EMULSION POLYMERIZATION USING SWITCHABLE SURFACTANTS

By

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Abstract

The work presented herein focuses on expanding the use of CO₂-triggered switchable surfactants in emulsion polymerization of hydrophobic and hydrophilic monomers. Bicarbonate salts of the following compounds were employed as surfactants in the emulsion polymerization of styrene, methyl methacrylate (MMA) and/or butyl methacrylate (BMA): N’-hexadecyl-N,N-dimethylacetamidine (1a), N’-dodecyl-N,N-dimethylacetamidine (2a) and N’-(4-decylphenyl)-N,N-dimethylacetamidine (3a). A systematic study of the effects of surfactant and initiator concentrations and solids content on the resulting particle size and ζ-potential was carried out, showing that a wide range of particle sizes (40 – 470 nm) can be obtained. It was found that as the basicity of the surfactant decreased, the particle size generated from emulsion polymerization increased. Destabilization of these latexes did not require the addition of salts and was carried out using only non-acidic gases and heat. It was shown that solids content, temperature, particle size and surfactant basicity greatly affect the rate of destabilization of latexes. The area occupied by N’-dodecyl-N,N-dimethylacetamidinium acetate on PMMA particles was determined to be 104 Å². The monomer-D₂O partition coefficient of 2a was determined to be 21 for styrene and 2.2 for MMA. The monomer-D₂O partition coefficient of the bicarbonate salt of 2a was determined to be 1.2 for styrene and 0.85 for MMA. An initial assessment of the use of switchable surfactants in the generation of inverse emulsions was carried out. It was determined that butylated polyethyleneimine (BPEI) can successfully stabilize inverse emulsions of cyclohexane and aqueous 2-(dimethylamino)ethyl methacrylate. Upon CO₂ introduction, this emulsion separates into two distinct phases.
Acknowledgements

“What you’ve done is not yours alone...”

So this is it. This marks the end of an important chapter in my life, and it’s been quite a ride.

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...*what you've done echoes on and on*”
- HR!
# Table of Contents

Abstract ........................................................................................................................................... i

Acknowledgements .......................................................................................................................... ii

Table of Contents ............................................................................................................................. iv

List of Tables ...................................................................................................................................... vii

List of Figures ..................................................................................................................................... viii

List of Symbols and Abbreviations .................................................................................................... x

List of Numbered Compounds ........................................................................................................ xii

Chapter 1  Introduction ....................................................................................................................... 1

1.1  Surfactants .................................................................................................................................... 2
    1.1.1 Micelles and the Critical Micelle Concentration (CMC) ......................................................... 3
    1.1.2 Surfactant Hydrophile-Lipophile Balance (HLB) ................................................................. 4
    1.1.3 Surfactant Solubility and Partitioning ..................................................................................... 5
    1.1.4 Surfactant Adsorption at Interfaces ......................................................................................... 5
    1.1.5 Switchable Surfactants ........................................................................................................... 6

1.2  Colloidal Stability ....................................................................................................................... 10
    1.2.1 Electrostatic Stabilization ...................................................................................................... 11
    1.2.2 Steric Stabilization ............................................................................................................... 13

1.3  Polymers ...................................................................................................................................... 14
    1.3.1 Free Radical Polymerization ................................................................................................. 14
    1.3.2 Properties of Polymers ......................................................................................................... 15

1.4  Emulsion Polymerization ........................................................................................................... 17
    1.4.1 Mechanism of Emulsion Polymerization\textsuperscript{21,25,26} ..................................................... 17
    1.4.2 Determination of Particle Size\textsuperscript{e} ............................................................................ 20
    1.4.3 Applications to Polymer Colloids ........................................................................................... 22

1.5  Latex Destabilization .................................................................................................................. 22
    1.5.1 Altering Latex pH .................................................................................................................. 23
1.5.2 Temperature Effects ................................................................. 24
1.5.3 Aggregation Rate ............................................................... 25

1.6 Inverse Emulsions and Inverse Emulsion Polymerization ............... 27

1.7 Project Overview and Objectives .................................................. 28

Chapter 2 Experimental Methods ..................................................... 30

2.1 Materials .................................................................................. 30

2.2 Emulsion Polymerization ............................................................ 32

2.3 Latex Destabilization .................................................................. 34

2.4 Latex Characterization ................................................................ 34

2.5 Assessing Surfactant Switchability ................................................. 35

2.6 Conversion to Bicarbonate ........................................................... 36

2.7 Determination of Surfactant Partitioning Behaviour ....................... 37

2.8 Determination of Surfactant Coverage .......................................... 38

2.9 Inverse Emulsion Generation and Polymerization ......................... 40

2.9.1 Using Surfactant 1b .............................................................. 40

2.9.2 Using Compound 6 .............................................................. 41

Chapter 3 Emulsion Polymerization and Latex Destabilization using Alkyl Amidine Switchable Surfactants ..................................................... 42

3.1 Emulsion Polymerization ............................................................. 42

3.1.1 Choosing an Initiator ............................................................. 42

3.1.2 Styrene Polymerization .......................................................... 44

3.1.3 Methyl Methacrylate and Butyl Methacrylate Polymerization .... 46

3.1.4 Long Term Latex Stability ...................................................... 49

3.2 Latex Destabilization ................................................................. 51

3.2.1 The Effect of Surfactant Concentration and Initial Particle Size .... 52

3.2.2 The Effect of Polymer Concentration and Temperature ............... 59

3.3 Determining Surfactant Partitioning Behaviour ............................... 61

3.4 Determining Particle Coverage ................................................... 63
Chapter 4  Emulsion Polymerization and Latex Destabilization using Alkylphenyl Amidine and Tertiary Amine Switchable Surfactants ........................................ 70

4.1 Surfactant Switchability ................................................................. 70

4.2 Emulsion Polymerization .............................................................. 75
   4.2.1 Initiator Choice ........................................................................ 75
   4.2.2 Methyl Methacrylate Polymerization ....................................... 75
   4.2.3 Effect of Initiator Type, Additives and CO₂ Pressure on Particle Size ...... 79
   4.2.4 Long Term Latex Stability ............................................................ 82

4.3 Latex Destabilization ..................................................................... 83
   4.3.1 Destabilization and the Change in ζ-Potential ......................... 84
   4.3.2 Effect of Additives on Destabilization .................................... 86

4.4 Conclusions .................................................................................. 87

Chapter 5  Inverse Emulsion Polymerization ........................................ 90

5.1 Generation of a Stable Inverse Emulsion Using 1b ................................ 91

5.2 Generation of a Stable Inverse Emulsion Using Compound 6 .......... 95

5.3 Inverse Emulsion Polymerization of DMAEMA ............................... 97

Chapter 6  Conclusions and Recommendations ................................... 99

6.1 Conclusions .................................................................................. 99

6.2 Future Work and Recommendations .............................................. 100

References .......................................................................................... 103

Appendix A  A Study of the Interactions Between Two PMMA Particles using DLVO Theory ................................................................. 108

Appendix B  Key Spectra and Data Tables ............................................. 113
List of Tables

Table 3.1 Stability of PMMA latexes formed using 1b and different azo-based initiators.\(^a\) .................................................................................................................................................. 43

Table 3.2 Variation in particle size and \(\zeta\)-potential of polystyrene latexes using different solid contents, surfactant concentrations and initiator concentrations.\(^a\) ................. 46

Table 3.3 Variation in particle size and \(\zeta\)-potential of PMMA latexes using different solid contents, surfactant concentrations and initiator concentrations.\(^a\) ..................... 47

Table 3.4 Variation in particle size and \(\zeta\)-potential of PBMA latexes using different solid contents, surfactant concentrations and initiator concentrations.\(^a\) ......................... 48

Table 3.5 Assessment of the long term stability of PMMA latexes stabilized by 2b that are exposed to air and those that were saturated with \(\mathrm{CO}_2\) for 30 min once a day for 7 days.\(^a\) .................................................................................................................................................. 50

Table 3.6 Variation in \(\zeta\)-potential with time during destabilization (sparging with air and heating to 65 °C) of the PMMA latex formulated according to conditions in Table 3.3, entry 11 (23.5 wt % MMA, 0.07 mol % 2b, 0.07 mol % 3).\(^a\) ........................................ 57

Table 3.7 Percentage of 2a and 2b partitioned into a D\(_2\)O phase from the monomer phase when the monomer phase was styrene or MMA. ................................................................. 63

Table 4.1 Variation in particle size and \(\zeta\)-potential of PMMA particles synthesized using different concentrations of 2b, 3b or 4b and 3.\(^a\) .............................................................................................................................................. 78

Table 4.2 Variation in emulsion polymerization conditions and their effect on the particle size and \(\zeta\)-potential of the resulting PMMA particles.\(^a\) ................................................................................ 79

Table 4.3 Changing the conditions under which emulsion polymerization is carried out to promote the formation of <200 nm PMMA particles.\(^a\) ................................................................. 81

Table 4.4 Assessment of the long term stability of a latex synthesized according to the conditions in Table 4.1, entry 7 (13.5 wt % MMA, 0.25 mol % 3b, 0.25 mol % 3).\(^a\) .................. 82

Table 4.5 A list of amines with pKa\(_H\) values between 11 and 12. ................................................................. 89

Table 5.1 An overview of the typical components (oil phase, emulsifier and initiators) used in the inverse emulsion polymerization of acrylamide. .............................................................. 90

Table 5.2 Type of emulsion generated from an aqueous phase with different oil phases using surfactant 1b, as determined by the droplet test method.\(^a,b\) ................................................. 92

Table 5.3 Type of emulsion generated from an aqueous phase with different oil phases using surfactant 1b, as determined by the conductivity test method.\(^a\) .......................... 92
List of Figures

Figure 1.1 Schematic of a typical surfactant and examples of commonly used surfactants. ................................................................................................................................. 3

Figure 1.2 Switchable surfactants containing (a) ferrocenyl,19 (b) viologen18 and (c) azobenzene26 functionality. ....................................................................................................................................................... 8

Figure 1.3 CO2 switchable surfactants with (a) amidine,27,28,29,30 guanidine30,31 and tertiary amine30 head groups and long alkyl chain tails and (b) amidine head groups and PEG containing tails.28,29 .............................................................................................................................................. 9

Figure 1.4 DLVO plot for the interaction of two silica particles in water at pH = 6 and [NaCl] = 0.01 M. ................................................................................................................................. 13

Figure 1.5 The three steps in free radical polymerization ................................................................. 15

Figure 1.6 Schematic of the general mechanism of emulsion polymerization ................................. 19

Figure 1.7 Structures of some non-ionic surfactants of the (a) SpanTM and (b) TweenTM series used in inverse emulsion polymerization ........................................................................... 28

Figure 2.1 The setup for the determination of the partition coefficient of 2a between MMA and water ............................................................................................................................... 38

Figure 2.2 Structure of the surfactant used to determine the % coverage of surfactant on the surface of PMMA particles ................................................................................................. 39

Figure 3.1 Conversion versus time profile for the polymerization of MMA using 1.0 mol % 2b and 1.0 mol % 3 (- - -); MMA using 0.07 mol % 2b and 0.07 mol % 3 (—); styrene using 1.0 mol % 2b and 1.0 mol % 3 (•••); and BMA using 0.5 mol % 2b and 0.5 mol % 3 (—) ............................................................................................................................................... 49

Figure 3.2 Photograph of PMMA latexes (prepared using 23.5 wt % MMA, 2.0 mol % 2b and 1.0 mol % 3) after 17 days with (at left) bubbling of CO2 for 30 minutes each day for the first 7 days and (at right) no CO2 bubbling (vials were inverted for the photograph to show the increased viscosity of the sample which received no CO2 treatment).57 ........................................................................................................................................ 51

Figure 3.3 (a) Particle size distribution of a polystyrene latex synthesized using 0.5 mol % 2b and 0.5 mol % 3 after treating with air at 65 °C for 100 min (b) Volume percent of polystyrene aggregates over time in latexes containing various amounts of 2b and 3 (mol % 2b/mol % 3 (initial particle size)) after treating with air at 65 °C (23.5 wt % polystyrene).57 The curves are added to guide the eye. ................................................................................................................................. 53

Figure 3.4 Change in particle size with time during destabilization (sparging with air and heating to 65 °C) of latex formulated according to conditions in Table 3.3, entry 11 (23.5 wt % MMA, 0.07 mol % 2b, 0.07 mol % 3) monitored with the (a) Zetasizer ZS and (b) Mastersizer 2000.57 ................................................................................................................................. 56

Figure 3.5 Photograph of a PBMA latex (left) and a destabilized PBMA latex (right) ... 58

Figure 3.6 Volume % of PMMA particles stabilized by 2b below 1.0 µm over time after heating and bubbling with air at different (a) polymer concentrations (temperature is
constant at 65 °C) and (b) temperatures (polymer concentration is constant at 5 wt %). The decrease in ζ-potential over time corresponding to destabilization of PMMA particles at 80 °C is also shown.

Figure 3.7 SEM images of particles from (a) a PMMA latex stabilized with 2b and (b) a similar PMMA latex treated with air and heat to remove the CO₂. In both cases, the latex was prepared using 13.5 wt % MMA, 0.07 mol % 2b and 0.07 mol % 3 (scale is 5 µm).

Figure 3.8 Soap titrations of three latexes at different polymer concentrations: 20 g L⁻¹ (▲), 8.3 g L⁻¹ (◆) and 2.0 g L⁻¹ (●).

Figure 3.9 A plot of surfactant concentration versus polymer concentration in three different latexes to determine the maximum amount of 5 adsorbed by PMMA particles at the surfactant CMC.

Figure 4.1 The conductivity of solutions during CO₂/Ar cycles in 20 mL ethanolic solutions containing 200 µL of water and 0.4 mmol of either (a) 3a or (b) 4a and the change in conductivity of wet ethanolic solutions of 2a (■), 3a (▲) and 4a (●) at room temperature when (c) CO₂ followed by (d) Ar are bubbled through the solutions.

Figure 4.2 Volume percent of PMMA particles below 1 µm as a function of time during destabilization using air at 65 °C (◆), 40 °C (●) and room temperature (▲) in a latex synthesized according to the conditions in Table 4.1, entry 7.

Figure 4.3 Change in ζ-potential with time of latexes destabilized using Ar and heat (65 °C) for 15 min followed by 45 min at 65 °C without Ar bubbling. Initial latexes were synthesized using (a) 1.0 mol % 2b and 0.25 mol % 3, (b) 0.07 mol % 2b and 0.07 mol % 3, (c) 1.0 mol % 3a and 0.25 mol % 3 and (d) 1.0 mol % 4a and 0.25 mol % 3.

Figure 4.4 Change in ζ-potential with time during the destabilization of latexes synthesized (●) with no CTAB (Table 4.1, entry 14) and (■) with CTAB (0.016 mol % with respect to monomer, Table 4.3, entry 6) as a co-surfactant mixed with 4a.

Figure 5.1 Photographs of emulsions generated using surfactant 1b (at 2 wt % and 0.5 wt %), at 2:1 and 4:1 weight ratios of cyclohexane to 1 M DMAEMA_{aq} in the presence and absence of Span 60™.

Figure 5.2 Photographs showing the temperature stability of cyclohexane – 1 M DMAEMA_{aq} emulsions, with and without Span 60™ as a co-surfactant.

Figure 5.3 Photograph showing the destabilization of a cyclohexane : 1 M DMAEMA_{aq} emulsion (stabilized by 6) with CO₂.
# List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>∞</td>
<td>infinity</td>
</tr>
<tr>
<td>$z$-potential</td>
<td>zeta potential</td>
</tr>
<tr>
<td>AIBN</td>
<td>2, 2’-azobisisobutyronitrile</td>
</tr>
<tr>
<td>BMA</td>
<td>butyl methacrylate</td>
</tr>
<tr>
<td>BPEI</td>
<td>butylated polyethyleneimine</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>CMC</td>
<td>critical micelle concentration</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyl trimethylammonium bromide</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>deuterated water</td>
</tr>
<tr>
<td>DLVO</td>
<td>Derjaguin-Landau-Verway-Overbeek</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>2-(dimethylamino)ethyl methacrylate</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
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<td>HLB</td>
<td>hydrophilic-lipophilic balance</td>
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<tr>
<td>$K$</td>
<td>partition coefficient</td>
</tr>
<tr>
<td>$M_n$</td>
<td>number average molecular weight</td>
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<tr>
<td>$M_w$</td>
<td>weight average molecular weight</td>
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<tr>
<td>MeOD-d$_4$</td>
<td>deuterated methanol</td>
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<tr>
<td>mol %</td>
<td>percentage based on the number of moles</td>
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<td>MMA</td>
<td>methyl methacrylate</td>
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<td>MWD</td>
<td>molecular weight distribution</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>------------</td>
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<tr>
<td>O/W</td>
<td>oil-in-water</td>
</tr>
<tr>
<td>PBMA</td>
<td>poly(butyl methacrylate)</td>
</tr>
<tr>
<td>PdI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>PEG</td>
<td>polyethylene glycol</td>
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<tr>
<td>pH</td>
<td>pKa value of the conjugate acid of a base</td>
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<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
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<td>PS</td>
<td>polystyrene</td>
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<td>glass transition temperature</td>
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<td>ultraviolet</td>
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<tr>
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<td>2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride</td>
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**List of Numbered Compounds**

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<tr>
<td>1a</td>
<td>(N')-hexadecyl-(N,N)-dimethylacetamidine</td>
</tr>
<tr>
<td>1b</td>
<td>(N')-hexadecyl-(N,N)-dimethylacetamidinium bicarbonate</td>
</tr>
<tr>
<td>2a</td>
<td>(N')-dodecyl-(N,N)-dimethylacetamidine</td>
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<td>2b</td>
<td>(N')-dodecyl-(N,N)-dimethylacetamidinium bicarbonate</td>
</tr>
<tr>
<td>3</td>
<td>2,2'-azobis[2-(2-imidazolin-2-yl)propane]bis(hydrogen carbonate)</td>
</tr>
<tr>
<td>3a</td>
<td>(N')-(4-decylphenyl)-(N,N)-dimethylacetamidine</td>
</tr>
<tr>
<td>3b</td>
<td>(N')-(4-decylphenyl)-(N,N)-dimethylacetamidinium bicarbonate</td>
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<td>(N,N)-dimethyl-(N)-dodecylammonium bicarbonate</td>
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<tr>
<td>5</td>
<td>(N')-dodecyl-(N,N)-dimethylacetamidinium acetate</td>
</tr>
<tr>
<td>6</td>
<td>butylated polyethyleneimine</td>
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Chapter 1  Introduction

Emulsion polymerization has been extensively used industrially to synthesize latexes, or emulsion polymers, since the early 20th century. As is often the case, the inspiration for synthetic latexes spawned from the need for solid dry rubber that could be produced from natural rubber latexes, by coagulation. Polychloroprene rubber, produced by DuPont USA, was the first product manufactured by emulsion polymerization in the late 1920’s or early 1930’s.¹ In the wake of World War II, and the possibility of importing rubber from Europe diminishing, the United States set up a Rubber Reserve Company and a program allowing for all research in the area of synthetic rubber to be open and accessible.¹ This caused a boost in the research and development of rubber, and accordingly, its synthetic rubber latex precursor. From this, many academics and industrialists alike realized the enormous potential of synthetic latexes for modified rubbers and for entirely new applications.

In modern society synthetic polymers are ubiquitous; many of the comforts we enjoy are made possible due to enormous investment in the research and development of these commodity chemicals. In 2000, the industry was worth more than US$200 billion worldwide, with 189 million metric tons of polymer being produced that year.² Of this, the mass of dry polymer in polymer dispersions accounted for 8.5 million metric tons, 1 million metric ton of this dry polymer was used as impact modifiers, which were produced by emulsion polymerization but were not sold as dispersions.² Three types of polymer classes comprise 95% of the products synthesized via emulsion polymerization; these are styrene-butadiene copolymers (37%) for synthetic rubbers,² ³ vinyl acetate polymers (28%) for binders and coatings (in 1995, 680 000 metric tons of vinyl-based
latexes were sold as exterior coatings)\textsuperscript{2,4} and acrylate polymers (30\%) for coatings, textiles, adhesives, caulks and sealants.\textsuperscript{2}

Surfactants are added to stabilize monomer emulsions in order to carry out emulsion polymerization. When the final use of the polymer dispersion is as a dry powder or solid, the stabilizing ability of the surfactant must be nullified, and this is typically carried out industrially using salts, acids for anionically stabilized latexes, or alkali for cationically stabilized latexes.\textsuperscript{1} This leads to an aqueous waste layer contaminated with a high concentration of ionic species that would require extra processing steps and further energy input to purify. The polymer particles also require extensive washing to remove the salt, acid or alkali. The ability to rapidly and easily alter the polymer dispersion from a suspended to an aggregated state without using salt or acid could provide significant environmental and economic benefits.

1.1 Surfactants

Surfactants, or surface active agents, are amphiphilic molecules that tend to reside at interfaces and act to lower the interfacial tension between two phases.\textsuperscript{5} Their amphiphilicity is derived from the hydrophilic head group at one end of the molecule and the hydrophobic tail group (typically a long chain hydrocarbon) at the other end\textsuperscript{5} (see Figure 1.1). These types of molecules can act as detergents, wetting agents, foam stabilizers, dispersing agents or emulsifiers depending on the relative hydrophilicity of the head and tail groups.\textsuperscript{6} There are many properties of a particular surfactant that may make it suitable for a certain application. In terms of emulsion polymerization, a few of the important parameters are the surfactant critical micelle concentration (CMC) in the
presence of monomer, surfactant adsorption at the polymer particle surface and the partitioning of surfactant between the monomer and water phases.

