AMPHIPHILIC DIBLOCK COPOLYMERS AS STABILIZERS IN EMULSION POLYMERIZATION

by

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Abstract

Emulsion polymerizations, used to produce many commodity materials, require stabilizing agents to prevent phase separation. Incorporation of these stabilizers in the final polymer may have negative effects on product properties, so the design of new stabilizers is worthwhile. Amphiphilic diblock copolymers are a promising type of emulsion polymerization stabilizer and are the focus of this work. First, the tolerance of an amphiphilic diblock copolymer stabilizer’s performance to high molecular weight dispersity and homopolymer impurity has been investigated. Polystyrene-b-poly(acrylic acid) block copolymers were studied due to their previously demonstrated efficacy as stabilizers in emulsion polymerization, and their similarity to commercially important polystyrene-r-poly(acrylic acid) stabilizers. Neither greater molecular weight dispersity nor homopolymer impurity was found to negatively impact the stabilization performance of these block copolymers, suggesting that the economically unfavorable conditions required to achieve low molecular weight dispersity and homopolymer impurity may be avoided. In addition to improving the economic outlook of amphiphilic block copolymer stabilizers, this work has also improved their technical feasibility. Novel polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers have been introduced which stabilize emulsion polymerizations with up to 50 weight percent solids content, exceeding what was possible using polystyrene-b-poly(acrylic acid) block copolymers. The block-random copolymers were also observed to have unusual solution behavior, self-folding rather than self-assembling. Emulsion polymerizations stabilized by these block-random copolymers had a total particle surface area which was directly proportional to the stabilizer concentration and was unaffected by polymerization kinetics. A novel “seeded-coagulative” emulsion polymerization mechanism has been proposed to explain these results, which were unexplainable by any known emulsion polymerization mechanism.
Co-Authorship

The bulk of this research was carried out independently by myself, under the supervision of Dr. Michael Cunningham, at Queen’s University. All of the material presented in Chapters 3 and 4 has been accepted and published as two separate publications in *Macromolecules*, a refereed journal; this content is republished here as permitted by the American Chemical Society’s Ethical Guidelines to Publication of Chemical Research. Rachel Champagne-Hartley assisted in many of the experiments in these Chapters, under my supervision. Dr. Gary Deeter and Dr. David Campbell (BASF Corporation, Wyandotte, MI), and Dr. Bernd Reck and Dr. Dieter Urban (BASF SE, Ludwigshafen, Germany) contributed to the creation and guidance of this project, as well as the preparation of manuscripts and many valuable discussions.
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<th>Description</th>
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<tr>
<td>AA</td>
<td>Acrylic acid</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>APS</td>
<td>Ammonium persulfate</td>
</tr>
<tr>
<td>ASR</td>
<td>Alkali-Soluble Resin</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom Transfer Radical Polymerization</td>
</tr>
<tr>
<td>BCP</td>
<td>Block Copolymer</td>
</tr>
<tr>
<td>BlocBuilder™</td>
<td>N-(tert-butyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine</td>
</tr>
<tr>
<td>C153</td>
<td>Coumarin 153, 2,3,6,7-Tetrahydro-9-(trifluoromethyl)-1H,5H,11H-[1]benzopyrano(6,7,8-ij)quinolizin-11-one</td>
</tr>
<tr>
<td>CAC</td>
<td>Critical Aggregation Concentration</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinylbenzene</td>
</tr>
<tr>
<td>FRP</td>
<td>Free Radical Polymerization</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>GTP</td>
<td>Group Transfer Polymerization</td>
</tr>
<tr>
<td>IPD</td>
<td>Interparticle Distance</td>
</tr>
<tr>
<td>L/CRP</td>
<td>Living/Controlled Radical Polymerization</td>
</tr>
<tr>
<td>MONAMS</td>
<td>methyl 2-((tert-butyl)(1-(diethoxyphosphoryl))-2,2-dimethylpropyl)amino)oxy) propanoate</td>
</tr>
<tr>
<td>MWD</td>
<td>Molecular Weight Distribution</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NMRP</td>
<td>Nitrooxide Mediated Radical Polymerization (a.k.a. NMP)</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity Index (from DLS)</td>
</tr>
<tr>
<td>PMeA</td>
<td>Poly(methyl acrylate)</td>
</tr>
<tr>
<td>PRE</td>
<td>Persistent Radical Effect</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>RAFT</td>
<td>Reversible Addition-Fragmentation Chain Transfer</td>
</tr>
<tr>
<td>RDRP</td>
<td>Reversible-Deactivation Radical Polymerization</td>
</tr>
<tr>
<td>ROMP</td>
<td>Ring-Opening Metathesis Polymerization</td>
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SG1  N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide
SLS  Static Light Scattering
TEM  Transmission Electron Microscopy
THF  Tetrahydrofuran
TPE  Thermoplastic Elastomer
VOC  Volatile Organic Compound

**Parameters**

\( A \)  Arrhenius coefficient (L mol\(^{-1}\) s\(^{-1}\))

\( a_s \)  Interfacial area occupied by a stabilizer molecule on latex particle surface (cm\(^2\))

\( D_n \)  Number-average hydrodynamic diameter (nm or cm)

\( D_N \)  Degree of neutralization

\( dn/dC \)  Refractive index increment (mL g\(^{-1}\))

\( d(wt)/d(logM) \)  Differential logarithmic molecular weight distribution

\( D_P \)  Number-average degree of polymerization

\( D_z \)  Intensity-average hydrodynamic diameter (nm or cm)

\( D \)  Molecular weight dispersity

\( E_a \)  Activation energy (kJ mol\(^{-1}\))

\( k_a \)  Activation rate constant (s\(^{-1}\))

\( k_d \)  Deactivation rate constant (L mol\(^{-1}\) s\(^{-1}\))

\( k_p \)  Propagation rate constant (L mol\(^{-1}\) s\(^{-1}\))

\( M \)  Molecular weight (g mol\(^{-1}\))

\( M_n \)  Number-average molecular weight (g mol\(^{-1}\))

\( M_w \)  Weight-average molecular weight (g mol\(^{-1}\))

\([M]\)  Concentration of monomer (mol L\(^{-1}\))

\([M]_0\)  Initial concentration of monomer (mol L\(^{-1}\))

\([M]_p\)  Concentration of monomer in latex particle (mol L\(^{-1}\))

\( \bar{n} \)  Average number of radicals in a latex particle

\( N_A \)  Avogadro’s constant (6.022 x 1023 mol\(^{-1}\))

\( N_{agg} \)  Aggregation number

\( N_{bca} \)  Number of block copolymer aggregates (L\(^{-1}\))

\( N_c \)  Number of stabilizer molecules per particle

\( N_m \)  Number of micelles (L\(^{-1}\))
\( \dot{n}_m \)  \text{Limiting interfacial mass transfer rate from the monomer phase (mol s}\(^{-1}\))

\( N_p \)  \text{Number of particles (L}\(^{-1}\)}

\( P_n \)  \text{Polymer with } n \text{ repeat units}

\( R \)  \text{Number-average particle radius (cm)}

\( R_i \)  \text{Rate of radical formation (mol s}\(^{-1}\) m\(^3\))

\( R_p \)  \text{Rate of polymerization (mol L}\(^{-1}\) s\(^{-1}\))

\(<r^2>_{1/2} \)  \text{Root-mean-square end-to-end distance (nm)}

\(<r^2>_{0.5} \)  \text{Unperturbed root-mean-square end-to-end distance (nm)}

\([S] \)  \text{Concentration of stabilizer (mol L}\(^{-1}\)}

\( t \)  \text{Time (s)}

\( T_g \)  \text{Glass transition temperature (°C)}

\( v_m \)  \text{Volume fraction of monomer in latex particle}

\( v_{\text{poly}} \)  \text{Volume fraction of polymer in latex particle}

\( w_i \)  \text{Weight fraction of polymer } i \text{ in block copolymer}

\( Z\text{-Avg} \)  \text{Intensity weighted mean hydrodynamic size assuming monomodal distribution (nm)}

\( \alpha \)  \text{Exponent of stabilizer concentration in proportion to number of particles (Np ~ [S]}^\alpha\)

\( \mu \)  \text{Rate of particle volume growth (cm}^3\text{s}^{-1}\)

\( \rho \)  \text{Density (g cm}^{-3}\)

\( \tau \)  \text{Solids content of latex (g L}^{-1}\)

\( \phi \)  \text{Volume fraction of particles}

\( \phi_m \)  \text{Volume fraction of particles at maximum packing}
Chapter 1

Introduction

Commodities such as synthetic rubber, adhesives, binders, and coatings are produced at megatonne scales each year through the process known as emulsion polymerization. Compared to homogeneous polymerization, the production of polymers via emulsion polymerization is advantageous, providing a higher rate of polymerization and greater thermal control; in addition, water is used as the solvent instead of a volatile organic compound (VOC), making the process more environmentally friendly. A disadvantage of emulsion polymerizations is their inherent thermodynamic instability, requiring stabilizing molecules to prevent particle coagulation and phase separation. While a stabilizer improves the stability of an emulsion polymerization, it is also incorporated into the final emulsion polymer and may affect final product properties. For example, the presence of a water soluble stabilizer in an emulsion polymer used as a coating may have a negative impact on the coating’s water resistance.

The design of new stabilizers for emulsion polymerization is driven by the need to create new or improved emulsion polymer properties, but the range of properties available from small molecule surfactants is limited. The design of polymeric surfactants for use as stabilizers in emulsion polymerization is promising due to the vast range of properties that may be achievable. Advances in polymerization chemistry, specifically living polymerization, have enabled the production of polymers with discrete “blocks” of differing composition. Copolymers with both hydrophobic and hydrophilic blocks are referred to as amphiphilic and may stabilize the interface between the dispersed and continuous phases of an emulsion. The identification of polymeric
structures which are both technically and economically practical will lead to the next generation of polymeric stabilizers in emulsion polymerization.

1.1 Overview

This work began as a collaboration with researchers from the chemical company BASF to experimentally evaluate the hypothesis that well-defined and pure block copolymer structures are required for satisfactory performance as stabilizers in emulsion polymerization. A significant obstacle to the commercial application of block copolymers is their economic production, but strategies to make production more economic may lead to undesirable effects. For example, broadened molecular weight distributions may result from high conversion or continuous production, while impurities such as homopolymers will result from a reduction in purification steps. Amphiphilic block copolymers of polystyrene-b-poly(acrylic acid) were chosen for this study due to their previously demonstrated efficiency as stabilizers in emulsion polymerization, and their similarity to commercially important polystyrene-r-poly(acrylic acid) random copolymer stabilizers. The effects of molecular weight dispersity of both the polystyrene and poly(acrylic acid) block on stabilizer performance were investigated, and are reported in Chapters 3 and 4, respectively. The effect of polystyrene homopolymer impurity was also investigated in Chapter 5, along with the effect of stabilizer concentration and degree of neutralization. The conclusion of these chapters was that block copolymer stabilizers can tolerate levels of dispersity and impurity greater than those likely to result from economic production without compromising their performance as stabilizers in emulsion polymerization.

The original scope of this project was extended beyond dispersity and impurity to identify the limitations of polystyrene-b-poly(acrylic acid) stabilizers in commercially relevant emulsion polymerizations conditions, e.g. high solids content. As reported in Chapter 6, it was discovered
that these block copolymer stabilizers fail at high solids content, inspiring the design of novel polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymer stabilizers which were demonstrated to overcome the high solids content limitation. The unusual solution behavior of the block-random copolymer stabilizers prompted the study of their emulsion polymerization mechanism, presented in Chapter 7, where it was concluded that emulsion polymerizations stabilized by the block-random copolymer follow a mechanism which is thermodynamically controlled, and unprecedented in the literature. In summary, this work began to determine the practicality of amphiphilic block copolymer stabilizers in emulsion polymerization, and through this pursuit, lead to the design of improved amphiphilic block copolymer stabilizers responsible for a novel emulsion polymerization mechanism.

1.2 Original Contributions

The original contributions of this work are summarized below:

- The solution behavior of amphiphilic polystyrene-b-poly(acrylic acid) block copolymer stabilizers is affected by molecular weight dispersity and homopolymer impurity, but there is no negative effect on the stabilization performance in emulsion polymerization. Block copolymer specifications may be relaxed and still achieve satisfactory results, meaning production through more economic conditions may be tolerable.

- Introduced an in situ dynamic light scattering technique to study the time evolution of emulsion polymerizations at very dilute block copolymer concentrations (below and above the critical aggregation concentration).

- A polyelectrolyte stabilizing block below full neutralization inhibits radical entry into seed aggregates and results in high particle size dispersity.
• Polyelectrolyte blocks of polystyrene-b-poly(acrylic acid) stabilizers decrease the effective interparticle distance and limit the achievable solids content in an emulsion polymerization.

• By replacing the poly(acrylic acid) stabilizing block with a polystyrene-r-poly(acrylic acid) block, emulsion polymerizations with up to 50 weight percent solids content can be stabilized.

• Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers with an overall molar acrylic acid composition of less than 20% readily form dispersed nanoparticles in alkaline media, consistent with the size of a single self-folded copolymer chain.

• Emulsion polymerizations stabilized by a block-random copolymer had a total particle surface area that was directly proportional to the stabilizer concentration and unaffected by polymerization kinetics. A “seeded-coagulative” emulsion polymerization mechanism was proposed in which particles grow by polymerization and continuously coagulate to conserve total surface area, i.e. number of particles controlled thermodynamically, rather than kinetically.

• Mathematical equations were derived for a seeded-coagulative mechanism which fit the experimental data well and explained the observed dependence of particle number, \( N_p \), on stabilizer concentration \( (N_p \sim [S]^3) \) and solids content \( (N_p \sim \tau^2) \).
2.1 Block Copolymers

Block copolymers are an exciting class of polymeric material in which two or more distinct polymer “blocks” are covalently attached, typically resulting in a material with unique properties compared to the individual blocks. By controlling the topology of individual polymer molecules, it is possible to design materials with well-defined structures at nanometer scales, and through the careful selection of thermodynamic compatibility of blocks, such structures may form thermodynamically, i.e. through self-assembly. When considering the broad range of available chemical structures available through modern polymer chemistry, one can quickly realize the number of possible block copolymer permutations and material properties is enormous. This section will give a brief introduction to the synthesis of block copolymers with a focus on nitroxide mediated radical polymerization (NMRP), and their applications.

2.1.1 Synthesis

The production of block copolymers relies on the “livingness” of the blocks, i.e. chemical functionality of the block that allows it to be extended or coupled with another block. During the last half of the 20th century, a variety of chemistries were developed that allowed for the production of “living” polymers, thus enabling the production of block copolymers. The first of these chemistries was anionic polymerization, developed in 1956 by Szwarc and co-workers, this work introduced the term “living” to describe styrene that was polymerized anionically and in the absence of a termination mechanism, resulting in polystyrene chains that could continue
polymerization when additional monomer was added. Historically, “living” was written in quotations to distinguish from any biological implications, but this practice is rarely observed in the contemporary literature.

For several decades, anionic polymerization was the only means by which polymers with controlled molecular weight distributions (MWD) or block topologies could be prepared. A renaissance of living and controlled polymerization began in the early 1980s with the discoveries of living cationic polymerization by Sawamoto and co-workers,3,4,5 group transfer polymerization (GTP) by Webster and co-workers,6,7 and nitroxide-mediated radical polymerization (NMRP) by Solomon and co-workers.8,9 Further developments of living polymerization were made in the 1990s with the discovery of atom transfer radical polymerization (ATRP) by the groups of Sawamoto and Matyjaszewski,10,11,12,13 followed by the discovery of reversible addition-fragmentation chain transfer (RAFT) radical polymerization by Moad and co-workers,14,15,16 and the development of practical catalysts for ring-opening metathesis polymerization (ROMP) by Grubbs.17 At the time of writing, these chemistries continue to be improved, and additional chemistries have been developed, such as catalyst-transfer polycondensation,18,19 and organotellurium-, organostibine-, and organobismuthine-mediated living radical polymerization.20 The technologies listed here are by no means exhaustive, but are representative of where substantial research has been focused; more comprehensive reviews of block copolymer synthesis are available.19,21

The current state of the art in block copolymer synthesis provides catalysts, initiators, and mediating agents that enable the production of block copolymers with a significant variety of chemical and physical properties. The greatest challenge that remains is the screening of innumerable permutations of block copolymers to discover materials that not only achieve specific
chemical and physical properties, but are also available through economically practical synthetic routes. Due to previous expertise in our research group with nitroxide mediated radical polymerization and its potential commercial viability, it was chosen as an appropriate synthetic route for the production of the block copolymers used in this work and is described in greater detail in the following section.

2.1.2 Nitroxide-Mediated Radical Polymerization

The first application of nitroxides in radical polymerization was not to create living polymers, but rather to study the mechanism of free radical polymerization by capturing, or trapping, radical species by termination with a nitroxide. It was observations by the Commonwealth Scientific and Industrial Research Organization (CSIRO) polymer research group that first showed the trapping of oligomeric radicals as alkoxyamines was reversible (e.g. by changing temperature or solvent; Figure 2.1), and this lead to the 1986 patent detailing the synthesis and use of nitroxides to control the growth of radical polymerizations.

![Deactivation-activation equilibrium between a persistent nitroxide radical, and an alkoxyamine](image)

**Figure 2.1.** Deactivation-activation equilibrium between a persistent nitroxide radical, and an alkoxyamine. General structures are shown.

NMRP garnered more attention in the early 1990s after work by Georges and co-workers and has been classified as a “living/controlled” (e.g. L/CRP) or “controlled” (e.g. CRP) radical polymerization, but herein will be referred to by the International Union of Pure and Applied Chemistry (IUPAC) recommended term “reversible-deactivation radical polymerization” (RDRP). A form of reversible-deactivation radical polymerization, NMRP involves the reversible termination of a growing polymer radical with a nitroxide radical (Figure 2.2) that
competes with the classical termination pathways of free radical polymerization (FRP) such as combination, disproportionation, and chain transfer. In NMRP, the reversibility of the termination with a nitroxide is owing to the instability of the alkoxyamine product under the reaction conditions.

![Diagram of Monomer, Termination or transfer, and Pn O NR2]

**Figure 2.2.** The equilibrium between an active polymer radical and dormant polymer radical via reversible termination with a stable nitroxide radical.

Reversibility of the termination mechanism is not enough to maintain a living polymerization; the reversible termination mechanism must prevail over termination by combination, disproportionation, and chain transfer. The dominance of the reversible termination mechanism in NMRP is owing to the persistent radical effect (PRE). The PRE describes an accumulation of persistent radicals, such that a small population of transient radicals has a much greater probability of terminating with a persistent radical than with another transient radical. To demonstrate this, consider a system that generates both transient R radicals (e.g. polymer radicals) and persistent Y radicals (e.g. nitroxide radicals), via the reactions in Figure 2.3:

\[
R_\cdot + R_\cdot \xrightleftharpoons[k_d]{k_a} R-R
\]

\[
Y_\cdot + R_\cdot \xrightarrow{k_d}{k_a} R-Y
\]

**Figure 2.3.** Reaction schemes of the fate of transient and persistent radicals leading to the persistent radical effect.\(^{29}\)
From these reactions, the rate equations for the concentrations of transient and persistent radicals can then be written by eqs 2.1 and 2.2, respectively.

\[
\frac{d[R \cdot]}{dt} = k_a[R - Y] - k_d[R \cdot][Y \bullet] - k_{t,R}[R \cdot]^2 \quad (2.1)
\]

\[
\frac{d[Y \bullet]}{dt} = k_a[R - Y] - k_d[R \cdot][Y \bullet] \quad (2.2)
\]

As the Y radicals are persistent, they will not self-terminate \((k_{t,Y}=0)\) and their cross-termination with transient (R) radicals is reversible. With the irreversible consumption of transient radicals through diffusion controlled self-termination, the system will rapidly accumulate persistent radicals such that the cross-termination equilibrium becomes the dominant reaction. At this equilibrium stage, the majority of self-termination will have occurred, and persistent and transient radicals will exist in equilibrium primarily with the cross-termination product R-Y. Due to the relatively high concentration of persistent radicals compared to transient radicals, when R-Y “activates” to release a transient radical, the chances of cross-terminating (or “deactivating”) with a persistent radical will be far greater than self-terminating with another transient radical. These cross-terminated R-Y “dormant” chains can then continue activation/deactivation cycles allowing for short propagation periods between cross-terminations; this is the persistent radical effect and is the fundamental concept behind NMRP.

When producing controlled and living block copolymers by NMRP, the first step is to select a nitroxide suitable for all monomers to be copolymerized. Nitroxides can be designed to have compatibility with specific monomers or monomer families, such that it is usually possible to find a nitroxide suitable for a given pair or even trio of monomers (See Tables 16-18 in review article\(^3\)). In some cases, it is not only the monomers that must be considered when selecting a nitroxide, but also the sequence that they will be polymerized in. For example, in the production of n-butyl
acrylate/styrene block copolymers, a poly(n-butyl acrylate) macroinitiator is capable of initiating and growing well-controlled poly(n-butyl acrylate)-b-polystyrene, but a polystyrene macroinitiator results in a poorly controlled polystyrene-b-poly(n-butyl acrylate).\textsuperscript{31}

With NMRP, the first block of a block copolymer can be produced by either a bimolecular or unimolecular initiation system. In a bimolecular initiation, traditional thermal initiators common in free radical polymerizations can be used to create propagating radicals which are then captured by a nitroxide radical. By altering the amount of free nitroxide, either by the initial amount added or by the use of nitroxide scavenging additives (e.g. camphorsulfonic acid, acetic anhydride) the rate of polymerization can be controlled;\textsuperscript{32} however, a potential disadvantage inherent to bimolecular initiating systems is that the efficiency of the initiator can be difficult to control, leading to problems with reproducibility.\textsuperscript{30} In a unimolecular initiation system, an alkoxyamine initiator thermally decomposes into an initiating radical and a mediating nitroxide radical, creating an immediate stoichiometric ratio between radical and nitroxide.\textsuperscript{33} In general, unimolecular initiation systems have a greater reproducibility and have been noted to perform better than their bimolecular counterparts.\textsuperscript{34} In both types of initiation systems, propagating radicals will reversibly deactivate with free nitroxide into an alkoxyamine that is reactivated by a thermal unimolecular reaction to allow propagation; this is unlike other reversible-deactivation techniques, where reactivation involves a bimolecular reaction, such as with a catalyst in atom-transfer radical polymerization or a radical species in reversible addition-fragmentation chain-transfer polymerization.

