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Synthesis of styrene and acrylic emulsion polymer systems by semi-continuous seeded polymerization processes

Lynley H. Guckian

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Synthesis of Styrene and Acrylic Emulsion Polymer Systems by Semi-continuous Seeded Polymerization Processes

Lynley H. Guckian

May, 2004

THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

APPROVED:

Grazyna Kmiecik-Lawrynowicz

Thomas W. Smith
Project Advisors

Department Head

Rochester Institute of Technology
Rochester, New York 14623
Center for Material Science & Engineering
Synthesis of Styrene and Acrylic Emulsion Polymer Systems by
Semi-continuous Seeded Polymerization Processes

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Lynley H. Guckian

18 June 2004
Date
Abstract

The synthesis of monodisperse styrene and acrylic core-shell polymer particles by semi-continuous seeded emulsion polymerization processes was investigated. 120 and 140 nm homopoly(styrene) seed particles were made for each batch and monodisperse 300 and 400 nm core-shell particles were synthesized therefrom. Divinylbenzene and poly(dimethylsiloxane) were compositional variables that were studied as part of the synthesis. The addition of DVB significantly increased the gel content of the particles. The incorporation of poly(dimethylsilocane) appeared to plasticize the particles. The particle size, morphology, surface charge, molecular weight, percent gel content, and glass transition characteristics of the particles were evaluated. It was found that the surface charge of the particles was affected by increasing particle size and by incorporating poly(dimethylsiloxane) or acrylic functionality in the shell.
Acknowledgements

I would like to extend my deepest gratitude to my advisors, Professor Thomas W. Smith and Dr. Grazyna Kmiecik-Lawrynowicz of Xerox Corporation, for their guidance and patience throughout the extent of my project. The knowledge I gained through working with them is indispensable. I would like to thank Professor Andreas Langner for his help in understanding and examining zeta potential and for contributing to the write-up of my project. I would like to thank Maura A. Sweeney and Robert D. Bayley of Xerox Corporation for their help in synthesizing the latex particles. I would also like to thank Witold Niedzialkowski, Kim Lander, Mike Mehan, Dennis Stearns, and Mark Monachino for their help in analyzing the latex particles. Lastly, I would like to thank my husband Ryan for his endless love and support.
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I. Introduction

Large monodisperse polymer particles have many applications including coatings, finishes\(^1\), photonic crystals\(^2\), chromatographic columns\(^3\), and biomedical devices.\(^4\) The synthesis of particles, ranging in size from 0.05 to 2000 \(\mu m\), has been a topic of interest in both academic and industrial laboratories. Polymer particles in this size range may be synthesized by suspension, dispersion, or emulsion polymerization.

Suspension polymerization entails the polymerization of a suspension of monomer droplets in a medium in which the monomer is not soluble. Typically it involves the polymerization of an "oil-soluble monomer" dispersed in water with the agency of a polymeric protective colloid or particulate suspension aid, initiating with an oil-soluble, free-radical catalyst. Suspension polymerization typically produces particles ranging from 50 to 2000 \(\mu m\) in size.\(^5\) The locus of polymerization in suspension polymerization systems is the monomer droplet and kinetics in suspension polymerization reactions, in which the polymer is soluble in the monomer, are identical to polymerization in bulk. Suspension polymerization yields readily isolable polymer particles that may be directly used in molding and extrusion of plastics. Suspension polymerization allows for facile dissipation of heat reaction and can be readily scaled up in batch and continuous reactor schemes. A disadvantage of suspension polymerization is that the protective colloid or particulate suspension aid most often has to be removed in a post-polymerization processing reaction.

Dispersion polymerization has been described by Barrett\(^6\) as a special case of precipitation polymerization in which flocculation is prevented and particle size is controlled by an amphipathic graft or block copolymer dispersant. The polymerization occurs predominantly in the polymer particle and the resulting particles are typically 0.1 to 1.0 \(\mu m\) in size. Dispersion polymerization is capable of producing monodisperse particles. A potential disadvantage of dispersion
polymerization is that organic solvents are generally used as the reaction medium when polymerizing oil-soluble monomers.

Classic emulsion polymerization involves an oil-soluble monomer in water mediated by a surfactant and a water-soluble initiator. The polymerization can be viewed as being initiated in micelles with the bulk of the polymerization occurring in monomer-swollen latex particles. Emulsion polymerization, in a batch process, typically produces particles that range in size from 0.05 to 0.3 μm. The locus and kinetics of polymerization differentiate emulsion polymerization from suspension and dispersion.

As compared to suspension and dispersion polymerization systems, emulsion polymerization offers the fastest polymerization rate and yields the highest molecular weight polymers. The degree and rate of polymerization are determined by the number of polymer particles,

\[ \text{DP} = \frac{k_p N [M]}{\rho} \]

and

\[ R_p = 10^3 N \bar{n} k_p [M] / N_A \]

where \( k_p \) is the propagation rate constant, \( N \) is number of particles per milliliter (typically \( 10^{14} \)), \([M]\) is the monomer concentration, \( \rho \) is the rate of radical production, \( \bar{n} \) is the average number of radicals per micelle, and \( N_A \) is Avogadro's number. The initially-formed particles are very small (typically 20-50 nm in diameter). Given the rapid diffusion rates for free-radicals in solutions, two radicals in any volume element of this size will immediately couple. Accordingly, there is, on average, only one radical per particle and thus, termination by recombination is suppressed. Emulsion polymerization systems can generally be driven to nearly quantitative conversion of monomer to polymer. This leads to reduced production costs and in many cases the resulting latex can be directly used in commercial applications.

Of the three polymerization processes described above, emulsion polymerization was chosen as our preferred method of synthesis. Specifically, we were interested in creating monodisperse polymer particles in the 0.2-0.5 μm size range. Suspension polymerization is particularly suited to produce much
larger particles and thus was not a viable process. While dispersion and emulsion polymerization are both capable of producing particles in the desired size range, dispersion polymerization of oil-soluble monomers with slight solubility in water is typically carried out in non-aqueous media. The use of volatile and sometimes toxic organic solvents requires substantial investment in systems to control emissions and is typically avoided in the modern industrial environment. The critical factor in our choice of emulsion polymerization, however, was that it is capable of producing particles in our desired size range.

The kinetics of emulsion polymerization were first described in the literature by Wendall Smith and Roswell Ewart.\textsuperscript{10} The Smith-Ewart theory describes the kinetics of initiation and propagation in the polymerization of an oil-soluble monomer, in water, initiated by a water soluble free radical initiator and mediated by a micellar surfactant.

In 1945, William Harkins reported a broadly applicable mechanism or model for emulsion polymerization.\textsuperscript{11,12} The Harkins model describes three distinct intervals or stages during the course of an emulsion polymerization. Interval I is the nucleation phase wherein polymer particles are first formed, ostensibly being nucleated in monomer swollen micelles. Interval II begins when particle nucleation stops and micelles are consumed. Monomer is still found in droplets and polymer particles and there are a constant number of particles in the system. Interval III is the final stage of the reaction and in this phase monomer droplets are no longer present. Monomer is only found in the polymer particles and the particle size is constant as the rest of the monomer is consumed. These mechanistic features were exploited in our seeded growth of polymer particles.
Figure 1. Schematic Representation of Emulsion Polymerization as Described by Harkins (From Polymer Chemistry, B. Vollmert, Springer-Verlag, 1973, p. 155)
The Smith-Ewart theory describes three cases.