![Schematic of a typical surfactant and examples of commonly used surfactants.](image)

**Figure 1.1** Schematic of a typical surfactant and examples of commonly used surfactants.

### 1.1.1 Micelles and the Critical Micelle Concentration (CMC)

Due to their amphiphilic nature, surfactant molecules tend to aggregate at interfaces, but they can also exist as single molecules in solution. The hydrophilic portion of a surfactant is easily solubilized by surrounding water molecules due to dipole-dipole or ion-dipole interactions. Solubilization of the corresponding alkyl chains causes an entropic decrease due to the formation of a cage-like structure of water molecules around the alkyl chain, which leads to an unfavourable free energy change. The large entropic
gain upon adsorption of a surfactant molecule onto a surface is the origin of a phenomenon known as the hydrophobic effect. The hydrophobic effect is the exclusion of hydrophobic groups from water due to water’s high cohesive energy, leading to an apparent attraction of hydrophobic groups in water.\(^7\)

Surfactant molecules will adsorb onto the air-water interface and along the walls of a vessel until both are saturated. Beyond a certain surfactant concentration, the entropic decrease associated with the organization of surfactant molecules into aggregate structures in solution is smaller than the entropic decrease associated with the reorganization of water molecules around the alkyl chains, leading to micellization.\(^8\) The concentration at which this occurs is called the critical micelle concentration (CMC), which is the surfactant concentration above which micelles are present in solution.

### 1.1.2 Surfactant Hydrophile-Lipophile Balance (HLB)

The HLB system was devised as a method of quantifying the ability of a surfactant to form different types of emulsions. It is a measure of the relative hydrophilicity of the head and tail groups of a surfactant and is measured on a scale of 0-20. Higher numbers indicate more hydrophilic surfactants, these molecules act as detergents and are used in the formation of oil-in-water emulsions. More lipophilic surfactants exist at the lower end of the scale and are used as anti-foaming agents and for the generation of water-in-oil emulsions.\(^5\) HLB values are typically calculated for non-ionic surfactants, but values have been calculated for frequently used ionic surfactants such as sodium dodecyl sulfate.
1.1.3 Surfactant Solubility and Partitioning

Bancroft’s rule states that the phase (oil or water) in which a surfactant is more soluble will be the continuous phase of the emulsion that forms from these two phases. This can be rationalized by considering the following: surfactants that are more easily wetted by a particular phase will preferentially orient themselves on the interface where they maximize their contact with that phase (when the interface is convex toward that phase). It is also important that the surfactant not be too soluble in either phase such that it will not partition at the interface in high enough concentrations to provide colloidal stability.

1.1.4 Surfactant Adsorption at Interfaces

Adsorption can be defined as the preferential location of one component of a system at an interface resulting in a concentration gradient of that species at the interface versus in the bulk. The Gibb’s method of determining surface excess concentration is the most widely used method of determining interfacial concentration profiles.

The Gibb’s approach defines an interface, also called a “Gibb’s dividing interface”, as a plane where the concentration of one phase component, α, (usually the solvent) becomes zero. From this, the relative excess number of moles of component $i$ ($n_i^\sigma$) with respect to α in a system with an interface of area $A^\sigma$ is termed the surface excess concentration, $\Gamma_i^{(\alpha)}$, and is defined as:

$$\Gamma_i^{(\alpha)} = \frac{n_i^\sigma}{A^\sigma} \quad (1)$$

When considering surfactants, which are generally used in small concentrations and have high surface activity, surface excess concentration can be related to experimentally
obtainable quantities such as interfacial tension using the Gibbs adsorption equation, which is given by:

$$\Gamma_2^{(1)} = \frac{-1}{RT} \left[ \frac{d\sigma}{d \ln c_2} \right]$$  \hspace{1cm} (2)

where $c_2$ is the molar concentration of adsorbate in the bulk phase (1) and $\sigma$ is the measured interfacial tension (liquid-liquid or liquid-air).

In the case of polymer latexes (where solid-liquid interfaces are concerned), interfacial tension is an important parameter to consider when understanding colloidal stability, although it is nearly impossible to determine directly. The Gibbs adsorption equation allows one to determine values of interfacial tension through experimental determination of the surface excess concentration.

The amount of solute adsorbed at a solid-liquid interface can be determined by measuring its concentration in solution after adsorption onto the solid has occurred. In the case where the solute is a surfactant, the decrease in surface tension of the liquid-air interface with an increase in bulk surfactant concentration can also be used to determine the maximum amount of surfactant adsorbed on the polymer surface.

1.1.5 Switchable Surfactants

Surfactants are used in many processes to stabilize a dispersion of two immiscible phases. Often, this stabilization is only required for one step of the process, such as in the cases of viscous oil pipelining, metal degreasing, oil sands separations and emulsion polymerization where the desired product is in the form of a polymer resin. To address this issue, a class of surfactants termed “switchable surfactants” has been developed,
whose surface activity can be reversibly altered by the application of a trigger, allowing for reversibly stabilized dispersions.

With particular application to the polymer colloids field, the presence of surfactants in the polymer dispersion can, in some cases, negatively affect the final performance of the material. This is the case with water-borne coatings, where the surfactant can migrate to the surface of the film leading to an undesirably hydrophilic surface.\(^2\) Thus for coatings applications, a preferred approach would be to use a surfactant capable of being switched off when its latex-stabilizing ability is no longer needed, and as such, reduce its tendency to migrate. Furthermore, polymer colloids stabilized by these switchable surfactants could potentially be used as fast-drying paints used, for example, on roads and highways. This would avoid the release of toxic fumes coming from ammonia, the release of which is currently used to accelerate film formation.\(^{10,11}\)

Switchability can be triggered by altering pH,\(^{12}\) adding redox reagents\(^{13}\) or applying UV light.\(^{14}\) Surfactants containing ferrocenyl moieties\(^{13(a-g)}\) and “pepfactants”\(^{12(b,c)}\) (which are switchable surfactants containing a series of amino acids) are expensive, those containing viologen moieties\(^{13(c)}\) are toxic, and all of the above rely on the addition of oxidants, reductants, acids or bases to trigger the switch. Photochemical azobenzene surfactants use only light as a trigger, but are limited to non-opaque samples and therefore cannot be applied in emulsion polymerization systems. Representative examples of these types of surfactants are shown in Figure 1.2.
The Jessop group first developed switchable surfactants containing long alkyl chains and amidine head groups in 2006. Since then, several variations of this initial surfactant have been developed by varying the head and tail groups. Switchable surfactants with guanidine head groups have been developed, as well as those with ethoxylated tails (Figure 1.3). These surfactants are charged in the presence of CO$_2$ due to the formation of bicarbonate salts, and uncharged upon removal of CO$_2$ (Scheme 1.1). The basicity of the surfactant’s head group is linearly correlated to its enthalpy of protonation. Guanidines are generally the most basic and have the highest conversion to the protonated form and therefore require high temperatures and faster gas flow rates to remove the CO$_2$. On the other hand, tertiary amines have relatively lower basicities such that CO$_2$ can be removed at more ambient conditions. This is evidenced by the lower conversions of tertiary amines versus guanidines to bicarbonate salts at a given temperature. The basicity of amidines generally lies between the above two cases. The head group basicity has implications in the applications in which these types of surfactants can be used.

Carbon dioxide has also been used as a trigger for latex destabilization when the dispersion is stabilized by anionic, fatty acid type surfactants. It was shown in 1985 by Moore that polymerization of monomer emulsions stabilized by these surfactants yields
polymer latexes that can be destabilized with the application of CO\textsubscript{2} followed by high shear. In this case, carbonic acid protonates the surfactant and decreases the electrostatic barrier between particles, causing aggregation.

![Figure 1.3](image)

**Figure 1.3** CO\textsubscript{2} switchable surfactants with (a) amidine\textsuperscript{15,16,18,19} guanidine\textsuperscript{16,17} and tertiary amine\textsuperscript{16} head groups and long alkyl chain tails and (b) amidine head groups and PEG containing tails\textsuperscript{18,19}.

![Scheme 1.1](image)

**Scheme 1.1** Reaction of long chain alkyl amidines with CO\textsubscript{2} to form amidinium bicarbonates\textsuperscript{15}.
1.2 Colloidal Stability

A colloid is a dispersion of particles with sizes between 1 nm and 10 µm (called the dispersed phase) into a second phase (called the continuous phase). Some common examples of colloidal systems are emulsions (liquid-in-liquid dispersions), aerosols (liquid-in-gas or solid-in-gas dispersions) or sols (solid-in-liquid dispersions). To carry out emulsion polymerization, the monomer phase must first be emulsified into the aqueous phase, creating a colloidal system. The emulsification of oil in water creates a large interfacial area between the two phases that is inversely proportional to the size of the droplets, so interfacial phenomena and colloidal stability play a large role in the emulsion polymerization process.

Upon emulsification, the change in free energy ($\Delta G$) is proportional to the change in area ($\Delta A$) between the two phases, leading to a thermodynamically unstable system.

$$\Delta G \propto \gamma \Delta A >> 0$$  \hspace{1cm} (3)

Surfactants decrease the interfacial tension ($\gamma$) between the two phases and thus decrease this free energy penalty. $\Delta G$ will never become negative so emulsions will always be thermodynamically unstable systems and will result in phase separation after a period of time. Understanding the factors that affect colloidal stability is crucial in developing a formulation that will be stable enough to conduct an emulsion polymerization.

In 1937, Hamaker described the van der Waals forces of interaction between two colloidal particles by considering the interaction energies between the molecules of each particle with the molecules of the other particle. From this, the following expression could be derived which shows that the free energy of interaction between two particles of the same material (regardless of their shape, plates, spheres etc.) is always going to be
attractive, regardless of the distance (denoted as l) between the particle surfaces and the medium in which they are dispersed\textsuperscript{23}

\[
\Delta G_{LW}(l) = -2\left(\sqrt{\gamma_{1LW}^L} - \sqrt{\gamma_{3LW}^L}\right)\left(\sqrt{\gamma_{2LW}^L} - \sqrt{\gamma_{3LW}^L}\right)\left(\frac{l_0^2}{l}\right)\pi R
\]

(4)

In this equation, \(\gamma_{1LW}^L\), \(\gamma_{2LW}^L\) and \(\gamma_{3LW}^L\), are Lifshitz-van der Waals surface tension values of materials 1 and 2 in a medium 3, R is particle radius, and \(l_0\) is the equilibrium distance between two semi-infinite surfaces when they are in van der Waals contact (experimentally determined to be \(\sim 1.57 \times 10^{-10}\) m). All of the variables in this equation are positive, such that if materials 1 and 2 are the same, this expression will always be negative, indicating an attractive interaction, thus creating an unstable dispersion.

1.2.1 Electrostatic Stabilization

Surfactants are typically added to counteract the van der Waals attraction and stabilize emulsions through an electrostatic stabilization mechanism. The surfactant will impart some charge, \(\psi_o\), on the surface of the droplet or particle. The particle will also have some associated water molecules, approximately two or three layers thick, that travel with the particle (this is called the Stern layer).\textsuperscript{9} Further out, counter-ions are found associated with the particle, which also move with the particle through the solution. The point at which the counter-ions cease to move with the particle and instead flow freely through solution is called the “shear plane” or “slipping plane” and the potential of the particle at the shear plane is called the zeta potential (\(\zeta\)-potential [=] mV).\textsuperscript{9} Another important parameter is the Debye length (1/\(\kappa\)), which is defined as follows:

\[
\frac{1}{\kappa} = \sqrt{\frac{\varepsilon kT}{4\pi \varepsilon_0^2 \Sigma_i \sigma_i^2 n_i}}
\]

(5)
where $\varepsilon$ is the electrical permittivity of the liquid medium, $e$ is the electronic charge, $v_i$ is the charge on a single ion and $n_i$ is the total number of ions per unit volume, $k$ is Boltzmann’s constant and $T$ is temperature. The Debye length is generally taken to be the thickness of the diffuse double layer (which is defined as the distance from the surface at which the potential is $\psi_0/e$). As the ionic strength of the solution is increased, the Debye length gets smaller due to shrinkage of the double layer, and there is a faster drop off of charge from the surface. Also, as the valency of the ion increases, the thickness of the diffuse double layer decreases.\(^9\)

The free energy of interaction due to electrostatics between two particles as a function of the distance between them ($l$) can be calculated using the following formula:\(^{23}\)

$$\Delta G_{\text{EL}}(l) = 0.5R\psi_0^2\varepsilon\ln[1-e^{-\kappa l}]$$ \hspace{1cm} (6)

where $R$ = the particle radius.

The sum of the attractive and repulsive free energies plotted against distance of separation gives a DLVO (Derjaguin-Landau-Verway-Overbeek) plot, an example is shown in Figure 1.4. The maximum shows the barrier towards aggregation and the primary minimum shows the most energetically favourable position for the particles. In some systems, the particles may enter a secondary minimum (which exists at larger interparticle distances than the energy barrier) that is accompanied by the formation of loose flocs.
1.2.2 Steric Stabilization

High molecular weight species or polymers can also be used to stabilize a colloidal system through a mechanism known as steric stabilization. The molecule must be large enough to adsorb onto the particle surface but still extend from the particle surface. When the hairy layers on the surface of two particles come in contact, there is a decrease in entropy due to the constriction of movement of the polymer chains. This decrease leads to an unfavourable free energy change and repulsive steric interactions, stabilizing the colloidal system.
1.3 Polymers

Polymers are macromolecules composed of several repeat units called monomers. Polymers can occur naturally (proteins and cellulose for example), or be produced synthetically (polystyrene and polyethylene for example). There are two main types of mechanisms by which polymers can be synthesized: step growth polymerization or chain growth polymerization.

1.3.1 Free Radical Polymerization

Free radical polymerization is a type of chain-growth polymerization whereby polymer growth occurs through the addition of monomer units at the end of a chain containing a radical. There are three characteristic steps: initiation, propagation and termination (shown in Figure 1.5). Initiation is the process whereby an initiator molecule dissociates into two free radicals and reacts with a monomer. During propagation, monomer units are sequentially added to the growing chain. The chain stops growing when termination occurs. Termination can occur by combination (which involves the formation of a covalent bond between two growing radical chains leaving one polymer chain) or disproportionation (which involves proton transfer from one chain to another, leaving two polymer chains).
1.3.2 Properties of Polymers

There are many properties of a polymer that will affect its performance, such as its chemical composition, chemical composition distribution, molecular weight, molecular weight distribution, branching, cross-linking and glass transition temperature, just to name a few.

The molecular weight of a polymer is measured as a distribution of molecular weights and reported as an average molecular weight, because each chain will not have grown to the same extent. Two commonly reported averages are the weight average molecular weight, given as:

**Figure 1.5** The three steps in free radical polymerization.
\[ M_w = \frac{\sum_{i=1}^{N} W_i M_i}{\sum_{i=1}^{N} W_i} \]  \hspace{1cm} (7)

and the number average molecular weight, given as:

\[ M_n = \frac{\sum_{i=1}^{N} W_i}{\sum_{i=1}^{N} \left( \frac{W_i}{M_i} \right)} \]  \hspace{1cm} (8)

where \( N_i \) is the number of moles of molecules with molecular weight \( M_i \) and \( W_i \) is the weight of molecules with molecular weight \( M_i \) (ie \( W_i = N_i M_i \)).

The polydispersity index (PDI) is a measure of the breadth of the molecular weight distribution, with PDI values equal to 1 meaning that the sample is monodisperse and each polymer chain has the same molecular weight. PDI is given as:

\[ \text{PDI} = \frac{M_w}{M_n} \]  \hspace{1cm} (9)

The glass transition temperature \( (T_g) \) of a polymer is the temperature at which the polymer changes from a glassy, amorphous, brittle material to a molten or rubbery material. When a polymer is cooled quickly from the melt, at the \( T_g \) of the polymer there is not enough energy for long-range chain movement, so the polymer “freezes” or turns to a glass. The chemical structure of a polymer is the most important factor in determining \( T_g \). Polymers with flexible backbones and small substituents have low \( T_g \) values because the polymer chains can flow past each other with very little energy.
1.4 Emulsion Polymerization\textsuperscript{25,26}

Emulsion polymerization is a free radical polymerization process where polymers are formed in a dispersed phase of a two-phase system. The product of this reaction is typically nanometer-sized polymer particles dispersed in an aqueous phase. This method of polymer synthesis eliminates the use of volatile organic solvents, making it more environmentally friendly than solvent based polymerization.

There are many distinct advantages of using emulsion polymerization rather than bulk polymerization. Most of these derive from the fact that the polymerization takes place in discrete, individual reactors. Typically in bulk polymerization, high molecular weights can only be achieved with low reaction rates and vice versa, but emulsion polymerization offers the unique advantage of maintaining high molecular weights with high reaction rates. As well, the viscosity of the system remains low even at high conversions because the polymer is not dissolved in the continuous phase. High viscosities in bulk polymerization lead to poor temperature control because the heat generated cannot be dissipated effectively through the polymer; this leads to increased radical production and the possibility of a “runaway reaction”. In emulsion polymerization, the surrounding aqueous phase can absorb the heat and allow it to be dissipated more effectively.

1.4.1 Mechanism of Emulsion Polymerization\textsuperscript{21,25,26}

Harkins\textsuperscript{27} pioneered much of the work in the development of a mechanism for emulsion polymerization in 1947. A typical emulsion polymerization begins with μm-sized monomer droplets dispersed in the aqueous phase with the help of a surfactant. The monomer must have some limited solubility in the aqueous phase. Polymerization then
begins in the aqueous phase after decomposition of a water-soluble radical initiator, leading to the formation of water-soluble oligomers. Once the oligomer reaches a critical chain length (which depends on the water solubility of the monomer), it becomes insoluble and a particle nucleus is formed (Figure 1.6).

There are two main nucleation mechanisms depending on the concentration of the surfactant. Micellar nucleation occurs if the surfactant is present in concentrations greater than the CMC. Monomer swollen surfactant micelles are typically 5-10 nm and therefore are present in much larger numbers ($10^{19}$-$10^{21}$ dm$^{-3}$) than the monomer droplets (~10 µm). The oligomer will enter (“sting”) a monomer swollen surfactant micelle, creating a polymer particle. It was proposed in 1965 by Fitch that homogeneous nucleation can also occur if the surfactant is present in amounts lower than the CMC. In this case, once the oligomer reaches the critical chain length, it becomes insoluble and coils up into a particle nucleus. Limited flocculation of these nuclei occurs until the interfacial tension of the particle is reduced sufficiently to be stable in the medium. Surfactant molecules migrate from the aqueous phase or the monomer droplets in order to stabilize the growing particles. When the surfactant concentration is above the CMC, it is likely that both nucleation mechanisms are occurring simultaneously.
The type of nucleation and the number of nucleated particles is important in determining the final particle size and particle size distribution of the polymer dispersion, which can have a great effect on the final properties of the latex. Many factors affect the number of nucleated particles, some of which include the type and concentration of surfactant, the rate of free radical generation, nature and concentration of the initiator, reaction temperature and monomer type and amount.

After the nucleation stage, the number of particles ideally remains constant and the polymer particles grow by diffusion of monomer through the aqueous phase into the monomer swollen polymer particles. The overall polymerization rate depends on the number of particles (N), the equilibrium concentration of monomer in the particles ([M]_p), the average number of radicals per particle (n) and the propagation rate constant of the monomer (k_p), according to the following equation:

\[
R_p = \frac{nNk_p[M]_p}{N_A} 
\]  

(10)
Because the monomer concentration in the particles remains constant when droplets exist, the polymerization rate is also constant as long as monomer droplets are present. When the droplets are depleted, the polymerization rate decreases due to a decrease in monomer concentration in the polymer particles.

1.4.2 Determination of Particle Size

The final size of the particles in a latex after polymerization can have a dramatic effect on latex properties such as rheology, colloidal stability and film formation. Determination of the absolute particle size and distribution, however, is not a trivial task. To obtain accurate results, use of the appropriate equipment and analytical technique is imperative.

Methods that measure the particle size by light scattering are widely used because the analysis time is fast, the resolution is good for monodisperse samples, no calibration is necessary and only a small amount of sample is required. Light scattering methods include static light scattering (used by the Mastersizer 2000) and dynamic light scattering (used by the Zetasizer ZS).

A particle will scatter light with an angular intensity that depends its size. Small particles scatter radiation at high angles with low intensity and as the particle size increases, the angle decreases and the intensity of scattered radiation increases. The Mastersizer 2000 is equipped with a HeNe laser (\( \lambda = 633 \) nm) and several detectors at different angles that collect the sample’s scattering pattern. An optical model based on Mie theory (which assumes that the size of the particles is on the same order as the wavelength of the laser) is applied to the scattering data and a particle size distribution is obtained. The Mastersizer 2000 is a useful instrument because it can analyze a broad
range of particle sizes (0.05 μm – 2000 μm), and it is particularly useful for bimodal
particle size distributions where it has been shown that it can measure the volume
percentage of each size population with an error of less than 5 %.\textsuperscript{30}

Dynamic light scattering works on the principle that particles diffuse in solution
due to Brownian motion, with smaller particles diffusing faster than larger ones. This
movement causes a fluctuation in the scattered light with time and this allows the
diffusion coefficient to be determined using digital autocorrelation. Using this method,
the signal intensity at time t is compared to that at time $t + \delta t$, $t + 2\delta t$, $t + 3\delta t$ etc. When
particles are diffusing through solution, the correlation in the signal will drop with time.
Larger particles diffuse slower and a steep drop in the correlation coefficient is observed
at longer times than that of smaller particles that diffuse quicker. If the decay in the
correlation is steep, the sample is monodisperse (low PdI) and vice versa. The diffusion
coefficient is related to the particle diameter by the Stokes-Einstein equation:

$$D = \frac{kT}{3\pi\mu d} \tag{11}$$

where $D$ is the diffusion rate coefficient, $k$ is Boltzmann’s constant, $T$ is temperature, $d$ is
the particle diameter and $\mu$ is the viscosity.