Production of block copolymers with NMRP is typically done by the sequential polymerization of each monomer,\textsuperscript{30} where the first block behaves as an alkoxyamine initiator, initiating the polymerization of the second block. In this case, the initiation of all subsequent blocks
will be unimolecular. Polymerization can be performed either \textit{in situ} by the addition of monomer, or by the purification of the macroinitiator prior to the polymerization of additional blocks. The \textit{in situ} method may be more industrial feasible, while the purification method is more academically useful in terms of characterization of each block and preventing gradients between blocks. There are several alternative routes to produce block copolymers using NMRP, including (i) termination of a polymerization using a functionalized alkoxyamine followed by NMRP, (ii) a double-headed initiator, where one end initiates NMRP and the other initiates a different polymerization type, and (iii) a pre-functionalized polymer coupled to a functionalized alkoxyamine followed by NMRP.\textsuperscript{35} Of course, this is not a comprehensive list of all NMRP techniques, but should demonstrate the variety of synthetic routes available for the production of block copolymers with NMRP. It must also be noted that while NMRP has been used as a convenient method to prepare block copolymers in this work, the specific synthetic route is of little importance compared to the final material properties and application; indeed, many alternative synthetic routes could have been used to produce the same materials and results.

\textbf{2.1.3 Molecular Weight Distribution and Topology}

Block copolymers, like most other polymers, do not have a single molecular weight but instead have a distribution of molecular weights that arise from the method of synthesis. The molecular weight distribution can be characterized by different averages, each carrying a different physical meaning. The simplest average is the number-average molecular weight ($M_n$), defined as:

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = \sum_i x_i M_i$$ \hspace{1cm} (2.3)

where $n_i$ and $x_i$ are the number and number (mole) fraction of polymer chains with a molecular weight of $M_i$, respectively. The $M_n$ of a polymer is simply the arithmetic mean of the molecular
weights of all individual chains and is directly controlled by the polymerization chemistry. Because $M_n$ does not provide any information on the breadth of the distribution, higher-order averages are useful. The weight-average molecular weight ($M_w$) is a second order average defined as:

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \sum_i w_i M_i$$

(2.4)

where $w_i$ is the weight fraction of polymer chains with a molecular weight of $M_i$. The $M_w$ of a polymer is biased towards the higher molecular weight chains in the distribution; it has a physical relationship with the intensity of scattered light in static light scattering and correlates well with the viscosity of polymer liquids. In general, higher order molecular weight averages can be calculated as:

$$M_{z+k} = \frac{\sum_i n_i M_i^{k+3}}{\sum_i n_i M_i^{k+2}}$$

(2.5)

For example, the third and fourth order molecular weight averages, $M_z$ and $M_{z+1}$, emphasize the high molecular weight tail of the distribution, and may prove to be physically meaningful, but are not considered in this work.

The breadth of the distribution is most commonly described by the molecular weight dispersity ($\mathcal{D}$), defined as:

$$\mathcal{D} = \frac{M_w}{M_n} = \left(\frac{\sigma_{M_n}}{M_n}\right)^2 + 1$$

(2.6)

where $\sigma_{M_n}$ is the standard deviation of $M_n$. For a uniform polymer where all chains have identical length, $\mathcal{D} = 1$, although this situation is most commonly produced in nature (e.g. polypeptides), and not in the laboratory. For synthetic polymers, $\mathcal{D} > 1$, with larger values indicative of broader, or more disperse molecular weight distributions. It should be noted that it is
still common to see older terms such as “monodisperse” and “polydispersity/PDI” in polymer journal articles, but IUPAC has stated: “‘Monodisperse’ is a self-contradictory term, and ‘polydisperse’ is tautologous”, recommending the use of “uniform” and “dispersity/ $D$”, respectively. The IUPAC recommended terminology is used herein.

In an ideal nitroxide mediated radical polymerization, the molecular weight dispersity can in principle be predicted by eq 2.7, although non-ideal kinetics are commonly observed:

\[
D = 1 + \frac{1}{DP_n} + (2x^{-1} - 1) \frac{k_p[P - X]}{k_d[X]},
\]

(2.7)

where $DP_n$ is the number-average degree of polymerization at a given conversion $x$, $k_p$ (L mol$^{-1}$ s$^{-1}$) the rate constant of propagation (average value in a copolymerization), $k_d$ (L mol$^{-1}$ s$^{-1}$) is the rate constant of reversible deactivation of the propagating radicals by nitroxide (average value in a copolymerization), $[P-X]$ (mol/L) is the concentrations of all active and dormant polymer chains, and $[X]$ is the concentration of nitroxide radicals at the conversion $x$, expressed as a function of monomer concentration in eq 2.8:

\[
x = \frac{[M]_0 - [M]}{[M]_0},
\]

(2.8)

where $[M]$ (mol/L) is the concentration of monomer and $[M]_0$ (mol/L) is the initial concentration of monomer in the system.

Although $D$ gives a general idea of the breadth of a molecular weight distribution, it is not an ideal parameter as it depends upon the number-average molecular weight of the distribution it parameterizes, e.g. two polymers with identical $D$ but different number-average molecular weights ($M_n$) will have different standard deviations of $M_n$. In other words, $D$ is more descriptive of the ratio of standard deviation and $M_n$ than the actual standard deviation, or breadth, of a molecular weight distribution. In addition, the simplicity of $D$ puts limitations on its utility, e.g. given values
of $D$ and $M_n$, there are an infinite number of molecular weight distributions that they could describe, including multimodal distributions.

While narrow molecular weight distributions are achievable through living polymerization, and aesthetically pleasing in academic literature, it can be argued that the true potential of living polymerizations lies in the ability to produce polymers with a broad range of topologies, resulting in novel properties and applications. The topology of a block copolymer refers to the physical arrangement of the blocks, and some examples of different topologies that are achievable are highlighted in Figure 2.4.

![Figure 2.4. Illustration of different block copolymer topologies.](image)

The simplest and most common block copolymer topology is a diblock, which will be the topology studied in this work.

### 2.1.4 Applications

To envisage where block copolymers may be applied in the future, it is useful to look at how they have been applied in the past. From a historical perspective, society is only at the beginning of the plastics age; while our ancestors built societies based on materials like stone, bronze, and iron, the past century has made plastic, or polymeric, materials ubiquitous in everyday life. From Figure 2.5, the exponential growth of the plastics industry over the last century can be seen along with the advents of important commercial product developments. At the time of writing, annual plastic production exceeds 300 million metric tons and is expected to triple by the year 2050.41
Figure 2.5. The annual production of plastics over the past century (data from Association of Plastics Manufacturers\textsuperscript{42,43}). Advents of commercial production processes for several important plastics are annotated.

With an increasing reliance on polymeric materials, the demand for new and better properties can be expected to increase, and a promising solution to this demand is block copolymers. As previously mentioned, the ability to synthesize block copolymers with a variety of topologies, molecular weights, and chemical structures allows for a broad range of potential applications. The first commercial application of block copolymers was in the 1950s with the development and use of triblock poly(alkylene oxide) copolymers known as Pluronics, for example, as surfactants in the emulsion polymerizations of poly(vinyl acetate).\textsuperscript{44} During the same period, another class of block copolymers known as thermoplastic elastomers (TPE) was developed. Unlike Pluronics, which have useful solution properties, TPE block copolymers have excellent bulk properties; some blocks will form thermodynamic “crosslinks” at nanometer scales that give strength and allow for remolding (i.e. thermoplastic) while other blocks will create soft regions and provide elasticity. Examples of commercial TPE materials include the polyester-polyurethane copolymer Fiber K
(a.k.a. Spandex, Lycra), and polystyrene-b-polybutadiene(or polyisoprene)-b-polystyrene (SBS or SIS).

While other examples of commercialized block copolymers exist, the list of commercial applications is dwarfed by the number of potential applications that have been identified for block copolymers. While the only requirement of good scientific research should be the creation of new and lasting knowledge about nature, the same cannot be said for commercialization. In order to transcend academic potential and become industrially successful, block copolymers must be both physically and economically practical to compete with existing technologies which are well-established, understood, and relatively inexpensive. The main objective of this work is, therefore, to create fundamental knowledge of block copolymers that may help bridge this gap between pure and applied science.

2.2 Emulsion Polymerization

Emulsion polymerization is a method of synthesizing sub-micron sized polymer particles dispersed in a continuous medium, most commonly water. In its most basic form, an emulsion polymerization requires water, a surfactant, a water-insoluble monomer, and a water-soluble initiator. After agitation and heating for some period of time, the monomer is polymerized, forming a latex; this name is borrowed from the Latin word meaning “liquid” or “fluid” which also describes the milky sap produced by many plants, for example, the aqueous dispersion of polyisoprene produced by the rubber tree. The usefulness of natural latex, e.g. natural rubber, inspired the first process to produce a synthetic latex in 1912, and led to the development of the first viable emulsion polymerization methods in the 1930s. Intensive research and development in emulsion polymerization did not occur until the Second World War when natural rubber shortages made the production of synthetic rubber critical. Since these early days, great advances
in the number and variety of products available through emulsion polymerization have been made. At the time of writing, the global demand for emulsion polymers exceeds 10 million metric tons, with large markets in paint, paper coatings, and general-purpose adhesives. These water-based technologies are especially attractive in countries where stringent environmental regulations concerning the emission of volatile organic compounds (VOCs) exist.

Prior to mechanistic theories, early emulsion polymerizations were designed empirically through trial and error; as Gilbert described, early emulsion polymerizations were “put together with some physical feeling and a lot of black magic, and are made after trying many different formulations”. The development of theories to describe the controlling mechanisms in emulsion polymerization has led to formulations that follow more intelligent, knowledge-based design, with greater reproducibility. Perhaps the most studied mechanisms of emulsion polymerizations are those of nucleation, i.e. the process by which dispersed polymer particles are formed and grow. The nucleation mechanism is arguably the most important aspect of an emulsion polymerization as it ultimately controls the number of polymer particles; this then controls process parameters such as the overall rate of polymerization and heat transfer requirements, as well as final product properties such as the rheology, film formation, and reproducibility. This section will summarize the modern mechanisms of emulsion polymerization, specifically those concerning the nucleation of polymer particles in free radical systems. For a more complete review, several textbooks have been published on the kinetics, formulations, and applications of emulsion polymerization and emulsion polymers.

2.2.1 General Kinetics and Seeded Systems

The first phase of an emulsion polymerization, often called Interval I, begins with initiation. Water-soluble initiators are typically used such that propagation begins in the aqueous
(continuous) phase, and these radicals either enter existing particles or form new particles, i.e. particle nucleation. It is commonly accepted that the oligomers must reach a critical length where they are sufficiently hydrophobic to enter a micelle or monomer droplet. Reported values of this critical length, or “z-mer” length, are typically between 2 and 5 monomer units, depending on the temperature and monomer/initiator structures; however, unambiguous experimental evidence has been provided by Tauer, concluding that primary initiating moieties may also directly enter particles. Irrespective of an entering radical’s structure, the entry of a radical into a surfactant micelle, swollen with monomer, results in the creation of a polymer particle that may continue to grow by the diffusion of additional monomer and surfactant. In the absence of any micelles or particles, oligomer radicals may also grow to a critical length at which they collapse to form a polymer particle, stabilized by free surfactant.

After particle nucleation is complete, the emulsion polymerization enters a period known as Interval II where the number of particles and the overall rate of polymerization remain constant. For any free radical emulsion polymerization, a general equation can be written for the instantaneous overall rate of polymerization, $R_p$:

$$R_p = \frac{d[M]}{dt} = \frac{k_p [M]_p N_p \bar{n}}{N_A}$$

(2.9)

where $k_p$ is the propagation rate coefficient of the monomer at a specific temperature (L mol$^{-1}$ s$^{-1}$), $[M]_p$ is the concentration of monomer in the particles (mol/L), $N_p$ is the number of particles per unit volume of the aqueous phase (L$^{-1}$), $\bar{n}$ is the average number of radicals per particle, and $N_A$ is Avogadro’s constant (6.022 x 10$^{23}$ mol$^{-1}$). During Interval II, the concentration of monomer in particles remains constant as monomer continuously diffuses through the aqueous phase to replace the monomer polymerized inside the particles. The final stage of an emulsion polymerization, Interval III, begins when the monomer droplets have been depleted, and continues
until the monomer inside the particles is also depleted. The three intervals of a conventional emulsion polymerization are illustrated in Figure 2.6.

**Figure 2.6.** Illustration of the three intervals of a conventional emulsion polymerization, (I) particle nucleation, (II) particle growth, and (III) monomer droplet depletion and full conversion. 

Eq 2.9 demonstrates the importance of the number of particles in an emulsion polymerization, as this directly affects the overall rate of polymerization, and therefore heat addition or removal requirements of the process. By directly controlling the number of particles by the addition of pre-made “seed” particles, the number of particles and thus the overall rate of polymerization can be held constant in what is called a seeded emulsion polymerization. Mechanistically, a seeded emulsion polymerization is very simple as the complications from particle nucleation can be ignored; this is advantageous for industrial processes as it results in greater batch reproducibility.

In seeded emulsion polymerization, a seed latex is prepared in the same manner as a conventional emulsion polymerization and follows a formulation chosen for being highly reproducible. Ideally, the seed latex particles will be very small (e.g. 30 nm) and versatile such that a single seed latex formulation can be used to produce a variety of different products. After synthesis and characterization of a seed latex, it can be used in a subsequent emulsion
polymerization where the number of latex particles is constant, i.e. each seed latex particle grows and no new particles are nucleated. Depending on the compatibility and sequence in which monomers are (co)polymerized, seeded emulsion polymerizations can result in different particle morphologies. Examples of particle morphologies are illustrated in Figure 2.7, and detailed reviews of latex particle morphology are available.\textsuperscript{61,62}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{particle_morphologies.png}
\caption{Illustration of possible particle morphologies that may be achieved through seeded emulsion polymerization of monomer 2, using seed particles of polymer 1. Copyright © 2008 by John Wiley & Sons, Inc. Reproduced with permission.\textsuperscript{58}}
\end{figure}

While seeded emulsion polymerization requires an additional preparation step, this drawback may be minor compared to the versatility and reproducibility that are gained.

\subsection*{2.2.2 Micellar Nucleation}

In the absence of seed particles, an emulsion polymerization is considered \textit{ab initio} and must begin with particle nucleation. If a surfactant is added to the system at a concentration greater than its critical micelle concentration (CMC), which is the case in the majority of commercial emulsion
polymerizations, the surfactant-formed micelles will act as the loci for particle nucleation. Although nucleation of both micelles and monomer droplets is possible, the total surface area of micelles is generally much larger than the surface area of monomer droplets, resulting in the majority of oligomer radicals being captured by micelles. The period during which micelles are nucleated to become particles is known as Interval I and ends when there are no longer any micelles remaining.

Harkins, along with Smith and Ewart, pioneered the study of particle nucleation in the late 1940s, forming the basis of modern particle nucleation theories. In their seminal work, Smith and Ewart derived a theory based on the idea of radical compartmentalization, following the time dependence of the number of particles, \( N_n \), with \( n \) radicals, where the average number of radicals in a particle is:

\[
\bar{n} = \sum_{n=0}^{\infty} nN_n, \quad \text{with: } \sum_{n=0}^{\infty} N_n = 1 \tag{2.10}
\]

This treatment led to an equation for the number of particles produced in an emulsion polymerization:

\[
N_p = k \left( \frac{R_i}{\mu} \right)^{\frac{2}{5}} (a_s[S])^{\frac{3}{5}} \tag{2.11}
\]

where \( R_i \) is the rate of radical formation (mol s\(^{-1}\) m\(^{-3}\)), \( \mu \) is the rate of particle volume growth (m\(^3\) s\(^{-1}\)), \( a_s \) is the interfacial area occupied by a surfactant molecule on the particle surface (m\(^2\)), \( k \) is a constant related to radical entry, \( N_A \) is Avogadro’s constant (6.022 x 10\(^{23}\) mol\(^{-1}\)), and \([S]\) is the surfactant concentration (mol m\(^{-3}\)). The derivation of eq 2.11 requires the following assumptions:
1. The concentration of surfactant that is stabilizing micelles and particles is much greater than the concentration of surfactant adsorbed to monomer droplets or dissolved in water, such that droplet and dissolved surfactant can be neglected:

\[
[S]_{\text{micelle}} + [S]_{\text{particle}} \gg [S]_{\text{droplet}} + [S]_{\text{dissolved}}
\]

\[
[S] \approx [S]_{\text{micelle}} + [S]_{\text{particle}}
\]

2. The interfacial area, \(a_s\), occupied by a surfactant molecule is the same in micelles and particles:

\[
a_s \approx a_{s,\text{micelle}} \approx a_{s,\text{particle}}
\]

\[
A_{\text{total}} = a_{s,\text{micelle}}[S]_{\text{micelle}} + a_{s,\text{particle}}[S]_{\text{particle}} \approx a_s[S]
\]

3. Nucleation ceases at the time when the total particle surface area equals the total surface area of all surfactant molecules, i.e. complete adsorption of surfactant on particle surfaces.

4. The rate of polymerization in particles remains constant, independent of particle size or radical entrance rate, i.e. “zero-one” kinetics are obeyed where an average number of radicals per particle is 0.5.

5. The ratio of monomer to polymer in particles remains constant during particle formation, such that particle density and volume growth rate are constant:

\[
\frac{dM_{\text{particle}}}{dt} = \rho \frac{dV_{\text{particle}}}{dt} = \text{Constant}
\]

\[
\frac{dV_{\text{particle}}}{dt} = \mu
\]

6. All particles are assumed to be spherical.
In this model, the constant $k$ is related to the entry of radicals into micelles versus particles; if radicals only enter micelles, $k = 0.53$, but if the rate of radical entry is equal for all surfaces regardless of particle size, $k = 0.37$. The experimental $k$ will, therefore, lie between 0.37 and 0.53.

Many refinements have been made in modern theories of micellar nucleation to account for mechanisms not considered in early theories, for example:55

- Propagation in the aqueous phase continues until oligomers become surface-active, and these aqueous phase oligomer radicals may terminate with each other.
- An aqueous phase oligomer may enter a micelle, or alternatively may aggregate with surfactant molecules to become a precursor particle; such particles may undergo coagulation with each other.
- A radical may exit from one particle and nucleate another.
- Particle nucleation ceases when newly formed radicals are captured by existing particles faster than they can nucleate new particles.

The majority of these theories are far more complex than the original Smith and Ewart treatment, and often lack analytical solutions, although numerical solutions are readily found with current computer processors.

2.2.3 Homogeneous-Coagulative Nucleation

In the case that neither seed particles nor micelles are present, particle nucleation is dominated by a homogeneous mechanism, first proposed by Priest,66 Roe,67 and Fitch and Tsai.68,69 This mechanism involves the decomposition of an initiator into water-soluble radicals which then propagate with monomer dissolved in the continuous phase to form oligomeric radicals. These water-insoluble oligomeric radicals then collapse into particles. Hansen and Ugelstad then considered that oligomeric radicals must reach a critical chain length before nucleating particles,
Further developments of this model by Lichti\textsuperscript{72} and Feeney\textsuperscript{73,74,75} postulated that particle formation is a two-step process, whereby oligomeric radicals first collapse into particle nuclei, followed by the coagulation of these particle nuclei into primary particles stabilized by the water-soluble initiator end-groups and by any free surfactant. This homogeneous-coagulative nucleation mechanism is illustrated in Figure 2.8.

\textbf{Figure 2.8.} An illustration of the homogeneous-coagulative nucleation mechanism. Copyright © 2008 by John Wiley & Sons, Inc. Reproduced with permission.\textsuperscript{58}

Emulsion polymerizations with exclusively homogeneous-coagulative nucleation mechanisms typically result in relatively low particle numbers, compared to conventional emulsion polymerizations, due to an inherent lack of surface active molecules. As a result,
homogeneous-coagulative nucleation will most often lead to large latex particles and a greater potential for scrap or coagulum, but may still be desirable because the lack of surface active molecules may improve coating properties such as water resistance or adhesion. It should be noted that in a conventional emulsion polymerization where a surfactant is present in a concentration greater than its CMC, although the micellar nucleation mechanism will be dominant, the homogeneous-coagulative nucleation mechanisms summarized in this section may still operate and should not be ignored, especially in the case of hydrophilic monomers such as methyl methacrylate or vinyl acetate.

2.3 Stabilizers in Emulsion Polymerization

Polymer emulsions, by nature, are thermodynamically unstable heterogeneous systems of two immiscible phases, where one phase is dispersed (dispersed phase) in the other (continuous phase). Although thermodynamically unstable, emulsions can be made kinetically stable through the use of a surface active agent (surfactant) which reduces the rate of phase separation. Commonly used surfactants are small molecules containing a short hydrophobic tail and a hydrophilic head, like those used in soaps and detergents. Before discussing surfactants and stabilizers in more detail, the nomenclature in this field should first be clarified. In surface and colloid science, many terms with similar meanings are often used interchangeably which can lead to confusion. For example, terms including surfactant, emulsifier, detergent, stabilizer, soap, wetting agent, dispersant, syndet, foaming agent, and amphiphile can all be used to describe similar molecules, but are more descriptive of the intended application. Surfactant is the more common term, and the origin of the word from the term “surface-active agent” reveals its basic definition, phrased by the International Union of Pure and Applied Chemistry (IUPAC) as:76
“A substance which lowers the surface tension of the medium in which it is dissolved, and/or the interfacial tension with other phases, and, accordingly, is positively adsorbed at the liquid/vapour and/or at other interfaces.”

While this definition makes it clear that a surfactant simply reduces the interfacial tension between two phases, it is uncommon to see this designation given to molecules which do not also lower the surface tension of the medium in which they are dissolved. According to this de facto nomenclature, the majority of block copolymers studied in this work would not be considered as surfactants, and are instead referred to as stabilizers as they stabilize the interface of the dispersed and continuous phases.