In case 1,
\[ \tilde{n} < 0.5 \quad \text{and} \quad \rho'/N \ll k_0a/v \]

\( \tilde{n} \) is the number of free radicals per reaction locus, \( \rho' \) is the rate of entrance of free radicals, \( N \) is the number of reaction loci, \( k_0 \) is the rate constant, \( a \) is the interfacial area of loci, \( v \) is the volume of loci, and \( k_t \) is the termination rate constant. Case 1 would be operative when radical desorption and termination in the aqueous phase are predominant.

In case 2,
\[ \tilde{n} = 0.5 \quad \text{and} \quad k_0a/v \ll \rho'/N < k_t/v. \]
Thus, at any given time half of the polymer particles contain a living free-radical and are active. Case 2 kinetics will typically predominate during interval II when the particle size is too small to accommodate more than one radical.

In case 3,
\[ \tilde{n} > 0.5 \text{ and } \rho' / N \gg k_v / v. \]

Case 3 would be operative when the particle size is large or the termination rate constant is low. Case 3 type kinetics may be used to describe seeded polymerization processes in which relatively large particles are being formed.

Since the seminal work of Harkins and Smith and Ewart, it has become understood that nucleation processes in emulsion polymerization can take place by two mechanisms, micellar and homogeneous nucleation-capture. Micellar nucleation is the classic mechanistic picture used to describe an emulsion polymerization. In micellar nucleation, primary and oligomeric radicals in the aqueous phase enter the surfactant micelles. Residual monomer dissolved in the aqueous phase also migrates into the micelles where it encounters initiating radicals. As the monomer is converted to polymer, the micelles become polymer particles. In homogeneous nucleation, free radicals react with monomer that is dissolved in the aqueous phase. The growing oligomeric radicals become insoluble and precipitate from solution to form primary particles. These primary particles typically undergo accretive growth increasing in volume until absorbed surfactant or ionizable surface species on the particle surface can produce charge stabilization. Homogeneous nucleation is the probable mechanistic process for the polymerization of monomers with appreciable water solubility (>1% by weight), surfactant-free systems, and systems wherein the concentration of surfactant is well below the critical micelle concentration.\(^{15}\)

Three reactor systems (batch, semi-continuous, and continuous) are commonly used in industrial emulsion polymerization, these are schematically shown in Figure 3. Batch reactors usually consist of a stirred tank equipped with a heat removal device such as a jacket or a reflux condenser. All of the ingredients are added at or near the beginning of the reaction and the reaction is carried out to conversion. Batch reactors are commonly used to make small
latex batches, typically less than 1000 gallons in size. The heat given off in a very short interval of time in polymerization reactions is quite large and despite the high heat capacity of water, the exotherm in large batch reactors can exceed the cooling capacity of state-of-the-art jacketed reactors. Batch reactors are thus suitable for the preparation of relatively small commercial volumes of polymer.

**Figure 3.** Emulsion Polymerization Reactor Systems

Semi-continuous or semi-batch reactors are similar to batch reactors in design. However, the polymerization in semi-continuous reactors proceeds in two stages. In the first stage, the polymerization is run like a batch reaction. All of the necessary ingredients are added and small initial particles, called seed particles, are formed. In the second stage, the polymerization reaction is continued with monomer and other ingredients being added at a controlled rate. This procedure allows for great flexibility in latex design. The semi-continuous process can be used to control reaction rate, particle size distribution, particle morphology and other properties of the resulting latex.\textsuperscript{16}
Continuous reactors typically consist of a number of reactors connected in series, each one controlling a different part of the polymerization. A steady flow of ingredients in and product out of the reactor is maintained. For example, in a continuous system reactor one may be used to make seed particles, reactor two may be used to start monomer feed and reactor three may be used to feed in a second monomer. Continuous reactors are complex and require engineering designs unique to each process. For these reasons, a continuous reactor system is not typically used for lab-scale batches. Continuous reactors are the desired state for manufacturing polymers because large volumes of material can be produced in reactor systems having minimal size. In addition, continuous reactors afford a great deal of flexibility in controlling the reaction.

A necessary condition for the formation of monodisperse latexes is that all particles be nucleated at essentially the same time and then subsequently grow at equal rates. A seeded polymerization is one way of achieving this. As additional monomer is fed to the reaction mixture under surfactant starvation conditions (100% monolayer coverage of the particles with negligible surfactant present in the aqueous phase) new polymer will be incorporated in the existing seed particles. It has been shown that it is possible to grow large monodisperse particles in the 0.2-0.5 μm size range in seeded growth systems.

The synthesis of monodisperse particles by semi-continuous seeded emulsion polymerization is well documented in the literature. Recently El-Aasser et al. reported the synthesis of well-defined, functionalized latex particles using n-butyl methacrylate/n-butyl acrylate/methacrylic acid monomers. Sajjadi et al. and Asua et al. presented models to predict kinetics in methyl methacrylate and n-butyl acrylate systems, respectively. Numerous mathematical models of semicontinuous seeded emulsion polymerization systems have been developed and kinetics studies have been carried out focusing on various reaction parameters and conditions.

In this study, we investigated seed formation and semi-continuous growth of monodisperse particles in styrene and styrene/methyl methacrylate emulsion polymerization systems. Our objective was to synthesize monodisperse particles
that were 0.3 and 0.4 μm in size. Moreover, we wanted to incorporate divinylbenzene and poly(dimethyl siloxane) (PDMS) in our polymer particles. We were specifically interested in crosslinking with divinylbenzene to increase the hardness of the particles. Adding PDMS macromer to the particle surface was viewed a means of lowering the surface energy of the particles. In this project, the particle size was evaluated by light scattering, morphology by scanning electron microscopy, surface charge by zeta potential, molecular weight and polydispersity by gel permeation chromatography, percent gel content by gravimetric filtration and glass transition characteristics by differential scanning calorimetry of the resulting polymer particles.
II. Experimental

i. Materials

Monomers and macromers employed in the preparation of specific latex batches were: styrene (99.5%, Scientific Polymer Products), inhibited with 10-15 ppm t-butyl catechol (t-BC); methyl methacrylate (99.9%, Rohm & Haas), inhibited with 10 ppm monomethyl ether hydroquinone; divinyl benzene (56% active, Scientific Polymer Products), inhibited with 1000 ppm t-BC; and monomethacryloxypropyl-terminated polydimethylsiloxane (Gelest Inc). Sodium lauryl sulfate (reagent, Sigma-Aldrich) was used as surfactant. Potassium persulfate (ACS reagent, J.T. Baker) was used as initiator. All materials were used as received.

ii. Latex Synthesis

All reactions were performed in 2-liter reactors equipped with a stainless-steel stirrer, condenser, nitrogen inlet, thermometer, temperature controller, and internal cooling coil. The internal temperature of the reactor was controlled at 75 ± 0.2°C. Two different reactors were used that differed in their aspect ratios for batches 1-4 and 5-12, respectively. Accordingly, to achieve approximately the same shear, different stirrer speeds were used in the two reactors. In the reactor used for batches 1-4 the stirrer speed was 150 rpm. In the reactor used for reactions 5-12 the stirrer speed was 200 rpm. Reactions 1-4 were polystyrene (PS) controls and polystyrene/divinylbenzene copolymer (PS/DVB) latexes. Reactions 5-8 were polystyrene controls and polystyrene/poly(dimethylsiloxane) (PS/PDMS), polystyrene/poly(methyl methacrylate) (PS/PMMA), and polystyrene/poly(methyl methacrylate)/poly(methyl methacrylate)-poly(dimethylsiloxane) core/shell latexes. Reactions 9-12 were poly(methyl methacrylate) (PMMA) latexes. Table 1 displays the recipes for each of the 12 latex batches. Note that the seed stage is identical for batches 1-4 and 5-8.