The Zetasizer ZS uses only one detector, placed at an angle of 173°, so it can be
used to measure particles in the low nanometer region (1 nm- 3000 nm). Bimodality is
difficult to detect using dynamic light scattering, especially if the population of the
species is a small fraction of the total population. Furthermore, the surface structure of
the particle will affect the reported particle size because the measured size is that of a
particle with the same translational diffusion. For this reason, particle sizes obtained
using this method will be larger than those obtained using methods based on microscopy (transmission electron or scanning electron microscopy).

1.4.3 Applications to Polymer Colloids

Traditionally, polymer colloids have found use in the paint, coatings, ink, adhesives and rubber industries. A particular challenge is in the coatings industry, which seeks to eliminate the use of solvent-based coatings due to the emission of volatile organic compounds into the atmosphere during their synthesis and use. The problem is that solvent-based coatings typically have superior properties and therefore much research is being carried out to make water-borne coatings a more viable option.

More recently, the use of surface functionalized polymer colloids and polymer colloids as “smart materials” has emerged. Smart materials, also called stimuli responsive materials, are those that can rapidly respond to a change in their environment such as a change in temperature, pH, chemical composition or the application of molecular stress or light. By altering the surface of latex particles, they can be made to respond to such stimuli. These particles are being used as attachment sites for biological ligands such as enzymes or antibodies, for drug delivery and for diagnostic testing.

1.5 Latex Destabilization

Colloidal destabilization of a latex results in the bulk separation of polymer particles from the aqueous phase, which is oftentimes necessary in industrial latex applications. The stabilization of colloidal systems was discussed previously, but one must also understand the factors that lead to the breakdown of such stability, and in doing so, one can determine if colloidal destabilization can be controlled. There are many
factors that can affect the integrity of a latex and destabilization can occur or be carried out through physical (high shear, heating or freezing) or chemical means.

### 1.5.1 Altering Latex pH

Latex stabilization can be altered using acids or bases depending on the nature of the surfactant species adsorbed onto the particle surface. In the case of carboxylate stabilized latexes, addition of acid will decrease the latex pH and protonate the surfactant so that it is no longer an ionic species. This causes gross destabilization due to the reduction of electric charge density and counter ion charge on the particle surface, which decreases the electrostatic barrier and allows for close approach of particles. Furthermore, the surface is less likely to be hydrated when these charges are reduced.\(^{35}\)

Maron and Bowler examined the effect of acid addition to styrene-butadiene particles stabilized by acidic carboxylate groups in 1948.\(^{36}\) A reduction in pH results in a decrease in electrophoretic mobility (or \(\zeta\)-potential). At higher pH’s, the \(\zeta\)-potential decreases only slightly due to gradual conversion of the surfactant to the neutral acid, and at a certain pH (approximately 8) the electrophoretic mobility decreases sharply due to the suppression of ionization of the acid groups. An important aspect to note is that no cases were observed in which the pH could be lowered below 5.5 without coagulation occurring, and that the particles at this point still had an appreciable electrophoretic mobility thus leading the authors to conclude that it is not necessary to fully reduce the surface charge in order to induce particle aggregation. The authors ensured that the ionic strength of the latexes were kept constant during these experiments, to rule out the idea that destabilization occurred through double layer suppression due to an increase in the ionic strength of the latex.
This phenomenon has also been studied with cationic latexes, although much less so. Naturally, the opposite trend is observed in latexes stabilized by cationic charges, like the styrene-vinylbenzylamine hydrochloride latex, stabilized by surface amino and amidine groups studied by Ganachaud.\textsuperscript{37} As pH increases in this case, the surface groups get deprotonated and thus the $\zeta$-potential decreases leading to destabilization.

1.5.2 Temperature Effects\textsuperscript{35}

The effect of temperature on particle aggregation is briefly considered in the context of the Gibbs free energy barrier between a single pair of particles, denoted as $\Delta G^*$. The relationship between this quantity and $\Delta H^*$, $\Delta S^*$ and $T$ is given by:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

For colloidal stability, $\Delta G^*$ has to be positive and there are three conditions under which this is possible. The colloidal system can be enthalpically stabilized, where $\Delta H^* > T\Delta S^*$ and $\Delta H^*$ and $\Delta S^*$ are both positive. In this case, increasing the temperature would destabilize the latex. If $\Delta H^*$ and $\Delta S^*$ are both negative and $|T\Delta S^*| > |\Delta H^*$| then the colloid is entropically stabilized and increasing the temperature in this case would further stabilize the latex. Finally, if $\Delta H^*$ is positive and $\Delta S^*$ is negative, increasing the temperature would also increase the stability of the latex. It is important to note that these conclusions are very general and will apply to any colloidal system regardless of attractive forces between particles and stabilization mechanisms (electrostatic or steric). Implementation of this analysis to a polymer latex system however would require sufficient knowledge of $\Delta H^*$ and $\Delta S^*$ values.

Temperature also has an effect on electrostatically stabilized latexes by altering the electric double layer and the permittivity of the medium. Considering the equation for
the thickness of the electrical double layer (equation 5), one notices that the Debye length is proportional to \((kT)^{1/2}\). Therefore, an increase in temperature would increase the thickness of the double layer. However, \(\varepsilon\) for water also decreases with increasing temperature thus these two effects oppose each other. The net effect is that an increase in temperature, for example, from 20 °C to 50 °C compresses the double layer and this reduces colloidal stability.

### 1.5.3 Aggregation Rate

The rate of aggregation in a colloidal system is governed by two main factors. The first factor is the frequency of collisions between particles; if the particles collide through Brownian motion alone the aggregation is called perikinetic, but if some external shear is supplied the aggregation is called orthokinetic. Typically, one mechanism dominates for a certain set of conditions. The second factor is the probability of cohesion during particle collisions. If there are no interactions between particles, every particle collision will result in sticking and the probability of cohesion is one; this is called diffusion limited (or rapid) aggregation. If a barrier exists between the particles (such as that shown in Figure 1.4), the aggregation is said to be reaction limited (or slow).

In 1916, Smoluchowski developed a theory to describe the kinetics of diffusion-limited aggregation of colloidal particles.\(^3\) By assuming only Brownian diffusion of particles, and that aggregation occurs first by the formation of a doublet particle followed by capture of primary particles onto the growing aggregate, the following expression can be derived to describe the half-life of a dispersion (the time at which half of the primary particles have disappeared):\(^7\)
$t_{1/2} = \frac{3\mu}{4kTn_0}$

(13)

where \( \mu = \) viscosity of the medium, \( n_0 \) is the initial number of particles per m \(^3\), \( k = \) Boltzmann’s constant and \( T = \) temperature. Further manipulation of this equation gives a more useful expression relating the dispersion half-life to the solids content and particle size:

$$t_{1/2} = \frac{\pi \mu d^3}{8kT\phi}$$

(14)

where \( \phi = \) volume fraction of particles and \( d = \) particle diameter. Essentially, the equation tells us that the half-life increases with increasing particle diameter, decreases with increasing solids content and decreases with increasing temperature. It is important to note that these expressions were developed for particles with no electrostatic or steric stabilization, and that in stabilized dispersions, \( t_{1/2} \to \infty \). Furthermore, they are most useful for low solids content latexes (\(< 20 \) wt %).

Reaction-limited aggregation was described first by Fuchs\(^3\) who showed that if the particles have a maximum potential energy of interaction (\( \Phi_{\text{max}} \)), the diffusion limited aggregation rate (\( k_r \)) is altered by a factor of \( 1/W \) (where \( W \) is called the stability ratio and is proportional to \( e^{(\Phi_{\text{max}}/kT)} \)):

$$k_r = \frac{k_r \text{ (rapid aggregation)}}{W}$$

(15)

For colloidally stable systems \( \Phi_{\text{max}} > 0 \) which typically leads to \( W \) values much greater than one and a reduction in the aggregation rate.

The effect of solid content on reaction-limited aggregation is the same as that for diffusion limited aggregation described above. Particle size has an effect on \( \Phi_{\text{max}} \) (shown
in Appendix A) that would lead to an increase in \( W \) and a reduction in aggregation rate. Finally, increasing temperature would increase the aggregation rate by lowering \( W \) (because \( W \propto e^{1/T} \), as shown above). This is intuitive, since a temperature increase would increase the thermal energy of the particles and allow them to more easily surmount the potential energy barrier that exists between them.

### 1.6 Inverse Emulsions and Inverse Emulsion Polymerization

Hydrophilic monomers cannot be polymerized in a conventional emulsion polymerization system. To overcome this problem, inverse emulsion polymerization is used. Using this method, polymerization occurs in an aqueous phase, containing a water-soluble monomer, which is dispersed in a low dielectric constant, non-polar oil phase. Emulsification in this system is typically achieved using low HLB surfactants that are typically non-ionic,\(^{40}\) some examples are shown in Figure 1.7.

Using this method, the same advantages of emulsion polymerization (high rates, high molecular weights, low viscosities) can be conferred to water-soluble monomers. Furthermore, the final product is a high molecular weight polymer dissolved in water, thus avoiding the problem of heating and excessive agitation that is necessary to dissolve a dry polymer powder in water. An aqueous solution of the polymer is typically the desired product, which can be used in secondary oil recovery, flocculation of solids in wastewater treatment and metal recovery.\(^{41}\)
The mechanism and kinetics of inverse emulsion polymerization are less understood than those of its conventional counterpart. Much of the work that has been carried out in this area involves the inverse emulsion polymerization of acrylamide, and shows that the mechanism depends highly on the chemical nature of the species involved (ionic versus non-ionic surfactants and oil versus water soluble initiators).\cite{40} Furthermore, colloidal stability is often an issue, and flocculation occurs much more easily in inverse emulsions. Typically, ionic emulsifiers do not prevent flocculation because the continuous oil phase has a low dielectric constant, and a charge sufficient enough to stabilize the emulsion is not able to build-up on the particle surface.\cite{42}

### 1.7 Project Overview and Objectives

The goals of this project were to: (1) establish the feasibility of, and then develop an emulsion polymerization process for common monomers such as styrene, methyl methacrylate and butyl methacrylate using amidine- and tertiary amine-based switchable surfactants.
surfactants; and (2) prepare latexes that could be destabilized using only air or inert gas as triggers. The synthesis of submicron particles using switchable surfactants has not been previously published, and only a small number of experiments have been carried out using these surfactants in an emulsion polymerization system. The effect of surfactant and initiator concentrations, as well as solids content, on the resulting particle size of the latexes was examined. A study of the effect of temperature, solids content, particle size and surfactant head group basicity on the rate of destabilization was carried out. Emulsion polymerization was conducted to synthesize highly stable latexes with a wide range of nm-sized particles (40 nm – 470 nm) to broaden the applicability of the products obtained using switchable surfactants.

Some fundamental aspects of surfactant behaviour were addressed in order to better understand the properties of switchable surfactants in an emulsion polymerization system, as opposed to in bulk solution. Such properties include: the amount of surfactant adsorbed on the polymer particle surface and the partitioning of the neutral and charged forms of the surfactant between the monomer and water phases.

Finally, the use of switchable surfactants and switchable polymers in the generation and stability of inverse emulsions was assessed. This was followed by attempted polymerization of a hydrophilic monomer in an inverse emulsion polymerization system.
Chapter 2  Experimental Methods

2.1 Materials

CO₂ (Praxair, Medical grade), N₂ and argon (Praxair, 99.998%) were used as received. 2, 2’-Azobisisobutyronitrile (AIBN), 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) and 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Styrene (99%) (containing 4-t-butylcatechol (TBC) inhibitor) and methyl methacrylate (MMA, 99%), butyl methacrylate (BMA, 99%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%) (containing monomethyl ether hydroquinone (MEHQ) inhibitor) were purchased from Aldrich. N,N-Dimethyl-N-dodecylamine (4a, 90%), 4-decylaniline (98%) and Span 60™ were purchased from Alfa Aesar. Dimethylacetamide dimethyl acetal (90%) was purchased from TCI. Disponil® A 3065 was purchased from Cognis as a 30 wt % solution of linear fatty alcohol ethoxylates in water. Paraffin (a mixture of aliphatic hydrocarbons, product code # 5530-1) was purchased from Caledon Laboratory Chemicals. All other chemicals were purchased from Aldrich. Inhibitor removal columns (purchased from Aldrich) were used to purify the monomers. All other chemicals were used without further purification.

Compounds 1a and 2a and their bicarbonate salts 1b and 2b were synthesized as described previously²⁶ (Scheme 2.1). N’-(4-Decylphenyl)-N,N-dimethylacetamidine (3a) has not previously been reported, so the synthetic method and characterization data are included below. The purity was determined by ¹H-NMR spectroscopy to be 92%. The major impurity is assumed to be N-(4-decylphenyl)-O-methylacetimidate.²⁷ This mixture was not purified before its use as a surfactant. Compound 5 was synthesized by mixing 0.5 g (1.6 mmol) of 2a with 1.6 mL of 1.0 M (1.6 mmol) of acetic acid in water. A
sample of butylated polyethyleneimine (6, Scheme 2.2) was provided by another member of the Jessop lab, and was synthesized according to a literature procedure.43

Scheme 2.1 Synthesis of the surfactants used in this study.

\[
\begin{align*}
R-NH_2 + H_2CO \xrightarrow{60^\circ C, 0.5 \text{ h}} R-\text{NH}_2-N-CO \xrightarrow{\text{CO}_2, \text{H}_2\text{O}} 2\text{CH}_3\text{OH} \\
\text{Air, Heat} \quad \text{R-}N=\text{CO}_3^- \\
1a \ R=C_{16}H_{33} \\
2a \ R=C_{12}H_{25} \\
3a \ R= \text{C}_{10}H_{21}
\end{align*}
\]

\[N’-(4-\text{Decylphenyl})-\text{N},\text{N}-\text{dimethylacetamidine (3a) was prepared by mixing 1.0 g (4.2 mmol) of 4-decylaniline with 0.62 g (4.2 mmol) of \text{N},\text{N}-\text{dimethylacetamide dimethyl acetal in a round bottom flask equipped with a condenser and heating to 60 }^\circ\text{C for 30 min. The methanol was removed by rotary evaporation to yield an orange liquid (1.34 g, 96%).}\]

\[1^H-\text{NMR (400 MHz, MeOD-d}_4): \delta = 0.79 \text{ (t, } J_{\text{HH}} = 7.9 \text{ Hz, 3 H, CH}_2\text{CH}_3), 1.18 \text{ (m, 14 H, C}_{7}\text{H}_{14}), 1.48 \text{ (multiplet, } J_{\text{HH}} = 6.8 \text{ Hz, 2 H, CH}_2\text{CH}_2), 1.73 \text{ (s, 3 H, CCH}_3), 2.44 \text{ (t, } J_{\text{HH}} = 6.8 \text{ Hz, 2 H, CH}_2\text{C}), 2.90 \text{ (s, 6 H, N(CH}_3)_2), 6.52 \text{ (d, } J_{\text{HH}} = 7.8 \text{ Hz, 2 H, CH}), 6.94 \text{ (d, } J_{\text{HH}} = 7.8 \text{ Hz, 2 H, CH}).\]

\[13C-\text{NMR (400 MHz, CDCl}_3): \delta = 14.2, 14.9, 22.7, 29.3, 29.4, 29.6, 29.7, 31.7, 31.9, 35.4, 38.0, 122.2, 128.6, 135.7, 149.8, 157.4.\]

HRMS (ESI+) calculated m/z for \([\text{C}_{18}\text{H}_{34}\text{N}_2+\text{H}]^+ = 303.2800, \text{ observed} = 303.2806.\] IR (neat, cm\(^{-1}\)): 845 (m), 1018 (m), 1188 (m), 1293 (m), 1390 (s), 1466 (m), 1620 (s, v, (C=N)), 2359 (w), 2853 (s), 2924 (s). See Appendix B, Figures B.1 and B.2 for NMR spectra.

The position of the \(^1\text{H-NMR peaks correspond to those reported for } N’-(4-\text{heptylphenyl})-\text{N},\text{N}-\text{dimethylacetamidine}.\]

31
2.2 Emulsion Polymerization

Carbonated water was prepared by bubbling carbon dioxide for 30 min through a needle into a round bottom flask containing distilled water. Emulsion polymerization reactions were carried out in 50 or 100 mL round-bottomed flasks equipped with a stir bar and a condenser or using a 12-reaction station carousel from Radley’s Innovation Technology (model # 201-2958). Typical reaction conditions are as follows: 1b, 2b, 3a or 4a was added to styrene, MMA or BMA in a 20 mL scintillation vial and, if necessary, sonicated using a Fisher Scientific Ultrasonic Cleaner (model FS30) for approximately one minute to dissolve the surfactant. The monomer/surfactant solution was then added to carbonated water in the round-bottomed flask. In the cases where 3a and 4a were used, their bicarbonate salts (3b and 4b) were formed in situ by bubbling CO\textsubscript{2} through the monomer/surfactant solution prior to its addition to carbonated water. CO\textsubscript{2} was bubbled through the mixture using a needle. The mixture was allowed to stir for 30 min at room temperature to form an emulsion. The initiator was dissolved in the monomer phase, distilled water or carbonated water in the cases of AIBN, VA-044, or VA-061, respectively. The initiator solution was added to the emulsion after which polymerization was carried out at 65 °C for 5 h (in cases where 1b and 2b used) and 2 h (in cases where 3a and 4a were used). When a round-bottomed flask was used, CO\textsubscript{2} was continuously
bubbled through the emulsion throughout the polymerization. When the carousel reactor was used, the liquid was flushed with CO\(_2\) and the vessel was then sealed.

An example of the conditions used to produce a 23.5 wt % PMMA latex is as follows: Methyl methacrylate (6.26 g, 62.5 mmol) was added to 2b (14 mg, 0.044 mmol) and the mixture was sonicated for 1 min at 100 W to dissolve the surfactant. This mixture was added to 18 mL of carbonated water in a 50 mL round-bottomed flask and an emulsion was allowed to form over 30 min. In a separate vial, carbonated water (2 mL) was added to VA-061 (11 mg, 0.044 mmol) and the resulting clear solution was added dropwise to the emulsion. The emulsion was heated for 5 h at 65 °C with continuous bubbling of CO\(_2\). These reaction conditions produced a latex with a particle size of 159 nm and a \(\zeta\)-potential of 33 mV. Conversion of monomer to polymer was determined gravimetrically (using equation 16) to be 97 %.

The molecular weight and polydispersity of the polymer was determined using Gel Permeation Chromatography (GPC). The system was a Viscotek GPCmax VE 2001 containing a PAS-106M mixed bed column (from the PolyAnalytik SupeRes Series), coupled with a Viscotek 3580 differential refractive index detector (calibrated with PS standards ranging from 6.90 to 860 kg mol\(^{-1}\)). THF was used as the eluent with a flow rate of 1.0 mL min\(^{-1}\). The number average molar mass (\(M_n\)), weight average molar mass (\(M_w\)) and the polydispersity (PDI) of the molecular weight distribution (MWD) of the PMMA synthesized above were determined to be 180 kg mol\(^{-1}\), 956 kg mol\(^{-1}\) and 5.30, respectively. These values were obtained using a polystyrene calibration curve and therefore are polystyrene equivalent molecular weights.
2.3 Latex Destabilization

Colloidal latexes of polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) prepared as described above were destabilized by continuous bubbling of a non-acidic gas (Ar, air or N\textsubscript{2}) through the latex (typically at 65 °C) using a needle while the sample was stirred. The polymer particles were either left to settle under gravity or centrifuged for 10 min at 3500 rpm. To assess the effectiveness of latex destabilization, the Mastersizer 2000 was used to track changes in particle size over time. In some cases, latex destabilization was assessed visually by an increase in viscosity and the presence of visible flocs.

2.4 Latex Characterization

To determine overall conversion and conversion over time, 1-2 g samples of latex were removed from the reaction vessel via syringe and were allowed to dry under a flow of air for 24 h followed by oven drying for 24 h at 85 °C. Conversion was determined using the following equation:

\[
\text{% conversion} = \frac{[m(\text{dried polymer})][m(\text{TOT})]}{m(\text{latex sample})[m(\text{monomer}) + m(\text{surf}) + m(\text{init})]}
\]  

(16)

where \(m(\text{dried polymer})\) is the mass of the dried polymer, \(m(\text{TOT})\) is the total mass of water, monomer, surfactant and initiator, \(m(\text{latex sample})\) is the mass of the latex sample removed, and \(m(\text{monomer})\), \(m(\text{surf})\), and \(m(\text{init})\) are the initial masses of the monomer, surfactant and initiator, respectively.

Particle size was determined using a Malvern Mastersizer 2000 (size range of 0.05 µm to 2000 µm) equipped with a Hydro2000S optical unit and/or a Zetasizer Nano ZS (size range of 0.6 nm to 6.0 µm). The instrument that was used depended on the
particle size of the sample. The particle size of the latex samples were typically at the lower end of the size range for the Mastersizer 2000, so the Zetasizer Nano ZS was used. After destabilization, the particle size fell at or above the upper end of the Zetasizer Nano ZS size range, necessitating the use of the Mastersizer 2000. Measurement with the Mastersizer 2000 requires a large sample dilution with de-ionized water, which causes quasi-stable particles to aggregate during the measurement, giving irreproducible results. A mixture of non-ionic surfactants called Disponil® A 3065 was added to the sample just prior to its addition to the machine to prevent particle aggregation and preserve the original particle size distribution. Representative examples of Mastersizer 2000 and Zetasizer ZS plots of particle size distribution are shown in Appendix B.

\[ \zeta \text{-Potentials} \] were measured using a Zetasizer Nano ZS by diluting the latex samples with distilled water that was pre-saturated with carbon dioxide and adding a portion of this to a clear folded capillary cell. Representative examples of Zetasizer ZS plots of \( \zeta \)-potential are shown in Appendix B.

Scanning electron microscopy of two PMMA samples was carried out. The samples were sputter coated with gold and images were obtained using a scanning electron microscope operated at 20 kV.