This section will summarize the mechanisms by which stabilizers can kinetically stabilize emulsions, and review stabilizer structures that have been used for this purpose. Specifically, polyelectrolyte block copolymer stabilizers will be reviewed as these materials are the focus of this work.

2.3.1 Stabilization Mechanisms

Despite their inherent thermodynamic instability, emulsions can be made kinetically stable by the addition of a stabilizer, which prevents degradation mechanisms such as phase separation, Ostwald ripening, aggregation, and phase inversion. The addition of a stabilizer to the dispersed-continuous interface alters the van der Waals attraction, electrostatic repulsion, and steric repulsion between dispersed particles. An ideal stabilizer will increase the energy barrier to particle aggregation, creating a kinetically stabilized emulsion, i.e. as two particles collide, the stabilizer will provide repulsive interactions greater than the kinetic energy of the particles, preventing the particles from entering a distance where attractive van der Waals forces dominate. The interactions
provided by a stabilizer may be electrostatic repulsions, steric repulsions, or a combination of both, and will be discussed in further detail.

Electrostatic stabilization occurs when stabilizers containing ionic moieties are used to stabilize dispersed particles. Depending on the chemical nature of the stabilizer, the particle surfaces will either acquire a positive or negative electric potential. In the ideal case of a smooth and rigid particle surface with an electrostatic charge, the ions at the particle surface will attract counter-ions from solution and form a tightly bound layer of hydrated counter-ions. At some small distance from the particle surface, on the order of magnitude of a solvated ion, ions will become more weakly bound to the surface and a shear plane is established, beyond which ions do not move with the particle. The electric potential at the particle shear plane is the so-called zeta potential.78

Electrostatic stabilization occurs due to all particles having the same sign of electric potential such that particle collisions are avoided through the electrostatic repulsion between particles; however, if the combined kinetic energy of both particles is sufficient to overcome this electrostatic repulsion, they will collide and be held together by van der Waals attractive forces. Stabilization can be improved by increasing the surface charge of particles, e.g. by adding additional surfactant, but a caveat of adding surface charge is that it may also increase ionic concentration. An increase in the concentration of ionic species in the continuous phase of an emulsion will lead to screening of the charged particle surfaces, decreasing the zeta potential, and may ultimately lead to coagulation.57 For example, an excessive concentration of an ionic surfactant in a system may inadvertently decrease, rather than increase, particle stability.

For traditional small molecule surfactants, electrostatic stabilization provides a good explanation of the particle stabilization, but when dealing with macromolecular and/or non-ionic stabilizers, stabilization by steric effects must also be considered. Steric stabilization arises from
the energy required for adsorbed molecules to mix; as two particles approach each other, the van der Waals attractive forces between them grow stronger, but as the adsorbed molecules on each particle surface begin to overlap, energy is required for these layers to mix. This energy can be represented as the Gibb’s free energy of mixing, $\Delta G_m$:

$$\Delta G_m = \Delta H_m - T \Delta S_m$$  \hspace{1cm} (2.12)

where $\Delta H_m$ is the enthalpy of mixing, $T$ is the temperature, and $\Delta S_m$ is the entropy of mixing. The sign convention here is such that the Gibb’s free energy will be positive if energy is required to mix the two layers, or negative if the mixing of the layers is spontaneous. As both layers are assumed to be chemically identical, the main contribution to the energy of mixing will be a change in entropy. Specifically, the overlap of the layers may cause compression or confinement of the adsorbed molecules, decreasing the entropy, as illustrated in Figure 2.9. If the energy required for mixing of the particle surfaces exceeds the kinetic energy of a particle collision, the particles will not coagulate and are considered sterically stabilized.

![Figure 2.9. Illustration of particles stabilized by electrostatic, steric, and electrosteric stabilization.](image)
The combination of both electrostatic and steric stabilization mechanisms, known as electrosteric stabilization, can combine the advantages of both mechanisms and lead to more robust systems. For example, the electrostatic stabilization of an emulsion may be compromised by the addition of salt, but the emulsion may remain stable if it also has a steric stabilization mechanism. Combining electrostatic and steric stabilization can be achieved simply by using a mixture of ionic and non-ionic stabilizers, or more elegantly by the use of polymeric stabilizers containing ionic groups.

2.3.2 Small Molecules and Polysoaps

The majority of stabilizers used in emulsion polymerization can be classified as either small molecule surfactants or polysoaps. Small molecule surfactants are amphiphilic molecules containing both hydrophobic (typically short alkyl chain) and hydrophilic regions. The hydrophilic region(s) of small molecule surfactants can be anionic (e.g. carboxylate and perfluorocarboxylate salts, sulfate and sulfonate salts, phosphate salts), cationic (e.g. primary amine salts, quaternary ammonium salts), zwitterionic (both cationic and anionic, e.g. β-N-alkylaminopropionic acids, imidazoline carboxylates), or non-ionic (e.g. polyethylene glycol alkylphenols, polyethylene glycol silicones, carboxylic acid esters, long-chain acetal of polysaccharides), with the most commonly used surfactants being anionic, specifically alkylbenzene sulfonates and alcohol ethoxysulfates. In general, anionic stabilizers are more commonly used in emulsion polymerization compared to cationic stabilizers; although the sign of charge does not fundamentally affect the electrostatic stabilization mechanism, many natural surfaces and additives are anionic, which presents an incompatibility with cationic materials.

While the field of small molecule surfactants has matured, advances in polymer chemistry, especially in living polymerization, are only beginning to unlock a variety of promising polymeric
surfactant structures. A classification scheme for polymeric surfactants is shown in Figure 2.10, where they are divided into three main classes: polysoaps, complex architectures, and macrosurfactants.

Figure 2.10. A classification scheme for polymeric surfactants.84

Polysoaps are defined as amphiphilic polymers where the hydrophilic and hydrophobic regions are spread randomly, or statistically, across the polymer backbone.85 Common polysoap structures include statistic or alternating amphiphilic copolymers, and homopolymers of polymerizable surfactants. A commercially relevant example is the copolymerization of styrene and acrylic acid to produce statistic amphiphilic copolymers that are water soluble at alkaline pH and have good surfactant properties; these materials are also known as alkali-soluble resins (ASR),86 examples of which include the products Joncryl,87 Neocryl,88 and Morez 101.89 ASRs are effective stabilizers in emulsion polymerization and can be used synergistically with small molecule surfactants.90,91

The advantages of using small molecule surfactants and polysoaps, compared to block architectures, are that they are relatively inexpensive, widely available, and have well-understood properties. Diblocks and other multiblock architectures, however, have their own advantages, offering a design space wherein a near-limitless amount of new properties and applications may
be discovered; economically practical synthesis is now the major obstacle to block copolymer surfactant design. The following section describes in more detail the design of block copolymer surfactants, specifically diblock copolymers, for use as stabilizers in emulsion polymerization.

### 2.3.3 Block Copolymer Stabilizers

The purpose of this section is to provide a background of block copolymers that could be used as stabilizers in emulsion polymerization. While this work will study block copolymers composed of styrene and acrylic acid, it is important to explain why this specific system was targeted and the alternatives that exist.

In the 1950s, non-ionic poly(alkylene oxide) block copolymers, sold as Pluronics, became the first block copolymers to be used as stabilizers in emulsion polymerization, and remain among the few amphiphilic block copolymers to have commercial success in this application. Pluronic stabilizers are copolymers of poly(ethylene oxide) (PEO), a hydrophilic block, and poly(propylene oxide) (PPO), a hydrophobic block, with the general topology of PEO-PPO-PEO, or occasionally PPO-PEO-PPO. The block copolymer flanked by hydrophobic PPO blocks forms “loops” of PEO at the oil-water interface, while the block copolymer flanked by PEO blocks forms “brushes” of PEO at the oil-water interface (Figure 2.11). In either case, steric stabilization is gained through steric repulsions between the PEO blocks.
Figure 2.11. Illustration of steric stabilization of a particle provided by different triblock copolymer topologies.

In the majority of non-ionic block copolymers used as stabilizers in emulsion polymerizations, the hydrophilic block is composed of poly(ethylene oxide) (PEO) or poly(ethylene oxide)methacrylate, while the hydrophobic block is composed of another poly(alkylene oxide) such as poly(propylene oxide) (PPO) or poly(butylene oxide) (PBO), a styrenic polymer, or a hydrophobic (meth)acrylate polymer. In addition to non-ionic monomers, the continuous development of living polymerization over the last several decades has enabled the study of block copolymers containing many more chemical structures, allowing the production of polyelectrolyte block copolymers. Compared to non-ionic block copolymers, polyelectrolyte block copolymers can provide both steric and electrostatic stabilization, and it was shown in the early 1990s by Leemans and co-workers that amphiphilic block copolymers containing a strong polyelectrolyte block could be used to produce very fine and stable emulsion polymerizations.

Further investigations into polyelectrolyte block copolymers have revealed a rich diversity of behaviours in solution, or as Eisenberg described, a “morphological wonderland”. Examples of this solution behaviour are shown in Figure 2.12.
Figure 2.12. A selection of morphologies formed by amphiphilic diblock copolymers in solution, produced and reviewed by Eisenberg and co-workers: (a) spherical micelles, (b) rods, (c) bicontinuous rods, (d) small lamellae, (e) large lamellae, (f) vesicles, (g) hexagonally packed hollow hoops, and (h) large compound micelles. Pictures Copyright © 2008 by Canadian Science Publishing, reproduced with permission.98 Figure reproduced with permission of The Royal Society of Chemistry.99

The understanding of polyelectrolyte block copolymer solution behavior is particularly important to their application as stabilizers in emulsion polymerization because these morphological structures will inevitably impact particle nucleation. Indeed, it was shown that spherical aggregates formed by polyelectrolyte block copolymers can act as seed particles in emulsion polymerization, but this behavior depends on the length of the hydrophobic block.100
Another interesting property of many polyelectrolyte block copolymers is their inherent lack of activity at the air/water surface. While non-ionic block copolymers have a tendency to lower the surface tension of their solution, many amphiphilic block copolymers containing a strong polyelectrolyte block have been found to have little effect on surface tension; polystyrene-b-poly(sodium acrylate), which is of particular significance to this work, is among those block copolymers which demonstrate negligible surface activity.

Polyelectrolyte block copolymers have been produced from a number of different monomers, and may carry a negative (anionic) and/or positive (cationic) charge, depending on the monomers selected. In some cases, a block (or multiple blocks) may be capable of switching between neutral and charged states reversibly (switchable). Perhaps the most widely researched family of ionic polymers are the anionic poly(carboxylates), readily prepared by the neutralization of a poly(carboxylic acid) with a base. Anionic block copolymer stabilizers can therefore be prepared by incorporation of a hydrophobic polymer block and a poly(carboxylate block) in the same polymer chain. Examples include polystyrene-b-poly(acrylic acid) and poly(methyl methacrylate)-b-poly(acrylic acid) block copolymers which successfully stabilized emulsion polymerizations using less than one weight percent of block copolymer with respect to monomer; for comparison, the required stabilizer in emulsion polymerization is typically 2-20 weight percent. In addition to carboxylate anions, copolymers containing sulfonate anions have also been used to produce anionic block copolymer stabilizers for emulsion polymerization, for example, poly(styrene sulfonate).

Cationic block copolymers, containing a block such as poly(vinylpyridine), poly(quaternized arylamine), or poly(alkylaminoacrylate) in their ionized forms, may also be used as stabilizers. As previously noted, however, cationic species may be more challenging to incorporate into
emulsion polymerization formulations due to the presence of anionic surfaces or additives. For example, in the study of a novel poly(methyl methacrylate-b-N,N’-dimethylaminoethyl methacrylate) block copolymer as a stabilizer in the emulsion polymerization of methyl methacrylate, it was found that the electrostatic attraction between the cationic polyelectrolyte block and anionic oligomer radicals produced by a persulfate initiator resulted in premature termination and retarded polymerization rate.\textsuperscript{117} In contrast, when a cationic initiator was used, the rate of polymerization increased with stabilizer concentration as would be expected in a conventional emulsion polymerization.

The block copolymers that will be studied in the following chapters are anionic polyelectrolyte block copolymers composed of styrene and acrylic acid; these monomers have been chosen as they are the same as those used in commercially important alkali soluble resins (recall Joncryl,\textsuperscript{87} Neocryl\textsuperscript{88} and Morez 101\textsuperscript{89}), and the solution behavior of this specific family of block copolymer has been well-studied.\textsuperscript{118,119,120,121,122,123} A more comprehensive review of amphiphilic block copolymers as stabilizers in emulsion polymerization is available in several reviews,\textsuperscript{94,124,125} and a review of block copolymer stabilizers has been recently published.\textsuperscript{84}

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Chapter 3

Effects of Stabilizing Block Molecular Weight Dispersity on Stabilization Performance

Abstract

Molecular weight dispersity is not typically studied as a design parameter of block copolymer stabilizers, but is often assumed to impact stabilization performance; low molecular weight dispersity is generally assumed to be associated with the best performance. This is the first quantitative investigation of the effects of block copolymer molecular weight dispersity with regards to stabilization performance in an emulsion polymerization. Polystyrene-b-poly(acrylic acid) block copolymers were synthesized by nitroxide-mediated radical polymerization and employed as stabilizers in the emulsion polymerization of styrene. The effect of the stabilizing poly(acrylic acid) block’s molecular weight dispersity on stabilization behavior was studied, independent of molecular weight and composition. Block copolymer stabilizers were evaluated in terms of critical aggregation concentration, dispersed phase particle size, distribution and zeta potential. The molecular weight dispersity of the stabilizing block affected the aggregation number and the final number of particles, but displayed no negative effects on stability or size distribution.
3.1 Introduction

Emulsion polymerization has been used at industrial scales since the mid-1930s and has been studied intensively since its important role in the first production of synthetic rubber.\textsuperscript{1} A basic emulsion polymerization involves the free-radical polymerization of a monomer or a mixture of monomers, typically in water and in the presence of a surface active agent (surfactant). The aqueous continuous phase provides good heat transfer, low viscosity, and a diffusive barrier between particles and monomer droplets. The surfactant concentration must be above its critical aggregation concentration (CAC) to provide sites for particle nucleation, and kinetic stability to the particle-water interfaces. The theory and applications of emulsion polymerizations have been comprehensively discussed in several textbooks.\textsuperscript{1,2,3}

Commonly, the small molecule surfactants used in emulsion polymerization are composed of a short hydrophobic alkyl tail and a hydrophilic ionic head. Beginning in the 1950s, the use of amphiphilic block copolymers was investigated when triblock poly(alkylene oxide) copolymers were used in vinyl acetate emulsion polymerization;\textsuperscript{4} since then, numerous block copolymer (BCP) designs have been investigated.\textsuperscript{5,6}

One of the key advantages of using block copolymers over traditional surfactants is the high level of tailoring that can be done to afford the best stabilization properties; chemical structure, composition, molecular weight, and topology are all commonly optimized properties. The molecular weight dispersity (Đ) is often neglected as a design parameter, with the general assumption that lower molecular weight dispersity will produce better performance. Investigations of block copolymer molecular weight dispersity have typically focused on bulk self-assembly and melt-phase morphological behavior.\textsuperscript{7}
Traditionally, block copolymers were made using anionic polymerization, which readily yields low molecular weight dispersity ($D = M_w/M_n < 1.1$). Reversible-deactivation radical polymerization (RDRP) techniques have enabled the synthesis of block copolymers with a broader range of monomers, but typically with broader molecular weight distributions ($D = 1.1-1.5$). In most cases, achieving lower $D$ will add cost, but without a clear understanding of the benefits. The purpose of this work is, therefore, to investigate the relationships between $D$ and block copolymer performance in emulsion polymerization.

Polystyrene-b-poly(sodium acrylate) stabilizers were chosen for this study as styrene-acrylic acid random copolymers represent a commercially important class of emulsion polymerization stabilizers. The term “stabilizer” to describe these ionic block copolymers, rather than “surfactant”, as they are not always surface-active, is often the case for ionic block copolymers. This family of block copolymers has been previously studied regarding their self-assembly properties and their use as stabilizers in emulsion polymerizations. Specifically, the effects of the poly(acrylic acid) block $D$ on the morphology of polystyrene-b-poly(acrylic acid) ($D_{PS} = 300-325$, $D_{PAA} = 10-210$) aggregates have been studied. The presented work examines the effects of the poly(acrylic acid) stabilizing block $D$ on stabilization performance, independent of the polystyrene anchoring block. Herein, “stabilizing” refers to the block responsible for preventing aggregation of the colloids, while “anchoring” refers to the block responsible for the adherence of the block copolymer to the colloidal structure it is stabilizing. Molecular weight dispersity is studied using a series of copolymers with constant number-average molecular weight and composition, but variable $D$. Stabilization behavior is evaluated in terms of dispersed phase particle size, stability, and distribution, as well as self-assembly properties including critical aggregation concentration and aggregation number.
3.2 Experimental

3.2.1 Materials

N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl) nitrooxide] (SG1, 85%) and methyl 2-((tert-butyl(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy)propanoate (MONAMS, 96%) were supplied by Arkema and used as received. Acrylic acid (anhydrous, 180-200 ppm MEHQ as an inhibitor, 99%), ammonium persulfate (>98%), toluene (99.9%, CHROMASOLV), sodium hydroxide (>98%), and coumarin 153 (C153, 99%) were purchased from Sigma-Aldrich and used as received. Styrene (4-tert-butylcatechol as a stabilizer, ≥99%) was purchased from Sigma-Aldrich and passed through a column of basic alumina to remove the 4-tert-butylcatechol inhibitor prior to use. Anhydrous ethanol was purchased from GreenField Specialty Alcohols and used as received. Methanol (99.8%), tetrahydrofuran (THF, 99%), and hexanes (98.5%) were purchased from ACP Chemicals and used as received. 1,4-dioxane (99.9%), hydrochloric acid (38% assay), and hydroquinone (crystalline/laboratory) were purchased from Fisher Scientific and used as received. Chloroform-D and dimethyl sulfoxide-D6 (100%, 99.96% D) were purchased from Cambridge Isotope Laboratories, Inc. and used as received. All water used in this work was in-house distilled water that was further purified (18.2 MΩ-cm) using a Millipore Synergy water purification system equipped with SynergyPak purification cartridges.

3.2.2 Characterization of Diblock Copolymers

Gel Permeation Chromatography (GPC) analysis was performed with a Waters 2690 Separation Module and Waters 410 Differential Refractometer with THF as the eluent. The column bank consisted of Waters Styrage HR (4.6x300 mm) 4, 3, 1, and 0.5 separation columns operating at 40°C and 0.3 mL/min. The poly(acrylic acid) blocks of the diblock copolymers were methylated to poly(methyl acrylate) before analysis by GPC. This was achieved by adding a slight excess of
trimethylsilyldiazomethane to the polymer sample dissolved in a THF:methanol mixture (3:1 volume ratio), an adaptation of previously reported techniques.\textsuperscript{21,22} All GPC data is reported as the polystyrene-equivalent, based on a calibration curve of narrow molecular weight distribution polystyrene standards purchased from Polymer Standards Service-USA.

\textsuperscript{1}H NMR spectroscopy was performed on an FT-NMR Bruker Avance 400 MHz spectrometer at room temperature. Spectra were recorded with a total of 64 scans, using a polymer concentration of 5 mg/mL in DMSO-d6. The composition of block copolymers was determined by integrating the carboxylic acid protons (11-13 ppm) from poly(acrylic acid), and the aromatic protons (6-7.5 ppm) from polystyrene. The chemical shift scale was calibrated on the basis of the solvent peak (2.50 ppm).

\subsection*{3.2.3 Synthesis of Polystyrene Macroinitiator}

The alkoxyamine initiator MONAMS (2.166 g, 0.0057 mol), styrene (44.4 g, 0.426 mol), and excess SG1 nitroxide (0.198 mL, 0.0006 mol, 10 mol\% based on initiator) were added to a 100 mL 3-necked round bottom flask with an attached condenser. This solution was bubbled with nitrogen for 30 minutes with stirring, followed by immersion in a 120 °C bath of silicone oil. The temperature of the solution was monitored with a mercury thermometer inserted into a side neck of the flask; after 10 minutes the temperature reached 115 °C where it remained for an additional 50 minutes before being cooled in an ice bath. The viscous product was slowly added to 300 mL of stirring methanol to precipitate the polymer. The methanol was then removed by decanting and the polymer residue dried under air. The polymer was re-dissolved in 50 mL of THF and this precipitation procedure was repeated twice more to remove all residual monomer, as confirmed by the absence of any vinyl peaks in the \textsuperscript{1}H NMR spectrum of the purified macroinitiator. The dried
polymer was easily crushed into a white powder (M_n=3400 g/mol, M_w=3800 g/mol, D=1.11 from GPC analysis).

### 3.2.4 Chain Extensions with Acrylic Acid

Polystyrene macroinitiator (0.30 g, 8.8x10^{-5} mol), SG1 nitroxide (3 µL, 1x10^{-5} mol, 10 mol% based on macroinitiator), 1,4-dioxane (3.4 mL), and acrylic acid (1.00 g, 0.014 mol) were added to a 10 mL round bottom flask. After the macroinitiator was dissolved, the solution was bubbled with nitrogen for 30 minutes, and immersed in a 115 °C bath of silicone oil for between 0.5 to 5 hours. The solution was then cooled in an ice bath, prior to being slowly added to 30 mL of stirring hexanes to precipitate the block copolymer. After decanting the hexanes, the polymer was redissolved in 10 mL of THF, and precipitation was repeated twice to remove residual monomer, as confirmed by the absence of any vinyl peaks in the ^1H NMR spectrum of the purified block copolymer. A series of eight block copolymers were prepared in this manner, with M_n ranging from 4200 g/mol to 12300 g/mol, based on GPC.