In batch 9, the recipe from batch 2 was duplicated substituting methyl methacrylate for styrene monomer. The particle size realized from this
polymerization was 174 nm. Accordingly, we were not able to make 400 nm particles as desired. In batches 10 and 11, the amount of monomer in the seed stage was reduced. In batch 12, the recipe from batch 11 was duplicated with the temperature of the reaction lowered to 65°C. These adjustments were made to the recipe to see their effects on particle size.
Table 1: Recipes for Semi-continuous Seeded Emulsion Polymerization of Styrene, Styrene/MMA and MMA Systems.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batches</td>
<td>1 2 3 4 5 6 7 8 9 10 11 12</td>
</tr>
<tr>
<td>Seed stage</td>
<td></td>
</tr>
<tr>
<td>DI water</td>
<td>1170 1170 1170 1170 990 990 990 990 990 990 990 990</td>
</tr>
<tr>
<td>SLS</td>
<td>0.26 0.26 0.26 0.26 0.26 0.26 0.26 0.26 0.26 0.26 0.26 0.26</td>
</tr>
<tr>
<td>Monomer</td>
<td>50 50 50 50 50 50 50 50 25 12.7 12.7</td>
</tr>
<tr>
<td>KPS</td>
<td>2.62 2.62 2.62 2.62 2.65 2.65 2.65 2.65 2.65 2.65 2.65 2.65</td>
</tr>
<tr>
<td>Feed stage</td>
<td></td>
</tr>
<tr>
<td>Monomer</td>
<td>81 312 79.2 307.1 550 540 450 440 312 312 312 312</td>
</tr>
<tr>
<td>DVB</td>
<td>1.8 4.9 10 10</td>
</tr>
<tr>
<td>PDMS</td>
<td></td>
</tr>
<tr>
<td>SLS</td>
<td>0.4 0.4 0.5 0.5 1.0 1.0 0.135 0.5 1.0 1.0</td>
</tr>
<tr>
<td>KPS</td>
<td>0.5 0.5 0.5 0.5</td>
</tr>
</tbody>
</table>
Batch 1: 300nm Polystyrene Control
Deionized (DI) water, 1170 g, and 0.26 g SLS were charged in the reactor. The reaction mixture was subjected to a nitrogen purge to displace the oxygen for a minimum of 30 minutes and was simultaneously heated to 75°C. The reactor was then charged with 50 g styrene monomer and stirred for 10 minutes to disperse the monomer droplets in the water phase. 2.62 g KPS dissolved in 20 mL DI water was added to initiate the polymerization. Within minutes of initiation, the appearance of a milky white emulsion made manifest the start of the polymerization. The initial 30 minute period of the polymerization was the seeding stage. After the seed particles reached 140 nm in size, 81 g styrene monomer was fed in over a period of 34 minutes. After monomer addition was complete, the polymerization was allowed to continue for 2 hours to complete conversion of monomer to polymer. The resulting particles were 292±34 nm in size.

Batch 2: 400nm Polystyrene Control
The same procedure was followed for the synthesis of seed particles as described for the 300 nm polystyrene control (Batch 1). After the seed particles reached 140 nm in size, 212 g styrene monomer was fed in over a period of 96 minutes. The monomer feed was stopped and the mixture was continually stirred for an additional 100 minutes. After the 100 minutes, the monomer feed was started again and an additional 100 g styrene monomer was fed in over a period of 50 minutes. After the second monomer addition was complete, the polymerization was allowed to continue for 2 hours to complete conversion of monomer to polymer. Due to a larger size particle, more surfactant was needed to provide stabilization. An additional 0.135 g SLS was added to the reaction mixture at three time intervals: 70 minutes after the end of the first monomer feed, at the start of the second monomer feed, and 60 minutes after the end of the second monomer feed. The resulting particles were 411±45 nm in size.
Batch 3: 300nm Polystyrene/DVB Latex
The same procedure was followed as described for the 300 nm polystyrene control (Batch 1) except that instead of using exclusively styrene, a solution of 1.8 g DVB and 131 g styrene was used. The resulting particles were 304±33 nm in size.

Batch 4: 400nm Polystyrene/DVB Latex
The same procedure was followed as described for the 400 nm polystyrene control (Batch 2) except that instead of using exclusively styrene, a solution of 4.9 g DVB and 362 g styrene was used. The resulting particles were 415±46 nm in size.

Batch 5: 350nm Polystyrene Control
The same procedure was followed for the synthesis of seed particles as described for the 300 nm polystyrene control (Batch 1) except that 2.65 g KPS was used. After the seed particles reached 119 nm in size, 550 g styrene monomer was fed in over a period of 250 minutes. After monomer addition was complete, the polymerization was allowed to continue for 2 hours to complete conversion of monomer to polymer. An additional 0.25 g SLS was added to the reaction mixture at two time intervals: 180 minutes after start of monomer feed and at the end monomer feed. An additional 0.5 g KPS was added to the reaction mixture 60 minutes after the end of monomer feed. The resulting particles were 351±38 nm in size.

Batch 6: 350nm Polystyrene/PDMS Latex
The same procedure was followed as described for the 350 nm polystyrene control (Batch 5) with the addition of 10 g PDMS macromer to the last 100 g of monomer feed (10 g PDMS: 90 g styrene). The resulting particles were 342±40 nm in size.
Batch 7: 320nm Polystyrene/PMMA Latex
The same procedure was followed for the synthesis of seed particles as described for the 350 nm polystyrene control (Batch 5). After the seed particles reached 121 nm in size, 450 g MMA monomer was fed in over a period of 212 minutes. After monomer addition was complete, the polymerization was allowed to continue for 2 hours to complete conversion of monomer to polymer. An additional 0.5 g SLS was added to the reaction mixture at two time intervals: 40 and 100 minutes after start of monomer feed. An additional 0.5 g KPS was added to the reaction mixture 60 minutes after the end of monomer feed. The resulting particles were 318±51 nm in size.

Batch 8: 320nm (Polystyrene/PMMA)/PDMS Latex
The same procedure was followed as described for the 320 nm PS/PMMA latex (Batch 7) with the addition of 10 g PDMS macromer to the last 100 g of monomer feed (10 g PDMS: 90 g MMA). The resulting particles were 319±25 nm in size.

Batch 9: 174nm PMMA Latex
DI water, 990 g, and 0.26 g SLS were charged in the reactor. The reaction mixture was subjected to a nitrogen purge to displace the oxygen for a minimum of 30 minutes and was simultaneously heated to 75°C. The reactor was then charged with 50 g MMA monomer and stirred for 10 minutes to disperse the monomer droplets in the water phase. 2.65 g KPS dissolved in 20 mL DI water was added to initiate the polymerization. Within minutes of initiation, the appearance of a milky white emulsion made manifest the start of the polymerization. The initial 30 minute period of the polymerization was the seeding stage. After the seed particles reached 81 nm in size, 312 g MMA monomer was fed in over a period of 153 minutes. After monomer addition was complete, the polymerization was allowed to continue for 2 hours to complete conversion of monomer to polymer. An additional 0.135 g SLS was added to the reaction mixture 34 minutes after start of monomer feed. The resulting particles were 174±28 nm in size.
Batch 10: 250nm PMMA Latex
The same procedure was followed as described for the 174 nm PMMA latex (Batch 9) with the following exceptions: 25 g MMA was initially charged to the reactor resulting in 77 nm seed particles and an additional 0.5 g SLS was added to the reaction mixture 100 minutes after start of monomer feed. The resulting particles were 250±31 nm in size.