2.5 Assessing Surfactant Switchability

Conductivity measurements of 20.0 mM solutions of 2a-4a in absolute ethanol (spiked with 200 \( \mu \)L of water) were obtained using a Jenway conductivity meter 4071. CO\(_2\) was bubbled through the solution using a needle at a flow rate of 70 mL min\(^{-1}\) (determined using a Varian Intelligent Digital Flowmeter), and the conductivity change over time was measured at room temperature (23 °C) until a constant value was obtained.
Air was subsequently bubbled through the solution using a needle at a flow rate of 70 mL min\(^{-1}\). This process was repeated for 3 cycles. As a control, the conductivity of a solution of water (200 µL) in ethanol (20 mL) was determined and changed by less than 5 µS cm\(^{-1}\) upon CO\(_2\) addition.

### 2.6 Conversion to Bicarbonate

Scheme 2.3 shows the compounds used and reactions carried out in this study. Due to the potential difficulty in purifying 3a, a pure sample of the shorter chain analogue \(N^\prime\)-(4-heptylphenyl)-\(N,N\)-dimethylacetamidine (3a\(^\prime\)) was provided by another member of the Jessop group and was used for this study. The conversion to the bicarbonate salt should not be affected by the alkyl chain length, only by the identity of the head group.

![Scheme 2.3 Compounds used in the study to determine of the extent of conversion of aryl amidine and tertiary amine surfactant precursors to their corresponding bicarbonate salts using CO\(_2\) and water.](image)

CO\(_2\) was bubbled through a solution of 3a\(^\prime\) or 4a (0.1 mmol) in MeOD-d\(_4\) (0.7 mL) spiked with 50 µL H\(_2\)O for 5 minutes (one sample at room temperature and one sample at 65 °C) and \(^1\)H-NMR and \(^{13}\)C-NMR spectra were recorded. \(^1\)H-NMR and \(^{13}\)C-NMR spectra of the neutral molecule as well as the hydrochloride salt of each were also recorded. The presence of peaks at 161 ppm (carbon of HCO\(_3^\)\(^-\)), and \(~164\) ppm (the
cationic carbon) in the $^{13}$C spectra was taken as evidence of bicarbonate salt formation. Conversion to $3b'$ and $4b$ was determined at room temperature and at 65 °C using $^1$H-NMR spectroscopy. Each spectrum ($3a'$, $3a'$•HCl, $3b'$, $4a$, $4a$•HCl and $4b$) was internally referenced against the signal for the methyl group at the end of the alkyl chain. The chemical shifts of protons contained close to the head group of the surfactant were determined. The HCl salt and neutral compounds were assumed to be converted 100 % and 0 % to the protonated form, respectively. Equations were developed correlating the chemical shift to % conversion and using the chemical shift obtained from the spectra of carbonated $3a'$ and $4a$, % conversion to the bicarbonate salt was determined. The data for this experiment is shown in Appendix B, Tables B.1 and B.2.

2.7 Determination of Surfactant Partitioning Behaviour

$^1$H-NMR spectroscopy was used to measure the partitioning behaviour of the charged ($2b$) and neutral ($2a$) forms of the amidine surfactant between the monomer and water phase. Four solutions were prepared: solutions of $2a$ in each of styrene and MMA as well as solutions of $2b$ in each of styrene and MMA, all with accurately known concentrations. A sample of each of these solutions (1.0 mL) was added to separate 6 mL vials each containing 1.0 mL of D$_2$O and shaken. CO$_2$ was added to the vials containing $2b$ to ensure ionization of the surfactant, and as expected, an emulsion resulted from the samples containing $2b$. All vials were sealed with Parafilm® and left for two days in the fridge to allow the layers to separate. Each experiment was carried out in duplicate. 200 µL of each D$_2$O layer, 25 µL of a 25.9 mM solution of DMF in D$_2$O and an extra 200 µL of D$_2$O were added to separate NMR tubes. 200 µL of each monomer layer, 25 µL of a 25.9 mM solution of DMF in CDCl$_3$ and an extra 200 µL of CDCl$_3$ were added to
separate NMR tubes. To increase the signal-to-noise for the samples of the monomer layer, some of the monomer was evaporated after adding the sample to the NMR tube but prior to the addition of the internal standard and extra solvent. The amount of surfactant in each phase was determined relative to the internal standard and the percentage in each phase was determined. The data for this experiment is shown in Appendix B, Table B.3. A scheme showing the setup for the determination of 2a in MMA can be seen in Figure 2.1.

**Figure 2.1** The setup for the determination of the partition coefficient of 2a between MMA and water.

### 2.8 Determination of Surfactant Coverage

A method called soap titration was used to determine the surface area occupied by a surfactant molecule on a polymer particle surface. Loss of CO$_2$ is an issue when working with amidine based switchable surfactants, and this loss would alter the surfactant concentration. For this reason, the following experiment was carried out using
surfactant 5, shown in Figure 2.2, which remains permanently charged under the experimental conditions.

![Structure of surfactant 5](image)

**Figure 2.2** Structure of the surfactant used to determine the % coverage of surfactant on the surface of PMMA particles.

Emulsion polymerization was carried out using 0.07 mol % (with respect to MMA) of 5 (0.0219 mmol, 8.1 mg) and 3 (0.0219 mmol, 5.5 mg) according to the conditions outlined in Section 2.2. CO₂ was not used at anytime during the experiment. The resultant Mastersizer particle size, $\zeta$-potential and conversion were 151 nm and 52 mV, and 97 %, respectively. The latex as synthesized contained 131 mg of PMMA/mL latex. This was diluted to make 20.0, 8.3 and 2.0 mg mL⁻¹ latexes. Each of these latexes was titrated with different concentrations of surfactant solution, with 3 min of stirring after each addition of surfactant. The surface tension was measured by the du Noüy ring method using a Fisher Surface Tensiometer Model 21 and plotted against the mass of surfactant added to the latex.
2.9 Inverse Emulsion Generation and Polymerization

2.9.1 Using Surfactant 1b

The effect of different parameters on the generation and stability of inverse (water-in-oil) emulsions using 1b was tested. Three oil phases (cyclohexane, toluene and paraffin liquid) were tested, each at different surfactant concentrations (0.5 and 2.0 wt % with respect to the oil phase) and different weight ratios of the oil to aqueous phase (4:1 and 2:1). The aqueous phase was 1.0 M 2-(dimethylamino)ethyl methacrylate (DMAEMA, a water soluble monomer), in order to simulate the conditions necessary for polymerization.

To generate the emulsion, 1b was added to a 6.0 mL vial and dissolved in the oil phase. Sonication and heating were sometimes necessary to dissolve the surfactant, depending on the oil phase used. 1.0 M DMAEMA was added and the mixture was purged with CO$_2$ for 5 min. The vial was sealed using Parafilm® and sonicated for a further 3 min. Emulsion stability was assessed visually and photos were taken after 5 minutes.

This series of tests was repeated using Span 60™ (a commercially available non-ionic surfactant) as a co-surfactant, added in the same weight percentage as the switchable surfactant.

The identity of the continuous phase was determined using the droplet test method and conductivity measurements. A droplet of the emulsion was added to a petri dish containing the oil phase of interest and to a petri dish containing water. If the droplet spread in a medium, that medium was determined to be the continuous phase of the
emulsion. The conductivity of the emulsions was also measured using a Jenway conductivity meter 4071.

The temperature stability of two cyclohexane:aqueous DMAEMA (4:1 by weight) emulsions was established, one containing only 2 wt % 1b (with respect to oil phase) and the other containing both 2 wt % 1b and 5 wt % Span 60™, by allowing one portion of the emulsion to remain at room temperature and heating the other portion to 65 °C and observing the emulsion stabilities over time.

2.9.2 Using Compound 6

Inverse emulsions of 2:1 cyclohexane:aqueous phase (by weight) were generated by dissolving 2 wt % 6 (with respect to the oil phase) in cyclohexane, adding water, and shaking by hand for 5 min. The stability of these emulsions in the presence and absence of CO₂ was tested by removing one half of the emulsion to a separate vial, bubbling CO₂ through it and observing the separation of the oil phase from water over time. The temperature stability of an emulsion generated using 6 was determined as mentioned previously and the continuous phase identity was determined using the droplet test method. Polymerization was carried out by adding the initiator VA-061 (2 wt % with respect to monomer, 9.0 mg) and 6 (2 wt % with respect to monomer, 110 mg) to cyclohexane (5.3 g) and emulsifying this into the aqueous phase (1 M DMAEMA, 2.85g) by shaking for 5 min. The resulting emulsion was heated to 65 °C with stirring for 5 h in a sealed vessel.
Chapter 3  Emulsion Polymerization and Latex Destabilization using Alkyl Amidine Switchable Surfactants


Emulsion polymerization of styrene and methyl methacrylate was carried out using the amidine switchable surfactants, 1b and 2b. Although this concept was demonstrated previously,\textsuperscript{15} the key difference and improvement in this work versus the previous work is that latexes can now be prepared with particle sizes in the nano-range versus the micron-range, making this a true emulsion polymerization. The process described previously was a microsuspension polymerization, with particle diameters ~20 µm. For this project, I have explored the factors (initiator type, initiator amount, surfactant amount and solids content) that affect particle size and latex stability and in particular, the role of the amidine surfactant in determining these properties. An understanding of the factors that affect controlled latex destabilization is also required in order to induce phase separation in an effective manner, to improve the industrial viability of this process.

3.1 Emulsion Polymerization

3.1.1 Choosing an Initiator

It was determined previously in the Jessop lab that the choice of initiator greatly affects the stability of the resultant polymer latex when surfactant 1b is used. Three different azo-based free radical initiators were used and it was determined that VA-061 (Table 3.1, Scheme 3.1) was the most suitable because stable latexes obtained in the presence of CO\textsubscript{2} could be aggregated upon CO\textsubscript{2} removal. In contrast, latexes generated
using the cationic, water-soluble initiator VA-044 showed no visible signs of polymer settling after the removal of CO₂. Even after treatment of the latex with heat and air, followed by centrifugation for 10 min at 3500 rpm, the polymer particles remained suspended. The reason for this is believed to be proton transfer from the initiator to the surfactant. The pKₐ of the amidine shown in Scheme 2.1, where R=C₆H₁₃, has been reported to be 12.37,⁴⁶ and is not expected to change appreciably with alkyl chain length. The pKₐ of 2-ethylimidazoline, which is a fair representation of the end groups that result from initiator decomposition, is 11.05.⁴⁷ Therefore, because the surfactant is more basic, transfer of protons is expected to occur from the hydrochloride initiator (which contains 2 moles of HCl per mole of initiator) to the surfactant resulting in sustained surface activity of 1b (as 1a • HCl) even in the absence of carbon dioxide.

Table 3.1 Stability of PMMA latexes formed using 1b and different azo-based initiators.⁴⁸

<table>
<thead>
<tr>
<th>Initiator Name</th>
<th>VA-044</th>
<th>VA-061</th>
<th>AIBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size (nm)</td>
<td>108</td>
<td>108</td>
<td>&gt;6000</td>
</tr>
<tr>
<td>Latex Stability</td>
<td>Stable</td>
<td>Stable only in the presence of CO₂</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

⁴⁸Reactions were carried out at 23.5 wt % monomer loading, using 5 wt % (with respect to monomer) of 1b, 4 wt % (with respect to monomer) of initiator for 5-6 h at 65 °C under 1 atm of CO₂.

⁴⁶Particle sizes were measured using the Mastersizer 2000.

⁴⁷Stability was determined visually. Samples where no visible settling occurred for at least 2 weeks were deemed stable.
VA-061 is the neutral form of VA-044 and contains a cyclic amidine group that can react with CO₂ in the same way as 1a, producing a bicarbonate salt 3 (Scheme 3.1). The water soluble salt 3 can then be used as the initiator for the polymerization reaction, and upon treatment of the resulting latex with air and heat, polymer particles containing these initiator end groups on the particle surface should be neutralized and the latex should be more easily aggregated. Unless otherwise stated, all of the experiments carried out during this project used the initiator 3, which was generated in situ prior to polymerization.

![Structured diagram showing the reaction of VA-061 with CO₂ and H₂O to form 3]

Scheme 3.1 Reaction of VA-061 with carbon dioxide and water to produce the bicarbonate salt, 3.

### 3.1.2 Styrene Polymerization

A series of PS latexes was prepared using the conditions shown in Table 3.2. The effects of solids content, initiator concentration, and surfactant concentration on particle size and ζ-potential were examined. It was found that the particle size was essentially independent of initiator concentration (entries 3 vs. 5 and 8 vs. 11). This is unexpected behaviour because higher initiator concentrations should favour nucleation of more micelles thus producing a larger number of particles and therefore smaller particles compared to those produced at lower initiator concentrations. The fact that the
particle size is independent of initiator concentration suggests that the primary mode of particle generation in this system may be homogeneous, rather than micellar, nucleation.

In contrast, particle size was highly dependent on surfactant concentration; increases in particle size were observed when the surfactant concentration was decreased (entries 2 vs. 5 and 9 vs. 11). Simultaneously decreasing both the surfactant concentration and the initiator concentration also produced an increase in particle size (entries 1-3 and 7-9). This is expected behaviour, as increasing the surfactant concentration increases the number of particles that can be stabilized, leading to smaller particle diameters. This effect has been noted numerous times in the batch emulsion polymerization of styrene using cationic surfactants.\textsuperscript{49,50,51,52}

The particle size generally decreased with increasing wt % of styrene (at constant ratios of surfactant to monomer and initiator to monomer) when the resultant latex contained <10% coagulum (entries 1-4 versus 7-10). This can be attributed to higher overall surfactant concentrations at higher styrene loadings.

Coagulum formation during polymerization was generally not a serious problem; most of the experiments produced <5% coagulum. However, it did become a problem at higher initial monomer concentrations. At 38.5 wt % of styrene, 53% of the resulting polymer was a large, white solid mass, rendering any conclusions about trends in particle size at higher initial styrene concentrations unreliable. $\zeta$-Potential measurements in all cases indicate that the latexes should be stable, as they have values greater than 30 mV.\textsuperscript{53}
Table 3.2 Variation in particle size and ζ-potential of polystyrene latexes using different solid contents, surfactant concentrations and initiator concentrations.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Wt % Styrene\textsuperscript{b}</th>
<th>Mol % 2b\textsuperscript{c}</th>
<th>Mol % 3\textsuperscript{c}</th>
<th>Particle Size (nm) (PdI)\textsuperscript{d}</th>
<th>ζ-Potential (mV)</th>
<th>Conv. (%)</th>
<th>Coagulum (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5</td>
<td>1.00</td>
<td>1.00</td>
<td>72±0.1 (0.05)</td>
<td>51±2</td>
<td>93</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
<td>0.50</td>
<td>0.50</td>
<td>129±1 (0.01)</td>
<td>45±1</td>
<td>89</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>0.25</td>
<td>0.25</td>
<td>198±2 (0.02)</td>
<td>49±1</td>
<td>92</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>13.5</td>
<td>0.10</td>
<td>0.10</td>
<td>222±2 (0.03)</td>
<td>44±0.3</td>
<td>85</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>13.5</td>
<td>0.25</td>
<td>0.50</td>
<td>203±3 (0.04)</td>
<td>59±2</td>
<td>94</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>22.8</td>
<td>3.00</td>
<td>1.00</td>
<td>58±1 (0.05)</td>
<td>31±2\textsuperscript{e}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>23.5</td>
<td>1.00</td>
<td>1.00</td>
<td>61±1 (0.12)</td>
<td>59±6</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>23.5</td>
<td>0.50</td>
<td>0.50</td>
<td>85±1 (0.06)</td>
<td>59±1</td>
<td>95</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>23.5</td>
<td>0.25</td>
<td>0.25</td>
<td>203±2 (0.03)</td>
<td>54±1</td>
<td>98</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>23.5</td>
<td>0.10</td>
<td>0.10</td>
<td>178±2 (0.02)</td>
<td>51±1</td>
<td>94</td>
<td>7</td>
</tr>
<tr>
<td>11</td>
<td>23.5</td>
<td>0.50</td>
<td>0.25</td>
<td>94±1 (0.08)</td>
<td>55±1</td>
<td>99</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>38.5</td>
<td>0.25</td>
<td>0.25</td>
<td>239±2 (0.09)</td>
<td>56±2</td>
<td>87</td>
<td>53</td>
</tr>
<tr>
<td>13</td>
<td>38.5</td>
<td>0.10</td>
<td>0.10</td>
<td>372±16 (0.19)</td>
<td>45±1</td>
<td>83</td>
<td>35</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reactions were carried out for 5 h at 65 °C under 1 atm of CO\textsubscript{2}

\textsuperscript{b}With respect to water.

\textsuperscript{c}With respect to styrene.

\textsuperscript{d}Values of PdI obtained from the Zetasizer ZS that are < 0.1 indicate a narrow, monomodal size distribution.

\textsuperscript{e}Measured using dip cell (all others measured using capillary cuvette).

3.1.3 Methyl Methacrylate and Butyl Methacrylate Polymerization

Polymerization of methyl methacrylate was also performed (Table 3.3). Although MMA is more hydrophilic and has a higher water solubility than styrene (159 versus 3.5 mmol dm\textsuperscript{-3}), similar trends between the monomers were observed. Decreasing the surfactant concentration increased the particle size (entries 1-2 and 8-11), and changes in the initiator concentration seemed to have little effect on particle size (entries 4 vs. 5 and 6 vs. 7). With all other ratios constant, increasing the solids content tended to slightly decrease the particle size (entries 1 vs. 10 and 2 vs. 11). Comparing the polymerization of styrene to that of methyl methacrylate, the particle size was larger in the case of polystyrene with otherwise equivalent conditions (Table 3.2, entry 8 versus Table 3.3,
entry 7). The fact that PMMA is more hydrophilic than PS allows more surface area to be stabilized by the same amount of surfactant, leading to a larger number of particles and therefore smaller particles.

Table 3.3 Variation in particle size and ζ-potential of PMMA latexes using different solid contents, surfactant concentrations and initiator concentrations.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>Wt % MMA(^b)</th>
<th>Mol % 2b(^c)</th>
<th>Mol % 3(^c)</th>
<th>Particle Size (nm) (PdI) Zetasizer</th>
<th>Particle Size (nm) (UnI)(^d) Mastersizer</th>
<th>ζ-Potential (mV)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5</td>
<td>0.12</td>
<td>0.07</td>
<td>143±1 (0.05)</td>
<td>-</td>
<td>27±2</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
<td>0.07</td>
<td>0.07</td>
<td>183±2 (0.04)</td>
<td>-</td>
<td>35±2</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>0.03</td>
<td>0.05</td>
<td>218±1 (0.15)</td>
<td>167 (0.511)</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>23.5</td>
<td>2.00</td>
<td>1.00</td>
<td>47±0.2 (0.06)</td>
<td>-</td>
<td>22±1</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>23.5</td>
<td>2.00</td>
<td>0.50</td>
<td>41±1 (0.06)</td>
<td>-</td>
<td>46±1</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>23.5</td>
<td>0.50</td>
<td>1.00</td>
<td>58±1 (^f) (0.11)</td>
<td>-</td>
<td>53±1</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>23.5</td>
<td>0.50</td>
<td>0.50</td>
<td>56±1 (0.09)</td>
<td>-</td>
<td>48±3</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>23.5</td>
<td>0.50</td>
<td>0.07(^e)</td>
<td>59±0.3 (0.12)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>23.5</td>
<td>0.25</td>
<td>0.07</td>
<td>101±1 (0.09)</td>
<td>-</td>
<td>44±2</td>
<td>86</td>
</tr>
<tr>
<td>10</td>
<td>23.5</td>
<td>0.12</td>
<td>0.07</td>
<td>134±1 (0.07)</td>
<td>-</td>
<td>31±2</td>
<td>92</td>
</tr>
<tr>
<td>11</td>
<td>23.5</td>
<td>0.07</td>
<td>0.07</td>
<td>159±2 (0.1)</td>
<td>-</td>
<td>33±0.5</td>
<td>97</td>
</tr>
<tr>
<td>12</td>
<td>23.5</td>
<td>0.03</td>
<td>0.05</td>
<td>244±2 (0.27)</td>
<td>316 (0.307)</td>
<td>-</td>
<td>88</td>
</tr>
<tr>
<td>13</td>
<td>38.5</td>
<td>0.03</td>
<td>0.05</td>
<td>227±5 (0.38)</td>
<td>319 (0.192)</td>
<td>-</td>
<td>93</td>
</tr>
</tbody>
</table>

\(^a\)Reactions were carried out for 5 h at 65 °C under 1 atm of CO\(_2\).

\(^b\)With respect to water.

\(^c\)With respect to monomer.

\(^d\)Particle size values obtained on the Zetasizer ZS are reliable as long the PdI values are less than 0.1. The Mastersizer was used to measure particle sizes of those samples having a particle size PdI ≥ 0.15.

\(^e\)Higher values of uniformity indicate less uniform particle sizes.

\(^f\)Large amounts of coagulum were produced (as much as 50%), due to a higher initiator than surfactant concentration. Coagulum amounts in all other cases was < 5 %.

\(^g\)VA-044 initiator was used.

Polymerization of butyl methacrylate was carried out as a proof of concept, and the results can be seen in Table 3.4. The results show that polymerization can be successfully carried out using surfactant concentrations as low as 0.25 mol % (with respect to monomer). Much less surfactant can be used to produce similar particle sizes.
when comparing MMA to BMA. This is expected due to the much higher water solubility of MMA \((159 \text{ mmol dm}^{-3})^{21}\) compared to BMA \((4.23 \text{ mmol dm}^{-3})^{21}\), indicating that less surfactant is needed to stabilize the total particle surface area. Styrene and BMA have similar water solubilities \((3.5 \text{ and } 4.23 \text{ mmol dm}^{-3}, \text{ respectively})\), which suggests that a similar amount of surfactant would be needed to stabilize the same surface area, which is the case when comparing Table 3.4, entry 2 to Table 3.2, entry 3. Similar particle sizes between PBMA and polystyrene were not obtained, however, in the cases where 0.5 mol % of \(2b\) was used (Table 3.4, entry 1 versus Table 3.2, entry 2). One possible explanation is that BMA polymerizes much faster than styrene\(^{5a}\) leading to a quick nucleation of many particles. The surfactant may not be able to stabilize this large surface area, thus causing particle aggregation to the size that was obtained with lower surfactant concentrations. This is likely the same reason why using more surfactant did not produce smaller particles. Both attempts to polymerize BMA with lower surfactant and initiator concentrations \((0.07 \text{ mol } % \text{ each})\) failed.

