of monomer added is increasing, new particles are being nucleated throughout the course of the reaction. If the slope of the curve is increasing as the percent of monomer added is increasing, latex is coagulating and larger particles are being formed, which is indicative that the latex is unstable.⁵

As seen in **Figure 16**, a linear function with R^2 value of 0.936 was obtained. It is difficult to conclude that particles were grown exclusively in a controlled manner because the slope appears to be decreasing around 70 wt.% monomer added. This may indicate that seed particles were being grown but that new particles were also being nucleated throughout the reaction. It also appears that beyond 70 wt.% monomer added, the slope begins to increase significantly. This may suggest that not enough surfactant was available to stabilize particles and that they may have aggregated or coagulated.

3.2 Optimization of Chem 547 Emulsion Polymerization Lab

Batch emulsion polymerization is the simplest of all emulsion polymerization processes and is therefore often used as a teaching tool in laboratory settings. However, due to its simplicity a batch polymerization is also the process most prone to coagulation.

This was clearly evident when running the original emulsion polymerization teaching lab recipe (Latex A) used in Chem 547. The agitation seized midway as the magnetic stir bar was covered entirely by the coagulum

formed, and soon enough, two separate layers formed in the RBF. Having micelles and monomer in two separate phases does not allow monomer molecules to be pulled into the micelles to continue the growth of particle chains and as a result, the polymerization was terminated prematurely.

Since an emulsion polymerization cannot be carried out with phase separation, Latex B was synthesized using a synthetic setup that included an overhead stirrer. This synthesis was carried out to completion, as agitation did not cease even with the formation of coagulum. However, as seen in **Table 14**, 6.1 wt.% of coagulum was observed. Coagulum observed could have resulted from a number of reasons including a high agitation speed. If it is set too high, the stirrer can disrupt micelles causing particles to crash out and coagulate onto other particles or growing z-mers in the aqueous phase. Coagulation could have also resulted from early termination, which can result from not having enough initiator molecules throughout the reaction. Once an initiator radical is generated, that radical can initiate a propagating chain, can be transferred to other components like water, or it can quench another radical. Since, not all radicals will initiate or can even terminate a propagating z-mer or chain, having a significant concentration of radicals throughout the reaction is vital to prevent early termination.

Table 14. Coagulation data

Latex	Surfactant	Wt.% Surf	Wt.% AA	Wt.% NaHCO ₃	Coagulum (%)
A	Triton X-200	0.4	0.94	0	N/A*
B	Triton X-200	0.4	0.94	0	6.1
C	Triton X-200	0.4	0.94	0	6.8
D	SDS	0.4	0.94	0	15.2
E	SDS	0.5	2	0	13.0
F	SDS	0.5	6	0	95.5
G1	SDS	1.0	6	0	92.7
G2	SDS	0.5	6	1	4.2
H	SDS	0.5	2	1	1.9
J1	Polystep-B5	0.5	2	0	10.3
J2	Polystep-B5	0.5	2	1	3.0

*Agitation seized due to coagulation; reaction was terminated early

Latex C was carried out using the same setup as Latex B but with a decrease in the agitation speed and the initiator reactor charge was added in 1.5 mL aliquots every 10 minutes until the end of the reaction to ensure a constant input of initiator radicals into the system. Coagulation observed increased to 6.8 wt.%. The wt.% of coagulum should have decreased due to the slower agitation speed, as it should have disrupted the system less. A decrease was also expected because having multiple additions of initiator should have guaranteed a constant input of radicals into the aqueous phase.

Latex D was synthesized using surfactant sodium dodecyl sulfate (SDS) as Triton X-200 was discontinued by the supplier, DOW Chemical Company. SDS consists of a 12-carbon tail attached to a sulfate head group and like Triton X-200, it is also an anionic surfactant. It has an HLB value of 40 and a CMC of 0.0081 mol/L. The wt.% of acrylic acid and surfactant were kept at 0.94 and 0.4, respectively. As seen in **Table 14**, 15.2 wt.% of coagulum was observed

suggesting thermodynamically unstable latex particles. This could have resulted from a low concentration of functional monomer on the surface of particles; particles with fewer repulsive surface charges attract each other resulting in the agglomeration of particles. Having a low concentration of surfactant may also result in unstable particles since there is an energy or cost associated with the creation of new interfaces. At a low surfactant concentration particles will agglomerate if not enough surfactant is present to accommodate new surfaces. Therefore, two particles will coagulate to lower their total surface area if their separate surface areas cannot be stabilized with present surfactant. In addition, the anionic segment of surfactant molecules increase the repulsion between particles.