Batch 11: 260nm PMMA Latex
The same procedure was followed as described for the 174 nm PMMA latex (Batch 9) with the following exceptions: 12.7 g MMA was initially charged to the reactor resulting in 60 nm seed particles and an additional 0.5 g SLS was added to the reaction mixture 30 and 120 minutes after start of monomer feed. The resulting particles were 262±35 nm in size.

Batch 12: 250nm PMMA Latex II
The same procedure was followed as described for the 260 nm PMMA latex (Batch 11) with the exception that the reaction temperature was lowered to 65°C. The resulting particles were 248±35 nm in size.

iii. Latex Characterization
Size of particles was evaluated by scanning electron microscopy (SEM) and light scattering. Compositional homogeneity was examined by differential scanning calorimetry (DSC). Molecular weight and polydispersity index was investigated by gel permeation chromatography (GPC). Percent total gel was determined by gravimetric filtration. Particle surface charge was monitored by zeta potential. Surface and particle composition were probed by x-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP). The polymer or copolymer was isolated before performing DSC, GPC, % total gel, and surface and particle composition analyses (XPS and ICP) by lyophilization.
Particle Analysis:
The SEM analysis\(^1\) was performed in a Hitachi S-4500 field-emission scanning electron microscope (FESEM) at 5 keV probe voltage. Samples were prepared for analysis by dropping undiluted latex from a pipette onto double-coated carbon conductive adhesive tabs affixed to aluminum sample studs. The samples were dried at room temperature. Dry samples were sputter coated with 150 Å gold in vacuo to eliminate electrostatic charging.
Dynamic light scattering was performed using a Microtrac UPA 150. Using a pipette 1-3 drops of sample was added to the sample compartment and diluted with DI water to an internal loading factor of 1.0±0.1. The samples were each run four times at 300s. Instrument settings were particle transparency, absorptive; particle shape, spherical; and fluid refractive index, 1.33. Each run directly gave a histogram of counts as a function of the scattered light. The mean particle diameter is reported as three separate quantities: \( m_v \), the volume distribution, \( m_n \), the number distribution, and \( m_a \), the area distribution. We report the particle size as \( m_v \) in all cases and also report the standard deviation as calculated. Latex samples were removed from the reactor using a pipette at intermittent time intervals and analyzed to measure seed particles, monitor particle growth throughout the polymerization, and measure final particle size.

Compositional Analysis:
The glass transition temperatures (\( T_g \)'s) of the latex polymers were measured with a differential scanning calorimeter (DSC; model Q-1000, TA Instruments, New Castle, DE)\(^2\). 10 mg of sample was used and two heat cycles were performed over a temperature range of 0 to 150°C at a heating rate of 10°C/min. All data was tabulated from the second heat cycle.
Molecular Weight Analysis:
The average molecular weight and polydispersity of polymers were determined by gel permeation chromatography (GPC, model 2690, Waters, Boston, MA). A mobile phase of THF and six Waters Styragel columns (HR6, HR5, HR4, HR3, HR2, HR1) were used. The samples were dissolved in THF, filtered through 0.2 micron Teflon filters and injected into the GPC system. Polystyrene standards ranging from 4,230,000 to 1,260 g/mol were used for the calibration.

Percent Total Gel:
The % total gel was determined by gravimetric filtration. Approximately 40 mg (W1) of each sample was weighed into a scintillation vial and 20 mL toluene was added. The samples were allowed to shake on a box shaker for 4 hours. Two filters, one Whatman Filter Paper 4.25 cm type GF/A and one MSI Micro Teflon Filter 47mm type PTEF, were placed in an aluminum pan and their weight recorded (W2). A filtration apparatus was assembled using a 1-Liter vacuum flask with vacuum pump and trap, ceramic filter support, and a Whatman 3-piece filter funnel. The Teflon filter was placed shiny side down on to the filter support and the Whatman filter was placed on top. The filter funnel was clipped to the filter support and the filters were wet with toluene. The contents of the vial were emptied onto the filter and the vial rinsed with 2 mL toluene. The wet filters were removed from the filter apparatus using forceps and the filters were allowed to air dry in the aluminum dish overnight. The weight of the aluminum filter dish was recorded the next day (W3). The % total gel was calculated using: (W3-W2)/W1 x 100.

Surface Charge Analysis:
The zeta-potential of the latex were measured with a Zeta Reader (Mark 21, ZPi Inc., Bedminster, NJ). Approximately 0.5 g of each sample was added to 500 mL deionized water. The sample was introduced to the instrument by cycling it through the sample accessory using the automated sample pumps. At this time
the sample was injected into the capillary sample cell using similar automated pumps. The cell image was scanned by a high resolution color ccd camera and displayed on a high resolution color monitor. When a voltage was applied, the particles moved across the capillary cell. Vertical scan lines, with 25 micron line spacing, were manually adjusted to mimic the movement of the particles and the zeta potential was manually recorded for a minimum of ten sample injections per latex batch. The voltage was set at 20 V/cm and the camera was operated in the darkfield mode.

Surface Composition:
The samples were analyzed for surface composition using a Physical Electronics 5800 ESCA X-ray Photoelectron Spectrometer (XPS)\textsuperscript{v}. A region about 800 microns in diameter was analyzed. The samples were presented to the x-ray source by depositing the polymers onto double-backed conductive copper adhesive tape adhered to a stainless steel sample holder. The limits of detection of the technique are about 0.1 atom percent for the top 2-5 nm. The samples were analyzed for composition on a TJA IRIS ICP (inductively coupled plasma) using matrix-matched standards\textsuperscript{v}. The samples were prepared for analysis by weighing 1.0 gram of dried latex into a platinum crucible and 0.6 grams of 50/50 Lithium Tetraborate/Lithium Metaborate flux were added to the sample. The sample was placed in a furnace with a fluxing program (300 °C/1hrs, 600 °C/4hrs, 950 °C/40min). 15 ml of 50 % HCl was added and heated on a hot plate until dissolved. The sample was transferred to a 100 mL plastic volumetric, 0.5 mL of concentrated HF was added, and it shook overnight. 7.5 mL of 4% H\textsubscript{3}BO\textsubscript{3} solution was added to neutralize any excess HF. 1 mL of 5% Triton X-100 was added as a wetting agent and the sample was brought to volume with DI water.

Analysis of Residual PDMS Macromer in the Aqueous Phase:
Sample preparation: 30 mL of each latex sample was placed in a PTFE ultracentrifuge tube. The samples were placed in a Beckman L-60
Ultracentrifuge and ran at 20,000 rpm for 1 hour under vacuum at < 200 mTorr at ambient temperature. The samples were then removed from the centrifuge and the aqueous phase was collected via pipette for analysis. A silicon standard and blank were also prepared. A 50 µg/mL silicon standard was prepared by the following procedure: pipet 5.0 mL of the 1000 µg/mL silicon solution into a 100 mL volumetric flask, add 2.0 mL of a 1% Triton X-100 solution, add 2.0 mL conc. HNO₃, and dilute with DI water to volume. A blank was prepared by the following procedure: pipet 2.0 mL of a 1% Triton X-100 solution into a 100 mL volumetric flask, add 2.0 mL conc. HNO₃, and dilute with DI water to volume.