**Table 3.4** Variation in particle size and \(\zeta\)-potential of PBMA latexes using different solid contents, surfactant concentrations and initiator concentrations.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>Wt % BMA(^b)</th>
<th>Mol % 2b(^c)</th>
<th>Mol % 3(^c)</th>
<th>Particle Size (nm) (PdI)</th>
<th>(\zeta)-Potential (mV)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5</td>
<td>0.50</td>
<td>0.50</td>
<td>219 ± 3 (0.04)</td>
<td>57 ± 1</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
<td>0.25</td>
<td>0.25</td>
<td>217 ± 4 (0.03)</td>
<td>55 ± 1</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>0.07</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Reactions were carried out for 5 h at 65 °C under 1 atm of CO\(_2\). Negligible amounts of coagulum were produced during each polymerization.

\(^b\)With respect to water.

\(^c\)With respect to BMA.

Conversion in all cases (for styrene, MMA and BMA) was over 80%; typical conversion profiles can be seen in Figure 3.1. The curves show the standard shape
associated with conventional batch emulsion polymerization. In the case of MMA polymerization, the induction time was longer when a lower initiator concentration (0.07 mol % versus 1.0 mol %) was used, leading to a longer time to reach maximum conversion, which was >95% in both cases. Furthermore, it is likely that the rate of polymerization of BMA was slower than MMA or styrene because less surfactant and initiator were used and fewer particles were present during the polymerization.

Figure 3.1 Conversion versus time profile for the polymerization of MMA using 1.0 mol % \(2b\) and 1.0 mol % \(3\) (---); MMA using 0.07 mol % \(2b\) and 0.07 mol % \(3\) (---); styrene using 1.0 mol % \(2b\) and 1.0 mol % \(3\) (-----); and BMA using 0.5 mol % \(2b\) and 0.5 mol % \(3\) (—).

3.1.4 Long Term Latex Stability

Long term stability of the latex formulated using the conditions in Table 3.3, entry 4 (2.0 mol % \(2b\) and 1.0 mol % \(3\)) was also assessed. The latex was divided into two samples, whose particle size and ζ-potential were measured each day for a week. The first sample was left under an atmosphere of CO\(_2\) between measurements and to ensure that the latex was saturated during the measurement, CO\(_2\) was bubbled through it for 30 min prior to analysis. It was found that this latex was stable (no changes in particle size or ζ-potential, see Table 3.5) for at least one week. After that, the sample remained capped
and untouched for 10 more days and the particle size only increased moderately (from 59 to 93 nm). The second sample was stored in a vial which was briefly opened to air each day (for the first 7 days) and not treated with CO$_2$ prior to analysis. This sample, which received no CO$_2$ treatment, showed a slight decrease in $\zeta$-potential throughout the first week. After 17 days, that sample became very viscous and turned to a gel (Figure 3.2). At this point, particle size was measured and it was determined that the latex was severely destabilized (the final particle size was 10.4 µm). From these results, we conclude that polymer latexes synthesized using amidine surfactants are stable as long as they are kept under an atmosphere of CO$_2$. Another important aspect worth noting is that the latexes are sufficiently stable that rigorous air-free conditions during synthesis are not necessary and that the latexes can be stored in air if stability is required for less than approximately one week.

**Table 3.5** Assessment of the long term stability of PMMA latexes stabilized by 2b that are exposed to air and those that were saturated with CO$_2$ for 30 min once a day for 7 days.$^a$

<table>
<thead>
<tr>
<th></th>
<th>Bubbling CO$_2$ for 30 minutes each day$^b$</th>
<th>No bubbling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\zeta$-Potential (mV)</td>
<td>Size (nm) (PdI)</td>
</tr>
<tr>
<td>3 days</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4 days</td>
<td>54±0.4</td>
<td>59 (0.09)</td>
</tr>
<tr>
<td>5 days</td>
<td>49±1</td>
<td>59 (0.11)</td>
</tr>
<tr>
<td>6 days</td>
<td>48±2</td>
<td>59 (0.10)</td>
</tr>
<tr>
<td>7 days</td>
<td>52±2</td>
<td>59 (0.11)</td>
</tr>
<tr>
<td>17 days</td>
<td>-</td>
<td>93 (0.21)</td>
</tr>
</tbody>
</table>

$^a$Measurements taken at room temperature.

$^b$CO$_2$ was bubbled through the latex each day until day 7, after which it was sealed under CO$_2$ for 10 further days.
Figure 3.2 Photograph of PMMA latexes (prepared using 23.5 wt % MMA, 2.0 mol % 2b and 1.0 mol % 3) after 17 days with (at left) bubbling of CO$_2$ for 30 minutes each day for the first 7 days and (at right) no CO$_2$ bubbling (vials were inverted for the photograph to show the increased viscosity of the sample which received no CO$_2$ treatment).

3.2 Latex Destabilization

Many factors can affect the colloidal stability of a latex and it is necessary to understand these factors in order to determine how and when destabilization occurs. Particle aggregation occurs when the free energy barrier between polymer particles is overcome, rendering the interactions between particles more favourable than their interaction with the aqueous phase. Salts can be added to electrostatically stabilized latexes to suppress the electric double layer and decrease the energy barrier toward aggregation. Furthermore, if the surfactant is pH sensitive, addition of acids or bases will decrease surface charge providing less stabilization and more rapid aggregation.\textsuperscript{35,37}

In the system currently under study, the surfactant is pH sensitive and has been designed to respond to the amount of CO$_2$ present. Removal of CO$_2$ causes neutralization of the surfactant resulting in a decreased surface charge and a decreased electrostatic barrier. The chemical reaction converting the bicarbonate salt form of the surfactant to the neutral amidine is endothermic and thus increasing the temperature helps the
conversion of the salt to its neutral form. This temperature increase also increases the average particle kinetic energy and the rate of particle encounters, leading to an increased rate of particle aggregation.

3.2.1 The Effect of Surfactant Concentration and Initial Particle Size

The polystyrene latexes synthesized as reported in Table 3.2, entries 7-9 were destabilized by bubbling air through the samples at 65 °C. Figure 3.3 shows the results of this study and provides insight into the factors that affect destabilization. Figure 3.3(a) shows that a second peak appears at approximately 20 µm after bubbling with air and heating for 100 min, signifying the formation of stable polystyrene aggregates. In numerous experiments, we consistently observed this trend with the appearance of large aggregates but without observing intermediate particle sizes. Furthermore, the time that it takes for the sample to become destabilized depends on the amount of amidine functionality present in the system and/or the initial particle size, which can be seen in Figure 3.3(b). At higher initial concentrations of 2b and 3 (1.0 mol % each vs. 0.25 mol % each), the volume percentage of particles below 1.0 µm (primary particles) decreases quickly during the destabilization procedure. This implies that higher amidine concentrations favour destabilization. However, higher initial concentrations of 2b and 3 also produce smaller initial particle sizes, so it is unclear whether small initial particle sizes or high surfactant/initiator concentrations lead to faster destabilization. If the bubbling and heating time is extended, no detectable primary particles remain as is evident from the single monomodal peak in the micron range for each latex sample at 24 h.
Figure 3.3 (a) Particle size distribution of a polystyrene latex synthesized using 0.5 mol % 2b and 0.5 mol % 3 after treating with air at 65 °C for 100 min (b) Volume percent of polystyrene aggregates over time in latexes containing various amounts of 2b and 3 (mol % 2b/mol % 3 (initial particle size)) after treating with air at 65 °C (23.5 wt % polystyrene). The curves are added to guide the eye.
Although a larger volume of stable aggregates is formed faster when amidine concentrations are high (initial particles sizes are small), the final particle size of the aggregates in polystyrene latexes after destabilization was consistently between 10 µm and 15 µm when the solids content was 13.5 wt %. This leads to the conclusions that final aggregate size does not depend on the amount of amidine functionality on the particles or the initial particle size. The latexes with solids contents of 23.5 wt % produce larger aggregates (24 µm – 26 µm), leading to the conclusion that final aggregate size has a slight dependence on the latex polymer concentration.

PMMA latexes were destabilized using heat and either argon or air, and again the latex was fully destabilized faster in the case where more surfactant was used (initial particles were smaller). Destabilization of the PMMA latex with 47 nm particles (Table 3.3, entry 4) was assessed visually. This was necessary because latex destabilization resulted in the formation of a viscous polymer gel. At this point the latex could not be stirred effectively and bubbling rates could not be maintained, so the mixture had to be diluted before the destabilization procedure could be continued. Upon addition of water, a mixture of latex and aggregated polymer particles resulted. With further treatment of air and heat, the polymer particles settled to reveal a clear water layer on top indicating that a negligible amount of primary particles were present. This clear water layer was observed after 120 min of total treatment time.

At larger primary particle sizes (159 nm, Table 3.3, entry 11), destabilization took longer (see Figure 3.4 which shows that a large population of primary particles are still present after 120 min), which is consistent with the aggregation kinetics described in equation 14. Effectively, at larger primary particle sizes and the same polymer
concentration there are fewer particles and therefore fewer particle-particle interactions, leading to a decreased rate of aggregation.

In the case of destabilization of the latex with 159 nm particles, changes in particle size and \( \zeta \)-potential with time were easily monitored. As expected, the \( \zeta \)-potential decreases with destabilization time (Table 3.6), indicating a decreased particle charge due to the surfactant and/or initiator end groups switching to their neutral form. The decrease in \( \zeta \)-potential corresponds to the growth of a peak in the micron range (approximately 6-8 \( \mu \)m) as the particles begin to aggregate due to the decrease in electrostatic stabilization (Figures 3.4 and 3.5). This does not correspond to removal of all of the surface charge, but enough charge has been neutralized that van der Waals attractive forces between particles become larger than electrostatic repulsion forces. After the appearance of the peak corresponding to the aggregated particles (after 80 min), measurements were recorded using both the Zetasizer ZS and the Mastersizer 2000. The Zetasizer ZS is a dynamic light scattering instrument and is most useful and accurate for monomodal samples whose particle size is < 1 \( \mu \)m. Because destabilization produces particles > 5 \( \mu \)m, measurements were also taken on the Mastersizer 2000, a static light scattering instrument that can measure samples up to 2000 \( \mu \)m. An overlay plot of the particle size distributions after destabilization for various time intervals using both instruments can be seen in Figure 3.4. Final average particle sizes in the case of PMMA did not appear to depend on polymer concentration or amidine concentration, and were all generally in the range of 6-7 \( \mu \)m. Extended treatment of polystyrene and PMMA latexes with air and heat caused further aggregation and sometimes produced particles with very large diameters (> 100 \( \mu \)m).
Figure 3.4 Change in particle size with time during destabilization (sparging with air and heating to 65 °C) of latex formulated according to conditions in Table 3.3, entry 11 (23.5 wt % MMA, 0.07 mol % 2b, 0.07 mol % 3) monitored with the (a) Mastersizer 2000 and (b) Zetasizer ZS.\textsuperscript{45}
Table 3.6 Variation in ζ-potential with time during destabilization (sparging with air and heating to 65 °C) of the PMMA latex formulated according to conditions in Table 3.3, entry 11 (23.5 wt % MMA, 0.07 mol % 2b, 0.07 mol % 3).  

<table>
<thead>
<tr>
<th>Treatment Time (min)</th>
<th>ζ-Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42±2</td>
</tr>
<tr>
<td>40</td>
<td>34±1</td>
</tr>
<tr>
<td>80</td>
<td>27±1</td>
</tr>
<tr>
<td>120</td>
<td>26±0.4</td>
</tr>
<tr>
<td>160</td>
<td>24±1</td>
</tr>
</tbody>
</table>

*Measurements taken at room temperature.

Another distinct difference in the destabilization behaviour of PMMA latexes with 47 nm versus 159 nm particles is the fact that gel formation does not occur at larger primary particle sizes. In our system, destabilization of the latex involves the removal of CO₂, which decreases the electrolyte concentration in the continuous phase, effectively increasing the thickness of the electric double layer surrounding the polymer particles. This has the effect of increasing the sample viscosity, and allowing gel formation in the case of the latex sample with 47 nm particles. Smaller particles have a larger effective volume fraction and this is a possible explanation for gel formation in the small particle size latexes. The thickness of the double layer will be the same in the case of both the small and large particles, but the volume of the excluded layer surrounding the particle due to double layer repulsion will be a greater fraction of the particles total volume in the case of particles with smaller diameters. This can be expressed mathematically using the following equation:  

\[
\phi_{eff} = \phi \left( 1 + \frac{6\delta}{d} \right)
\]  

(17)

where \(\phi_{eff}\) is the effective polymer volume fraction of polymer particles (ie- solid content), \(\phi\) is the actual volume fraction of polymer particles, \(\delta\) can be approximated as...
the double layer thickness and \( d \) is the particle diameter. The change in double layer thickness upon CO\(_2\) removal combined with the large effective volume fraction induces gel formation in the case of the 47 nm particles. Furthermore, the interparticle spacing is less with smaller particles, which exacerbates the tendency to higher viscosity.

Destabilization of the PBMA latex formulated in Table 3.4, entry 2 was carried out, again at 65 °C while sparging the latex with air. A solid, rubbery mass of polymer was obtained after destabilization along with a clear aqueous layer. The rubbery polymer was cut with a spatula into small pieces and the polymer and water were transferred to a 20 mL scintillation vial (shown in Figure 3.5). In the case of PBMA, the destabilization temperature is higher than the \( T_g \) (20 °C)\(^{21}\) of the polymer leading to a particle fusion during destabilization, likely by inter-diffusion of individual polymer chains of different particles. This produces one solid mass of rubbery polymer instead of the micron-sized aggregates produced during the aggregation of hard PMMA and PS spheres.

![Photograph of a PBMA latex (left) and a destabilized PBMA latex (right).](image)

**Figure 3.5** Photograph of a PBMA latex (left) and a destabilized PBMA latex (right).
3.2.2 The Effect of Polymer Concentration and Temperature

The effect of polymer concentration and temperature on destabilization time of PMMA latexes was examined, and the results of this study can be seen in Figure 3.6. Another member of the Jessop group showed that at higher temperatures (80 °C) destabilization occurs much faster. Increasing latex temperature increases the average kinetic energy of particles and the frequency of collisions between them. The thermal energy of the particles increases with temperature and this allows two particles to surmount the potential energy barrier that may exist between them and allows them to aggregate together. At higher polymer concentrations (25 wt %), aggregation also occurs much faster, which is consistent with equation 14. This again is due to the decrease in particle spacing, thus increasing the frequency of particle collisions and promoting aggregation.

SEM images were obtained of a PMMA latex before and after the destabilization procedure. The latex before the destabilization procedure shows primary particles with some aggregation (Figure 3.7(a)), which is most likely due to the evaporation of solvent during microscope sample preparation. In contrast, the latex sample that had been destabilized by treatment with air and heat showed extensive aggregation, producing aggregates that are ~ 5 µm (Figure 3.7(b)). It is important to note that the primary particles, while they are touching each other in the aggregates, remain spherical and do not fuse together. This is not observed during the destabilization of PBMA latexes, due to the low glass transition temperature \( T_g \) of this polymer.
Figure 3.6 Volume % of PMMA particles stabilized by 2b below 1.0 μm over time after heating and bubbling with air at different (a) polymer concentrations (temperature is constant at 65 °C) and (b) temperatures (polymer concentration is constant at 5 wt %). The decrease in ζ-potential over time corresponding to destabilization of PMMA particles at 80 °C is also shown.45
Figure 3.7 SEM images of particles from (a) a PMMA latex stabilized with 2b and (b) a similar PMMA latex treated with air and heat to remove the CO₂. In both cases, the latex was prepared using 13.5 wt % MMA, 0.07 mol % 2b and 0.07 mol % 3 (scale is 5 µm).

3.3 Determining Surfactant Partitioning Behaviour

The partitioning behaviour of surfactants between the monomer and water phases plays a key role in determining emulsion stability and the stability of the resultant latex upon emulsion polymerization. To be an effective surfactant, the molecule must not be so hydrophobic or hydrophilic that it will reside preferentially in one phase; it must reside at
the interface between the two phases. As well, the type of emulsion will be determined by the surfactant solubility, with more water-soluble surfactants creating oil-in-water emulsions.

An experiment was carried out to determine the partitioning behaviour of the alkyl amidine surfactant \(2b\) and its neutral precursor \(2a\) between a monomer phase and a D\(_2\)O phase. Table 3.7 shows the relative percentage of each of the uncharged (\(2a\)) and charged (\(2b\)) surfactant that partitioned into the D\(_2\)O phase for each monomer. From this, monomer-D\(_2\)O partition coefficients (K) were calculated using equation 18. The closer K is to 1, the more evenly distributed the molecule is between the two phases. The K values for compound \(2b\) in styrene and MMA are 1.2 and 0.85, respectively. This shows that the surfactant does not prefer one phase preferentially, which explains its ability to stabilize emulsions of these monomers and water. The K values of the uncharged compound \(2a\) in styrene and MMA are 21 and 2.2, respectively. The fact that the values are greater than 1 indicates that \(2a\) partitions more into the monomer phase than the D\(_2\)O phase. This was anticipated because of the expected low solubility of \(2a\) in D\(_2\)O (solubility of the 8-carbon chain analogue is 4.9 g L\(^{-1}\)),\(^{16}\) and the fact that the monomer phase is more likely to have the ability to solubilize the molecule’s long alkyl chain. In the case of partitioning between styrene and D\(_2\)O, \(2a\) almost exclusively resides in the monomer phase (shown by the high K value). This differs from MMA in which \(2a\) is present in only slightly higher concentrations in the monomer phase. The difference between styrene and MMA is likely due to the fact that styrene is less polar than MMA, which leads to its greater ability to solubilize the long alkyl chain of the neutral molecule.

\[
K = \frac{\% \text{ Molecule in the Monomer Phase}}{\% \text{ Molecule in the D}_2\text{O Phase}} \times 100
\] (18)
Table 3.7 Percentage of 2a and 2b partitioned into a D₂O phase from the monomer phase when the monomer phase was styrene or MMA.

<table>
<thead>
<tr>
<th></th>
<th>Styrene/D₂O Emulsion</th>
<th>MMA/D₂O Emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trial 1</td>
<td>Trial 2</td>
</tr>
<tr>
<td>2a</td>
<td>5.3</td>
<td>4.0</td>
</tr>
<tr>
<td>2b</td>
<td>47</td>
<td>45</td>
</tr>
</tbody>
</table>

3.4 Determining Particle Coverage

The ability of a surfactant to adsorb onto a polymer surface will also affect the stability of the resultant latex. The more surfactant that can adsorb, the more stable the polymer dispersion will be. As well, the hydrophilicity of a polymer will determine how much surfactant is needed to obtain sufficient stability; more hydrophilic surfaces need less surfactant to remain stabilized in water.

When a surfactant is added to a latex, the surfactant will dissolve in the aqueous phase, go to the polymer-water interface, go to the air-water interface or form aggregate structures such as micelles. The soap titration method of determining the coverage of surfactant molecules on the surface of polymer particles involves addition of surfactant while monitoring properties such as air-latex surface tension or latex conductivity and was developed by Maron in 1954. The point at which the addition of surfactant ceases to decrease the air-latex surface tension signifies the formation of micelles, in which case no more surfactant is being adsorbed onto the particle surface.

The surfactant used in this experiment was surfactant 5 shown in Figure 2.2. It contains the \( N' \)-dodecyl-\( N, N \)-dimethylamidinium cation with an acetate anion and it was used because it remains permanently charged under the experimental conditions. The switchable surfactant 2b (containing the bicarbonate anion) is sensitive to the
concentration of CO$_2$, and loss of CO$_2$ would alter the concentration of the surfactant and affect the resulting surface tension measurement. Surfactant 5 was used in the emulsion polymerization of MMA and the resulting PMMA latex was titrated using surfactant 5 according to the procedure outlined in Section 2.8. The titration results are shown in Figure 3.8. The break point of each curve signifies the formation of micelles and is the maximum amount of surfactant 5 that can be added to the latex before particle saturation occurs. As expected, this value increases as the concentration of polymer in latex increases. From this data, the following equation can be used to determine the area that one surfactant molecule occupies on the particle surface ($A_s$):

$$A_s = \frac{6}{S_i N_A \rho d}$$  \hspace{1cm} (19)

where $d$ = average particle diameter, $N_A$ = Avogadro’s number, $\rho$ = polymer density and $S_i$ is the experimentally determined number of moles of surfactant per gram of polymer particles at micellization. $S_i$ is actually the sum of two terms: $S_i$ which is the initial amount of surfactant per gram of polymer ($= C_i/m_o$ where $C_i$ is the initial surfactant concentration [$=\text{moles of surfactant per liter of latex}$, and $m_o$ is the initial polymer concentration [$=\text{grams of polymer per liter of latex}$] and $S_a$ which is the amount of surfactant per gram of polymer that needs to be added to attain the CMC ($= C_a/m$ where $C_a$ is the concentration of surfactant added and adsorbed [$=\text{moles of surfactant per liter of latex}$, and $m$ is the polymer concentration). Some unadsorbed soap will be present at the CMC that must be corrected for, its concentration is denoted as $C_f$ such that $C = S_a m + C_f$ where $C$ is surfactant concentration at micellization obtained from the break points in the plots (in moles per liter of latex). This is a linear equation, in which $S_a$ is the slope and $C_f$ is the intercept, which are both assumed to be constant, given that the size of the
particles or the adsorbing surface does not change. Figure 3.9 shows the linear plot constructed using the maximum concentration of surfactant adsorbed obtained at various polymer concentrations (C vs. m).