**Scheme 3.1.** The structure of MONAMS, SG1, and the diblock copolymers prepared via MONAMS.
3.2.5 Generation of Block Copolymer Library via Blending

A library of block copolymers was prepared by blending varying amounts of the eight synthesized polystyrene-b-poly(acrylic acid) block copolymers, a previously reported technique for studying block D.\textsuperscript{19,20} Blending was achieved by weighing appropriate amounts of each block copolymer into a vial (Appendix A), dissolving the polymers in THF, and then removing the THF under a gentle stream of air. By blending different block copolymers on a molar basis, the number-average molecular weight was easily controlled, while allowing for an artificial broadening of the molecular weight distribution. Molecular weight dispersity of the block copolymer library varied between 1.13 and 1.54, a typical range found for polymers synthesized by RDRP. The D of the poly(acrylic acid) block (D\textsubscript{PAA}) in each block copolymer was estimated from rearrangement of eq 3.1,\textsuperscript{2}

\[
D_{PAA-b-PS} = 1 + w_{PAA}^2 (D_{PAA} - 1) + w_{PS}^2 (D_{PS} - 1) \tag{3.1}
\]

where D\textsubscript{PAA-b-PS} is the molecular weight dispersity of the total block copolymer and D\textsubscript{PS} is the molecular weight dispersity of the polystyrene macroinitiator. w\textsubscript{PAA} and w\textsubscript{PS} are the weight fractions of poly(acrylic acid) and polystyrene in the block copolymer, respectively.

3.2.6 Block Copolymer Aggregate Preparation

A block copolymer (10 mg) was added to a 20 mL glass vial, to which appropriate amounts of water and a 1 M sodium hydroxide solution were added to produce a final block copolymer concentration of 1x10\textsuperscript{-4} M with a four-fold stoichiometric excess of base relative to carboxylic acid units. The vial was then tightly sealed with a plastic cap, and heated at 90 °C with magnetic stirring for 24 hours.
3.2.7 Emulsion Polymerization Procedure

A semi-batch emulsion polymerization of styrene was chosen as a standard test procedure wherein 0.5 weight percent (based on styrene, \( \approx 8 \times 10^{-5} \text{ mol/L} \)) of the block copolymer was used as the stabilizer. Styrene was chosen to achieve maximum compatibility between the anchoring block of the block copolymer stabilizers and the growing particles. The general procedure began by adding a block copolymer aggregate dispersion to a 10 mL round bottom flask and bubbling the dispersion with nitrogen for 30 minutes. The flask was then sealed with a rubber septum and immersed in an 85 °C bath of silicone oil. After 10 minutes, the feed of styrene (0.4 g over 2 hours) to the flask was started. After 5 minutes of feeding the polymerization was initiated by the addition of an ammonium persulfate solution (1 wt% based on styrene, 4 mg, 0.0044 mol/L). The polymerization was allowed to continue for 2 hours after the feed to achieve high conversion of the monomer. Each emulsion became a translucent blue color after 10-15 minutes and was completely white/opaque after 30 minutes.

3.2.8 Evaluation of Block Copolymer Aggregate and Emulsion Properties

Conversion of emulsion polymerizations was determined gravimetrically by the addition of 100 μL of a 0.1 mol/L hydroquinone solution to 500 μL of the emulsion, followed by drying in an 85 °C vacuum oven. In all cases, high conversion (>95%) was calculated.

Size, aggregation number, and zeta potential were determined with a Malvern Zetasizer Nano ZS (size range 0.3 nm to 10 μm) at 25°C with non-invasive backscatter optics (173°), using a 4 mW He-Ne (633 nm) laser. All samples were measured in quartz cuvettes, and a universal dip cell (DTS1070) was used for measuring zeta potential. All data was processed using the Malvern Dispersion Technology Software (version 5.00). Block copolymer aggregate dispersions were measured directly, while latex dispersions were diluted by a factor of 200 to obtain a good fit to
the cumulant data. All reported dynamic light scattering (DLS) measurements are an average of
30 sequential measurements. Aggregation numbers of the block copolymer aggregates were
determined by static light scattering (Appendix A) according to eq 3.2,

\[ N_{agg} = \frac{M_{w,aggregate}}{M_{w,copolymer}} \] (3.2)

where \( M_{w,aggregate} \) is the weight-average molecular weight of the block copolymer aggregate
determined by static light scattering, and \( M_{w,copolymer} \) is the weight-average molecular weight of a
block copolymer determined by GPC. A refractive index increment \( (dn/dC) \) of 0.14 mL/g was
determined for a representative block copolymer aggregate (M1 from Table 3.1) using a Wyatt
Optilab rEX with a 690 nm LED light source (Appendix A); this value is in good agreement with
the \( dn/dC \) values previously determined for polystyrene-b-poly(potassium acrylate) block
copolymer aggregates.\(^{18}\) Using the aggregation number calculated from eq 3.2, the number of
block copolymer aggregates \( (N_{bca}; \text{L}^{−1}) \) was determined according to eq 3.3,

\[ N_{bca} = \frac{(C_p - CAC)N_A}{N_{agg}} \] (3.3)

where \( C_p \) is the concentration of block copolymer (mol/L), CAC is the critical aggregation
concentration of the block copolymer (mol/L, explained in the following section), and \( N_A \) is the
Avogadro constant \( (6.022 \times 10^{23} \text{ mol}^{-1}) \).

In order to estimate the size of the polystyrene cores of both block copolymer aggregates and
latex particles, the thickness of the poly(acrylic acid) corona was estimated. According to a
previously reported technique,\(^{17}\) slow addition of hydrochloric acid reduced the diameter of
particles by reducing the degree of neutralization of the poly(acrylic acid) chains, allowing for
their collapse. The gradual addition of strong acid showed that there was a minimum diameter at
a pH of approximately 3, after which additional acid caused aggregation of the block copolymer
aggregates/particles. The thickness of this collapsed corona was estimated as the root-mean-square end-to-end distance of an ideal linear poly(acrylic acid) chain in a good solvent:

\[ \sqrt{\langle r^2 \rangle} = \alpha L \sqrt{NC} \]  

(3.4)

with \( \alpha = 1.33 \) as the expansion coefficient of PAA in water (pH = 3, [NaCl] = 0.01 M)\(^{23} \), \( L = 0.154 \) nm as the length of a C-C (sp\(^3\)-sp\(^3\)) bond\(^{24} \), \( N \) the number of C-C bonds (estimated as twice the number-average degree of polymerization of PAA), and \( C = 6.7 \) as the characteristic ratio of PAA.\(^{25} \) Calculated thicknesses varied between 4-5 nm. It must be noted that these values are only approximations, as eq 3.4 assumes that the polymer chain is a completely uncharged linear homopolymer in an ideal dilute solution.

The number of latex particles (L\(^{-1}\)) was calculated using eq 3.5.

\[ N_p = \frac{6\tau}{\pi \rho D_n^3} \]  

(3.5)

with \( \tau \) the polymer content of the latex (g/L) determined by gravimetry, \( \rho \) the density of polystyrene (1.05 g/cm\(^3\)), and \( D_n \) the number-average diameter of the polystyrene core measured by DLS and corrected to exclude coronal thickness.

In addition to static light scattering, aggregation numbers were also estimated from the relationship between the surface area of the block copolymer aggregate core and the surface area per stabilizer chain, using eq 3.6.\(^{26} \)

\[ N_{agg} = \frac{4\pi R_c^2}{b^2} \]  

(3.6)

with \( R_c \) the number-average radius of the polystyrene block copolymer aggregate core measured by DLS and corrected to exclude coronal thickness, and \( b^2 \) the surface area per stabilizing molecule. Values of \( b^2 \) were estimated from a previously reported empirical
relationship (eq 3.6) between $b^2$ and the degree of polymerization of polystyrene ($N_{PS}$) in polystyrene-b-poly(acrylic acid) block copolymers.

$$b^2 = 1.47 + 0.027N_{PS}$$

Eq 3.6 yields $b^2$ in nm$^2$, and was determined for $N_{PS}$ values between 6-86.

3.2.9 Determination of Critical Aggregation Concentration

A stock dispersion of each block copolymer was made by heating the block copolymer in an alkaline solution of sodium hydroxide (four-fold stoichiometric excess relative to acid groups) at 90 °C for 24 hours. Each stock dispersion was then used to produce a series of dilutions (adding additional base to maintain ionic strength and pH), each of which was heated overnight at 90 °C to ensure equilibration. All dispersions were placed in a sonication bath for 15 minutes prior to measurements. The intensity of scattered light in each sample was measured with attenuator and measurement position held constant, a strategy recently reported as a sensitive technique for determining the CAC of a block copolymer.$^{27}$

Fluorescence spectroscopy was performed using a Photon Technology International (PTI) QuantaMaster QM-6/2005 spectrofluorometer equipped with a dual photomultiplier detection system (Model 814) and using a Xenon arc lamp at 65W. Samples were measured in quartz fluorescence cuvettes purchased from Starna Scientific. Block copolymer dispersions were made in the same manner as for DLS, except that a fluorescent probe was added prior to sonication. CAC was determined using coumarin 153 (C153, Scheme 3.2) as a fluorescent probe as per a recently reported technique,$^{28}$ using an excitation wavelength of 410 nm and scanning emission wavelengths from 450-650 nm to determine maximum fluorescence intensity. Spectra were analyzed using the PTI Felix32 Analysis software. A C153 concentration of 1 μM was used in all samples, achieved by the addition of 10 μL of a 500 μM stock solution of C153 in ethanol to 5 mL
of a block copolymer dispersion. It was assumed that the small quantity of ethanol did not affect the micellar properties.

**Scheme 3.2.** The structure of coumarin 153.

\[ \text{N} \quad \text{O} \quad \text{O} \quad \text{CF}_3 \]

### 3.3 Results and Discussion

#### 3.3.1 Block Copolymer Library Preparation and Characterization

Using a single polystyrene macroinitiator, several block copolymers of varying molecular weights were prepared by chain extension with acrylic acid (Appendix A). By combining the molecular weight distributions of the chain extended polymers in different molar ratios, it was possible to design a library of blend copolymers with approximately equal number-average molecular weight and composition, but different \( \bar{D} \). A molar composition of approximately 55 percent poly(acrylic acid) was targeted, as previous studies of poly(methyl methacrylate)-b-poly(acrylic acid) \(^{29} \) (\( \text{DP}_{\text{PMMA}} = 10-570 \)), and polystyrene-b-poly(acrylic acid) \(^{17} \) (\( \text{DP}_{\text{PS}} = 11-30 \)), observed that block copolymers were not water soluble until the molar composition of the hydrophilic block exceeded 50 percent. This library enabled the study of \( \bar{D} \), independent of composition, molecular weight, and topology. The GPC molecular weight distributions of the chain extensions and a resultant library of blend copolymers are plotted in Figure 3.1. The characterization data for the final blend library is summarized in Table 3.1.
Figure 3.1. Molecular weight distributions of the polystyrene macroinitiator and block copolymer extensions (left) and the final blended block copolymer library (right).

Table 3.1. Molecular weight, dispersity, and composition of the polystyrene-b-poly(acrylic acid) block copolymer blend library.

<table>
<thead>
<tr>
<th>Name</th>
<th>DP&lt;sub&gt;PS&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DP&lt;sub&gt;PAA&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>mol% AA&lt;sup&gt;c&lt;/sup&gt;, GPC</th>
<th>mol% AA&lt;sup&gt;c&lt;/sup&gt;, ¹H NMR</th>
<th>D&lt;sub&gt;PS-b-PAA&lt;/sub&gt;</th>
<th>D&lt;sub&gt;PAA&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
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<td>56</td>
<td>1.54</td>
<td>3.32</td>
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<sup>a</sup> Degree of polymerization based on GPC block copolymer composition.

<sup>b</sup> M<sub>n</sub> for methylated copolymer, polystyrene-b-poly(methyl acrylate), reported as polystyrene equivalent. Same macroinitiator used for all block copolymers (M<sub>n</sub>=3396 g/mol, D<sub>PS</sub> = 1.11).

<sup>c</sup> Molar percentage of poly(acrylic acid) in the block copolymer.

<sup>d</sup> D of the stabilizing block estimated from eq 3.1.
3.3.2 Critical Aggregation Concentrations of the Block Copolymer Library

To determine the effect of $D$ of the stabilizing (PAA) block on self-assembly of the block copolymer, the critical aggregation concentration (CAC) was measured for each block copolymer in the library. Static light scattering (SLS) and fluorescence spectroscopy were both used to determine CAC values.

Using static light scattering, the intensity of scattered light is proportional to the number of scattering particles, the square of their volume, and to the square of the difference between particle and solvent refractive indices. Due to the significant effect of particle size on the scattering intensity, there is a sharp increase in scattering intensity when small unimers form larger aggregates. Thus, block copolymer CAC was taken to be the concentration at which this sudden increase in scattering intensity occurred (Figure 3.2; left).

Coumarin 153 was used in determining block copolymer CAC by fluorescence spectroscopy. The fluorescence quantum yield of this molecule is much higher in an apolar environment than polar, such that the partitioning of C153 into an apolar block copolymer aggregate core will lead to a higher maximum fluorescence intensity.\(^{28}\) Therefore, the block copolymer concentration at which a sudden slope change in fluorescence intensity occurred was assumed to be the CAC (Figure 3.2; right), under the experimental conditions.
Figure 3.2. Critical aggregation concentration of block copolymer M2 determined by both static light scattering intensity (left), and fluorescence spectroscopy (right).

Figure 3.3. CACs of the block copolymer library plotted as a function of stabilizing block molecular weight dispersity, determined by both fluorescence spectroscopy (○) and static light scattering (●) are shown. Error bars for each technique represent the standard deviation of triplicate experiments.

The CAC values determined for this library were comparable to the CAC value determined for a similar block copolymer (PS$_{28}$-b-PAA$_{73}$, D=1.06), previously reported as approximately 0.02
Values of CAC determined from both SLS and fluorescence spectroscopy were in good agreement, although the fluorescence determined CAC values were consistently lower. Fluorescence intensity is proportional to the aggregate volume while scattering intensity is proportional to the aggregate volume squared; therefore, the discrepancy between CAC values from fluorescence and scattering intensity may be due to the higher sensitivity of fluorescence to smaller aggregates near the CAC. It is evident from Figure 3.3 that in the range of PAA block dispersity studied in this work, there was no measurable effect on the CAC.

3.3.3 Effect of Stabilizing Block Molecular Weight Dispersity on Emulsion Properties

Although the PAA block dispersity showed no measurable effect on CAC values, it was of interest to determine if there was an effect on the stabilization properties in emulsion polymerization, such as particle number, diameter, size distribution, and stability. A semi-batch emulsion polymerization of styrene was chosen as a standard test procedure wherein 0.5 weight percent (based on styrene, \( \approx 8 \times 10^{-5} \text{ mol/L} \)) block copolymer was used as the stabilizer. Table 3.2 summarizes the particle size and number for block copolymer aggregates and emulsion polymers stabilized by each block copolymer listed in Table 3.1.
**Table 3.2.** The number and diameter (DLS) of initial block copolymer aggregates and final particles from emulsions stabilized by block copolymers with varying Đ. The aggregation numbers determined from eqs 3.2 and 3.6 are also given for each block copolymer aggregate.

<table>
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<th>Stabilizer</th>
<th>Đ</th>
<th>pH &gt; 9</th>
<th>pH ≈ 3</th>
<th>pH &gt; 6</th>
<th>pH ≈ 3</th>
<th>Dn (nm)a</th>
<th>Dn (nm)b</th>
<th>Nbcac</th>
<th>Np</th>
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</table>

aNumber-average hydrodynamic diameter determined from DLS.
bVariation in final latex particle diameter of duplicate experiments was less than 5%.
cNumber of block copolymer aggregates (Nbcac) determined using aggregation numbers from eq 3.2.

It was observed from DLS that the number-average diameter of both block copolymer aggregates and latex particles increased as a function of the block copolymer Đ, shown in Table 3.2. Atomic force microscopy images of M1 and M8 block copolymer aggregates and particles confirm this trend (Appendix A). Given that the block copolymer concentration was held constant, the increase in block copolymer aggregate diameter suggests an increase in aggregation number.

Particle nucleation and growth was studied by varying the concentration of M1 in otherwise identical emulsion polymerizations. It was observed that the number of particles produced was directly proportional to the number of block copolymer aggregates initially present (Figure 3.4).
Figure 3.4. The number of particles ($N_p$) produced in an emulsion polymerization as a function of the number of block copolymer (M1) aggregates ($N_{bca}$) initially present. An $N_{bca}$ of $1 \times 10^{17}$ L$^{-1}$ corresponds to an M1 concentration of approximately 21 μM. The ratio of $N_{bca}:N_p$ remained close to unity (dashed line) in each polymerization. Each emulsion polymerization was conducted under the conditions outlined in the Experimental section, with the exception of block copolymer concentration which was varied, but always above the CAC.

In emulsions stabilized by block copolymers M1-M8, the ratio of the initial number of block copolymer aggregates to the number of particles, $N_{bca}/N_p$, varied between 0.7-1.2 (Figure 3.5).
Figure 3.5. The ratio of the initial number of block copolymer aggregates and the final number of particles as a function of stabilizing block Đ. N_{bca} was calculated with aggregation numbers from both eq 3.2 (●) and eq 3.6 (○). Error bars were propagated from the uncertainty in aggregate and particle diameters (± 1 nm) and the surface area per chain (± 0.5 nm²).

Figures 3.4 and 3.5 are consistent with a seeded emulsion polymerization mechanism where the number of initial particles is equal to the final number of particles; for comparison, in a non-seeded emulsion polymerization this ratio of micelles to particles is normally between 100-1000.\textsuperscript{1} The linear relationship between the number of particles and block copolymer aggregates suggests that the exchange of stabilizer molecules through the aqueous phase occurs on a slower timescale than particle nucleation, i.e. aggregates are in a frozen state. This is expected for polystyrene-based block copolymers as their hydrophobicity has been directly linked to a decreased rate of exchange between block copolymer aggregates,\textsuperscript{30} where the rate of exchange is hypersensitive to the polystyrene anchoring block length.\textsuperscript{31,32} This frozen state has been previously studied in emulsion polymerizations using block copolymer stabilizers.\textsuperscript{18,29}

Assuming a constant block copolymer concentration, a larger aggregation number leads to fewer block copolymer aggregates, which leads to fewer particles if those aggregates exist in a frozen state, a trend observed in Figure 3.6. If control of the number and size of particles is
required, then the effect of molecular weight dispersity on aggregation number is an important consideration.

![Graph](image)

**Figure 3.6.** The number of particles produced during an emulsion as a function of the stabilizing block $D$. The line is provided as a guide to the eye and does not represent a fit to the data.

Although it is easily understood that the aggregation number of frozen block copolymer aggregates will control the number and size of latex particles, the relationship between the aggregation number and stabilizing block dispersity is not as clear. As seen in Table 3.2, larger stabilizing block dispersity results in larger aggregation numbers, despite a constant number-average molecular weight of the stabilizing block. This effect can be explained by considering a simple aggregate model, such as that proposed by Tanford for small molecule surfactants.\(^{33}\) In this model, the aggregation number is determined by a balance between the electrostatic repulsion of charged head groups, favoring smaller aggregation numbers, and the reduction of interfacial energy between the anchoring block and solvent, favoring larger aggregation numbers. In the case of a block copolymer where the stabilizing group is a polyelectrolyte, the electrostatic potential energy between neighboring polyelectrolyte blocks will be a function of the total charge of each block. Assuming a constant anchoring block, as in this work, shorter stabilizing blocks will reduce
electrostatic repulsion and favor larger aggregation numbers, while longer stabilizing blocks will have the opposite effect. Therefore, in order for the stabilizing block dispersity to affect the aggregation number, it must alter the effective length of stabilizing blocks contributing to the electrostatic potential energy. Figure 3.7 illustrates how dispersity may lower the average stabilizing block repulsions without altering the number-average molecular weight.

Figure 3.7. Illustration of the effect that stabilizing block molecular weight dispersity has on the aggregation number of block copolymer aggregates. Surfaces of two block copolymer aggregates with the same stabilizing block number-average molecular weight are drawn. The aggregate with uniform stabilizing block molecular weight (left) is shown to have a higher average repulsive energy between stabilizing blocks compared to a block copolymer aggregate with more disperse stabilizing block molecular weights (right).

It is expected that during aggregate formation, stabilizing blocks are distributed on the aggregate surface in a manner that reduces the change in free energy of aggregation; larger differences in the lengths of neighboring stabilizing blocks will be favored due to the lower electrostatic potential energy. Thus, an increase in stabilizing block molecular weight dispersity will decrease surface curvature and increase the aggregation number. In block copolymers M1-8, this effect was intensified by the increase in the molar fraction of smaller chains as dispersity was increased, demonstrated in Figure 3.8. This will amplify the reduction of the effective length of stabilizing blocks contributing to electrostatic repulsion and result in a further increase in the aggregation number. Greater increases in the stabilizing block dispersity (Đ > 2) have been shown
to change aggregate morphology to rods and vesicles, attributed to a reduction in the stretching of anchoring blocks.\textsuperscript{20}

\textbf{Figure 3.8.} (Left) The molecular weight distributions of M1-8 plotted on a molar basis showing a greater molar fraction of smaller chains at higher dispersity. (Right) The molar fraction of M1-8 block copolymer chains below the number-average molecular weight (●; left axis) and the aggregation number (○; right axis) as a function of stabilizing block $\mathcal{D}$.

An additional mechanism that may contribute to increasing aggregation number is the swelling of aggregates by block copolymer chains with very short stabilizing blocks. In the lattice theory for spherical micelles proposed by Dill and Flory,\textsuperscript{34} the aggregation number is limited by the length of the core block, such that a void at the center is avoided. Harboring non-surface active chains inside an aggregate would prevent such a void, and increase the limit on aggregation number. A similar effect was previously found with polystyrene-b-poly(acrylic acid) aggregates in aqueous dispersion, where the addition of homopolymer polystyrene led to an increase in aggregate diameter and aggregation number.\textsuperscript{16} The authors argued that the entropic penalty of stretching the polystyrene blocks was reduced as the amount of homopolymer polystyrene in the aggregate core was increased. It is suggested that increasing the stabilizing block dispersity will
result in a population of non-surface active block copolymer chains that may increase aggregation number through this swelling mechanism, but this remains only conjecture as there was no direct evidence to support this theory.