Sample analysis: The standard, blank, and samples were ran on a Thermo Jarrell Ash IRIS ICP. The instrument was calibrated at the silicon wavelength, 251.6 nm, using the standard and blank solutions. A solution containing 20 µg/mL of lutetium was split into the standard, blank, and sample solution lines and used as an internal standard (a ratio of analyte to internal standard intensity was applied to compensate for fluctuations due to sample introduction and matrix differences). The lutetium wavelength of 261.5 nm was used. The sample solutions were introduced to the instrument by direct aspiration to obtain a value for Si concentration in µg/mL.
III. Results

As described in detail in the experimental section, eight different batches of polystyrene core latex were synthesized. The relevant characteristics of these 8 batches (seed size, particle size, zeta potential, weight average molecular weight, molecular weight polydispersity, gel content, and glass transition temperature) are summarized in Table 2. Monodisperse seed latexes of two sizes were made, 140 nm for batches 1 through 4 and 120 nm for batches 5 through 8.

Reactions 1 and 2 were styrene controls. Both reactions entailed the polymerization of styrene onto 140 nm seed particles. The gel content and glass transition temperatures were unaffected by the change in particle size. Figures 6 and 7 display DSC scans for the 300 and 400 nm particles. The glass transition curve had a smooth sigmoidal shape indicative of a well-formed polymer, and the onset $T_g$ of 98-100°C is close to that reported in the Polymer Handbook for poly(styrene). The change in particle size affected the molecular weight, polydispersity, and zeta potential. The molecular weight of the 400 nm control was double that seen in the 300 nm control. The PDI also increased with size. The absolute value of the zeta potential was lower in the 400 nm particles. As seen in Figures 4 and 5, both reactions produced spherical and relatively monodisperse particles.
# Table 2: Characterization of Semi-continuous Seed Emulsion Polymers

<table>
<thead>
<tr>
<th>Rxn</th>
<th>Polymer (w/w)</th>
<th>Size</th>
<th>Particle Size</th>
<th>Mw</th>
<th>Gel Content (%)</th>
<th>Onset Tg (°C)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300nm PS Control</td>
<td>138±26</td>
<td>292±34</td>
<td>175.0</td>
<td>4.9</td>
<td>97.9</td>
<td>-76.3±0.3</td>
</tr>
<tr>
<td>2</td>
<td>400nm PS Control</td>
<td>139±30</td>
<td>411±45</td>
<td>407.8</td>
<td>6.5</td>
<td>99.7</td>
<td>-59.5±2.4</td>
</tr>
<tr>
<td>3</td>
<td>300nm PS/DVB (98.6/1.4)</td>
<td>141±32</td>
<td>304±33</td>
<td>n/a</td>
<td>n/a</td>
<td>95.5</td>
<td>-76.3±0.2</td>
</tr>
<tr>
<td>4</td>
<td>400nm PS/DVB (98.6/1.4)</td>
<td>137±31</td>
<td>415±46</td>
<td>n/a</td>
<td>n/a</td>
<td>87.4</td>
<td>-58.7±1.1</td>
</tr>
<tr>
<td>5</td>
<td>350nm PS Control</td>
<td>119±17</td>
<td>351±38</td>
<td>584.0</td>
<td>7.3</td>
<td>100.8</td>
<td>-67.7±0.4</td>
</tr>
<tr>
<td>6</td>
<td>350nm PS/PDMS (98/2)</td>
<td>123±19</td>
<td>342±40</td>
<td>493.6</td>
<td>7.4</td>
<td>96.6</td>
<td>-76.6±0.8</td>
</tr>
<tr>
<td>7</td>
<td>350nm PS/PMMA (90/10)</td>
<td>121±16</td>
<td>318±42</td>
<td>195.5</td>
<td>3.0</td>
<td>101.7,118.0</td>
<td>-55.2±1.2</td>
</tr>
<tr>
<td>8</td>
<td>350nm(PS/PMMA)/PDMS (88/10/2)</td>
<td>120±19</td>
<td>319±25</td>
<td>207.4</td>
<td>3.4</td>
<td>102.9,116.6</td>
<td>-60.0±0.2</td>
</tr>
</tbody>
</table>
Figure 4. SEM of 292 nm polystyrene particles.

Figure 5. SEM of 411 nm polystyrene particles.
Figure 6. Differential scanning calorimetry thermogram of 300 nm PS control latex.

Figure 7. Differential scanning calorimetry thermogram of 400 nm PS control latex.
In batches 3 and 4, the effect of the addition of DVB was evaluated. 1.4% weight percent DVB was incorporated in the monomer feed for reactions 3 and 4 and the particles were grown to nominally 300 and 400 nm in size, respectively. The incorporation of DVB had little effect on the particle size, glass transition temperature, and zeta potential. The glass transition curves, shown in Figures 10 and 11 had the same shape characteristics as the controls; the absolute value of the onset Tg was minimally elevated. As expected the gel content of the polymer was dramatically affected by the incorporation of a difunctional monomer. The gel content was greater than 85% in both materials. The incorporation of DVB does not appear to have had a significant effect on the morphology of the particles. The particles, shown in Figures 8 and 9, appear to be relatively monodisperse in size.
Figure 8. SEM of 304 nm polystyrene particles crosslinked with 1.4% DVB.

Figure 9. SEM of 415 nm polystyrene particles crosslinked with 1.4% DVB.

Figure 10. Differential scanning calorimetry thermogram of 300 nm PS/DVB latex.
Figure 11. Differential scanning calorimetry thermogram of 400 nm PS/DVB latex.

In reactions 5 and 6, 350 nm PS and PS/PDMS core/shell particles were made from 120 nm seed particles. The ultimate particle size, molecular weight, polydispersity, and gel content were not significantly affected by the addition of PDMS. The molecular weight in batches 5 and 6 were both over 400,000 and were comparable to that of the 400 nm PS control. The glass transition and zeta potential were affected by the incorporation of PDMS to the outer shell. The glass transition curves are shown in Figures 14 and 15. The glass transition for the PS particles was similar to the controls. The glass transition temperature was 4°C lower for the core-shell particles incorporating PDMS macromer. A single glass transition was observed. By incorporating PDMS, the absolute zeta potential was increased by 10 mV. The surface composition for the batches in which PDMS macromer was incorporated into PS and PS/PMMA particles is summarized in Table 3. XPS is a technique used to examine the top 2-5 nm of a given surface. XPS was unable to detect silicon in the surface of the PS/PDMS
particles. ICP is a common technique used for elemental analysis of the bulk of a material. ICP analysis confirmed the presence of silicon in the particles at 0.1% in the aqueous phase at 6.9 ppm.