![Figure 3.9 showing the linear plot constructed using the maximum concentration of surfactant adsorbed obtained at various polymer concentrations (C vs. m).](image)

**Figure 3.8** Soap titrations of three latexes at different polymer concentrations: 20 g L\(^{-1}\) (▲), 8.3 g L\(^{-1}\) (●) and 2.0 g L\(^{-1}\) (●).
Figure 3.9 A plot of surfactant concentration versus polymer concentration in three different latexes to determine the maximum amount of 5 adsorbed by PMMA particles at the surfactant CMC.

The value of $S_i$ from the initial polymerization is $7.2 \times 10^{-6}$ mol g$^{-1}$ (0.0219 mmol of 5 was used in the polymerization of 3.13 g of MMA, with a PMMA yield of 97 %). The value of $S_a$ (slope of the line in Figure 3.9) was determined to be $4.7 \times 10^{-5}$ mol g$^{-1}$. The sum of these values ($S_t$) is $5.4 \times 10^{-5}$ mol g$^{-1}$. Using equation 18, the area occupied by a single surfactant molecule on the PMMA polymer particle surface is calculated to be $104 \text{ Å}^2$.

It is now possible to determine what fraction of the particles surface is covered in surfactant by simply determining the ratio of total surface area occupied by surfactant molecules to the total particle surface area. The equation is:

$$
\text{Fraction covered} = \frac{S_t}{\text{Total surface area}}
$$
% Coverage = \frac{\frac{m_s}{M_s} A_s N_A}{m_{pol} \rho_d} \tag{20}

where m_s is the mass of surfactant, M_s is the molecular weight of surfactant, A_s is the area occupied by a surfactant molecule, m_{pol} is the mass of polymer. From this, the calculated percent coverage of surfactant on PMMA particles synthesized for this experiment is 15%. This means that the amidine surfactant, 5, is very effective at stabilizing PMMA particles, and a very small amount can be used without sacrificing latex stability.

Research has been carried out on the adsorption behaviour of both cationic and anionic surfactants on the surface of polystyrene particles synthesized via emulsion polymerization. The following values have been obtained for various surfactants: 47 Å², 56 Å² and 71 Å² for cetyl, dodecyl and octyltrimethyl ammonium bromide surfactants, respectively, 47 Å² for potassium oleate and sodium dodecyl sulphate and 53 Å² for sodium dodecyl benzenesulfonate. For PMMA particles the authors only studied anionic surfactants, with the following results: 152 Å² for sodium dodecyl sulphate and 131 Å² for sodium dodecyl benzenesulfonate. The similarity in values within polystyrene latexes as well as within PMMA latexes but the difference in values between different polymers led all authors to conclude that the value for A_s depends very little on the emulsifier itself, and more on the identity of the polymer. In other words, more hydrophilic polymers require less surfactant to be stabilized, and thus the numerical value for the occupied area of a surfactant is much larger.

In light of this, the experimental value of 104 Å² for the surfactant studied in this thesis appears somewhat low, and there could be many explanations for this. One factor in particular could lead to a decrease in A_s: increased salt concentration in the latex. The
The surfactant used for this experiment was synthesized by adding an equimolar amount of acetic acid to 2a, but it was neither isolated nor purified before use. It could be possible that some residual acetic acid was present, which would increase the ion concentration. However, it is unlikely that such a small concentration of ions would have such a dramatic effect on the results obtained in this experiment.

The fact that the surface coverage of the polymer particles using surfactant 5 is only 15% at micellization shows that this surfactant is very effective at stabilizing the PMMA particles of this latex. Each molecule is able to stabilize a large area of the surface of a polymer particle, indicating that fewer surfactant molecules are necessary for stabilization. This has implications in the determination of the amount of surfactant required to effectively stabilize a PMMA latex using a surfactant with a similar structure to the switchable surfactant 2b and explains why very low surfactant concentrations can be used to obtain stable polymer latexes of PMMA.

3.5 Conclusions

Switchable long chain alkyl amidine surfactants can be used in the emulsion polymerization of styrene, methyl methacrylate and butyl methacrylate. Emulsion polymerization conducted using the azo-based free radical initiator VA-061 yields stable colloidal polymer latexes with controllable particle sizes ranging from 41 to 372 nm. The latex samples are stable as long as they are saturated with CO₂.

Treatment of latexes stabilized by surfactants such as 1b and 2b with heat and air, Ar or N₂ results in the formation of micron-sized polymer aggregates that can be readily separated from the aqueous phase. This destabilization procedure does not involve the addition of copious amounts of salts, strong acid or strong base and thus has the benefits
of contaminating neither the water (which would then subsequently need further purification) nor the product (which could alter its final properties). The use of air and heat rather than salt, acid or base in the destabilization of latex samples could reduce the environmental impact of latex processing.

The aggregation behaviour of polystyrene and poly(methyl methacrylate) latexes depends heavily on the amount of surfactant and initiator in the system, the initial particle size, the polymer concentration and the temperature. Latex destabilization is faster when the latex contains smaller particles, has higher solids contents and at higher temperatures. The final size of the polymer aggregates depends on the choice of monomer (styrene versus MMA) and the polymer concentration (in the case of polystyrene).

Because these switchable surfactants are known to be able to undergo multiple switching cycles, redispersion of the destabilized polymer aggregates by providing energy and reintroducing carbon dioxide is possible and has been shown in the case of PS.\textsuperscript{48} It is, however, important to note that redispersibility would likely only be possible if the particles do not fuse together during the destabilization procedure, which is true in the cases of polystyrene and PMMA but not in the case of PBMA.
Chapter 4  Emulsion Polymerization and Latex Destabilization using Alkylphenyl Amidine and Tertiary Amine Switchable Surfactants

Switchable surfactants containing amidine\textsuperscript{15,16,18,19} or guanidine\textsuperscript{16,17} head groups and long chain alkyl or ethoxylated\textsuperscript{18,19} tails have recently been developed. These surfactants are charged in the presence of CO\textsubscript{2} due to the formation of bicarbonate salts, and uncharged upon removal of CO\textsubscript{2}. The basicity of the surfactant head group affects the reaction equilibrium and thus the ratio of charged to uncharged forms at a given temperature and CO\textsubscript{2} partial pressure. Guanidines are generally the most basic and require the most forcing conditions (high temperatures, faster gas flow rates) to remove the CO\textsubscript{2}, whereas CO\textsubscript{2} can be removed from less basic amines at more ambient conditions. This is evidenced by the lower conversions of tertiary amines versus guanidines to bicarbonate salts at a given temperature.\textsuperscript{16} The basicity of amidines generally lies between the above two cases.

In this chapter, the use of less basic amidine and tertiary amine surfactants with more facile switching is described. Emulsion polymerization of MMA was carried out using these surfactants, and it was hypothesized that more rapid aggregation of polymer latexes would be possible.

4.1  Surfactant Switchability

The two surfactant precursors chosen were the long chain alkyl tertiary amine, 4a, and the alkyl phenyl dimethylacetamidine, 3a (Scheme 4.1). These compounds were chosen based on the reported aqueous pKa\textsubscript{H} values of their shorter alkyl chain analogues (10.0 for N,N-dimethylbutylamine\textsuperscript{60} and 10.8 for N'-tolyl-N,N-dimethylacetamidine,\textsuperscript{61} compared to 12.2 for 2a).
Scheme 4.1 The reaction of “easy off” amidines and amines with CO₂ and water to form bicarbonate salts.

Tertiary amine 4a was purchased and 3a was synthesized according to a previously developed procedure (outlined in Section 2.1). Formation of the bicarbonate salts was achieved by purging CO₂ through solutions of 3a and 4a in various solvents, but their isolation was unsuccessful. Therefore, bicarbonate formation was confirmed by the presence of peaks at 161 ppm (carbon of HCO₃⁻), and ~164 ppm (the cationic carbon) in the ¹³C-NMR spectra of solutions of 3a and 4a in CO₂ saturated MeOD-d₄. It has been shown previously in our lab that amidine type surfactants form bicarbonate (HCO₃⁻) rather than carbonate salts (CO₃²⁻) when reacted with CO₂ and water. As well, it has been shown that the carbon in CsHCO₃ in MeOD-d₄ gives a peak at 161 ppm in its ¹³C-NMR spectrum, which shifts downfield to 170 ppm in the ¹³C-NMR spectrum of Cs₂CO₃. Conversion to 3b⁺ (7-carbon chain analogue of 3b) and 4b was 98 % and 94 % at room temperature and 54 % and 47 % at 65 °C, respectively.

Reversibility of charge was demonstrated by bubbling CO₂ followed by argon through solutions of 3a and 4a in wet ethanol and measuring the change in conductivity of the solution. The conductivity increased almost immediately when CO₂ was bubbled through the solution and decreased again when sparged with Ar. The maximum conductivities reached after 20 min of bubbling with CO₂ for 2b, 3b and 4b were 347,
164 and 75 µS cm\(^{-1}\), respectively. The minimum conductivities reached after 20 min of bubbling with Ar for 3a and 4a were 3.0 and 5.1 µS cm\(^{-1}\), respectively. The conductivity of the mixture of 2a/2b after bubbling with Ar for 20 min was still 299 µS cm\(^{-1}\). The CO\(_2\)/Ar cycle was carried out three times to show repeatability of the switching (Figure 4.1(a) and (b)). The experiment was also carried out using 2a, and the average results of the three cycles for each surfactant can be seen in Figure 4.1(c) and (d). The application of Ar to 3b or 4b causes a rapid reduction in conductivity, and the original solution conductivity is restored after only 20 min, indicating that the surfactant is fully converted to the uncharged form. In the case of 2b, after 20 min the conductivity is only reduced by 14 % indicating that most of the surfactant remains in the charged form. Thus, surfactants 3b and 4b would be significantly more effective than 2b in applications where rapid removal of charge is desired.

The extent of switching is related to the enthalpy of protonation of the surfactant. The enthalpies of protonation of the 7-carbon chain analogue of 3a and the 8-carbon chain analogue of 4a are 48 and 53 kJ mol\(^{-1}\), respectively. These values are much lower than the enthalpy of protonation of the 8-carbon chain analogue of 2a, which is 71 kJ mol\(^{-1}\).\(^{16}\) Therefore, it requires more energy to remove the proton from the 2b, which explains why the conductivity of an ethanolic solution of 2b is only reduced by 14 % versus the complete reduction in conductivity of solutions of 3b and 4b when the same destabilization conditions are used.
Figure 4.1 The conductivity of solutions during CO$_2$/Ar cycles in 20 mL ethanolic solutions containing 200 µL of water and 0.4 mmol of either (a) 3a or (b) 4a and the change in conductivity of wet ethanolic solutions of 2a (■), 3a (▲) and 4a (●) at room temperature when (c) CO$_2$ followed by (d) Ar are bubbled through the solutions.
4.2 Emulsion Polymerization

4.2.1 Initiator Choice

VA-044 (whose 10 h half-life temperature is 44 °C) and VA-061 (whose 10 h half-life temperature is 61 °C) were both used in the emulsion polymerization of MMA. VA-061 was added as an aqueous solution of its bicarbonate salt, 3. Another member of the Jessop group has shown that the 10 h half-life temperature of 3 is dramatically decreased compared to that of VA-061 (45 °C versus 61 °C), so 3 should have a similar initiator decomposition rate as VA-044. One significant difference between the VA-044 and 3, however, is that 3 will revert back to its neutral form when CO₂ is removed from the system. At the emulsion polymerization temperature, the ratio of 3 to VA-061 will likely decrease. For this reason, even if the same concentration of VA-044 and 3 are initially added to the polymerization, at the polymerization temperature the number of radicals produced from initiator decomposition is likely to be higher in cases where VA-044 is used.

4.2.2 Methyl Methacrylate Polymerization

Isolation of the bicarbonate salts of 3a and 4a was unsuccessful, so 3b and 4b were formed in situ by bubbling CO₂ through the solution of 3a or 4a in MMA prior to emulsification. CO₂ was bubbled continuously through the emulsion while polymerization was being carried out to ensure the maximum amount of the surfactant was converted to the bicarbonate salt. Emulsion polymerization was carried out using surfactants 3b and 4b using an initial concentration of 13.5 wt % MMA to show that stable latexes could be obtained. By investigating the effect of surfactant and initiator concentrations, temperature and type of surfactant on the resultant particle size and ζ-
potential of the latex, key aspects of the surfactant behaviour in emulsion polymerization systems were addressed (Tables 4.1 and 4.2). With the same surfactant type, as the surfactant concentration decreases, the particle size increases, which is expected due to the decrease in the number of particles that can be stabilized. This is the same trend that was observed with 2b. Unexpected however, is the increase in particle size with increasing initiator concentration which occurs with both 3b and 4b, but not 2b45 (Table 4.1, entries 4-6 and 9-11, compared to Table 3.2, entries 3 and 5 and entries 8 and 11 and Table 3.3, entries 6-7). The most likely explanation is that higher initiator concentrations favour the formation of small water-soluble oligomers containing charged initiator end groups, which increase the ionic strength of the aqueous phase, decreasing colloidal stability and increasing particle size.63

A large increase in particle size is noted for surfactants 3b and 4b versus 2b under equivalent conditions (Table 4.1, entries 1, 6 and 11), which is most likely due to the decreased basicity of these surfactants. The polymerization reactions are carried out at 65 °C, and the ratio of charged to uncharged form of the surfactant will be much less in the case of the 3b and 4b, effectively decreasing the amount of charged surfactant available for particle stabilization. This hypothesis was tested by carrying out the emulsion polymerization using the hydrochloride salts of 3a and 4a (Table 4.2, entries 2 and 4) because these surfactants should be permanently charged; and it was found that much smaller particles (45 and 34 nm versus 275 and 316 nm) were produced. This shows that the large particle size (in the cases where surfactants 3b and 4b are used) is not due to the decreased ability of the surfactant molecules with these head groups to pack on the particle’s surface, but is likely due to significant conversion of 3b and 4b to
3a and 4a under the polymerization conditions. Another possibility is that the neutral tertiary amine 4a is acting as a chain transfer agent,\textsuperscript{64} decreasing the amount available for reaction with CO\textsubscript{2} to form 4b. This would decrease the amount of active surfactant and increase the particle size. The same conclusion cannot be made for 3a because it is unknown whether 3a can act as a chain transfer agent.

In an attempt to make smaller particles, polymerization at 50 °C (to ensure greater ratios of 3b:3a and 4b:4a) was attempted (Table 4.2, entry 6) but this simply increased reaction time and decreased the number of radicals formed by initiator decomposition producing larger particles.

A significant decrease in particle size was noted when 4a was dissolved in the aqueous phase versus the monomer phase prior to polymerization (Table 4.2, entries 3 and 5). This may be due to a greater solubility of the surfactant in the monomer phase, causing some of the surfactant to remain in this phase, leaving it unavailable to stabilize growing particles during the polymerization. While surfactant 2b can be used in very low concentrations (0.07 mol % of MMA) and still provide adequate stabilization, such a small concentration of 3b produces a latex containing very large particles with low conversion of monomer and significant amounts of coagulum (17 %) (Table 4.1, entry 8).

ζ-Potential values of all the latexes synthesized were over 30 mV, indicating that the latexes should be stable. It appears that the ζ-potential depends on the basicity of the surfactant, with less basic surfactants producing particles with smaller ζ-potentials (Table 4.1, entries 1, 6 and 11). This is not surprising in lieu of the previous discussion concerning the conversion of the less basic surfactants 3b and 4b to their neutral forms under the polymerization conditions.
Table 4.1 Variation in particle size and ζ-potential of PMMA particles synthesized using different concentrations of 2b, 3b or 4b and 3.\textsuperscript{a}

<table>
<thead>
<tr>
<th>No.</th>
<th>Surf. Identity\textsuperscript{b}</th>
<th>Mol % Surf. Precursor added\textsuperscript{c}</th>
<th>Mol % 3\textsuperscript{c}</th>
<th>Particle Size\textsuperscript{d} (nm) (PdI)</th>
<th>ζ-Pot.\textsuperscript{d} (mV)</th>
<th>Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>1.0</td>
<td>0.25</td>
<td>46 ± 0.2 (0.07)</td>
<td>67 ± 3</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>0.25</td>
<td>0.14</td>
<td>83 ± 2 (0.07)</td>
<td>45 ± 4</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>2b</td>
<td>0.07</td>
<td>0.07</td>
<td>183 ± 2 (0.04)</td>
<td>35 ± 4</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>3b</td>
<td>1.0</td>
<td>1.0</td>
<td>465 ± 8 (0.05)</td>
<td>56 ± 1</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>3b</td>
<td>1.0</td>
<td>0.5</td>
<td>334 ± 2 (0.07)</td>
<td>52 ± 2</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>3b</td>
<td>1.0</td>
<td>0.25</td>
<td>316 ± 3 (0.12)</td>
<td>34 ± 4</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>3b</td>
<td>0.25</td>
<td>0.25</td>
<td>369 ± 2 (0.04)</td>
<td>41 ± 2</td>
<td>78</td>
</tr>
<tr>
<td>8</td>
<td>3b</td>
<td>0.07</td>
<td>0.07</td>
<td>852 ± 117 (0.2)</td>
<td>32 ± 2</td>
<td>72</td>
</tr>
<tr>
<td>9</td>
<td>4b</td>
<td>1.0</td>
<td>1.0</td>
<td>408 ± 9 (0.10)</td>
<td>44 ± 1</td>
<td>91</td>
</tr>
<tr>
<td>10</td>
<td>4b</td>
<td>1.0</td>
<td>0.5</td>
<td>347 ± 2 (0.06)</td>
<td>44 ± 0.4</td>
<td>93</td>
</tr>
<tr>
<td>11</td>
<td>4b</td>
<td>1.0</td>
<td>0.25</td>
<td>275 ± 5 (0.14)</td>
<td>35 ± 0.7</td>
<td>94</td>
</tr>
<tr>
<td>12</td>
<td>4b</td>
<td>0.5</td>
<td>0.5</td>
<td>352 ± 2 (0.09)</td>
<td>32 ± 0.6</td>
<td>85</td>
</tr>
<tr>
<td>13</td>
<td>4b</td>
<td>0.5</td>
<td>0.25</td>
<td>308 ± 2 (0.07)</td>
<td>45 ± 3</td>
<td>93</td>
</tr>
<tr>
<td>14</td>
<td>4b</td>
<td>0.25</td>
<td>0.25</td>
<td>397 ± 6 (0.06)</td>
<td>32 ± 1</td>
<td>86</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Polymerization was carried out at 65 °C for 2 h, at 13.5 wt % MMA.

\textsuperscript{b}A blank run was also carried out using no surfactant and 0.25 mol % 3 and a stable latex was not formed.

\textsuperscript{c}With respect to MMA.

\textsuperscript{d}Ranges indicate the standard deviation in the particle size and ζ-potential measurements using the Zetasizer ZS.
Table 4.2 Variation in emulsion polymerization conditions and their effect on the particle size and ζ-potential of the resulting PMMA particles. 

<table>
<thead>
<tr>
<th>Change in procedure</th>
<th>Surf.</th>
<th>Particle Size (b) (nm) (PdI)</th>
<th>ζ-Potential (b) (mV)</th>
<th>Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 None</td>
<td>3b</td>
<td>316 ± 3 (0.12)</td>
<td>34 ± 4</td>
<td>96</td>
</tr>
<tr>
<td>2 Hydrochloride version of surfactant used(^c)</td>
<td>3a•HCl</td>
<td>34 ± 0.5 (0.18)</td>
<td>70 ± 6</td>
<td>100</td>
</tr>
<tr>
<td>3 None</td>
<td>4b</td>
<td>275 ± 5 (0.14)</td>
<td>35 ± 0.7</td>
<td>94</td>
</tr>
<tr>
<td>4 Hydrochloride version of surfactant used(^c)</td>
<td>4a•HCl</td>
<td>45 ± 0.3 (0.08)</td>
<td>46 ± 1</td>
<td>100</td>
</tr>
<tr>
<td>5 Surfactant dissolved in aqueous phase</td>
<td>4b</td>
<td>222 ± 7 (0.08)</td>
<td>42 ± 1</td>
<td>92</td>
</tr>
<tr>
<td>6 Polymerization temperature is 50 °C</td>
<td>4b</td>
<td>363 ± 4 (0.04)</td>
<td>45 ± 0.8</td>
<td>85</td>
</tr>
</tbody>
</table>

\(^a\)Polymerization was carried out with 13.5 wt % MMA (with respect to water), 1.0 mol % of 3a or 4a and 0.25 mol % of 3 (with respect to MMA), at 65 °C (unless otherwise noted). All reactions were carried out in the presence of CO\(_2\), except in the cases where the hydrochloride versions of the surfactants were used (entries 2 and 4).

\(^b\)Ranges indicate the standard deviation in the particle size and ζ-potential measurements using the Zetasizer ZS.

\(^c\)VA-044 was used.