The size distribution of block copolymer aggregates and latex particles showed a similar trend to diameter, as block copolymers with larger $D$ led to aggregates and latex particles with broader size distributions. The effect on size distribution was much less noticeable, and arguably negligible, with the ratio of peak width (standard deviation) and number-average diameter only varying by 5% (Figure 3.9). Although it is intuitive to think that self-assembled structures with a high degree of order must be composed of uniform building blocks, this is not always required. For example, it has been observed that polystyrene-b-poly(acrylic acid), with high $D (> 2)$ polystyrene blocks, form solvent-cast films exhibiting well-ordered lamellar and hexagonally packed cylindrical structures.35

**Figure 3.9.** The ratio of particle peak width (standard deviation) and number-average diameter of block copolymer aggregates and latex particles as a function of the stabilizing block $D$.

An important characteristic of an emulsion polymerization is the stability of the final latex, especially if shelf-life is a concern. The zeta potential of electrostatically stabilized particles can
be used as a measure of stability, i.e. the resistance to particle aggregation. Zeta potentials of both block copolymer aggregates and latex particles were measured and were not found to vary with the block copolymer molecular weight dispersity (Figure 3.10). This observation suggests that in the range of block copolymer stabilizers studied, the stabilizing block Đ does not have a significant effect on the stability of the self-assembled block copolymer aggregates or latex particles.

**Figure 3.10.** Zeta potential of both block copolymer aggregates and latex particles as a function of the molecular weight dispersity of the block copolymer used for stabilization.

The difference between zeta potentials of block copolymer aggregates and latex particles in Figure 3.10 can be attributed to the non-ideality and differences between the aggregate and particle surfaces. The Smoluchowski equation used to calculate these values is only appropriate for smooth, non-porous, and rigid particle surfaces where the thickness of the electrical double layer is small compared to the particle radius; therefore, the zeta potentials calculated for the soft, thick polyelectrolyte-covered surfaces in this work are only valid for a relative comparison. The apparent increase in the zeta potential of latex particles compared to block copolymer aggregates may be attributable to the average slipping (shear) plane shifting closer to the latex particle surface due to the lower charge density and inter-chain repulsion at higher particle surface area. The
potential at the slipping plane of the latex particles would then be expected to be higher than the potential at the slipping plane of the aggregates. It must also be considered that latex particles may have an overall greater charge due to the presence of initiator sulfate groups at the surface, which may lead to an increase in zeta potential.

3.4 Conclusions

Block copolymer aggregate and particle diameters increased with the molecular weight dispersity of a block copolymer stabilizer’s stabilizing block. This effect was dominated by the aggregation number of the block copolymer aggregates, which increased with $\bar{D}$ of the stabilizing block; it is suggested that increasing the stabilizing block dispersity will increase the aggregation number due to a reduction in the average length of stabilizing blocks contributing to the electrostatic potential energy, and that this effect is intensified by an increase in the molar fraction of shorter stabilizing blocks at higher dispersity.

The frozen state of the aggregates resulted in the number of particles being controlled by the number of aggregates. Size distributions of block copolymer aggregates and particles were observed to increase with stabilizing block $\bar{D}$, but the effect was much less noticeable than the effect on diameters. The stability of the block copolymer aggregates and latex particles, as evaluated by zeta potential, was not observed to be affected by the stabilizing block dispersity. In conclusion, the dispersity of the stabilizing block added another dimension of property control in emulsion polymerizations, including the number and size of latex particles, but did not demonstrate any significant negative effects on stability or particle size distributions. It is now of interest to study the effects of the anchoring block molecular weight dispersity in order to further the understanding of block copolymer stabilizers.
3.5 References

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Chapter 4

Effects of Anchoring Block Molecular Weight Dispersity on Stabilization Performance

Abstract

Poly(sodium acrylate)-b-polystyrene block copolymers were employed as stabilizers in the emulsion polymerization of styrene. Previous work by our group has shown that the molecular weight dispersity of the stabilizing block is an important design parameter of block copolymer stabilizers; herein, the molecular weight dispersity of the anchoring polystyrene block, $D_{PS}$, was investigated. Stabilization performance was evaluated by the critical aggregation concentration, aggregation number, and surface activity of the block copolymers, and the size, distribution, and zeta potential of the polystyrene latex particles. It was observed that $D_{PS}$ had a strong effect on aggregation number, which led to a change in the number of latex particles in the seeded emulsion polymerization of styrene. Surface activity decreased with increasing $D_{PS}$ due to a greater diversity of copolymer compositions, supporting the idea that copolymers of different composition play different roles in the stabilization of an emulsion. The performance of block copolymer stabilizers, evaluated by the stability and size distribution of latex particles, was indistinguishable over the range of $D_{PS}$ studied; narrow stabilizer molecular weight distributions were not necessary for satisfactory performance.
4.1 Introduction

Block copolymers are continuously finding new applications,¹ but superior performance does not guarantee commercial success. Along with performance, block copolymers must be available at competitive cost, a difficult task considering that expensive catalysts, reagents, and/or procedures are regularly required in their production. Reduction of cost may involve the use of less expensive reagents, high conversion or continuous production processes, and fewer purification steps. While reducing costs may be achievable technically, the properties and specifications of those block copolymers are likely to be negatively impacted, e.g. homopolymer impurities and higher molecular weight dispersity (Đ) can be expected; therefore, it would be advantageous to know the degree to which impurities and dispersity may be tolerated in a specific application, as obtaining satisfactory performance from lower purity materials could lead to the usage of block copolymers where previously prohibited by cost considerations.

The effects of molecular weight dispersity on melt-phase self-assembly have been reviewed;² increasing the Đ of block copolymers has been observed to increase the domain spacing due to decreased stretching energy,³ or in the case of ionomers, as a result of the largest chains dictating the domain radii.⁴ It is both interesting and perhaps counter-intuitive that increasing the Đ of block copolymers does not prevent the formation of well-ordered morphologies,⁵,⁶,⁷ and can even enhance structure stability.⁸ Consequently, the impact of high molecular weight dispersity requires further investigation.⁹ Few studies have investigated the effects of Đ on block copolymer self-assembly in a selective solvent. In “crew-cut micelles” of polystyrene-b-poly(acrylic acid) dispersed in water, the Đ of the poly(acrylic acid) block had an effect on the morphology of the self-assembled structures, with larger Đ shifting morphology from vesicles to spherical micelles.¹⁰,¹¹ A study of a diblock copolymer with a thermosensitive anchoring block found that
increasing the Đ of the anchoring block yielded micelles with a broader size distribution.\textsuperscript{12} More recently, the effect of Đ on the physical gelation behavior of amphiphilic triblock copolymers has been investigated, finding the Đ of both soluble and insoluble blocks important in the tuning of sol-gel transitions and self-assembly.\textsuperscript{13,14} Recognizing the importance of Đ to polymer properties, recent efforts have been directed toward developing synthetic strategies to control Đ and molecular weight distribution shape.\textsuperscript{15,16,17}

In this spirit, the previous chapter examined the effect of the poly(sodium acrylate) block Đ on the stabilization performance of poly(sodium acrylate)-b-polystyrene block copolymers in emulsion polymerization.\textsuperscript{18} Interest in this specific block copolymer stems from previous academic studies of their self-assembly\textsuperscript{19,20,21,22} and stabilization of emulsion polymerizations,\textsuperscript{18,23,24} and from the commercial success of styrene-acrylic acid random copolymers as emulsion polymerization stabilizers. Emulsion polymerization has been a well-studied field over the last century, both academically and industrially,\textsuperscript{25,26,27} with numerous block copolymer stabilizer designs investigated,\textsuperscript{28,29} but the molecular weight dispersity of block copolymer stabilizers is usually disregarded as a design parameter. While it was found that the Đ of the stabilizing poly(sodium acrylate) block could control the size of block copolymer aggregates, the performance of the block copolymer stabilizers in emulsion polymerization was otherwise indistinguishable.

It is now of interest, and the purpose of this work, to investigate the effect of the anchoring block Đ on block copolymer stabilization performance in emulsion polymerization. For comparative reasons, the experimental conditions have been maintained from the previous chapter; poly(sodium acrylate)-b-polystyrene block copolymers are investigated as stabilizers in the emulsion polymerization of styrene. A blending technique is used to vary the Đ of the anchoring block, independent of the block copolymer number-average molecular weight and composition.
The stabilization performance of block copolymers is evaluated by the latex particle size, stability, and dispersity. Effects on the self-assembly of block copolymers are also evaluated through the critical aggregation concentration, surface activity, and aggregation number.

4.2 Experimental

4.2.1 Materials

N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1, 85%) and N-(tert-butyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder™, 99%) were supplied by Arkema and used as received. Acrylic acid (anhydrous, 180-200 ppm MEHQ as an inhibitor, 99%), ammonium persulfate (>98%), toluene (99.9%, CHROMASOLV), sodium hydroxide (>98%), and coumarin-153 (C153, 99%) were purchased from Sigma-Aldrich and used as received. Styrene (4-tert-butylcatechol as a stabilizer, ≥99%) was purchased from Sigma-Aldrich and passed through a column of basic alumina to remove the 4-tert-butylcatechol inhibitor prior to use. Anhydrous ethanol was purchased from GreenField Specialty Alcohols and used as received. Methanol (99.8%), tetrahydrofuran (THF, 99%), and hexanes (98.5%) were purchased from ACP Chemicals and used as received. 1,4-dioxane (99.9%) hydrochloric acid (38% assay), and hydroquinone (crystalline/laboratory) were purchased from Fisher Scientific and used as received. Chloroform-D and dimethyl sulfoxide-D6 (100%, 99.96% D) were purchased from Cambridge Isotope Laboratories, Inc. and used as received. All water used in this work was in-house distilled water that was further purified (18.2 MΩ-cm) using a Millipore Synergy water purification system equipped with SynergyPak purification cartridges.
4.2.2 Characterization of Diblock Copolymers

Gel Permeation Chromatography (GPC) analysis was performed with a Waters 2690 Separation Module and Waters 410 Differential Refractometer with THF as the eluent. The column bank consisted of Waters Styragel HR (4.6x300 mm) 4, 3, 1, and 0.5 separation columns operating at 40°C and 0.3 mL/min. The poly(acrylic acid) blocks of the diblock copolymers were methylated to poly(methyl acrylate) before analysis by GPC as previously reported.\textsuperscript{18} All GPC data is reported as the polystyrene-equivalent, based on a calibration curve of narrow molecular weight distribution polystyrene standards purchased from Polymer Standards Service-USA.

\textsuperscript{1}H NMR spectroscopy was performed on an FT-NMR Bruker Avance 400 MHz spectrometer at room temperature. Spectra were recorded with a total of 64 scans, using a polymer concentration of 5 mg/mL in DMSO-d\textsubscript{6}. The composition of block copolymers was determined by integrating the carboxylic acid protons (11-13 ppm) from poly(acrylic acid), and the aromatic protons (6-7.5 ppm) from polystyrene. The chemical shift scale was calibrated on the basis of the solvent peak (2.50 ppm).

4.2.3 Synthesis of the Poly(acrylic acid) Macroinitiator

The alkoxyamine initiator BlocBuilder\textsuperscript{TM} (2.6 g, 0.0068 mol), acrylic acid (49.2 g, 0.682 mol), 1,4-dioxane (175 mL), and excess SG1 nitroxide (0.238 mL, 0.00068 mol, 10 mol% based on initiator) were added to a 500 mL 3-necked round bottom flask with an attached condenser. This solution was bubbled with nitrogen for 30 minutes with stirring, followed by immersion in a 120 °C bath of silicone oil. The temperature of the solution was monitored with a mercury thermometer inserted into a side neck of the flask; after 10 minutes the temperature reached 110 °C where it remained for 6 hours before being cooled in an ice bath. The solution was slowly added to 300 mL of stirring hexanes to precipitate the polymer. The hexanes were then removed by decanting and
the polymer residue dried under air. The polymer was re-dissolved in 50 mL of THF and this precipitation procedure was repeated twice more to remove all residual monomer, as confirmed by the absence of any vinyl peaks in the $^1$H NMR spectrum of the purified macroinitiator (M$_n$=3800 g/mol, M$_w$=4900 g/mol, D=1.20 from GPC analysis).

4.2.4 Chain Extensions with Styrene

Poly(acrylic acid) macroinitiator (7 g, 1.8x10$^{-3}$ mol), SG1 nitroxide (63 µL, 1.8x10$^{-4}$ mol, 10 mol% based on macroinitiator), 1,4-dioxane (24 g), and styrene (14 g) were added to a 250 mL round bottom flask. After the macroinitiator was dissolved, the solution was bubbled with nitrogen for 30 minutes, and immersed in a 120 °C bath of silicone oil for 5 hours. Samples were taken throughout the polymerization to obtain a range of polystyrene block lengths. Each sample was cooled in an ice bath, prior to being slowly added to 30 mL of stirring hexanes to precipitate the block copolymer. After decanting the hexanes, the polymer was re-dissolved in 10 mL of THF, and precipitation was repeated twice to remove residual monomer, as confirmed by the absence of any vinyl peaks in the $^1$H NMR spectrum of the purified block copolymer. A second reaction was performed in an identical manner, but with twice the amount of styrene and dioxane to target higher molecular weight extensions. From these two reactions, a series of fifteen block copolymers were prepared with M$_n$ ranging from 4500 g/mol to 16300 g/mol, based on GPC.
Scheme 4.1. The structure of BlocBuilder™, SG1, and the diblock copolymers prepared via BlocBuilder™.

4.2.5 Generation of Block Copolymer Library via Blending

As previously reported,\textsuperscript{10,11,18} block Đ was controlled independently of molecular weight by blending varying amounts of previously synthesized poly(acrylic acid)-b-polystyrene block copolymers. Blending was achieved by weighing appropriate amounts of each block copolymer into a vial (Appendix B), dissolving the polymers in THF, and then removing the THF under a gentle stream of air. Molecular weight dispersity of the block copolymer library varied between 1.30 and 1.77, and the Đ of the polystyrene block (Đ\textsubscript{PS}) in each block copolymer was estimated from rearrangement of eq 4.1,\textsuperscript{2}

\[
Đ\textsubscript{PAA-b-PS} = 1 + w\textsubscript{PAA}^2 Đ\textsubscript{PAA} - 1 + w\textsubscript{PS}^2 Đ\textsubscript{PS} - 1 \quad (4.1)
\]

where Đ\textsubscript{PAA-b-PS} is the molecular weight dispersity of the total block copolymer and Đ\textsubscript{PAA} is the molecular weight dispersity of the poly(acrylic acid) macrorinitiator. \(w\textsubscript{PAA}\) and \(w\textsubscript{PS}\) are the weight fractions of poly(acrylic acid) and polystyrene in the block copolymer, respectively.
4.2.6 Block Copolymer Aggregate Preparation

A block copolymer (10 mg) was added to a 20 mL glass vial, to which appropriate amounts of water and a 1 M sodium hydroxide solution were added to produce a final block copolymer concentration of $1 \times 10^{-4}$ M with a four-fold stoichiometric excess of base relative to carboxylic acid units. The vial was then tightly sealed with a plastic cap and heated at 90 °C with magnetic stirring for 24 hours.

4.2.7 Emulsion Polymerization Procedure.

A batch emulsion polymerization of styrene was used as a standard test procedure wherein 0.5 weight percent (based on styrene, $\approx 8 \times 10^{-5}$ mol/L) of the block copolymer was used as the stabilizer. The general procedure began by adding a block copolymer aggregate dispersion to a 10 mL round bottom flask and bubbling the solution with nitrogen for 30 minutes. The flask was then sealed and immersed in an 85 °C bath of silicone oil. After 10 minutes, styrene (0.4 g) was injected into the flask. After 5 minutes of stirring, the polymerization was initiated by addition of an ammonium persulfate solution (1 wt% based on styrene, 4 mg, 0.0044 mol/L). The polymerization was allowed to continue for 4 hours to achieve high conversion of the monomer. Each emulsion became a translucent blue color after 10-15 minutes and was completely white/opaque after 30 minutes.

4.2.8 Evaluation of Block Copolymer Aggregate and Emulsion Properties

Conversion of emulsion polymerizations was determined gravimetrically by the addition of 100 μL of a 0.1 mol/L hydroquinone solution to 500 μL of the emulsion, followed by drying in an 85 °C vacuum oven. In all cases, high conversion (>95%) was obtained.

Size, weight-average molecular weight, and zeta potential were determined with a Malvern Zetasizer Nano ZS at 25°C with non-invasive backscatter optics (173°), using a 4 mW He-Ne (633
nm) laser. All samples were measured in quartz cuvettes, and a universal dip cell (DTS1070) was used for measuring zeta potential. All data was processed using the Malvern Dispersion Technology Software (version 5.00). Block copolymer aggregate dispersions were measured directly, while latex dispersions were diluted by a factor of 200 to obtain an appropriate level of scattering for measurement. All reported dynamic light scattering (DLS) measurements are an average of 30 sequential measurements. Weight-average aggregation numbers for the block copolymers were determined according to eq 4.2,

$$N_{agg} = \frac{M_{w,aggregate}}{M_{w,copolymer}}$$  \hspace{2cm} (4.2)$$

where $M_{w,aggregate}$ is the weight-average molecular weight of the block copolymer aggregate determined by static light scattering (Debye plot), and $M_{w,copolymer}$ is the weight-average molecular weight of a block copolymer determined by GPC. A refractive index increment ($dn/dC$) of 0.14 mL/g was used as previously determined for neutralized poly(acrylic acid)-b-polystyrene block copolymer aggregates.$^{18,24}$ Using the aggregation number calculated from eq 4.2, the number of block copolymer aggregates ($N_{bca}$; L$^{-1}$) was determined according to eq 4.3,

$$N_{bca} = \frac{(C_p - CAC)N_A}{N_{agg}}$$  \hspace{2cm} (4.3)$$

where $C_p$ is the concentration of block copolymer (mol/L), CAC is the critical aggregation concentration of the block copolymer (mol/L, explained in the following section), and $N_A$ is the Avogadro constant ($6.022 \times 10^{23}$ mol$^{-1}$).

The thickness of the poly(acrylic acid) corona, $L_{corona}$, was estimated from eq 4.4,

$$L_{corona} = R_{h,collapsed} - R_{core,th}$$  \hspace{2cm} (4.4)$$

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\( R_{h, \text{collapsed}} \) is the hydrodynamic radius of an aggregate with collapsed corona determined by gradual addition of hydrochloric acid and was the minimum observed size from DLS before agglomeration.\(^{18,23}\) \( R_{\text{core,th}} \) is the theoretical polystyrene core diameter estimated from eq 4.5,

\[
R_{\text{core,th}} = \left( \frac{3N_{\text{agg}}DP_{n,PS}v_m}{4\pi} \right)^{\frac{1}{3}}
\] (4.5)

where \( N_{\text{agg}} \) is the aggregation number of the block copolymer aggregate from eq 4.2, \( DP_{n,PS} \) is the number-average degree of polymerization of the polystyrene block, and \( v_m \) is the volume per polystyrene repeat unit (0.167 nm\(^3\)).\(^{30}\) Calculated coronal thickness was between 3-4 nm, which was slightly lower than the thickness of approximately 5 nm previously approximated\(^{18}\) for a completely uncharged linear poly(acrylic acid) chain in an ideal dilute solution from eq 4.6,

\[
\langle r^2 \rangle^{\frac{1}{2}} = \alpha L \sqrt{NC}
\] (4.6)

with \( \alpha = 1.33 \) as the expansion coefficient of PAA in water (pH = 3, [NaCl] = 0.01 M)\(^{31}\), \( L = 0.154 \) nm as the length of a C-C (sp\(^3\)-sp\(^3\)) bond\(^{32}\), \( N \) the number of C-C bonds (estimated as twice the number-average degree of polymerization of PAA), and \( C = 6.7 \) as the characteristic ratio of PAA.\(^{33}\)

The number of latex particles (L\(^{-1}\)) was calculated using eq 4.7.

\[
N_p = \frac{6\tau}{\pi\rho D_n^3}
\] (4.7)

with \( \tau \) being the polymer content of the latex (g/L) determined by gravimetry, \( \rho \) the density of polystyrene (1.05 g/cm\(^3\)), and \( D_n \) the number-average diameter of the polystyrene core measured by DLS and corrected to exclude coronal thickness from eq 4.4. Using the number of particles calculated from eq 4.7, the average number of block copolymer chains per particle (\( N_c \)) was determined according to eq 4.8,
\[ N_c = \frac{(C_p - CAC)N_A}{N_p} \]  \hspace{1cm} (4.8)

4.2.9 Determination of Critical Aggregate Concentration

The Critical Aggregate Concentration (CAC) of each block copolymer was determined using both static light scattering intensity and a fluorescence probe (coumarin 153) technique with the same procedures as previously reported.\(^{18}\)

4.2.10 Surface Tension Measurements

A TensioCAD-M tensiometer from CAD Instruments was used to determine the surface tension of samples using the Wilhelmy plate method. All surface tension measurements were at room temperature (20 °C) where the surface tension of water was measured as 72.8 mJ/m\(^2\).

4.3 Results and Discussion

4.3.1 Block Copolymer Library Preparation and Characterization

Using a single poly(acrylic acid) macroinitiator, several block copolymers of varying overall molecular weight were made by chain extension with styrene (Appendix B). By combining different chain extended polymers in varying molar ratios, it was possible to design a library of blend copolymers with approximately equal number-average molecular weight and composition, but different \( \mathcal{D} \). As all block copolymers were produced from the same poly(acrylic acid) macroinitiator, the \( \mathcal{D} \) of the polystyrene anchoring block can be studied independently. The GPC molecular weight distributions of the chain extensions and the resultant library of blend copolymers are plotted in Figure 4.1. The characterization data for the final blend library is summarized in Table 4.1. By utilizing eq 4.1, the \( \mathcal{D} \) of the polystyrene block can be estimated from
the total block copolymer $\mathcal{D}$. Table 4.1 illustrates that the anchoring block $\mathcal{D}$ can be significantly higher than the overall block copolymer $\mathcal{D}$. While the overall block copolymer $\mathcal{D}$ varies from 1.30 to 1.77, the corresponding polystyrene block $\mathcal{D}$ ranges from 1.52 to 2.52.