**Table 3.** Characterization of Incorporation of PDMS Macromer in PS and PS/PMMA Particles

<table>
<thead>
<tr>
<th>Analysis</th>
<th>PS/PDMS</th>
<th>PS/PMMA/PMMA-PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS Added</td>
<td>1.67%</td>
<td>2.00%</td>
</tr>
<tr>
<td>Si Added</td>
<td>0.51%</td>
<td>0.61%</td>
</tr>
<tr>
<td><strong>Si Detected</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XPS</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>ICP-particles</td>
<td>0.1%</td>
<td>0.1%</td>
</tr>
<tr>
<td>ICP-aqueous</td>
<td>6.9 ppm</td>
<td>4.4 ppm</td>
</tr>
</tbody>
</table>

Figures 12 and 13 display the particles prepared in reactions 5 and 6. The particles have self-assembled in a structured lattice. This is indicative of highly monodisperse, spherical particles. The addition of PDMS did not adversely affect the morphology of the core/shell particles.
Figure 12. SEM of 351 nm polystyrene particles.

Figure 13. SEM of 342 nm polystyrene/PDMS particles.

Figure 14. Differential scanning calorimetry thermogram of 350 nm PS latex.
Figure 15. Differential scanning calorimetry thermogram of 350 nm PS/PDMS latex.

In reactions 7 and 8, 320 nm PS/PMMA and (PS/PMMA)/PDMS core/shell particles were made. The particle size, molecular weight, polydispersity, and gel content were similar for the two reactions. The glass transition and zeta potential were perturbed by the addition of a PMMA and PMMA-PDMS shell. The DSC curves of the particles from both reactions, shown in Figures 18 and 19, exhibited long, broad transition zones as compared with the styrene homopolymers. Such broad transitions are indicative of a substantially miscible mixture of copolymers of differing composition and molecular weight. One might interpret the data as being indicative of two glass transitions; one at 100°C and another at 115°C. The zeta potential measurements gave two significant results. First, with the addition of PDMS to the reaction, the absolute zeta potential was increased by 5 mV. Second, the zeta potential was lower for the PS/PMMA particles than for similar PS particles. The (PS/PMMA)/PDMS latex was similar to the PS/PDMS latex in that XPS was unable to detect silicon in the top 2-5 nm of the surface. ICP
analysis confirmed the presence of silicon in the particles at 0.1% and in the aqueous phase at 4.4 ppm.

As seen in Figures 16 and 17 the core/shell particles were spherically-shaped, but the surface does not appear as smooth as those in the PS controls. However, the particles still appear monodisperse and to some degree still arrange in a structured lattice.

**Figure 16.** SEM of 318 nm polystyrene/PMMA core/shell particles.

**Figure 17.** SEM of 319 nm polystyrene/PMMA/PDMS core/shell particles.
**Figure 18.** Differential scanning calorimetry thermogram of 320 nm PS/PMMA core/shell latex.

**Figure 19.** Differential scanning calorimetry thermogram of 320 nm PS/PMMA/PMMA-PDMS core/shell latex.
In reaction 9, the intent was to repeat the same recipe used for PS particles to make similar PMMA particles. Instead, the polymerization yielded PMMA particles that were much smaller than those produced with styrene. The seed particles were 81 nm in size and the ultimate particles were 174 nm, nearly half the size of those produced with styrene. Reactions 10-12 were carried out in an effort to see the effects of varying seed monomer and reaction temperature on particle size.
IV. Discussion

Seed Stages

The critical micelle concentration (CMC) of a surfactant or amphipathic molecule is the concentration above which molecules aggregate to form micelles. Below this concentration surfactant molecules are not associated and micelles are not formed. For classical emulsion polymerization recipes in which nucleation is pictured as being nucleated in micelles, the surfactant concentration is typically 10 x CMC. The initial seed stages of the polymerizations in this research were all run at surfactant concentrations well below the critical micelle concentration of SLS. The CMC of SLS is 8x10^{-3} M^{25} and we were operating at 9x10^{-4} M. Thus, the nucleation was not mediated by micelles and may have proceeded by homogeneous nucleation in the aqueous phase (see section I). In a typical emulsion polymerization system, the number of polymer particles formed is a function of the surfactant^{26} and initiator^{15,27} concentration. As compared to a classical emulsion polymerization recipe, we were operating in a system with 1/10 the surfactant and four times the initiator concentration. The recipe we used resulted in seed particles that were twice as large as those typically obtained in emulsion polymerizations carried out with SLS in excess of 10^{-3} M. With no micelles present, the monomer molecules in the aqueous phase are initiated by free radicals. This results in oligomeric chains with, in our case, sulfate end groups. The oligomers grow to a critical size and then precipitate out of solution to nucleate polymer particles. The number of particles formed depends on the number of these primary particles that accrete to form larger secondary particles and the degree to which new oligomeric chains are captured by existing particles and do not nucleate new particles.

The diffusion capture theory proposed by Fitch and Tsai^{28} describes this process of controlled nucleation and capture of oligomers. Their theory states that each oligomer molecule initiated in the aqueous phase will form a new particle if it reaches some threshold degree of polymerization, P, before being captured by an existing particle. The time it takes to grow to this size is given by:
\[ t_n = \frac{P}{k_p[M]} \]

where \( k_p \) is the propagation rate constant and \([M]\) is the monomer concentration.

**Figure 20.** Schematic Representation of Oligomer Precipitating to Form a New Particle (From *Polymer Colloids* (Ed. R. M. Fitch), Plenum Press, 1971, p. 94.)

The particle size was also controlled by dispersant-limited agglomeration.\(^6\) With such a high concentration of initiator, a large number of primary particles are initially formed. The theory of dispersant-limited agglomeration states that the resulting particles are formed by the agglomeration of much smaller, primary particles. The primary particles will accrete and the total surface area of the particles is reduced to an area that can be fully covered by the available dispersant. Thus our seed particles were much larger than those seen in typical emulsion polymerizations.

The initiator concentration determines the number of free radicals in the aqueous phase and thus, the number of particles initially formed is a function of the initiator concentration, \( E^{3/5} \).

\[ N = F(p/\mu)^{2/5}(A_s[E])^{3/5} \]

Where \( N \) is the number of particles, \( p \) is the rate of radical production, \( \mu \) is the rate of volume increase of a particle, \( A_s \) is the area occupied by one emulsifier molecule, \([E]\) is the concentration of emulsifier, and \( F \) is a numerical factor (between 0.37 and 0.53). As the concentration of initiator increases, the rate of
radical production and the number of particles formed will increase. In the present study, the amount of initiator added was slightly different for batches 1-4 and batches 5-8. This may explain why two different seed sizes were obtained. Batches 5-8 employed a higher initiator concentration and this may have led to the formation of a smaller seed particle.

The seed particles for all eight latex batches were prepared by the same general procedure. The concentration of monomer, surfactant, and initiator was held constant in batches 1-4 and in batches 5-8, respectively, and the seed stage of the polymerization was carried out over a period of 30 minutes. The formation of the seed is important in that it provides a specific number of polymer particles and given no nucleation of new particles the seed particles can be grown to a size that can be predicted by the amount of monomer subsequently added. When this is the case, any additional monomer will be incorporated in the existing particles. Particle size was monitored by removing latex samples at 30 minute intervals through out the polymerization.

Semi-continuous Growth

The semi-continuous process can be viewed as extending interval II in a Harkins type mechanism for polymerization with added monomer imbibed at a constant rate into existing polymer particles. In interval II, there is a constant number of particles and continuous or incremental addition of monomers maintains a nearly constant concentration of monomer in the polymer particles. As the polymerization progresses, the monomer droplets become exhausted and disappear. This marks interval III in which only monomer swollen polymer particles and aqueous phase are present. The growth of the polymer particles was monitored by intermittent removal of samples for particle size measurements. The growth of particles was similar for systems in which the added monomer was comprised of DVB/styrene or PDMS macromer/styrene mixtures. The monomer feed rate can affect particle size and growth because in monomer flooded conditions secondary nucleation can occur by initiation of
polymer chains in the aqueous phase. Our polymerizations were run under monomer starved conditions, in which secondary nucleation was unfavorable.