4.2.3 Effect of Initiator Type, Additives and CO\(_2\) Pressure on Particle Size

To broaden the applicability of these surfactants, a wide range of particle sizes must be attainable with variations in the polymerization conditions. Three strategies were developed to promote the production of smaller particles: using VA-044 as an initiator, adding CTAB (cetyl trimethylammonium bromide) as an extra stabilizer, and carrying out the reaction under increased CO\(_2\) pressure. The results of these experiments can be seen in Table 4.3. The use of VA-044 as an initiator allowed the reaction to be carried out at lower temperatures (50 °C) while maintaining a high rate of initiator decomposition. However, this initiator is a hydrochloride salt and remains charged even after CO\(_2\) is removed from the system. It has been shown previously in our group that when VA-044 is used with surfactant 2b, sparging with air and heating does not
destabilize the latex.\textsuperscript{45,48} It is postulated in the case of 3\textbf{b} and 4\textbf{b} that no transfer of protons will occur from the initiator to the surfactant, because the imidazoline fragments are more basic than the phenyl amidine or tertiary amine head groups of 3\textbf{a} and 4\textbf{a}, thus the surfactant would remain switchable. The results in Table 4.3 show that the particle size does decrease when this initiator is used and the polymerization is carried out at 50 \degree C (Table 4.3, entry 1 versus entries 2-4), which is likely due to the presence of more bicarbonate surfactant, 4\textbf{b}, at lower temperatures. The second strategy involved adding CTAB as a co-surfactant to impart extra stability to the emulsion and subsequent latex. This strategy also produced smaller particles, as is shown in Table 4.3, entries 5 and 6. It is important to note that in both of the above cases, only a very small amount of VA-044 or CTAB was used to ensure that the synthesized latex was not too stable. The third strategy involved pressurizing the reaction vessel to ensure that more CO\textsubscript{2} was dissolved in the emulsion in order to increase the amount of surfactant in the charged form. When the polymerization was carried out at a higher pressure (5 atm) in a stainless steel Parr vessel, the particle size decreased compared to the same reaction at atmospheric pressure (Table 4.3, entry 1 versus entry 7). This is an indication that more bicarbonate surfactant is present in the aqueous phase at higher CO\textsubscript{2} pressures. This makes sense because CO\textsubscript{2} is a reactant in an equilibrium reaction so increasing the CO\textsubscript{2} pressure would increase the ratio of 4\textbf{b} to 4\textbf{a} according to the equilibrium expression shown in equation 21, assuming that the equilibrium constant does not change with pressure (in equation 21, 4\textbf{b} is BH\textsuperscript{+} and 4\textbf{a} is B). The particle size is not as small as it is in the case where 4\textbf{b}•HCl was used, indicating that some of the surfactant remains in the uncharged form, likely dissolved in the monomer phase where it is not as easily converted to a bicarbonate salt.
Table 4.3 Changing the conditions under which emulsion polymerization is carried out to promote the formation of <200 nm PMMA particles.\(^a\)

<table>
<thead>
<tr>
<th>Change in procedure</th>
<th>Mol % 4a Added</th>
<th>Mol % Initiator(^b)</th>
<th>Particle Size(^e) (nm)</th>
<th>ζ-Potential(^e) (mV)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>1.0</td>
<td>275 ± 5</td>
<td>35 ± 0.7</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>Initiator is VA-044</td>
<td>1.0</td>
<td>0.25</td>
<td>167±2</td>
<td>41±2</td>
</tr>
<tr>
<td>3</td>
<td>Initiator is VA-044</td>
<td>1.0</td>
<td>0.10</td>
<td>154±2</td>
<td>39±2</td>
</tr>
<tr>
<td>4</td>
<td>Initiator is VA-044</td>
<td>1.0</td>
<td>0.05</td>
<td>161±2</td>
<td>34±2</td>
</tr>
<tr>
<td>5</td>
<td>CTAB was added(^c)</td>
<td>1.0</td>
<td>0.25</td>
<td>78±1</td>
<td>43±4</td>
</tr>
<tr>
<td>6</td>
<td>CTAB was added(^c)</td>
<td>0.25</td>
<td>0.25</td>
<td>126±1</td>
<td>39±2</td>
</tr>
<tr>
<td>7</td>
<td>Increased CO(_2) pressure(^d)</td>
<td>1.0</td>
<td>0.25</td>
<td>174±1</td>
<td>44±1</td>
</tr>
</tbody>
</table>

\(^a\)Polymerization was carried out at 65 °C when the initiator was 3 and 50 °C when the initiator was VA-044, for 2 h, at 13.5 wt % MMA.

\(^b\)Initiator was 3 unless otherwise indicated.

\(^c\)6.3 mol % (with respect to 4a) was used.

\(^d\)Pressure was 5 atm.

\(^e\)Ranges indicate the standard deviation in the particle size and ζ-potential measurements using the Zetasizer ZS.

Attempts at making polymer latexes with 24 wt % polymer using 4b and 3 failed.

The reaction resulted in high amounts of coagulum, high viscosities and significant aggregation. The strategy employed above to make smaller, more stable particles, by using VA-044 as an initiator and lower reaction temperatures, was employed to make 24 wt % latexes. As an example, 1.5 mol % 4b and 0.05 mol % VA-044 were used at 50 °C to make a latex with 193 ± 3 nm particles (PdI = 0.07) with a ζ-potential of 36 ± 1 mV.
There was no coagulum or aggregates formed during the synthesis and the latex was successfully destabilized using only air at 65 °C.

### 4.2.4 Long Term Latex Stability

Long term stability of the polymer latex synthesized using the conditions in Table 4.1, entry 7 was assessed by exposing one half of the latex to air and storing it in a loosely capped vial, and storing the other half under an atmosphere of CO$_2$ in a capped vial with Parafilm®. Initial particle size and $\zeta$-potentials were compared to those taken after 3 weeks for both samples and the data is summarized in Table 4.4. The particle size of the sample exposed to air dramatically increases and the $\zeta$-potential decreases, while no changes are observed in the case of the latex sealed under CO$_2$. From this data, we conclude that the latexes remain stable as long as they are under an atmosphere of CO$_2$.

**Table 4.4** Assessment of the long term stability of a latex synthesized according to the conditions in Table 4.1, entry 7 (13.5 wt % MMA, 0.25 mol % **3b**, 0.25 mol % **3**).

<table>
<thead>
<tr>
<th></th>
<th>Particle Size</th>
<th>$\zeta$-Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zetasizer (nm) (Pdl)</td>
<td>Mastersizer (nm)</td>
</tr>
<tr>
<td>Initial</td>
<td>381 ± 5 (0.10)</td>
<td>278</td>
</tr>
<tr>
<td>After 3 weeks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(stored under CO$_2$)</td>
<td>419 ± 3 (0.10)</td>
<td>261</td>
</tr>
<tr>
<td>After 3 weeks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(exposed to air)</td>
<td>-</td>
<td>4500</td>
</tr>
</tbody>
</table>

*Measurements were taken at room temperature.*
4.3 Latex Destabilization

Destabilization of the polymer latexes was achieved by sparging the latexes with air or Ar to remove the CO\textsubscript{2}. During PMMA latex destabilization using 2b, a distinct population of particles at \(\sim 6\ \mu m\) forms, creating a bimodal particle size distribution (the other peak in the distribution being the original particle size).\textsuperscript{45} This bimodal distribution was also observed during the destabilization of latexes synthesized using 3b and 4b. One way to determine the efficiency and rate of the destabilization process is to calculate the volume percentage of each of the particle populations over time. This type of analysis was carried out for the destabilization of latexes formed with 3b using the conditions of Table 4.1, entry 7 (Figure 4.2). After sparging the latex with air at 40 or 65 °C, there are no initial nanometer-sized particles remaining after 20 min. Furthermore, it was found that the destabilization could be carried out to completion after 30 min at room temperature by simply sparging the latex with air with no additional heat supplied. Using surfactant 2b, higher solid content latexes synthesized under similar conditions required 4 h of sparging with air and heating (65 °C) to be fully destabilized.\textsuperscript{45}
Figure 4.2 Volume percent of PMMA particles below 1 μm as a function of time during destabilization using air at 65 °C (◆), 40 °C (●) and room temperature (▲) in a latex synthesized according to the conditions in Table 4.1, entry 7.

4.3.1 Destabilization and the Change in ζ-Potential

In order to show that latex destabilization occurred due to the decreased surface charge on the polymer particles upon CO₂ removal, the ζ-potential was monitored over time during Ar and heat (65 °C) treatment. Figure 4.3 shows that the ζ-potential decreases more rapidly when sparging with inert gas is combined with heating; but that simply heating the latex also decreases the ζ-potential, albeit at a slower rate. It has been shown previously for PMMA latexes synthesized using 2b that the ζ-potential beyond which destabilization occurs is ~25 mV. Figure 4.3(a), (c) and (d) show that the surface charge of the PMMA particles decreases below that threshold within the first 20 min in the cases where surfactants 3b and 4b are used, in contrast to the latex produced using 2b, whose particle surface charge did not decrease below 25 mV even after 60 min.
Destabilization (appearance of flocs and an increase in latex viscosity) was observed visually in the latexes synthesized using 3b and 4b after the first 15 min of destabilization. To ensure that it was not simply a higher starting ζ-potential causing the greater stability of the latex synthesized using 2b (Figure 4.3(a)) another latex was synthesized using less 2b and 3 (0.07 mol % each) to ensure that the starting ζ-potential matched those in Fig. 4.3(c) and (d). In this case (Fig. 4.3(b)), the initial surface charge was 37 mV and it was found that Ar and heat treatment caused little change in the ζ-potential. Thus in both cases, latexes synthesized using 3b and 4b destabilized much more rapidly than those synthesized using 2b.
Figure 4.3 Change in ζ-potential with time of latexes destabilized using Ar and heat (65 °C) for 15 min followed by 45 min at 65 °C without Ar bubbling. Initial latexes were synthesized using (a) 1.0 mol % 2b and 0.25 mol % 3, (b) 0.07 mol % 2b and 0.07 mol % 3, (c) 1.0 mol % 3a and 0.25 mol % 3 and (d) 1.0 mol % 4a and 0.25 mol % 3.

4.3.2 Effect of Additives on Destabilization

In the case where VA-044 was used as an initiator to promote the formation of small particles, latex destabilization occurred only when a very small amount of initiator was used (0.05 mol % with respect to monomer). This indicates that the charged initiator end groups contribute greatly to latex stability, and that their concentration must be minimized in order to ensure that the latex can be destabilized using only air and heat. When CTAB was used as a co-surfactant, the same phenomenon was observed; latex destabilization was possible as long as the concentration of CTAB was kept low enough. Increased sample viscosity was observed after the first 30 min of treatment when 0.016 mol % was used. This corresponds to a decrease ζ-potential from 40 mV to 27 mV (Figure 4.4), where the ζ-potential levels off (which is expected since CTAB will remain
in its charged form). The low concentration of CTAB used in this experiment ensures that this leveling off will happen at or below the “threshold of destabilization”, which is \(~ 25 \text{ mV}\). In contrast, destabilization of the latex synthesized with 0.063 mol % CTAB did not occur in the first 60 min of treatment (determined visually).

![Figure 4.4](image)

**Figure 4.4** Change in \(\zeta\)-potential with time during the destabilization of latexes synthesized (●) with no CTAB (Table 4.1, entry 14) and (■) with CTAB (0.016 mol % with respect to monomer, Table 4.3, entry 6) as a co-surfactant mixed with 4a.

### 4.4 Conclusions

In summary, two recently developed, less basic switchable surfactants (where the trigger to go between the uncharged and charged forms is \(\text{CO}_2\)) have been used in the emulsion polymerization of MMA. The resulting latexes were stable if kept under an atmosphere of \(\text{CO}_2\). Upon \(\text{CO}_2\) removal using a non-acidic gas, heat or a combination of both, the surfactant becomes uncharged and the latexes can be destabilized. These less
basic surfactants offer an advantage over the previously developed surfactants due to their ability to easily and rapidly revert to their uncharged forms. Both surfactants have similar basicities and yield similar results when used in emulsion polymerization. However, the long chain tertiary amine offers a clear advantage over the aryl amidine due to the lower cost and commercial availability of the amine.

The real advantage of using 3b and 4b in emulsion polymerization is the ease of post-polymerization latex destabilization compared to 2b. The problem with these surfactants is that they are not basic enough to remain fully charged under the polymerization conditions and because of this large concentrations of surfactants must be used. The fate of the excess neutral amine or amidine is unknown, but it is likely trapped in the polymer particles, and this could alter the properties of the final product. A possible solution is to find a switchable surfactant with an intermediate pKa$_H$ (between 10.8 and 12.2) such that the polymerization can be carried out with low surfactant concentrations, but latex destabilization using air and heat does not take a long time. Structures of amine containing molecules that have the proper pKa$_H$ values are shown in Table 4.5. One possibility is the use of secondary amines. Typically, secondary amines are not used as switchable surfactants due to the formation of carbamates, a reaction that is irreversible under our desired switching conditions. One way to prevent carbamate formation is through the use of bulky substituents on or around the amine. Another option is to use surfactant molecules with pyrroline or tetrahydropyridine head groups (see Table 4.5). Each of these amines has a pKa$_H$ value that is between 11-12, fulfilling the criteria described above.
**Table 4.5** A list of amines with $pK_{a_H}$ values between 11 and 12.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$pK_{a_H}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td>11.94</td>
<td>66</td>
</tr>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td>11.9</td>
<td>66</td>
</tr>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td>11.57</td>
<td>66</td>
</tr>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td>11.42</td>
<td>66</td>
</tr>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td>11.25</td>
<td>60</td>
</tr>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td>11.23</td>
<td>60</td>
</tr>
</tbody>
</table>
Chapter 5  Inverse Emulsion Polymerization

Inverse emulsion polymerization involves the emulsification of an aqueous solution of a water-soluble monomer into an oil phase typically using a non-ionic or low HLB surfactant. Polymerization of acrylamide has been carried out using this method numerous times. Table 5.1 shows the typical reagents and conditions used in these systems. The most important aspects to note are: the emulsifiers can be used as mixtures (better emulsion stability is often obtained in these cases), the emulsifiers are typically non-ionic and have an HLB ~6.0, the emulsifiers can be polymeric, the initiator used can be ionic or non-ionic (each resulting in a different mechanism for inverse emulsion polymerization), and the weight ratio of the oil phase to the aqueous is typically somewhere between 3:1 and 2:1.

Table 5.1 An overview of the typical components (oil phase, emulsifier and initiators) used in the inverse emulsion polymerization of acrylamide.

<table>
<thead>
<tr>
<th>Oil Phase</th>
<th>Oil Phase: Aqueous Phase Ratio</th>
<th>Emulsifier</th>
<th>Initiator</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>3:1</td>
<td>Tween 85&lt;sup&gt;TM&lt;/sup&gt;, Span 80&lt;sup&gt;TM&lt;/sup&gt;, non-ionic block copolymer Hypermer&lt;sup&gt;TM&lt;/sup&gt; B246SF</td>
<td>Ammonium peroxodisulfate (APS), AIBN, VA-044</td>
<td>67(a,b,e)</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.3:1</td>
<td>Graft copolymer of polystyrene and polyethylene oxide (PSt-g-PEO), Span 80&lt;sup&gt;TM&lt;/sup&gt; + Tween 80&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>AIBN</td>
<td>67(c)</td>
</tr>
<tr>
<td>Paraffinic Mixtures, xylene</td>
<td>2:1</td>
<td>ABA block copolymer of polyester-polyethylene oxide-polyester + sorbitan sesquioleate + polyoxyethylene sorbitol hexaoleate</td>
<td>2,2’-azobis(2,4-dimethylvaleronitrile) (V-65)</td>
<td>67(d,f)</td>
</tr>
</tbody>
</table>
Inverse latexes and the polymer products of inverse emulsion polymerization are high molecular weight, water soluble polymers that are used in a variety of applications including solid-liquid separation, rheology modification, targeted drug delivery, and wastewater treatment.\textsuperscript{67(d,f)} For these applications, a solution of the polymer in water is desired, and as such, after polymerization the emulsion must undergo a phase inversion. Typically, phase inversions are carried out by adding the inverse latex to a large volume of water or brine (high ionic strength) solution, or with the help of a high HLB surfactant known as a wetting agent (also called an emulsion breaker or an inverting surfactant).\textsuperscript{67(f)}

To investigate the use of switchable surfactants in this field, two surfactants were chosen: 1b and butylated polyethyleneimine (6, shown in Scheme 2.2). The following is a preliminary investigation into the ability of these surfactants to generate inverse emulsions stable enough to be used in the polymerization of water-soluble monomers.

### 5.1 Generation of a Stable Inverse Emulsion Using 1b

Surfactant 1b is an ionic amidinium bicarbonate surfactant with a 16-carbon chain tail (Scheme 2.1). Our hypothesis was that the long alkyl chain tail would make the surfactant waxy enough to generate an inverse emulsion.

Four parameters were varied in order to determine the optimal conditions to form a stable water-in-oil emulsion using surfactant 1b: the oil phase identity, the oil phase concentration, the surfactant concentration, and the presence of a co-surfactant (Span 60\textsuperscript{TM}). Emulsions of 1 M dimethylaminoethyl methacrylate (DMAEMA) with each oil phase were generated by first dissolving 1b in the oil phase, adding the aqueous phase and sonicating to generate an emulsion. It is also important to note that at higher surfactant concentrations, sonication was necessary to dissolve the surfactant in the oil
phase. Each emulsion was tested to determine the continuous phase (Table 5.2). Conductivity tests were also performed to further confirm the identity of each continuous phase (Table 5.3). The droplet and conductivity tests showed that a water-in-oil emulsion was only obtained in the case of cyclohexane. Furthermore, phase separation generating a clear oil layer was observed faster when toluene and paraffin liquid were used. Because cyclohexane is more commonly used in inverse emulsion polymerization and was the only solvent to generate a W/O emulsion, it was used for all further tests.

**Table 5.2** Type of emulsion generated from an aqueous phase with different oil phases using surfactant 1b, as determined by the droplet test method.\(^a,b\)

<table>
<thead>
<tr>
<th>Oil Phase</th>
<th>4:1(^c) Oil Phase: Aqueous Phase</th>
<th>2:1(^b) Oil Phase: Aqueous Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>O/W</td>
<td>O/W</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>W/O</td>
<td>W/O</td>
</tr>
<tr>
<td>Paraffin</td>
<td>O/W</td>
<td>O/W</td>
</tr>
</tbody>
</table>

\(^a\)Aqueous phase is 1 M DMAEMA.  
\(^b\)O/W signifies an oil-in-water emulsion was formed, W/O signifies a water–in-oil emulsion was formed.  
\(^c\)Weight ratios.

**Table 5.3** Type of emulsion generated from an aqueous phase with different oil phases using surfactant 1b, as determined by the conductivity test method.\(^a\)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Conductivity (mS cm(^{-1}))</th>
<th>Type of Emulsion(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + DMAEMA</td>
<td>8.73</td>
<td>-</td>
</tr>
<tr>
<td>Toluene Emulsion</td>
<td>3.82</td>
<td>O/W</td>
</tr>
<tr>
<td>Cyclohexane Emulsion</td>
<td>0.0012</td>
<td>W/O</td>
</tr>
<tr>
<td>Paraffin Emulsion</td>
<td>5.02</td>
<td>O/W</td>
</tr>
</tbody>
</table>

\(^a\)All emulsions were made from a 2:1 weight ratio of oil phase to 1 M DMAEMA\(_{\text{aq}}\).  
\(^b\)O/W signifies an oil-in-water emulsion was formed, W/O signifies a water–in-oil emulsion was formed.
Emulsion stability was assessed visually by examining the separation of the two phases over time (Figure 5.1). Emulsions were stable initially (for at least 5 min) in all cases except when 0.5 wt % of 1b was used without a co-surfactant. In all cases, after 16 h two phases had appeared, although neither phase was clear. Furthermore, the presence of Span 60™ increased initial emulsion stability when 0.5 wt % 1b was used, but did not prevent the emulsion from phase separating over time. In fact, emulsion stability over time was poorer when the non-ionic surfactant was added to the system, because two phases started appearing after only 1 h.

![Figure 5.1 Photographs of emulsions generated using surfactant 1b (at 2 wt % and 0.5 wt %), at 2:1 and 4:1 weight ratios of cyclohexane to 1 M DMAEMA(aq) in the presence and absence of Span 60™.](image)

**Figure 5.1** Photographs of emulsions generated using surfactant 1b (at 2 wt % and 0.5 wt %), at 2:1 and 4:1 weight ratios of cyclohexane to 1 M DMAEMA(aq) in the presence and absence of Span 60™.
Emulsion polymerizations are generally carried out at elevated temperatures because of the use of thermal radical initiators. It is important that the emulsions are stable at these temperatures in order to provide the compartmentalization that is necessary to achieve high rates of reactions and high molecular weights. The thermal stability of emulsions generated using 2 wt % 1b and 2 wt % 1b + 5 wt % Span 60™ at 65 °C was investigated and the photos are shown in Figure 5.2. The emulsion generated using only 1b was stable for at least 1 h at room temperature but two clear layers resulted when heated to 65 °C. In the case where a non-ionic co-surfactant was added, the emulsion was again less stable at room temperature and still separated into two phases upon heating. It is known that 1b loses CO₂ more readily at higher temperatures and this would revert the surfactant to its neutral form, effectively decreasing the amount of available surfactant. Electrostatic stabilization is much less effective in inverse emulsion than regular emulsions, such that a decrease in the effective amount of surfactant at higher temperatures is more detrimental to emulsion stability.⁴²
5.2 Generation of a Stable Inverse Emulsion Using Compound 6

To circumvent the problem of decreased emulsion stability at higher temperatures due to the deprotonation of the switchable surfactants, compound 6 was used as a switchable surfactant for the generation of inverse emulsions.