To increase the stability of the latex, the acrylic acid content was increased to 2 wt.% and the surfactant concentration was increased to 0.50 wt.% for the synthesis of Latex E. The amount of coagulum decreased from 15.2 wt.% to 13.0 wt.%. As predicted, the increase in functional monomer and surfactant increased the stability of latex particles. As more functional monomer became incorporated onto the particle surfaces, repulsion among particles increased and particle agglomeration decreased. Having additional surfactant increased the stability of particle interfaces and increased particle-particle repulsion to lower coagulation.

Latex F was synthesized with an increase in the amount of acrylic acid (6 wt.%), to provide additional stability to latex particles. This run was not successful as the entire flask coagulated with little remaining latex. This was unexpected as

it was previously seen that increasing the amount of functional monomer decreased particle coagulation. To resolve the stability issue, two different routes were attempted: For Latex G1, the surfactant concentration was increased to 1 wt.%, double the concentration used in Latex F in case the instability was the resultant of insufficient surfactant amounts; for Latex G2, sodium bicarbonate was included as a buffer with the intention of regulating the pH of the system. As seen in **Table 14** the additional surfactant in Latex G1 did not yield a more stable latex as nearly the entire latex coagulated. However, the inclusion of a buffer significantly improved the stability of the particles in Latex G2.

When ammonium persulfate is used as the initiator, sulfuric acid is a side product of radical production. The acid produced lowers the pH of the reaction mixture protonating the acid groups on latex particles. As a result, latex particles cannot repel each other and coagulation ensues. As predicted, adding a buffer significantly decreased the amount of coagulation observed to only 4.2 wt.%. However, the latex was extremely viscous. This was most likely due to the high percentage used of acrylic acid. Acrylic acid can homopolymerize in the aqueous phase due to its high solubility in water to form polyacrylic acid, which is a thickener under alkaline conditions of the latex.

Latex H was synthesized with a buffer, but the amount of acrylic acid was decreased back to 2 wt.%. As seen in **Table 14**, the amount of coagulum decreased to only 1.9 wt.% and the resulting latex was also less viscous than Latex G2. This is desired and suggests that acrylic acid was incorporated as appose to homopolymerizing in the aqueous phase to make polyacrylic acid.

To test the validity of these results and to investigate the performance of another surfactant, two additional latexes (Latex J1 and J2) were synthesized using surfactant SLS (Polystep-B5). In literature SDS and SLS are often used interchangeably. However, the two are not the same: SDS is a pure C-12 surfactant while SLS only has about 30% of SDS by weight and instead has a broad distribution of chain length making it a better emulsifier.

Both latexes were synthesized with 2 wt.% and 0.50 wt.% AA and surfactant, respectively. Latex J1 was synthesized with no buffer while Latex J2 was synthesized including sodium bicarbonate as a buffer. Analogous to Latexes G1 and G2, the inclusion of a buffer decreased the amount of coagulum from 10.3 wt.% (Latex J1) to 3.0 wt.% (Latex J2).

After comparing Latexes E and J1, it is evident that SLS is a better emulsifier as the amount of coagulum decreased from 13 wt.% to about 10 wt.% with the change in surfactant. This was expected since Polystep B-5 (29 wt.% solids) has a CMC of 127 mg/L while SDS (98 wt.% solids) has a CMC of 2,332 mg/L or 18 times larger than SDS. Therefore, at a surfactant concentration of 0.50 wt.%, the Latex E system was only around 2 times the CMC while in the synthesis of Latex J1, the system was around 40 times the CMC.

4 Conclusions and Future Work

Three different methods were used in the synthesis of acrylic latex: semi-batch, starved-feed, and in-situ seeded polymerizations. These processes were found to affect the resulting latex properties (such as T_g) as they are strongly impacted by the distribution and sequence of monomers within polymer chains.

It was discovered that using a semi-batch polymerization is not suitable for the natural production of a random or alternating copolymer as differences in reactivity ratios resulted in the addition of one monomer over its comonomer. Therefore, a monomer starving polymerization should be used in the synthesis of a random or alternating copolymer. One major limitation found with this process, however, is that it is difficult to control the particle size of latex particles.

In-situ seeded polymerization was found to be the best process overall when a target glass transition temperature and particle size is desired. However, additional work is needed to optimize the polymerization, as it appears that new particles were being nucleated throughout the reaction. One thing that is not verified was whether or not this type of polymerization was truly ran under monomer starving conditions, which is required for a successful in-situ seeded process. Therefore, both particle size and kinetics should be probed in any future work.

Regarding the optimization of the Chem 547 teaching lab, synthesis was improved considerably. Two key changes that should be implemented are: (1) the inclusion of a buffer and (2) a low concentration of acrylic acid around 2 wt.%. Further optimization is suggested. Future experiments include: increasing the

weight percent of surfactant used beyond 0.5 wt.%, testing out a different functional monomer like methacrylic acid and investigating other SLS based surfactants such as Polystep B-3.

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