PS and PS/DVB Latexes (Batches 1-4)

The intent of these batches was to synthesize 300 and 400 nm PS particles and then to repeat the syntheses with the incorporation of DVB. The differences resulting from particle size and crosslinking with DVB were examined. In batches 1 and 2, the change in particle size did not affect the gel content or glass transition characteristics of the particles. We did not expect these properties to change because the particles size was the only variable between the two batches. The increase in particle size did affect the molecular weight and polydispersity of the polymer in the particles. The molecular weight of the 400 nm control particles was twice that of the 300 nm particles. The polydispersity index (PDI) also increased in the 400 nm particles. The PDI is the ratio of the weight average to the number average molecular weight for a given sample. For a free-radical polymerization, the PDI of a system considered to have a narrow molecular weight distribution is typically ~2.5. The PDI of both samples was considerably higher than this value. When a polymerization is carried out in the presence of already form particles (seeds), the new monomer may form new polymer chains or may be incorporated, by chain transfer, as grafted chains on pre-existing polymer molecules. This will serve to dramatically increase the molecular weight and PDI of the final polymer.\textsuperscript{29,30}

The zeta potential, or surface charge, was also affected by the particle size. Zeta potential is a measurement of the electrophoretic movement of particles and is defined as the potential of a particle or colloid in an electric field at the shear plane. The shear plane, or surface of shear, is an imaginary surface separating the layer of immobilized liquid from the rest of the mobile liquid. In a typical emulsion polymerization, the possible sources of surface charge are the surfactant, initiator, and ionic comonomer, if present.\textsuperscript{31} In an electric field, the latex particles are attracted and will migrate toward an oppositely charged electrode. The rate of migration of the particle is a function of its mobility. The
Particle mobility is related to zeta potential through the Huckel equation: $u = (2\varepsilon\zeta)/3\eta$ where $u$ is the electrophoretic mobility, $\varepsilon$ the permittivity, $\zeta$ the zeta potential and $\eta$ the viscosity. The Zeta Reader instrument we used in taking our measurements actually measures the mobility of the particles. When operating in darkfield mode, software imbedded with the instrument calculates the zeta potentials based on the Huckel equation. The Huckel equation is useful in the limit of relatively small particle radius and weak ionic strength. The Helmholtz-Smoluchowski equation describes the upper limit of relatively large particle radius and strong ionic strength. The Huckel and Helmholtz-Smoluchowski equations are related through a constant factor equal to $2/3$. We found that the ionic strength of solution and radius of our particles fall between these two limiting cases. Zeta potential is used to measure the surface charge of latex particles. A larger absolute zeta potential value is indicative of a more stable system with respect to coagulation.\textsuperscript{32} The absolute value of zeta potential was higher for the 300 nm styrene particles. The initiator and initial surfactant concentrations were the same for batches 1 and 2. The amount of monomer added in the feed stage was the factor differentiating the recipes. Thus, the larger 400 nm particles will have fewer ionic species per unit surface area or a lower surface charge. As we expected, the 400 nm particles had a lower zeta potential. As a general rule the smaller the particle the more stable the dispersion.\textsuperscript{33}

The effect of the incorporation of 1.4 wt.% DVB was also examined in batches 3 and 4. DVB is commonly used as a crosslinking agent to help increase the hardness and robustness of a polymer. The addition of DVB did not affect the particles size, glass transition characteristics, particle morphology, or zeta potential of the styrene particles. Using a semi-continuous feed, we were able to control the rate at which monomer was added to the particles resulting in a random copolymerization of styrene and DVB. Thus, the size, shape, and charge of the particle should not have been greatly affected. The DVB greatly increased the gel content of the particles, as would be expected from a bifunctional monomer. The gel content is a viable comparison between the polymers as the crosslinked polymer is considered to be of infinite molecular
weight. A crosslinked polymer acts as one molecule and thus, the percent gel content is a measure of the degree or extent of crosslinking in a given polymer. Both polymers contained greater than 85% gel content. The notable results from these four latex batches were that the increase in particle size served to decrease the zeta potential and that while the incorporation of DVB did not affect the surface properties, it served to greatly increase the gel content of the particles.

PS and PS/PDMS Latexes (Batches 5 and 6)

The intent of these batches was to synthesize a reference PS latex in batch 5 and then to repeat the syntheses with the incorporation of PDMS macromer in the particle surface in batch 6. The particle size, molecular weight, polydispersity, and gel content were unaffected by the addition of PDMS to the particles. The incorporation of PDMS did affect the glass transition characteristics and zeta potential of the particles. The glass transition was 4°C lower in batch 6 with PDMS incorporated. This is likely a result of plasticization accompanying the addition of the macromer. The most significant difference attributed to the addition of PDMS was the difference in zeta potential. The zeta potential was 10 mV higher in the particles with PDMS. This is a significant result because we were specifically interested in the particle surface charge.

The extent to which the PDMS was incorporated in the particles was also examined. Silicon was used as the tag to determine where and how much PDMS was in the particles. XPS analysis did not find any silicon in the top 2-5 nm of the surface of particles from batch 6. When we attempted to cast films from the batch 6 latex, pronounced dewetting was observed. Such effects are typically seen when there is PDMS in the aqueous phase. The particles and aqueous phase of batch 6 were analyzed for silicon. Silicon was found to be present in the aqueous phase and the bulk of the particles, but not at the particle surface. The aqueous phase was found to contain silicon on the part per million levels, accordingly most of the PDMS was incorporated into the particles. However, less than 20% of the PDMS macromer was incorporated in the
particles. The balance of the PDMS macromer was apparently lost from the system. Although our intent was to add PDMS to the surface of the particles; given that ICP validated the presence of Si in the bulk of the particle while XPS analysis detected no Si at the particle surface, it must be assumed that the PDMS chain segments migrated into the particles so as not to have low surface energy chain segments at the aqueous interface.

PDMS is an unusual molecule. It both repels and wets with water, ostensibly because the oxygens in the siloxane backbone hydrogen bond with water. When PDMS finds itself at an air/polymer or air/water interface, it spreads and dramatically lowers the surface energy. However, when placed at a water/polymer interface the PDMS chain segments migrate into the particle and away from the water interface. When incorporated in our PS particles, the PDMS increased the zeta potential of the particles. The higher zeta potential is indicative of higher surface charge or the more ionizable groups per surface area. While it is difficult to be absolutely certain as to why the zeta potential changed, we speculate that it is due to an enhancement of the number of ionizable surface groups that accompanies the migrations of the PDMS chain segments into the bulk of the particle. With the migration of PDMS chain segments into the particles, more hydrophilic sulfate groups from the initiator and surfactant populated the surface. Consequently, the zeta potential of the particles increased.