Butylated polyethyleneimine (BPEI, 6) was synthesized from polyethyleneimine (PEI) by another member of the Jessop group according to a literature procedure. This polymer consists only of tertiary amine groups which can be protonated by the introduction of CO$_2$ to form a bicarbonate salt (Scheme 5.1). Compound 6 is sparingly water-soluble in its neutral form and fully water soluble in its protonated form. The fact that 6 is more soluble in cyclohexane than water is important because Bancroft’s rule states that the phase in which the emulsifier is most soluble will be the continuous phase.
of the emulsion.\textsuperscript{6} It was hypothesized that in its neutral form, the polymer could act as a non-ionic emulsifier for water-in-oil emulsions, and upon protonation, it would become fully water-soluble and partition into the aqueous phase causing emulsion destabilization, both due to a lack of steric stabilization and an increase in the ionic strength of the aqueous phase. This was tested by dissolving 6 into cyclohexane, adding a 1 M solution of DMAEMA and shaking by hand for 5 minutes. The resulting emulsion was divided into two samples, one that received no gas treatment and one that was subjected to 5 min of CO\textsubscript{2} bubbling through a needle. The carbon dioxide treatment caused emulsion destabilization (Figure 5.3). The emulsion in the absence of CO\textsubscript{2} is stable on the order of hours, but in the presence of CO\textsubscript{2} destabilizes within minutes. Upon exposure of the CO\textsubscript{2}-free emulsion to heat (65 °C) without stirring, the aqueous phase begins to separate within minutes but when it is cooled and shaken again, the emulsion reforms and is stable again on the order of hours. When the emulsion is stirred while it is being heated, no visible separation of phases occurs.

\[
\begin{align*}
\text{Scheme 5.1 Reaction of 6 with CO}_2 \text{ and water to form the bicarbonate salt.}
\end{align*}
\]
Figure 5.3 Photograph showing the destabilization of a cyclohexane : 1 M DMAEMA\(_{\text{aq}}\) emulsion (stabilized by 6) with CO\(_2\).

The use of 6 as opposed to 1b as a switchable surfactant for inverse emulsion generation is beneficial for three reasons: the emulsion generated using 6 is more stable at higher temperatures, the emulsifier is soluble in all proportions with the oil phase, and no sonication is necessary to create the emulsion.

5.3 Inverse Emulsion Polymerization of DMAEMA

Polymerization was carried out by adding the initiator and emulsifier to the cyclohexane phase, adding the aqueous phase, shaking, and heating to 65 °C for 5 h, with stirring. The conversion of monomer to polymer was 57 %. While the reaction mixture was stirring, it appeared as a white emulsion with no apparent phase separation. After removal of the mixture from heat and stirring, the phases separated immediately without the addition of CO\(_2\). This is not ideal, as we would like CO\(_2\) to be a trigger for phase separation.

In many inverse emulsion polymerization systems, the concentration of emulsifier is at least 5 wt % with respect to the oil phase.\(^{67(a,b)}\) In this trial, only 2 wt % emulsifier
was used, which is likely not enough to offer steric stabilization of the emulsified polymer solution.

It has been shown here that inverse emulsions can be generated using the switchable surfactant 6 and that the stability of these emulsions is dependent on the absence or presence of CO₂. A preliminary investigation into the use of 6 in the inverse emulsion polymerization of DMAEMA has been carried out but much more work is necessary to develop an ideal system where phase separation of the polymer dispersion only occurs when triggered by CO₂.
Chapter 6   Conclusions and Recommendations

6.1 Conclusions

The switchable surfactants presented herein have been successfully employed in the emulsion polymerization of the monomers styrene, methyl methacrylate and butyl methacrylate. The conditions were varied to produce a range of nanometer-sized particles, which could make this process amenable to a variety of applications. These latexes are stable under an atmosphere of CO$_2$ but upon exposure to air, the particles aggregate to form large, easily filterable aggregates (high $T_g$ polymers), or a large mass of coagulum (low $T_g$ polymers). The rate at which this occurs depends on the temperature of aggregation, the solid content of the latex and the polymer particle size. As well, altering the basicity of the surfactant can alter the stability of the latexes. When the surfactant is a long chain alkyl amidinium bicarbonate, the latexes are quite stable and require heat and long times (on the order of hours) to become destabilized. By using less basic tertiary amines or alkyl phenyl amidines as surfactant precursors, the latexes are less stable initially but require less forceful conditions to separate the polymer from the aqueous phase.

The ultimate advantage of using emulsion polymerization over bulk or solution polymerization is the fact that the polymerization reaction is compartmentalized. This compartmentalization is achieved through the use of surfactants, so the behaviour of the surfactant in these types of systems must be thoroughly studied. Through studies of surfactant partitioning, this work has shown that the alkyl amidine surfactant, in its protonated form, partitions almost equally into the monomer and aqueous phases, which is a key property that it must possess in order to adequately stabilize emulsions and dispersions. In its unprotonated form, its partitioning into water is much lower. Through
studies of the surfactant adsorption onto the surface of polymer particles, this work has shown that the percentage of a similarly structured surfactant, 5, on the surface of PMMA particles is only 15%, meaning that it is effective at stabilizing a dispersion of PMMA in water at very low surfactant concentrations.

Switchable surfactants can also be used for the generation of inverse emulsions. Water-in-oil emulsions can be formed when the oil phase is cyclohexane and the most stable emulsions are formed when the emulsifier is a non-ionic, poly-tertiary amine. Polymerization of aqueous dimethylaminoethyl methacrylate emulsified in cyclohexane was carried out with a monomer conversion of 57%.

6.2 Future Work and Recommendations

Much of the future work in this area should concentrate on the understanding of switchable surfactants in emulsion polymerization systems. Three aspects in particular should be addressed: the ratio of charged to uncharged amidine at various stages in the process, the fate of the amidine after destabilization, and the reaction of the amidine with CO$_2$ on a surface rather than in solution.

The surfactants studied in this work have the ability to convert between ionic and non-ionic species, so understanding how much surfactant is actually in the protonated form (especially in the case of the less basic tertiary amines) during polymerization and after the destabilization procedure is crucial if this system is to be optimized for a particular application. For example, if most of the surfactant is in the non-protonated form during polymerization, it is likely that some of it will be lost to the monomer phase and ultimately get trapped inside the polymer particles, which could alter the properties of the final material. Alternatively, determining how much of the surfactant is in the
charged form after destabilization could have implications in the ability of the particles to be redispersed. It is likely that the energy required for redispersion will be correlated to the amount of residual charge on the particles after destabilization.

The procedure developed herein avoids the use of salts and acids in the destabilization of polymer latexes. High concentrations of salts or acids would contaminate the aqueous layer, which would either end up as wastewater or require high-energy methods to purify. The purity of the aqueous layer that results from the destabilization of latexes presented in this work is unknown. After the destabilization procedure, the amidine will be in its uncharged form and it is likely that it will be poorly soluble in the aqueous phase and would prefer to reside on the polymer surface. The amount of amidine on the surface of the particle versus the amount lost to the aqueous phase will determine how rigorous the water purification will have to be, as well as how much additional surfactant would be necessary for the redispersion process.

The switchability of the amidines presented in this work has been studied as solutions in DMSO or ethanol, but has never been studied when the amidine is close to or attached to a surface. It is known that formation of the bicarbonate salt is more difficult in non-polar solvents due to the reduced ability of the charge to be stabilized compared to in polar solvents. It is likely that similar behaviour will be exhibited when the amidine is close to a non-polar surface, and so surfactant switchability and efficiency of protonation should be studied under these conditions.

A preliminary investigation into the use of switchable surfactants in inverse emulsion polymerization has been carried out in this work and much more research is necessary to optimize this system. Some suggestions include: (1) the use of higher
molecular weight butylated polyethyleneimine or PEI with longer alkyl chains to further decrease the HLB of the emulsifier, (2) the use of a higher concentration of emulsifier, (3) the use of different initiators or initiation methods to decrease the temperature at which polymerization needs to be carried out and (4) the use of a homogenizer or overhead propeller type stirrer as higher energy methods to form more stable emulsions. As well, further characterization of the final polymer and polymeric dispersion needs to be carried out. These include but are not limited to: polymer molecular weight, particle size, amount of polymer in the aqueous phase and oil phase after destabilization and monomer conversion.
References

(1) Blackley, D. C. *High Polymer Latices: Their Science and Technology*; Palmerton


(31) *Dynamic Light Scattering: An Introduction in 30 Minutes*; MRK656-01; Malvern Instruments: Worcesthershire, UK.


Appendix A. A Study of the Interactions Between Two PMMA Particles using DLVO Theory

The purpose of this discussion is to use DLVO theory to investigate the colloidal stability of a latex under the conditions typical to the destabilization conditions described in this thesis. Four factors will be discussed in terms of their effect on the size of the energy barrier to destabilization: pH, ζ-potential, size and temperature.

DLVO theory was developed by Derjaguin, Landau, Verway and Overbeek and can be used to determine the interactions between colloidal particles suspended in a medium. Two main forces exist between two spherical particles stabilized by an ionic surfactant, electrostatic (repulsive) and van der Waals (attractive). A stable suspension can be created if the maximum of repulsion is larger than the energy possessed by the two particles coming in contact with each other.

The equations that describe the variation in free energy with distance of separation between particles for two identical spheres of PMMA in an aqueous medium are:

\[
\Delta G^{LW}(l) = -2\left(\sqrt{\frac{L}{L_1}} - \sqrt{\frac{L}{L_2}}\right)\left(\sqrt{\frac{L}{L_2}} - \sqrt{\frac{L}{L_3}}\right)\left(\frac{L^2}{L}\right)(\pi R)
\]

(4)

\[
\Delta G^{EL}(l) = 0.5R\psi_o^2e\ln[1-e^{-\kappa l}]
\]

(6)

\[
\psi_o = \zeta\left(1+\frac{a}{R}\right)e^\kappa a
\]

(22)

\[
\frac{1}{\kappa} = \sqrt{\frac{\varepsilon kT}{4\pi e^2\Sigma v_i^2n_i}}
\]

(5)

\[
R = \frac{R_1R_2}{R_1 + R_2}
\]

(23)

\[
\Delta G_{int}(l) = \Delta G^{LW}(l) + \Delta G^{EL}(l)
\]

(24)
where the following variables and constants were used:

\[ R_1 \text{ and } R_2 = \text{particle radii (in m)}, \zeta = \text{zeta potential (in V)}, T = \text{temperature (in K)}, \]
\[ v_i = \text{the valency of each ionic species and } n_i = \text{the number of ions of each species (ions cm}^{-3} \text{ liquid)}, \]
\[ \varepsilon = \text{the electrical permittivity of the liquid medium (6.9 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \text{ for water})}, k = \text{Boltzmann’s constant (1.38 \times 10^{-23} \text{ J K}^{-1})}, e = \text{charge of the electron (1.602 \times 10^{-19} \text{ J})}, a = \text{the distance from the particle’s surface to the shear plane (3-5 \times 10^{-10} \text{ m})}, l_o \text{ is the equilibrium distance between two semi-infinite surfaces when they are in van der Waals contact (experimentally determined to be } \sim 1.57 \times 10^{-10} \text{ m})}, \gamma_{LW}^1, \gamma_{LW}^2 \text{ and } \gamma_{LW}^3 \text{ are the apolar surface tension values of materials 1 and 2 in a medium 3 (for PMMA are 0.0406 mJ m}^{-2} \text{ and } \gamma_{LW}^2 \text{ for water is 0.0213 mJ m}^{-2} \text{).} \]

These equations were used in the generation of the DLVO plots in Figure A1. It is important to note that each graph only shows the change in the size of the energy barrier with a change in one of the variables. For instance, with switchable surfactants, changing the pH will also change the \( \zeta \)-potential, but this is not taken into account in these graphs (each variable is treated separately).

Figure A1(a) shows that the pH affects the maximum of repulsion. At neutral pH (no ions present), the electrical double layer is very diffuse; this is shown by the much higher energies at farther distances from the particles surface. By decreasing the pH (increasing the number of ions in solution), the electrical double layer becomes suppressed and moves closer to the particles surface, and the energy barrier for particle aggregation also decreases slightly. It appears that high ion concentrations would be necessary to decrease the energy barrier enough to cause a \( \Delta G \) value less than 0. Another point of note is that at high pH, the DLVO plot flattens, albeit at high \( \Delta G \) values. Figure
A1(b) shows the effect of decreasing the ζ-potential on the shape of the DLVO plot. It shows that high values of ζ-potential create high-energy barriers and that the energy barrier decreases quite rapidly with decreasing ζ-potential. Figure A1(c) shows that the temperature has quite a small effect on the shape of the DLVO plot and position of the energy barrier. This is not to say that temperature does not have an effect on the ability of the particles to overcome this barrier. Figure A1(d) shows that the particle size has quite a large effect of the height of the energy barrier, with larger particles having a higher energy barrier.

The destabilization procedure presented in this work involves sparging the latex with air in order to remove CO₂ from the system (typically at 65 °C). From the analysis of the DLVO plots, it appears that the factor that contributes most to latex destabilization is the decrease in ζ-potential. The increase in temperature has little effect on the energy barrier and the decrease in pH appears to increase the energy barrier toward aggregation. An important aspect to note however is that the ΔG value becomes negative before the ζ-potential reaches zero (Figure A1(b)). This indicates that the surface can still have some residual charge and the particles will still aggregate, which is consistent with the observations made in this work, where particle aggregation typically occurred at ζ-potentials from 15 – 25 mV. The ζ-potential at which particle aggregation can occur will of course depend on the latex pH and particle size. Also consistent with experimental data presented in this thesis is the fact that larger particles tend to be more stabilized.
Figure A.1 The effect of (a) pH (at ζ-potential = 60 mV, particle size = 50 nm and temperature = 293 K), (b) ζ-potential (at pH = 5, particle size = 50 nm and temperature = 293 K), (c) temperature (at pH = 5, ζ-potential = 60 mV, and particle size = 50 nm) and (d) particle size (at pH = 5, ζ-potential = 30 mV and temperature = 293 K) on the dependence of the ΔG of interaction of two spherical PMMA particles in water on the distance between the particle surfaces.
Appendix B. Key Spectra and Data Tables

$N'$-(4-decylphenyl)-$N,N$-dimethylacetamidine (3a)

Appearance: Orange liquid

Figure B.1 $^1$H-NMR spectrum of $N'$-(4-decylphenyl)-$N,N$-dimethylacetamidine.

Figure B.2 $^{13}$C-NMR spectrum of $N'$-(4-decylphenyl)-$N,N$-dimethylacetamidine.
Typical Mastersizer Output Reports
For latexes synthesized using 2b:

Figure B.3 Mastersizer report for the particle size determination of the latex synthesized in Table 3.3 – Entry 12.
Figure B.4 Mastersizer report for the particle size determination of the latex synthesized in Table 4.1 – Entry 7.
For destabilized latexes:

**Figure B.5** Mastersizer report for the particle size determination of the latex synthesized in Table 4.1 – Entry 7 after destabilization using air and heat (65 °C) for 20 min.
Typical Zetasizer Output Reports

For particle size analysis:

- **Sample Name:** c101A
- **SOP Name:** Catherine-PMMMA-disposable.scp
- **File Name:** 29Nov10.dls
- **Dispersant Name:** Water
- **Record Number:** 5
- **Material Rt:** 1.44
- **Material Absorption:** 0.00
- **Dispansant Rt:** 1.330
- **Viscosity (cP):** 1.0000
- **Measurement Date and Time:** November-29-10 1:25:46 PM

- **Temperature (°C):** 25.0
- **Count Rate (kcps):** 433.3
- **Measurement Position (mm):** 5.50
- **Attenuator:** 7

### Size Distribution by Intensity

- **Z-Average (d. nm):** 368.4
- **PDI:** 0.015
- **Intercept:** 0.076
- **Result quality:** Good

<table>
<thead>
<tr>
<th>Size (d. nm)</th>
<th>% Intensity</th>
<th>Width (d. nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1:</td>
<td>303.6</td>
<td>81.81</td>
</tr>
<tr>
<td>Peak 2:</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Peak 3:</td>
<td>0.000</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Figure B.6** Zetasizer report for the particle size determination of the latex synthesized in Table 4.1 – Entry 7.
For ζ-potential analysis:

**Sample Name:** cf101A  
**SOP Name:** Zeta pot-Candace-PIMMA-disposable sop  
**File Name:** 29Nov10.xls  
**Dispersant Name:** Water  
**Record Number:** 1  
**Date and Time:** November 29, 2010 1:13:26 PM  
**Dispersant Ratio:** 1.330  
**Viscosity (cp):** 0.8872  
**Dispersant Dielectric Constant:** 78.5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25.0</td>
</tr>
<tr>
<td>Count Rate (kcps)</td>
<td>0.0</td>
</tr>
<tr>
<td>Cell Description</td>
<td>Clear disposable zeta cell</td>
</tr>
<tr>
<td>Zeta Runs</td>
<td>13</td>
</tr>
<tr>
<td>Measurement Position (mm)</td>
<td>2.00</td>
</tr>
<tr>
<td>Attenuator</td>
<td>0</td>
</tr>
<tr>
<td>Zeta Potential (mV)</td>
<td>39.0</td>
</tr>
<tr>
<td>Zeta Deviation (mV)</td>
<td>4.16</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>0.0513</td>
</tr>
</tbody>
</table>

**Result quality:** Good

![Zeta Potential Distribution](image)

**Figure B.7** Zetasizer report for the ζ-potential determination of the latex synthesized in Table 4.1 – Entry 7.
Equations for the determination of conversion from $3a'$ to $3b'$:

![Chemical structure](image)

**Table B.1** Table showing the change in chemical shifts of protons close to the head group of $3a'$ upon protonation with a strong acid (HCl) or a weak acid (H$_2$CO$_3$) at room temperature and 65 °C.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$A (% Conv.)</th>
<th>$\delta$B (% Conv.)</th>
<th>$\delta$C (% Conv.)</th>
<th>Average % Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3a'$</td>
<td>2.949</td>
<td>6.555</td>
<td>2.482</td>
<td></td>
</tr>
<tr>
<td>$3a'$•H$_2$CO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial 1 at Room Temperature</td>
<td>3.199 (91.6)</td>
<td>7.002 (91.6)</td>
<td>2.577 (94.1)</td>
<td>92.4</td>
</tr>
<tr>
<td>$3a'$•H$_2$CO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial 1 at 65 °C</td>
<td>3.077 (46.9)</td>
<td>6.785 (47.1)</td>
<td>2.528 (45.5)</td>
<td>46.5</td>
</tr>
<tr>
<td>$3a'$•HCl</td>
<td>3.222</td>
<td>7.043</td>
<td>2.583</td>
<td></td>
</tr>
</tbody>
</table>

\[
\% \text{ Conversion} = 366\delta A - 1080 \quad 205\delta B - 1343 \quad 990\delta C - 2457
\]

*All spectra were referenced to the chemical shift for the protons at position D ($\delta = 0.825$).
Equations for the determination of conversion from 4a to 4b:

\[
\begin{align*}
\text{Table B.2} & \quad \text{Table showing the change in chemical shifts of protons close to the head group of 4a upon protonation with a strong acid (HCl) or a weak acid (H}_2\text{CO}_3\text{) at room temperature and 65 °C.} \\
\delta A & \quad (\% \text{ Conv.}) \quad \delta B \quad (\% \text{Conv.}) \quad \delta C \quad (\% \text{ Conv.}) \quad \text{Average \% Conversion} \\
4a & \quad 2.251 \quad 2.322 \quad 1.512 \quad \text{Blank line} \\
4a\cdot\text{H}_2\text{CO}_3 & \quad \text{Trial 1 at Room Temperature} \quad 2.619 \quad (98.8) \quad 2.788 \quad (99.6) \quad 1.650 \quad (102.9) \quad 100.4 \\
4a\cdot\text{H}_2\text{CO}_3 & \quad \text{Trial 2 at Room Temperature} \quad 2.612 \quad (96.9) \quad 2.778 \quad (97.4) \quad 1.653 \quad (88.3) \quad 94.2 \\
4a\cdot\text{H}_2\text{CO}_3 & \quad \text{Trial 1 at 65 °C} \quad 2.455 \quad (54.8) \quad 2.569 \quad (52.7) \quad 1.633 \quad (46.7) \quad 53.8 \\
4a\cdot\text{HCl} & \quad 2.623 \quad 2.790 \quad 1.649 \quad \text{Blank line} \\
\% \text{ Conversion} = & \quad 268\delta A - 604 \quad 214\delta B - 497 \quad 730\delta C - 1104 \\
^a & \quad \text{All spectra were referenced to the chemical shift for the protons at position D (δ = 0.9277).}
\end{align*}
\]
Partitioning of \(2a\) and \(2b\) in monomer and D\(_2\)O phases by \(^1\)H-NMR:

**Table B.3** Integration of \(^1\)H-NMR peaks used to determine the relative percentage of \(2a\) or \(2b\) in monomer and D\(_2\)O phases after phase separation of an emulsion formed by these two phases.

<table>
<thead>
<tr>
<th></th>
<th>Trial #</th>
<th>Integration(^a) (Corresponding # of Protons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2a) (Uncharged)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene/D(_2)O Emulsion</td>
<td>1</td>
<td>1.62 (18)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.18 (18)</td>
</tr>
<tr>
<td>Monomer Phase</td>
<td>1</td>
<td>4.80 (3)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.65 (3)</td>
</tr>
<tr>
<td>MMA/D(_2)O Emulsion</td>
<td>1</td>
<td>8.04 (18)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.70 (18)</td>
</tr>
<tr>
<td>Monomer Phase</td>
<td>1</td>
<td>3.29 (3)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.78 (3)</td>
</tr>
<tr>
<td>(2b) (Charged)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene/D(_2)O Emulsion</td>
<td>1</td>
<td>25.72 (18)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>24.89 (18)</td>
</tr>
<tr>
<td>Monomer Phase</td>
<td>1</td>
<td>4.79 (3)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.01 (3)</td>
</tr>
<tr>
<td>MMA/D(_2)O Emulsion</td>
<td>1</td>
<td>24.60 (18)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>26.19 (18)</td>
</tr>
<tr>
<td>Monomer Phase</td>
<td>1</td>
<td>3.44 (3)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.67 (3)</td>
</tr>
</tbody>
</table>

\(^a^\) Integration is relative to the integration of the methyl group of the DMF internal standard.

\(^b^\) The equation used to determine the relative amount of \(2a\) or \(2b\) in the D\(_2\)O phase is:

\[
\% \text{ in D}_2\text{O phase} = \frac{\text{Integration}_D}{\# \text{ of protons}_D} \times 100 \%
\]