**Figure 4.1.** Molecular weight distributions of the poly(acrylic acid) macroinitiator and block copolymer extensions (left), and the final blended block copolymer library (right).
Table 4.1. Molecular weight, dispersity, and composition of the poly(acrylic acid)-b-polystyrene block copolymer library.

<table>
<thead>
<tr>
<th>Name</th>
<th>DP&lt;sub&gt;PAA&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DP&lt;sub&gt;PS&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>mol% AA&lt;sup&gt;c&lt;/sup&gt;, GPC</th>
<th>mol% AA&lt;sup&gt;c&lt;/sup&gt;, &lt;sup&gt;1&lt;/sup&gt;H NMR</th>
<th>D&lt;sub&gt;PAA-b-PS&lt;/sub&gt;</th>
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<td>M11</td>
<td>40</td>
<td>32</td>
<td>7200</td>
<td>55</td>
<td>56</td>
<td>1.43</td>
<td>1.79</td>
</tr>
<tr>
<td>M12</td>
<td>40</td>
<td>32</td>
<td>7200</td>
<td>55</td>
<td>56</td>
<td>1.47</td>
<td>1.89</td>
</tr>
<tr>
<td>M13</td>
<td>40</td>
<td>31</td>
<td>7100</td>
<td>56</td>
<td>60</td>
<td>1.55</td>
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<tr>
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<td>32</td>
<td>7100</td>
<td>56</td>
<td>56</td>
<td>1.62</td>
<td>2.22</td>
</tr>
<tr>
<td>M15</td>
<td>40</td>
<td>32</td>
<td>7200</td>
<td>55</td>
<td>61</td>
<td>1.72</td>
<td>2.42</td>
</tr>
<tr>
<td>M16</td>
<td>40</td>
<td>32</td>
<td>7100</td>
<td>56</td>
<td>62</td>
<td>1.77</td>
<td>2.52</td>
</tr>
</tbody>
</table>

<sup>a</sup> Degree of polymerization based on GPC block copolymer composition.
<sup>b</sup> M<sub>n</sub> for the methylated copolymer, polystyrene-b-poly(methyl acrylate), reported as polystyrene equivalent. Same macroinitiator used for all block copolymers (M<sub>n</sub>=3814 g/mol, D<sub>PAA</sub> = 1.20).
<sup>c</sup> Molar percentage of poly(acrylic acid) in the block copolymer.
<sup>d</sup> D of the anchoring block estimated from eq 4.1.

4.3.2 Critical Aggregate Concentrations of the Block Copolymer Library.

The effect of the anchoring (PS) block D on the critical aggregate concentration (CAC) was experimentally measured for each block copolymer in Table 4.1. Both static light scattering (SLS) intensity and fluorescence intensity were used to determine the CAC, as previously detailed,18 and are plotted in Figure 4.2. The average CAC value of this block copolymer library was 3.1 ±0.8 µM, which is comparable to the average CAC determined in the previous chapter’s library, 3.8 ±0.7 µM; this is expected as the molecular weight and compositions of the two libraries are very similar. It is theoretically predicted from a mixed micelle model<sup>34,35</sup> (Appendix B) that CAC<sub>mix</sub> will decrease with increasing anchor block D, as the fraction of block copolymers with lower CAC would be expected to show an earlier onset of aggregation; however, this effect was not observed.
experimentally in the range of PS block $D$ studied (1.52-2.52). It is possible that the experimental error associated with each technique is greater than the expected change in CAC due to dispersity.

**Figure 4.2.** CACs of the block copolymer library plotted as a function of anchoring block molecular weight dispersity, determined by both fluorescence spectroscopy (○) and static light scattering (●) are shown. The dashed line is the theoretical CAC predicted from a mixed micelle model (Appendix B). Error bars for each technique represent the standard deviation of triplicate experiments.

### 4.3.3 Effect of Anchoring Block Molecular Weight Dispersity on Emulsion Properties

To determine the effect of the PS block $D$ on the emulsion polymer properties such as the number of particles, particle diameter, particle size distribution, and stability, a batch emulsion polymerization of styrene was chosen as a standard test procedure wherein 0.5 weight percent (based on styrene, $\approx 8 \times 10^{-5}$ mol/L) of the block copolymer was used as the stabilizer. Table 4.2 summarizes the number and size of initial block copolymer aggregates and final particles in emulsions stabilized by each block copolymer from Table 4.1.
Table 4.2. The number and diameter (DLS) of initial block copolymer aggregates and final particles from emulsions stabilized by block copolymers with varying stabilizing block $D^a$.

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>$D_{PS}$</th>
<th>pH &gt; 9</th>
<th>pH ≈ 3</th>
<th>pH &gt; 6</th>
<th>pH ≈ 3</th>
<th>N_{bca}</th>
<th>N_p</th>
<th>N_{agg}</th>
<th>N_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9</td>
<td>1.52</td>
<td>17</td>
<td>14</td>
<td>71</td>
<td>67</td>
<td>6.5</td>
<td>7.9</td>
<td>67</td>
<td>55</td>
</tr>
<tr>
<td>M10</td>
<td>1.69</td>
<td>17</td>
<td>14</td>
<td>67</td>
<td>64</td>
<td>7.0</td>
<td>9.5</td>
<td>62</td>
<td>45</td>
</tr>
<tr>
<td>M11</td>
<td>1.79</td>
<td>17</td>
<td>14</td>
<td>82</td>
<td>71</td>
<td>8.8</td>
<td>6.6</td>
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<td>67</td>
</tr>
<tr>
<td>M12</td>
<td>1.89</td>
<td>19</td>
<td>15</td>
<td>77</td>
<td>70</td>
<td>7.4</td>
<td>6.9</td>
<td>61</td>
<td>66</td>
</tr>
<tr>
<td>M13</td>
<td>2.06</td>
<td>23</td>
<td>18</td>
<td>98</td>
<td>88</td>
<td>4.0</td>
<td>3.4</td>
<td>111</td>
<td>131</td>
</tr>
<tr>
<td>M14</td>
<td>2.22</td>
<td>28</td>
<td>19</td>
<td>110</td>
<td>99</td>
<td>2.7</td>
<td>2.4</td>
<td>162</td>
<td>183</td>
</tr>
<tr>
<td>M15</td>
<td>2.42</td>
<td>27</td>
<td>20</td>
<td>116</td>
<td>105</td>
<td>2.0</td>
<td>1.9</td>
<td>222</td>
<td>231</td>
</tr>
<tr>
<td>M16</td>
<td>2.52</td>
<td>31</td>
<td>23</td>
<td>122</td>
<td>111</td>
<td>1.6</td>
<td>1.7</td>
<td>271</td>
<td>250</td>
</tr>
</tbody>
</table>

$^a$The average number of block copolymer chains per aggregate and particle, determined from eqs 4.2 and 4.8 respectively, are also given.

$^b$Number-average hydrodynamic diameter determined from DLS.

$^c$Variation in final latex particle diameter of duplicate experiments was less than 5%.

$^d$Number of block copolymer aggregates (N_{bca}) determined from eq 4.3.

In emulsions stabilized by block copolymers M9-M16, the ratio of initial number of block copolymer aggregates to the number of particles, N_{bca}/N_p, varied between 0.7-1.2 (Figure 4.5), consistent with the well-known seeded behavior of kinetically-frozen block copolymer aggregates; this ratio may have been affected by the rearrangement of monomer swollen aggregates had there been sufficient equilibration time for the hydrophobic anchor blocks to exchange through the continuous phase, but the short time (5 minutes) between monomer addition and initiation likely resulted in negligible rearrangement of aggregates prior to particle nucleation.
Figure 4.3. The ratio of the initial number of block copolymer aggregates to the final number of particles as a function of anchoring block $\mathcal{D}$. Error bars were propagated from the uncertainty in particle diameters ($\pm 1$ nm) and static light scattering molecular weights.

As expected for a given concentration of block copolymers in a kinetically frozen state, a larger aggregation number leads to fewer block copolymer aggregates and thus fewer latex particles, as shown in Figure 4.6. It is also noted that the aggregation number remained relatively constant until the anchoring block $\mathcal{D}$ exceeded approximately 2. This is hypothesized to be a result of larger anchoring blocks that are only present in appreciable amounts beyond a specific $\mathcal{D}$; this idea is explored in more detail in the following paragraphs.
Figure 4.4. The aggregation number of block copolymer aggregates (○; left) and the number of particles produced during an emulsion (●; right) as a function of the anchoring block Đ. Larger aggregation number leads to fewer aggregates/seeds and therefore fewer particles.

It can be concluded from Figures 4.3 and 4.4 that the molecular weight dispersity of the anchoring block is an important design parameter when controlling the number and size of particles in an emulsion polymerization seeded with block copolymer aggregates. It is therefore of interest to understand why an increase in anchoring block dispersity results in a larger aggregation number. It is proposed that this effect is entropy-driven, dominated by an increase in the number of higher molecular weight anchoring blocks; this is illustrated in Figure 4.5 by comparing two block copolymers with equivalent number-average anchoring block degree of polymerization, but with different anchoring block Đ. The block copolymer with uniform anchoring blocks will form smaller aggregates as increasing aggregate size would require each block to stretch from the surface of the aggregate to near-center and eventually produce a void. With more disperse anchoring blocks, larger aggregates become favorable as larger anchor blocks fill the aggregate center without stretching and reduce the required stretching of shorter blocks;
this reduction in the entropic penalty of larger aggregates should favor a higher aggregation number at thermodynamic equilibrium.

Figure 4.5. Illustration of the change in anchoring block organization in a block copolymer aggregate as the anchoring block dispersity is increased from uniform (top) to disperse (bottom). Uniform anchoring blocks are unable to form larger aggregates due to the energetic penalty of stretching. More disperse anchoring blocks favor larger aggregates due to the presence of large anchor blocks (largest shown in black) which reduce the required stretching of smaller anchor blocks.

To investigate this qualitative treatment in a quantitative manner, a simple model is proposed in which the largest probable anchoring block in an aggregate has a root-mean-square end-to-end distance \( \langle r^2 \rangle_{lp} \) equivalent to its unperturbed root-mean-square end-to-end distance \( \langle r^2 \rangle_{lp,o} \). Under the requirement that an anchoring block must have both ends inside of the aggregate core, one may estimate the diameter of the aggregate to be greater than or equal to the end-to-end distance of the largest anchoring block.

\[
D_{agg} \geq \langle r^2 \rangle_{lp,o}^{\frac{1}{2}}
\]  

(4.9)
A similar approach has been used to approximate the size of aggregates composed of small molecule surfactants, where the aggregate radius is assumed to be the length of the fully extended hydrocarbon tail,\textsuperscript{37,38} however, unlike a small molecule surfactant, a block copolymer stabilizer has a broad distribution of molecular weights, and the largest probable block copolymer in an aggregate will be a function of both the molecular weight distribution and aggregation number. A convenient method to determine the largest probable block copolymer in an aggregate is the repeated random sampling, or Monte Carlo, method. By using a block copolymer’s number fraction molecular weight distribution as the probability distribution, a random sample of $N_{\text{agg}}$ block copolymer chains can be taken, and the largest block copolymer in the sample recorded; with repeated random sampling, an average value for the largest block copolymer is calculated, i.e. the largest probable block copolymer in an aggregate. This method was used to determine the largest probable block copolymer in aggregates of M9-M16 over an aggregation number range of 5-400, and details are provided in Appendix B.

For each value of the largest probable block copolymer, the $<r^2>^{1/2}_o$ of the anchoring block was determined according to eq 4.10:

$$<r^2>^{1/2}_{lp,o} = L \sqrt{N_{lp} C} \quad (4.10)$$

with $L = 0.154$ nm as the length of a C-C (sp$^3$-sp$^3$) bond,\textsuperscript{32} $N_{lp}$ the number of C-C bonds in the anchoring block (estimated as twice the number-average degree of polymerization of PS), and $C$ as the characteristic ratio of PS.\textsuperscript{39} The $<r^2>^{1/2}_{lp,o}$ of M9-M16 aggregates is plotted as a function of aggregation number in Figure 4.6. As expected, increasing the anchoring block dispersity and/or aggregation number results in a higher probability of larger anchoring blocks in an aggregate. The diameter of an aggregate, $D_{\text{agg}}$, as a function of aggregation number is calculated using eq 4.5 and plotted in Figure 4.6. In this model, the predicted aggregation number is the point at which $D_{\text{agg}}$
and $<r^2>^{1/2}$ intersect; if the aggregate diameter is less than $<r^2>^{1/2}$, the largest probable anchor block will be compressed, while a diameter larger than $<r^2>^{1/2}$ would require increased stretching, and increased repulsive energy between stabilizing blocks due to lower surface curvature. In other words, block copolymer aggregates are predicted to accommodate larger anchoring blocks by increasing in size, but not more than necessary due to stretching and repulsion penalties. There was a surprisingly good agreement between the aggregation numbers found experimentally and this model. Despite the simplicity of this model, it appears to be roughly predictive of the relationship between anchoring block $D$ and aggregate size, suggesting the largest anchoring blocks in an aggregate may have a dominant role in determining aggregate size.

**Figure 4.6.** The root-mean-square end-to-end distance of the largest probable anchoring block in an aggregate as a function of aggregation number. Colored solid lines correspond, from bottom to top, to M9-16 (increasing $D_{PS}$). The dashed line corresponds to the diameter of an aggregate, $D_{agg}$, as a function of aggregation number from eq 4.5. Experimentally determined aggregation numbers
and the number of chains per particle (●; Table 4.2) for block copolymers M9-M16 are placed on the respective lines.

It is also worth considering that the anchoring block dispersity affects the compositional heterogeneity of the block copolymers, and therefore their stabilization properties. Consider that for a given number-average molecular weight of each block, compositional heterogeneity may divide the chains of a block copolymer into four behavioral types, as illustrated in Figure 4.7.

![Figure 4.7](image)

**Figure 4.7.** Amphiphilic block copolymers are categorized into four types based on their dispersion behavior: (I) chains with high anchoring block composition are not active at the interface and reside in the dispersed phase core; (II) chains are active at the interface, but exchange slowly through the continuous phase, i.e. kinetically frozen; (III) chains are active at the interface and exchange readily through the continuous phase, i.e. dynamic; (IV) chains with high stabilizing block composition are less active at the aggregate surface and exist as single chains in the continuous phase. The compositional plot on the left is for an arbitrary system and for illustrative purposes only.

Increasing the molecular weight dispersity of a block copolymer stabilizer will increase the compositional heterogeneity, and therefore change the stabilizing character of the block copolymer. For example, the introduction of Type I and II chains will result in block copolymer...
aggregates that behave as seeds in an emulsion polymerization. The exact compositions dividing these chain types will be specific to a given system. In this work, increasing the Đ of the anchoring block decreased the number fraction of chains near the average composition, while increasing the number fraction of chains with high stabilizing block composition, as shown in Figure 4.8. The number fraction of block copolymer chains active at the air/water interface decreased with anchor block Đ, as observed by an increase in surface tension in Figure 4.8; it should be noted that all surface tension values were close to the value measured for pure water (≈73 mJ/m²) as expected for block copolymers in a kinetically frozen aggregate state.

Figure 4.8. (Left) Theoretically calculated compositional heterogeneity of block copolymers M9-16 (average f_PAA ≈ 0.55) where each block is approximated by a Shulz-Zimm distribution (details in Appendix B), and (Right) the measured surface tension of 0.15 mM dispersions of block copolymers M9-16 as a function of their anchor block Đ.

Previous studies on the surface activity of polystyrene-b-poly(sodium acrylate) block copolymers and other ionic block copolymers have demonstrated that surface activity is typically limited by the combination of image charge repulsions at the air/water interface and stable aggregate formation, and is dependent on both composition and absolute block lengths. In this
work, surface tension measurements (Appendix B) revealed that block copolymers with a composition between approximately 50-90% poly(sodium acrylate), corresponding to anchor block degree of polymerizations between 5-40, demonstrate the greatest surface activity. Thus, it is evident from Figure 4.8 that as anchoring block Đ increases, the number fraction of surface active chains (Type II/III copolymers in Figure 4.7) decreases, explaining the increase in surface tension. The effect of the anchoring block Đ on compositional heterogeneity is, therefore, an important design consideration since properties such as surface tension, foaming, and even the emulsion polymerization mechanism may be affected.

Neither the block copolymer aggregates nor the final latex particles showed any significant trends in their size dispersity as a function of Đ (Figure 4.9). While increasing the anchoring block Đ to 2.5 had an obvious effect on the size of block copolymer aggregates and the resulting latex particles, there was no significant effect on the particle size dispersity. Recalling previous literature, this result is not surprising as block copolymers are known to build order from disorder given the proper conditions.
Figure 4.9. The particle size dispersity of both block copolymer aggregates and latex particles, measured by dynamic light scattering, as a function of anchoring block molecular weight dispersity.

As shown in Figure 4.8, anchor block dispersity directly affects compositional heterogeneity and could affect particle stability as a result. For example, an increase in anchor block dispersity will increase the fraction of block copolymer chains that exist either buried within particles (Type I) or primarily in the continuous phase (Type IV), resulting in fewer chains contributing to particle stabilization; however, similar to the particle size dispersity, an increase in anchoring block Đ appeared to have a negligible effect on the zeta potentials of both block copolymer aggregates and latex particles (Figure 4.10). As previously observed, the magnitude of the zeta potential for block copolymer aggregates was consistently lower than the latex particles, which may be attributed to latex particles having a slipping (shear) plane closer to the surface, as well as the presence of additional anionic sulfate groups. The zeta potential of electrostatically stabilized particles can be used as a measure of colloidal stability, (also effectively a measure of shelf-life); these results suggest that anchoring block Đ can be increased without sacrificing the stability of the emulsion, at least in the range of Đ studied in this work.
Figure 4.10. Zeta potential of latex particles as a function of anchoring block molecular weight dispersity.

4.4 Conclusions

The practical implementation of block copolymers will certainly favor the facility and economy of synthesis, but likely at the expense of increased molecular weight dispersity and homopolymer impurities; therefore, it is important to understand the effect of these properties on the performance of block copolymers in specific applications. By preparing a library of poly(sodium acrylate)-b-polystyrene block copolymers with varying molecular weight dispersity in the anchoring polystyrene block ($D_{PS}$), the effect of this dispersity on the aggregation and emulsion stabilization properties was studied. Increasing the $D_{PS}$ resulted in a greater number fraction of smaller and larger anchoring blocks, and as a consequence, the aggregation number of block copolymer aggregates was observed to increase. Based on a simple model it is proposed that the aggregation number, and therefore aggregate size, increases to accommodate the larger anchoring blocks and avoid the entropic penalty of compression. Higher $D_{PS}$ also led to the greater compositional heterogeneity of the block copolymers, and a decrease in the number of surface
active chains was inferred from the observation of increased surface tension. Despite theoretical predictions that the critical aggregation concentration of the block copolymers would decrease with $D_{\text{PS}}$, no such trend was observed experimentally.

Due to the kinetically frozen nature of the block copolymer aggregates and the effect of $D_{\text{PS}}$ on aggregate size, it was observed that when the block copolymers were used as stabilizers in the emulsion polymerization of styrene, $D_{\text{PS}}$ controlled the particle size; interestingly, there was no observed effect of the $D_{\text{PS}}$ on the size dispersity or stability of these particles. In combination with the conclusions from the previous chapter on the molecular weight dispersity of the stabilizing block, these results suggest that high molecular weight dispersity and compositional heterogeneity do not preclude the use of block copolymers as stabilizers in emulsion polymerization, but are rather another parameter to be tuned by the polymer chemist. To reiterate Hillmyer, polydisperse block polymers can be practically implementable macromolecules, and it is worthwhile to study how composition and molecular weight distributions influence their behavior.

4.5 References


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Chapter 5

Amphiphilic Polyelectrolyte Block Copolymers: Effects of Concentration, Degree of Neutralization, and Homopolymer Impurity
Abstract

Amphiphilic polyelectrolyte block copolymers have been known for decades as efficient stabilizers in emulsion polymerization, and have a great potential to be tailored for specific applications. Previous studies have afforded a better understanding of the effects of stabilizer structure (e.g. composition, block length, topology, and molecular weight dispersity) on stabilization performance, but rarely discuss the importance or optimization of process conditions. To better understand the behavior and limitations of block copolymer stabilizers, a polystyrene-b-poly(acrylic acid) stabilizer is studied in the emulsion polymerization of styrene, investigating the effects of concentration, degree of neutralization, and added polystyrene homopolymer impurity. An in situ DLS technique is introduced to study the time evolution of emulsion polymerizations at very dilute block copolymer concentrations, revealing a transition from a homogenous to seeded particle nucleation mechanism as the block copolymer concentration increased beyond the critical aggregation concentration (CAC). It was also observed that polyelectrolyte blocks below full neutralization result in high particle size dispersity, suggesting they inhibit radical entry into aggregates. Finally, it is observed that a polystyrene macroinitiator impurity (up to 30 wt% based on block copolymer), a realistic block copolymer impurity, increased the aggregation number and eliminated the existence of a CAC; although the impurity affected the number of particles, it had no significant effects on block copolymer stabilization other than dilution. These results are valuable to the intelligent design and implementation of block copolymer stabilizers in emulsion polymerization.
5.1 Introduction

Amphiphilic diblock copolymers, often called macrosurfactants, represent a promising future in surfactant technology due to the enormous possibility of structures, properties, and applications. Concurrent with advances in living radical polymerization, amphiphilic block copolymers containing a polyelectrolyte block have been synthesized and studied. The incorporation of a polyelectrolyte block provides electrostatic stabilization in addition to steric stabilization and represents an advantage over non-ionic block copolymer stabilizers. A commonly studied family of amphiphilic polyelectrolyte block copolymers are those containing an ionizable poly(acrylic acid) block and hydrophobic polystyrene block; these copolymers are attractive for several reasons, including: (i) the simplicity of the system; (ii) the commercial importance and availability of both monomers; (iii) the successful commercialization of random copolymers of styrene and acrylic acid as polymeric surfactants (e.g. alkali soluble resins). Eisenberg’s group has conducted many studies on the behavior of styrene-acrylic acid block copolymers in aqueous solution, including their self-assembly into aggregates above a critical concentration and the existence of a multitude of aggregate morphologies.