PMMA Latex (Batch 9)

It was our intent to make PMMA particles similar to those in batches 1 and 2 using an analogous procedure. Instead, both the seed and final particle size were much smaller, nearly half the size, than those in the targeted case of styrene. There is limited literature on the synthesis and kinetics of the semi-continuous emulsion polymerization of MMA particles. Sajjadi et. al.\textsuperscript{20} studied the effect of different variables on the particle size and particle number in the semibatch emulsion polymerization of MMA. Using a similar system to that which we employed in batch 9 with SLS as surfactant, KPS as initiator, but a
50°C reaction temperature, he found that when operating under monomer starved conditions a large number of very small particles were formed. Monomer starved conditions were described as a system in which the monomer distribution ratio (monomer in initial charge/total monomer added) was 0.20 or less. Our process had a monomer distribution ratio of 0.14 (50 g seed/362 g total feed), well within the range of operating under a monomer starved condition. We adjusted our procedure by decreasing the amount of seed monomer to 25 g and then to 12.5 g, neither of which yielded the desired result. As we decreased the amount of seed monomer, we were actually driving our process toward an increasingly starved condition and a larger number of particles. To better understand the behavior of MMA and styrene systems, the solubility of the monomers was examined. The solubility of MMA and styrene in water are 0.15 M and 0.005 M respectively. Thus, MMA is sparingly water-soluble and styrene is water-insoluble. For sparingly water-soluble monomers such as MMA, the water phase can delay the formation of monomer droplets because of its solubility. This results in appreciably more nucleation in the aqueous phase. Therefore in a given period of time, this may explain why a larger number of smaller particles were formed. In hindsight, the wrong steps were taken to achieve the desired increase in particle size. In order to accommodate the behavior of MMA monomer, the recipe would have to be drastically altered. Since we were limited in the flexibility of our recipe design, we took the more expedient path and opted to make core/shell particles to achieve the desired effect of PMMA.

PS/PMMA and PS/PMMA/PMMA-PDMS Latexes (Batches 7 and 8)

As a consequence of the results obtained in batch 9, we decided to synthesize core/shell particles (PS core/PMMA shell) to simulate the effects of a system with PMMA at the particle surface.

There is a great deal of literature on the synthesis of core/shell composite latex particles. However, there is limited research involving styrene as the core and MMA as the shell. Winnik et. al.34 used electron microscopy to study
PS/PMMA and PMMA/PS core/shell latex particles. Their recipe used 5PS/2PMMA resulting in 475 nm particles. The scope of their study did not include the synthesis of the particles. Dimonie et. al.\textsuperscript{35} studied the particle morphology of composite latexes of a series of acrylate esters (including MMA) on PS seeds. They found that when the monomer was added continuously under starved conditions that a near complete core/shell morphology could be obtained. In a related study Ferguson et. al.\textsuperscript{36} examined the use of polystyrene seeds in the synthesis of PS/PVAc latexes. He found that for PS seeds with a radius much less than 200 nm the formation of new particles could be avoided. All of these studies were relevant to our work, but none of them addressed the underlying behavior of MMA/styrene systems. To understand the behavior of MMA/styrene systems, the solvent and polymer solubility parameters were examined. The solubility parameters, $\delta$ (MPa)$^{1/2}$, of MMA and styrene solvent and polymer are 18.9 and 22.7 and 19.1 and 22.5 respectively.\textsuperscript{37} PMMA and PS are known to be mutually immiscible. Thus the polymers should form two distinct regions resulting in true core/shell particles. Though there is limited literature on styrene/MMA core/shell synthesis, there is considerably more on MMA/styrene systems. Lee et. al.\textsuperscript{38} studied the kinetics of MMA/styrene by soapless emulsion polymerization. He proposed a three region core/shell model in which the propagation and termination rate constants, gel effect, and glassy effect were considered respectively. Rudin et. al.\textsuperscript{39} studied the control of MMA/styrene core/shell morphology. He discussed the thermodynamic and kinetic variables that control core/shell structure such as particle surface polarity, monomer ratio, core particle size, mode of monomer addition, and degree of crosslinking. Both studies demonstrate the compatibility of the monomers.

As we were confident in our control of particle size and number, we made seeds, or cores, of PS for batches 7 and 8 in a similar manner to that used to prepare particles in batches 5 and 6. The intent of these batches was to make a PMMA shell latex in batch 7 and then to repeat the procedure with the incorporation of MMA and PDMS macromer in the shell in batch 8. The styrene seed particles in batches 5 and 6 were 120 nm in size, nearly twice as large as
those produced with MMA in batch 9. We then added MMA in the monomer feed to obtain a PMMA shell. The core/shell particles were much larger than the seed particles and thus, could still serve to impart the desired acrylic properties. Using the core/shell method we were successful in obtaining 320 nm sized particles.

The addition of PMMA to a PS core affected the molecular weight and polydispersity of the particles. The PS/PMMA particles had much lower molecular weights than the similar PS particles. The PS/PMMA systems had relatively small PDI's ranging in values from 3.0-3.4 compared with those of PS at 7.3-7.4. This is probably a result of the polymerization of MMA in the aqueous phase with oligomeric chains being absorbed on the preformed PS core particles. Thus, there was not substantial grafting of new PMMA onto pre-existing PS chains. The addition of a PMMA shell also affected the glass transition characteristics of the resulting latexes. The PS/PMMA and PS-PMMA/PMMA-PDMS core/shell particles both exhibited marked broadening of the thermogram. This broadening may be interpreted as two glass transitions. We speculate this is the case for our particles as the glass transition temperatures of the homopolymers are close.

Zeta potential measurements of the PS/PMMA and PS/PMMA/PMMA-PDMS core/shell particles provided two significant results. First, the zeta potential increased by 5 mV with the incorporation of PDMS to the outer shell of the particles. The PDMS served to increase the particle surface charge. This is similar to what was seen in the PS/PDMS particles. Second, the zeta potential was lower for the PS/PMMA particles compared with similar PS particles. Using a similar argument to that put forth to explain how redistribution of apolar polymer chain segments into the bulk of the particle enhanced the number of ionizable moieties at the polymer water interface, one could speculate that the hydrophilic acrylic chain segments are more disposed to be at the polymer water interface. Accordingly, the number of ionizable moieties at the polymer water interface is not enhanced when MMA is incorporated in the shell.
V. Conclusions

The synthesis of styrene and methyl methacrylate polymers by semi-continuous seeded emulsion polymerization was investigated. Similar styrene seed particles were made for each batch and monodisperse 300 and 400 nm sized particles were synthesized. The properties, morphology, and surface charge of the resulting particles were studied and four significant results were found. First, the addition of DVB served to significantly increase the particle gel content of the particles. This result was, of course, expected. Second, increasing particle size served to decrease the zeta potential of the particles. This was understood by fewer charge groups per unit surface area as particle size increased. Third, incorporating PDMS macromer in the shell of particles served to increase the zeta potential in both PS/PDMS and PS/PMMA-PDMS particles. Lastly, the addition of a PMMA shell to PS core particles also resulted in a decrease in zeta potential. The results relative to these systems was unexpected and was attributed to redistribution of surface groups with an increase in the number of ionizable moieties at the polymer/water interface with the incorporation of hydrophobic (siloxane) chain segments and a decrease in the number of ionizable moieties at the polymer/water interface with the incorporation of hydrophilic (acrylic) polymer chains.
End Notes

i SEM analysis was performed by Witold Niedzialkowski at Xerox Corporation.

ii DSC analysis was performed by Kim Lander at Xerox Corporation.

iii GPC analysis was performed by Kim Lander at Xerox Corporation.

iv XPS analysis was performed by Mike Mehan at Xerox Corporation.

v ICP analysis was performed by Dennis Stearns at Xerox Corporation.

vi ICP analysis of aqueous phase was performed by Mark Monachino at Xerox Corporation.
References