Although it was already shown in the 1950s that amphiphilic block copolymers are effective as stabilizers in emulsion polymerization, it was not until the 1990s that amphiphilic block copolymers containing a strong polyelectrolyte block were studied as stabilizers in emulsion polymerization. The theory and mechanisms of emulsion polymerization have been summarized elsewhere, but a basic conventional recipe requires a hydrophobic monomer, surfactant, water soluble initiator, and aqueous medium. Amphiphilic polyelectrolyte block copolymers are a promising class of emulsion polymerizations stabilizers due to their unusual solution behavior; while they are very active at the particle/water interface, their hydrophobic
block can reduce their critical aggregation concentration to a very low value such that all chains are effectively “anchored” to either an aggregate or particle interface and exhibit negligible surface activity. The high efficiency of these stabilizers may be advantageous in emulsion polymers intended for film formation, where the lack of water-labile molecules may improve coating properties such as water resistance and adhesion.

Many studies have been published on the use of amphiphilic block copolymers as stabilizers in emulsion polymerization, but the variable in the majority of these studies has been the chemical composition of the block copolymers (i.e. the novel combination of monomers and subsequent application as stabilizer) whereas few studies exist that have investigated more fundamental questions, such as the effects of structure (e.g. block length, topology, and molecular weight dispersity), or conditions (e.g. concentration, degree of neutralization, impurities, etc.). Accordingly, further research of amphiphilic polyelectrolyte diblock copolymers is required to understand their behavior and limitations in the stabilization of emulsion polymerizations. In this work, polystyrene-b-poly(acrylic acid) block copolymers are utilized as stabilizers in the emulsion polymerization of styrene, and their performance at varying concentration, pH, and impurities is studied. Specifically, this chapter investigates how particle nucleation and stabilization are affected by stabilizer concentration, especially near the critical aggregation concentration (CAC), the sensitivity of stabilization to a stabilizers degree of neutralization, and the effect of an impurity (e.g. dead macroinitiator) on stabilization. A specialized in situ dynamic light scattering technique is utilized to monitor particle size and particle size dispersity of emulsion polymerizations as a function of time, which has allowed for both kinetic insights and the estimation of particle number at low stabilizer concentration and solids content.
5.2 Experimental

5.2.1 Materials

A polystyrene macroinitiator (M_n = 3400 g/mol, D = 1.11) and polystyrene-b-poly(acrylic acid) block copolymer (M1, M_n = 7000 g/mol, D = 1.13, 55 mol% acrylic acid) that were previously synthesized and characterized were used in this work (Scheme 5.1). Scheme 5.1. Structures of the polystyrene macroinitiator and polystyrene-b-poly(acrylic acid) block copolymer used in this work.

A commercial polystyrene-r-poly(acrylic acid) stabilizer (M_n = 2800 g/mol, D = 3.1, 30 mol% acrylic acid) was kindly provided by BASF for comparison to the analogous block structure. Ammonium persulfate (>98%) and sodium hydroxide (>98%) were purchased from Sigma-Aldrich and used as received. Styrene (4-tert-butylcatechol as a stabilizer, ≥99%) was purchased from Sigma-Aldrich and passed through a column of basic alumina to remove the 4-tert-butylcatechol inhibitor prior to use. Tetrahydrofuran (THF, 99%) was purchased from ACP Chemicals and used as received. All water used in this work was in-house distilled water that was further purified (18.2 MΩ-cm) using a Millipore Synergy water purification system equipped with SynergyPak purification cartridges.

5.2.2 Polystyrene Seed Particles

Free radical emulsion polymerization was used to prepare well-defined polystyrene seed particles. In a 20 mL round bottom flask, 0.3 g of styrene was added to 14.2 g of a 10 mM sodium
dodecylbenzenesulfonate (SDBS) solution in water. This heterogeneous system was sealed, lowered into an 80 °C oil bath, and stirred for 20 minutes before initiation with 0.5 g of a 30 g/L ammonium persulfate (APS) solution in water (0.1 wt% APS based on monomer). The temperature was then held at 80 °C for 18 hours to decompose the majority of the initiator and achieve high conversion. The resulting latex was filtered through a 0.45 µm filter, followed by a 0.2 µm filter to remove any large aggregates or dust. The solids content (17 g/L) of the filtered latex was determined gravimetrically and a number-average hydrodynamic diameter was determined to be 20 nm using dynamic light scattering. The particle number determined using eq 5.2 was 3.9x10^{18} L^{-1}.

**5.2.3 In situ Dynamic Light Scattering**

In a typical experiment, 1 mL of water containing 2 mM of APS and a known concentration of either seed particles or a stabilizer was added to a 3.5 mL cuvette. Fused quartz cuvettes purchased from Thorlabs Inc. were used. Styrene (0.5 g) was then carefully layered on top of the water phase using a needle, and the cuvette was closed with a plastic cap. Polymerization was started by placing the cuvette into a Malvern Zetasizer Nano ZS and heating to 85°C. *In situ* dynamic light scattering measurements were obtained during these emulsion polymerizations using non-invasive backscatter optics (173°) with a 4 mW He-Ne (633 nm) laser. All data was processed using the Malvern Dispersion Technology Software (version 7.11). The attenuator and measurement position were optimized between each measurement to account for the increase in scattering intensity and to avoid multiple scattering. With this continuous optimization procedure, a size measurement was obtained approximately every three minutes.

Due to the low interfacial area between the monomer and water phase (approximately 1 cm²) relative to the particle/water interface (e.g. 500 cm² for 1x10^{13} particles with 20 nm radius) it was
assumed that interfacial mass transfer from the monomer phase becomes the limiting step in particle growth, where the rate of particle volume growth, $\mu$ (cm$^3$/s), can be described by eq 5.1:

$$\mu = \frac{\dot{n}_m M}{\rho_p N_p}$$  \hspace{1cm} (5.1)$$

where $\dot{n}_m$ is the limiting interfacial mass transfer rate from the monomer phase (mol s$^{-1}$), $M$ is the molecular weight of the monomer (g/mol), $N_p$ is the total number of particles, and $\rho_p$ is the density of particles (g/cm$^3$) approximated as the homopolymer density under diffusion-limited conditions. In this diffusion-limited case, the rate of particle volume growth will be inversely related to the number of particles in the system. By measuring the rate of particle volume growth for a known number of well-defined polystyrene seed particles, the limiting interfacial mass transfer rate under the experimental conditions can be determined, thereby allowing the determination of an unknown $N_p$ by measurement of $\mu$.

5.2.4 Block Copolymer Dispersions

A block copolymer (100 mg) was added to a 20 mL glass vial, to which appropriate amounts of water and a 1 M sodium hydroxide solution were added to produce a final block copolymer concentration of 1x10$^{-3}$ M with a four-fold stoichiometric excess of base relative to carboxylic acid units. The vial was then tightly sealed with a plastic cap, and heated at 90 °C with magnetic stirring for 24 hours. The procedure for preparing block copolymer dispersions containing a polystyrene homopolymer impurity (macroinitiator) required an extra mixing step prior to addition of water and base; the impurity and block copolymer were first added to the vial and dissolved in THF, and following complete dissolution the THF was removed under a gentle stream of air.
5.2.5 **Emulsion Polymerization Procedure**

The batch emulsion polymerization of styrene was performed by adding a dispersion of block copolymer aggregates to a 10 mL round bottom flask, followed by the addition of styrene (0.4 g). The flask was then sealed with a rubber septum and immersed in an 85 °C bath of silicone oil for 5 minutes prior to initiation by injection of an ammonium persulfate solution (2 mM). The polymerization was allowed to continue for 4 hours to achieve high conversion of the monomer. Conversions of emulsion polymerizations were determined gravimetrically by the addition of 100 μL of a 0.1 mol/L hydroquinone solution to 1 mL of the emulsion, followed by drying in an 85 °C vacuum oven. In all cases, high conversion (>95%) was calculated. The number of latex particles (L⁻¹) was calculated using eq 5.2.

\[
N_p = \frac{6\tau}{\pi \rho D^3}
\]  

with τ the polymer content of the latex (g/L) determined by gravimetry, ρ the density of polystyrene (1.05 g/cm³), and D the number-average diameter of the polystyrene core measured by DLS.

5.3 **Results and Discussion**

5.3.1 **In situ Dynamic Light Scattering Measurements**

*In situ* dynamic light scattering measurements were made during emulsion polymerizations seeded with a varying number of the previously prepared 20 nm polystyrene seed particles. Dilutions of these seed particles contained the surfactant SDBS at concentrations below 0.2 mM, at least one order of magnitude below the CMC, such that micellar nucleation would be negligible. Measurement of particle size as a function of reaction time confirmed a constant growth rate as expected for an emulsion polymerization with a constant number of particles in the presence of
monomer droplets. Preliminary experiments keeping the seed particle number and monomer/water interfacial area constant but using 1 mL or 2 mL of the water phase showed no difference in the rate of particle volume growth, suggesting that diffusion of monomer through the aqueous phase was not limiting and Brownian mixing was sufficient in the small system volume.

By plotting the particle volume growth as a function of time for a varying number of seed particles (Figure 5.1, left), it was observed that above a critical number of seed particles ($\approx 1.5 \times 10^{15}$ L$^{-1}$) the system followed the diffusion-limited relationship predicted by eq 5.1. Figure 5.1 (right) shows the clear transition from a rate-limited to a diffusion-limited system as a critical number of particles is reached, supporting the scenario of limited interfacial mass transfer from the monomer phase; if transfer of monomer from the continuous phase to particles was limiting, the rate of particle volume growth would be independent of the number of particles. By fitting the diffusion-limited region of Figure 5.1 (right) with eq 5.1, the limiting interfacial mass transfer rate from the monomer phase ($\bar{n}_m$, mol s$^{-1}$) was determined to be $1.8 \times 10^{-8}$ mol/s.

![Figure 5.1](image)

**Figure 5.1.** (Left) The number-average particle volume in seeded emulsion polymerizations as a function of reaction time. Beyond a critical number of seed particles, increasing the number of seed particles results in a decrease in the slope, i.e. the rate of particle volume growth. (Right) The
rate of particle volume growth is plotted as a function of the number of polystyrene seed particles. The non-constant region of volume growth rate is fit to a diffusion-limited model with eq 5.1.

Along with the number of particles, the concentration of monomer in the particles can also be determined by measurement of the rate of particle volume growth. A particle will increase in size due to polymerization and monomer swelling, such that the rate of particle volume growth (µ; L s⁻¹) can be described as a function of both the volume fraction of polymer and the rate of polymerization in the particle in eq 5.3:

\[
\mu = \frac{dV}{dt} = \frac{R_p M}{v_{poly} \rho_{poly}} \tag{5.3}
\]

with M the molecular weight of the monomer (104.15 g mol⁻¹), \(\rho_{poly}\) the density of the polymer (1050 g L⁻¹), \(v_{poly}\) the volume fraction of polymer in a particle, and \(R_p\) the rate of polymerization in a particle (mol s⁻¹):

\[
R_p = \frac{k_p [M]_p \bar{n}}{N_A} \tag{5.4}
\]

with \(k_p\) the rate constant for chain propagation (L mol⁻¹ s⁻¹), \([M]_p\) the monomer concentration in a particle (mol L⁻¹), \(\bar{n}\) the average number of radicals in a particle (assumed to be 0.5 for hydrophobic monomers in small particles¹⁸), and \(N_A\) the Avogadro constant (mol⁻¹). The \(k_p\) for styrene under the reaction conditions was estimated as 950 L mol⁻¹ s⁻¹ from an activation energy \((E_a)\) of 33.6 kJ/mol and Arrhenius coefficient (A) of 7.6x10⁷ L mol⁻¹ s⁻¹).³⁵ \(v_{poly}\) in eq 5.3 accounts for the volume growth of a particle due to monomer swelling and is related to the monomer concentration in particles:

\[
v_{poly} = 1 - v_m = 1 - \frac{[M]_p M}{\rho_m} \tag{5.5}
\]

With \(\rho_m\) the density of the monomer (909 g L⁻¹). Combining eqs 5.3-5.5, the rate of particle volume growth is found as a function of \([M]_p\):
Finally, rearrangement of eq 5.6 allows for \([M]_p\) to be determined from the rate of particle volume growth, eq 5.7.

\[
[M]_p = \left( \frac{k_p \bar{n}M}{\mu N_A \rho_{poly}} + \frac{M}{\rho_m} \right)^{-1}
\]  

For each experiment using the polystyrene seed particles, \([M]_p\) was calculated using eq 5.7 and plotted in Figure 5.2 as a function of the number of seed particles \((N_s)\).

**Figure 5.2.** Monomer concentration in particles as a function of the number of seed polystyrene particles, \(N_s\), determined from the in situ dynamic light scattering measurements. A clear transition is seen between the rate-limited and diffusion-limited regions at approximately 1.5x10^{12} particles (equivalent to 1.5x10^{15} particles/L in the 1 mL system).

In Figure 5.2 where particle volume growth rate was constant (< 1.5x10^{12} particles) the average value of \([M]_p\) was 5.8 mol/L. This concentration is in good agreement with the commonly accepted values for the styrene concentration in particles during interval II of emulsion
polymerizations, i.e. constant number of particles in the presence of monomer droplets. Therefore, in the case of styrene, the number of particles produced by homogeneous nucleation was considered low enough to allow the study of all particle numbers (N_p) in the diffusion-limited regime below approximately 1x10^{18} L^{-1}, after which the polymer growth rate becomes too low; this was not the case for preliminary experiments with butyl acrylate and methyl methacrylate, where significant homogeneous nucleation (N_p \approx 1x10^{16} L^{-1}) and high k_p led to severely diffusion-limited particle growth rates regardless of the number of seed particles, and precluded the accurate study of particle numbers as a function of particle volume growth rate.

5.3.2 Stabilizer Concentration

Using the previously determined interfacial mass transfer rate under the experimental conditions, the number of particles in emulsion polymerizations was determined by measurement of the rate of particle volume growth and the rearrangement of eq 5.1:

\[ N_p = \frac{\dot{n}_M M}{\rho_p \mu} \] (5.8)

Determination of the number of particles with this technique was reproducible (from triplicate experiments at 3 and 10 \( \mu \)M, standard error of N_p was 0.6x10^{16}) and offered additional information such as the concurrent measurement of the particle size dispersity. The technique was ideal for emulsion polymerizations with a low number of particles where the solids content is consequently low. Preliminary experiments using the more common gravimetric technique resulted in a larger error and poor reproducibility when used to determine the number of particles in a very low solids content latex (<1 wt%) with eq 5.2. In contrast to a gravimetric technique, high conversion (absence of monomer swelling) is not required, allowing for the determination of particle number throughout the emulsion polymerization, rather than at the end. By studying particle growth in...
situ, a linear profile can be used to support a constant number of particles. This technique is, therefore, a convenient way to study the growth of particles in the emulsion polymerization of styrene where the number of particles is below \( \sim 1 \times 10^{18} \text{ L}^{-1} \).

The most important aspect of stabilizer concentration is the effect it has on particle nucleation, where the number of particles is proportional to \([\text{stabilizer}]^\alpha\). For stabilizer molecules that readily exchange through the continuous medium, \(\alpha\) is expected to be close to the theoretical value of 0.6.\(^{37}\) If the mobility of stabilizers is restricted, as is often the case for block copolymer stabilizers, each micelle/aggregate of stabilizers can be nucleated as particle and result in a number of particles that is directly proportional to the stabilizer concentration, i.e. \(\alpha = 1\).\(^{28,30}\) Comparing two stabilizers at the same concentration, the stabilizer that results in a greater number of particles is considered more efficient.

The block copolymer stabilizer concentrations used in emulsion polymerization are often at least an order of magnitude greater than the critical aggregation concentration of the block copolymer, and the effects of block copolymers near or below the critical aggregation concentration have not been studied. Understanding the effects on particle nucleation at these lower concentrations is valuable for the design of new processes, e.g. the semi-batch of block copolymer stabilizer to make multi-modal particle size distributions. It is also valuable to know what concentration of block copolymer stabilizer, relative to the critical aggregation concentration, is required to obtain seeded polymerization mechanism. Using the in situ DLS technique introduced earlier, a plot of the number of particles produced at block copolymer concentrations near the CAC, Figure 5.3, was produced by calculating the number of particles using eq 5.8. The relationship between particle nucleation and block copolymer concentration shown in Figure 5.3 suggests that below approximately double the CAC, the block copolymer affects particle
nucleation in the same manner as a dynamic surfactant, where \( \alpha \approx 0.6 \). Above the critical aggregation concentration, it is apparent that a critical number of aggregates must be reached before the seeded behavior of the block copolymer dominates particle nucleation; below this critical number of aggregates, a mixed nucleation mechanism of homogeneous-coagulative and seeded nucleation likely prevails.

**Figure 5.3.** The number of particles produced in an emulsion polymerization as a function of the concentration of block copolymer stabilizer chains (\( N_c; 100 \times 10^{16} \text{ L}^{-1} \) equivalent to 1.66 \( \mu \text{M} \)). A linear fit is shown for higher concentrations of the block copolymer, while a power fit is used for the lower concentration data. Critical aggregation concentration of the block copolymer is plotted as an empty circle, ○.

As previously mentioned, the *in situ* DLS technique becomes limited at high \( N_p \), as the particle growth rate varies less with \( N_p \), so higher block copolymer concentrations were investigated using a traditional (non-diffusion limited) emulsion polymerization using a gravimetric approach to determine the number of particles after complete conversion. The number of particles as a function of higher stabilizer concentrations are plotted in Figure 5.4, overlaid with the data points from Figure 5.3, and show a linear trend consistent with block copolymer aggregates acting as seed particles in this concentration region.
Further insight from plots like Figure 5.4 can be gained by assuming a perfectly seeded mechanism at concentrations much greater than the CAC. In a perfect seeded mechanism, each block copolymer aggregate becomes nucleated into a particle, and the number of particles may be related to the number of block copolymer chains through eq 5.9:

\[ N_p = N_{bca} = \frac{N_c - N_{Avg} CAC}{N_{agg}} \]  

(5.9)

Where \( N_{bca} \) is the number of block copolymer aggregates (L\(^{-1}\)), \( CAC \) is the critical aggregation concentration of the block copolymer (mol/L) under the reaction conditions, and \( N_{agg} \) is the aggregation number of the block copolymer. By simple rearrangement, it is evident that a linear fit of \( N_p \) as a function of \( N_c \) may be used to determine both \( N_{agg} \) and \( CAC \).

\[ N_p = \frac{1}{N_{agg}} N_c - \frac{N_{agg} CAC}{N_{agg}} \]  

(5.10)

Applying eq 5.10 to the data in Figure 5.3, the \( N_{agg} \) and \( CAC \) for M1 were 57 and 2.2 µM, respectively. In comparison, from the emulsion polymerizations performed at higher BCP concentrations...
concentration, Figure 5.4, the $N_{\text{agg}}$ and CAC for M1 were 74 and 3.8 µM, respectively. These values are comparable to the $N_{\text{agg}}$ and CAC determined for this block copolymer by static light scattering and fluorescence spectrometry, which were 107 and CAC 3.2 µM, respectively.\textsuperscript{33}

The \textit{in situ} DLS technique was also used to study the effect of an analogous random copolymer stabilizer on particle nucleation, the results of which are plotted in Figure 5.5. Compared to an analogous commercial random copolymer (dynamic surfactant), the block copolymer is extremely efficient at particle nucleation, i.e. a much higher total particle number and surface area is achieved with the same concentration.

![Graph](image)

**Figure 5.5.** Comparison between the block copolymer stabilizer (●) and an analogous random copolymer stabilizer (○) on particle nucleation.

### 5.3.3 Degree of Neutralization

As in most chemical reactions that occur in an aqueous medium, pH is an important condition to control during emulsion polymerization, especially when electrostatic stabilization is used. In order for electrostatic stabilization to be effective, the stabilizer molecules must maintain an electrostatic charge, and this is dependent on pH. For example, in a stabilizing block like
poly(acrylic acid), an increase in pH will increase the percentage of carboxylic acid groups that are neutralized to carboxylate anions, i.e. the degree of neutralization. Achieving complete neutralization of the poly(acrylic acid) block will provide the greatest electrostatic stabilization, but although using a strong base or buffer to achieve this high pH may appear like a simple solution, it may not be practical in many situations, e.g. a high pH could result in the undesirable hydrolysis of (meth)acrylate monomers. It is, therefore, important to study the effect of the degree of polyelectrolyte block neutralization on the stabilization of emulsion particles, in order to understand the limitations of their use.

The degree of neutralization of a poly(acrylic acid) is more complicated than a simple weak acid as the neutralization of one carboxylic acid unit will increase the barrier to neutralization of the remaining carboxylic acids due to intramolecular electrostatic repulsion; the acid dissociation constant, $K_a$, of poly(acrylic acid) decreases exponentially with the degree of neutralization, i.e. $pK_a$ increases with degree of neutralization. If the relationship between the $pK_a$ and degree of neutralization is known, a solution can be found for a given pH where $pK_a$ and degree of neutralization (DN) satisfy the Henderson-Hasselbalch equation:

$$pK_a = pH + \log \left( \frac{1 - DN}{DN} \right)$$  \hspace{1cm} (5.11)

where DN is the degree of neutralization as a fraction between 0 and 1. Figure 5.6 shows the Henderson-Hasselbalch equation plotted for the pH values used in this section (6, 9, 10, and 12), along with the experimental $pK_a$ of poly(acrylic acid) as a function of degree of neutralization from Sakurai et al.\textsuperscript{38} From Figure 5.6, the degree of neutralization predicted for poly(acrylic acid) is approximately 0.3 at pH 6, 0.9 at pH 9, and 1 at pH 10 and above.
**Figure 5.6.** Henderson-Hasselbalch equations for a weak acid at pH 6, 9, 10, and 12, plotted over the pKₐ of poly(acrylic acid) as a function of the degree of neutralization (○).³⁸

The experiments used to produce Figure 5.3, which had a pH of approximately 12, were repeated at pH 6, and the results are plotted in Figure 5.7. A decrease in the degree of neutralization at lower pH decreased both the apparent onset of seeded behavior and the slope of Nₚ versus Nₖ; the decrease in the onset of seeded behavior suggests that the CAC decreases with degree of neutralization, resulting from the reduced solubility of chains, while the decrease in slope suggests that the number of block copolymer chains per particle (Nₐₚ) increased.
Figure 5.7. The number of particles produced in an emulsion polymerization as a function of the concentration of block copolymer stabilizer chains ($N_c$) at pH 6 (low degree of neutralization) and 12 (high degree of neutralization).

Regardless of the degree of neutralization studied (0.3-1) a dominantly seeded behavior was observed beyond a critical block copolymer concentration, but kinetic observations showed that the degree of neutralization had a significant dependence on the particle nucleation. It is shown in Figure 5.8 that emulsion polymerizations stabilized with the same concentration of block copolymer resulted in very different particle size dispersity depending on the pH, and thus the degree of neutralization of the block copolymer stabilizer. Although the degree of neutralization only had a minor effect on the number of particles, the particle size dispersity increased significantly as the pH decreased below 10, corresponding to a degree of neutralization between 0.9 and 1.
Figure 5.8. (Left) Hydrodynamic diameter as a function of reaction time in emulsion polymerizations seeded with 5 µM of the block copolymer at different pH. (Right) Comparison of the polydispersity (PDI) in particle size shows that a higher pH (resulting in higher degree of neutralization) in block copolymer aggregate seeds resulted in more uniform latex particles.

It is proposed that below complete neutralization the nucleation of block copolymer aggregates by radicals may become inhibited by a more semi-collapsed conformation of polyelectrolyte blocks, i.e. a partially neutralized polyelectrolyte block will adopt a semi-collapsed conformation and create a more tortuous path for radical entry compared to a fully neutralized polyelectrolyte block in a rod-like conformation (Figure 5.9). The retardation of radical entry into aggregates will have the same effect as the semi-batch feed of seed particles into an emulsion polymerization, resulting in a greater particle size dispersity.
Figure 5.9. The degree of neutralization of a stabilizing polyelectrolyte block affects its conformation; radical entry is inhibited by partially neutralized block assuming a collapsed conformation (left), compared to a fully neutralized block in a rod-like conformation (right).

Assuming a constant number of block copolymer chains per particle, the effect of the stabilizing block on radical entry will presumably be negligible after the particle is nucleated and begins growing, due to the increasing distance between neighboring stabilizing blocks. This theory is supported by the molecular weight distributions of the emulsion polymers prepared at pH 6 and 12. If radical entry was retarded for the entire polymerization, the time between termination events in each particle would be increased, resulting in polymer chains of greater molecular weight; however, as shown in Figure 5.10, there was little difference between the molecular weight distributions at different pH, suggesting that radical entry into particles was only affected prior to significant growth. In this case, the retardation of radical entry into block copolymer aggregates can be overcome by increasing the concentration of radicals. It is shown in Figure 5.10 that at a pH of 6, an increase in initiator concentration does indeed result in dramatically decreasing the particle size dispersity.
Figure 5.10. (Left) The molecular weight distributions of emulsion polymers stabilized by 5 µM of block copolymer remain unchanged when decreasing pH from 12 to 6. (Right) Increased initiator concentration results in lower particle size dispersity, presumably due to the faster nucleation of all block copolymer aggregates.

5.3.4 Homopolymer Impurity

The cost of block copolymer synthesis remains a significant obstacle to commercial use, and it is likely that compromises in structure and purity will be necessary to achieve economic practicality. An example of a structural compromise is the use of block copolymers with broad molecular weight distributions resulting from high conversion and/or continuous production, a compromise studied in the previous two chapters. A realistic purification compromise would be the presence of a homopolymer; a homopolymer impurity could result from unreacted macroinitiator (e.g. from irreversible termination, poor re-initiation of macroinitiator, chain transfer, or a broad residence time distribution in the case of continuous production), or from the free radical polymerization of residual monomer to avoid additional purification steps. Assuming that a homopolymer is a likely impurity in a block copolymer produced by an economic process, the effects of such an impurity should be known, specifically, those effects which are not simply dilution.
In this section, the block copolymer is intentionally doped with varying amounts of the polystyrene macroinitiator to simulate a block copolymer produced in a process with varying chain extension efficiencies. Block copolymer dispersions were prepared in the same manner as those containing no impurity, and it was noted that beyond an impurity weight fraction of 30 percent, an insoluble fraction remained in the dispersions even after heating for 24 hours. Emulsion polymerizations seeded by these block copolymer dispersions were conducted using the same \textit{in situ} DLS technique as before, with the number of particles plotted against the concentration of block copolymer not including impurity concentration, to ignore dilution effects (Figure 5.11). As macroinitiator impurity increased, the number of particles decreased, suggesting an increase in the number of block copolymer chains per aggregate. This is an intuitive result as one may imagine the hydrophobic impurity swelling the interior of aggregates and forcing their increase in size. Analysis of the linear trends in Figure 5.11 with eq 5.10 results in sub-zero CAC values for the dispersions containing the macroinitiator impurity, which would suggest a complete lack of a CAC in the presence of a hydrophobic polymer impurity, i.e. aggregates must form at all concentrations to protect the hydrophobic homopolymer components. Despite the effect on the number of particles, the presence of the macroinitiator impurity did not affect the particle size dispersity of the emulsion polymerizations.
Figure 5.11. The number of particles produced in an emulsion polymerization as a function of the concentration of block copolymer stabilizer chains with varying weight fractions of polystyrene homopolymer impurity (9, 20, 30 wt%).

5.4 Conclusions

In this work, the effects of concentration, degree of neutralization, and homopolymer impurity on the stabilization performance of polystyrene-b-poly(acrylic acid) copolymers in the emulsion polymerization of styrene have been investigated. An \textit{in situ} DLS technique has been introduced to study the time evolution of these emulsion polymerizations at very dilute block copolymer concentrations (below and above the CAC). It was observed that block copolymers behave similarly to small molecule surfactants below the CAC, likely in a mixed seeded-homogenous nucleation mechanism, while a seeded mechanism dominated particle nucleation at approximately double the CAC and above. Assuming a perfectly seeded nucleation mechanism, a linear fit of the number of particles versus stabilizer concentration provided both aggregation number and CAC of the block copolymer. The degree of neutralization of a polyelectrolyte block copolymer was shown to play an important role in aggregate nucleation, as polyelectrolyte blocks below full
neutralization appear to inhibit radical entry into aggregates resulting in high particle size dispersity. The inhibition of radical entry appeared to exist only prior to significant growth where polyelectrolyte brushes are closely packed, due to the negligible observed effect on the molecular weight distribution of the emulsion polymer. The elongated nucleation time of aggregates was equivalent to the semi-batch addition of seed particles to an emulsion but could be counteracted by either increasing neutralization with higher pH or increasing the radical concentration by adding more initiator. It was also shown that although a hydrophobic homopolymer impurity increased aggregation number and thus the number of particles, and eliminated the existence of a CAC, it had no significant effects on block copolymer stabilization other than dilution. The conclusions of this work increase the fundamental understanding of polyelectrolyte block copolymer stabilizers in emulsion polymerization that is necessary for developing and defining their potential commercial use.

5.5 References


(21) Matsuoka, H.; Chen, H.; Matsumoto, K. Molecular Weight Dependence of Non-Surface


Chapter 6

Amphiphilic Block-Random Copolymers: Self-folding and Stabilization of High Solids Emulsion Polymerization

= Styrene
= Acrylic Acid
Abstract

Polystyrene-b-poly(acrylic acid) block copolymers are shown to have significant limitations as stabilizers in emulsion polymerization; it is proposed that the polyelectrolyte block limits the achievable solids content in an emulsion polymerization by increasing particle volume fraction relative to the weight fraction. To overcome this problem, a new stabilizer structure is introduced, where the poly(acrylic acid) stabilizing block is replaced with a polystyrene-r-poly(acrylic acid) block. The resulting polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers were synthesized by nitroxide mediated radical polymerization, and have a molar composition of over 80% polystyrene. Despite having a highly hydrophobic structure, the block-random copolymers dispersed quickly and easily into alkaline water and formed very small (<5 nm) nanoparticles, consistent with very small aggregation numbers or possibly single-chains. Emulsion polymerizations of styrene were successfully stabilized by the block-random copolymers at high solids content (50 weight percent polymer), which was unachievable with polystyrene-b-poly(acrylic acid) stabilizers. Block-random copolymers are a promising new stabilizer structure for high solids content emulsion polymerization, and merit further research to optimize their structure and to understand their effects on particle nucleation.
6.1 Introduction

It is well known that amphiphilic block copolymers are efficient stabilizers in emulsion polymerizations, but their advantages in this field are often overshadowed by the cost and complexity of synthesis. A breakthrough in block copolymer surfactants requires both advances in synthetic strategies and a deeper understanding of structure-property relationships; satisfying these two requirements will enable the intelligent design of block copolymers that may surpass the capabilities of modern surfactants not only in the laboratory but in commercial applications as well. Indeed, recent advances in polymer synthesis have produced an unprecedented variety of structures and topologies of block copolymer surfactants, and their application as stabilizers in emulsion polymerization has been reviewed.

Amphiphilic block copolymers containing a polyelectrolyte block were first studied as stabilizers in emulsion polymerization during the 1990s, and are an attractive class of stabilizers due to their efficiency and electrosteric stabilization. It was later found that a sufficiently large hydrophobic block could “anchor” block copolymer chains to particle interfaces, leading to block copolymer aggregates acting as seed particles in emulsion polymerization; other studies of polyelectrolyte block copolymers have investigated block length, topology, and molecular weight dispersity. A particularly well-studied family of polyelectrolyte block copolymer surfactants are those composed of styrene and acrylic acid; not only are these monomers commercially important and available, but random copolymers of these monomers have been effectively commercialized as polymeric surfactants (e.g. alkali soluble resins, ASR). The solution behavior of styrene-acrylic acid block copolymers has been extensively investigated, including their self-assembly into aggregates above a critical concentration, the
existence of a multitude of aggregate morphologies,\textsuperscript{25,26,27} and the absence of surface activity;\textsuperscript{28} the lack of surface activity may improve coating properties such as water resistance and adhesion.

In the majority of work published using polyelectrolyte block copolymers as stabilizers in emulsion polymerization, the solids content of the emulsion polymerization, i.e. the mass fraction of polymer relative to the system, is comparatively low (5-30 wt\%) to what is expected in commercial applications (>40 wt\%). Herein, the limitations of polyelectrolyte block copolymers in high solids emulsion polymerization are investigated, and it is demonstrated that a block-random copolymer provides better performance in such applications. Specifically, it was found that a polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymer, with similar composition to commercial ASRs, outperforms polystyrene-b-poly(acrylic acid) block copolymers while presenting unusual solution behavior. Block-random copolymers, where at least one block is a random copolymer, provide another way to tune copolymer properties through the continuous variation of individual block compositions and have been studied both in the melt-phase\textsuperscript{29,30,31} and solution phase, with self-assembly demonstrated in both aqueous\textsuperscript{32,33} and non-aqueous media;\textsuperscript{34} specific structures have been designed to be pH\textsuperscript{35} and/or thermoresponsive\textsuperscript{36,37,38} in aqueous media, with potential applications in drug delivery.\textsuperscript{39,40} While block-random copolymers have recently been investigated as surfactants in non-aqueous dispersions,\textsuperscript{41,42} the work presented here is, to the best of our knowledge, the first report of a block-random copolymer used to stabilize an emulsion polymerization.

6.2 Experimental

6.2.1 Materials

N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl) nitroxide] (SG1, 85\%) and N-\textit{(tert-butyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine}
(BlocBuilder™, 99%) were supplied by Arkema and used as received. Acrylic acid (anhydrous, 180-200 ppm MEHQ as an inhibitor, 99%), styrene (4-tert-butyl catechol as a stabilizer, ≥99%), ammonium persulfate (>98%), and sodium hydroxide (>98%) were purchased from Sigma-Aldrich and used as received. Methanol (99.8%), tetrahydrofuran (THF, 99%), and hexanes (98.5%) were purchased from ACP Chemicals and used as received. 1,4-dioxane (99.9%) hydrochloric acid (38% assay), and hydroquinone (crystalline/laboratory) were purchased from Fisher Scientific and used as received. Chloroform-D and dimethyl sulfoxide-D6 (100%, 99.96% D) were purchased from Cambridge Isotope Laboratories, Inc. and used as received. All water used in this work was in-house distilled water that was further purified (18.2 MΩ-cm) using a Millipore Synergy water purification system equipped with SynergyPak purification cartridges.

6.2.2 Characterization of Copolymers

Gel Permeation Chromatography (GPC) analysis was performed with a Waters 2690 Separation Module and Waters 410 Differential Refractometer with THF as the eluent. The column bank consisted of Waters StyrageL HR (4.6x300 mm) 4, 3, 1, and 0.5 separation columns operating at 40°C and 0.3 mL/min. The poly(acrylic acid) blocks of the diblock copolymers were methylated to poly(methyl acrylate) before analysis by GPC. This was achieved by adding a slight excess of trimethylsilyldiazomethane to the polymer sample dissolved in a THF:methanol mixture (3:1 volume ratio), an adaptation of previously reported techniques. All GPC data is reported as the polystyrene-equivalent, based on a calibration curve of narrow molecular weight distribution polystyrene standards purchased from Polymer Standards Service-USA.

1H NMR spectroscopy was performed on an FT-NMR Bruker Avance 400 MHz spectrometer at room temperature. Spectra were recorded with a total of 64 scans, using a polymer concentration of 5 mg/mL in DMSO-d6. The composition of block copolymers was determined by integrating
the carboxylic acid protons (11-13 ppm) from poly(acrylic acid), and the aromatic protons (6-7.5 ppm) from polystyrene. The chemical shift scale was calibrated on the basis of the solvent peak (2.50 ppm).

6.2.3 Synthesis of the Polystyrene Macroinitiator

The alkoxyamine initiator BlocBuilder™ (18.5 g, 0.049 mol) and styrene (500 g, 4.8 mol) were added to a 1000 mL 3-necked round bottom flask with an attached condenser. This solution was bubbled with nitrogen for 30 minutes with stirring, followed by immersion in a 120 °C bath of silicone oil. The temperature of the solution was monitored with a mercury thermometer inserted into a side neck of the flask; after 15 minutes the temperature reached 110 °C where it remained for either 1.5 hours (PS1) or 3 hours (PS2) before being cooled in an ice bath. The viscous product was precipitated in methanol. Residual monomer was removed by redissolving the polymer in a minimal amount of THF followed by reprecipitation in methanol and drying under vacuum for one day, as confirmed by the absence of any vinyl peaks in the 1H NMR spectrum of the purified macroinitiator. The dried polymer was easily crushed into a white powder (PS1, Mn=3300 g/mol, Đ=1.13; PS2, Mn=5600 g/mol, Đ=1.10; from GPC analysis).

6.2.4 Chain Extensions with Acrylic Acid

Polystyrene macroinitiator (1 g), SG1 nitroxide (10 mol% based on macroinitiator), acrylic acid, and 1,4-dioxane (3:1 molar ratio with acrylic acid) were mixed in a 20 mL glass flask until homogeneous (recipes in Table 6.1). The solution was bubbled with nitrogen for 30 minutes, then sealed and immersed in a 115 °C bath of silicone oil for between 1 to 3 hours. The solution was then cooled in an ice bath, prior to being slowly added to 30 mL of stirring hexanes to precipitate the block copolymer. After decanting the hexanes, the polymer was washed twice more with hexanes and dried for one day in a vacuum oven at 40 °C. The removal of residual monomer was
confirmed by the absence of any vinyl peaks in the $^1$H NMR spectrum of the purified block copolymer. A series of four block copolymers were prepared in this manner, B1-4, with characteristics reported in Table 6.3.

Table 6.1. Chain extensions of polystyrene macroinitiators with acrylic acid.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$[\text{macroinitiator}]_0$ (mol/L)</th>
<th>$[\text{SG1}]_0$ (mol/L)</th>
<th>$[\text{AA}]_0$ (mol/L)</th>
<th>[dioxane] (mol/L)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.031 (PS2)</td>
<td>0.0031</td>
<td>2.8</td>
<td>8.3</td>
<td>2</td>
</tr>
<tr>
<td>B2</td>
<td>0.019 (PS1)</td>
<td>0.0019</td>
<td>2.9</td>
<td>8.6</td>
<td>1</td>
</tr>
<tr>
<td>B3</td>
<td>0.019 (PS1)</td>
<td>0.0019</td>
<td>2.9</td>
<td>8.6</td>
<td>2</td>
</tr>
<tr>
<td>B4</td>
<td>0.019 (PS1)</td>
<td>0.0019</td>
<td>2.9</td>
<td>8.6</td>
<td>3</td>
</tr>
</tbody>
</table>

6.2.5 Chain Extensions with Styrene and Acrylic Acid

Polystyrene macroinitiator (1 g), SG1 nitroxide (10 mol% based on macroinitiator), acrylic acid, styrene, and 1,4-dioxane (1:1 molar ratio with monomer) were mixed in a 20 mL glass flask until homogeneous (recipes in Table 6.2). The molar ratio between styrene and acrylic acid (7:3) was chosen to result in a random block with the same composition of commercial styrene-acrylic acid random copolymers, which is typically between 15-30 mol% acrylic acid. The solution was bubbled with nitrogen for 30 minutes, then sealed and immersed in a 125 °C bath of silicone oil for 1.5 hours. The solution was then cooled in an ice bath and purified with the same procedure used for the block copolymers.

Table 6.2. Chain extensions of polystyrene macroinitiators with acrylic acid and styrene.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$[\text{macroinitiator}]_0$ (mol/L)</th>
<th>$[\text{SG1}]_0$ (mol/L)</th>
<th>[acrylic acid]$_0$ (mol/L)</th>
<th>[styrene] (mol/L)</th>
<th>[dioxane] (mol/L)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR1</td>
<td>0.046 (PS1)</td>
<td>0.005</td>
<td>1.4</td>
<td>3.2</td>
<td>4.6</td>
<td>1.5</td>
</tr>
<tr>
<td>BR2</td>
<td>0.030 (PS2)</td>
<td>0.003</td>
<td>1.3</td>
<td>3.1</td>
<td>4.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Two block-random copolymers were prepared in this manner, BR1 and BR2, with characteristics reported in Table 6.5. The structures of both block and block-random copolymers are shown in Scheme 6.1.

**Scheme 6.1.** Structures of both polystyrene-b-poly(acrylic acid) block copolymer and polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymer used in this work, as well as the BlocBuilder™ alkoxyamine and polystyrene macroinitiator used in their synthesis.

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### 6.2.6 Preparation of Aqueous Block Copolymer Dispersions

A block copolymer was added to a 20 mL glass vial, to which appropriate amounts of water and a 1 M sodium hydroxide solution were added to produce a final block copolymer concentration of 0.7 g/L with a four-fold stoichiometric excess of base relative to carboxylic acid units. The vial was then tightly sealed with a plastic cap and heated at 90 °C with magnetic stirring for 24 hours.

### 6.2.7 Preparation of Aqueous Block-Random Copolymer Dispersions

A block-random copolymer was added to a 20 mL glass vial, to which appropriate amounts of water and a 1 M sodium hydroxide solution were added to produce a final block-random copolymer concentration of 70 g/L with a stoichiometric equivalent of base relative to carboxylic
acid units. The vial was then tightly sealed with a plastic cap and heated at 80 °C with magnetic stirring for 30 minutes, after which a colorless transparent dispersion was formed.

6.2.8 Emulsion Polymerization Procedure

A batch emulsion polymerization of styrene was used as a standard test procedure wherein either a block or block-random copolymer was used as the stabilizer. The general procedure began by adding styrene monomer (1 g), deionized water, sodium hydroxide (0.1 g of 1 M solution), and ammonium persulfate (0.1 g of 30 g/L solution) to an aqueous copolymer dispersion, such that the mixture was 50% styrene by weight. This mixture was then sealed in a 5 mL round bottom flask and immersed in an 85 °C bath of silicone oil with stirring. Emulsion polymerizations were closely monitored and allowed to continue for 4 hours unless significant coagulum was noticed in which case the polymerization was stopped earlier.

6.2.9 Evaluation of Block Copolymer Aggregate and Emulsion Properties

Conversion of emulsion polymerizations was determined gravimetrically by the addition of 100 μL of a 0.1 mol/L hydroquinone solution to 500 μL of the emulsion, followed by drying in an 85 °C vacuum oven. Hydrodynamic diameters of particles were determined with a Malvern Zetasizer Nano ZS at 25°C with non-invasive backscatter optics (173°), using a 4 mW He-Ne (633 nm) laser. All samples were measured in quartz cuvettes. All data was processed using the Malvern Dispersion Technology Software (version 7.11). Block copolymer aggregate dispersions were measured directly, while latex dispersions were diluted by a factor of 200 to obtain an appropriate level of scattering for measurement. All reported dynamic light scattering (DLS) measurements are an average of 30 sequential measurements.

The number of latex particles (L⁻¹) was calculated using eq 6.1.
\[ N_p = \frac{6\tau}{\pi \rho D_n^3} \]  \hspace{1cm} (6.1)

with \( \tau \) being the polymer content of the latex (g/L) determined by gravimetry, \( \rho \) the density of polystyrene (1.05 g/cm\(^3\)), and \( D_n \) the number-average diameter of the polystyrene core measured by DLS.

The average distance between latex particles in an emulsion polymerization, i.e. the interparticle distance (IPD), was estimated using the model of Hao and Riman for uniform spherical particles in a suspension:\(^45\)

\[ IPD = D \left( \left( \frac{\varphi_m}{\varphi} \right)^{1/3} - 1 \right), \text{ for } \varphi \leq \varphi_m \]  \hspace{1cm} (6.2)

Where \( D \) is the diameter of uniform spherical particles, \( \varphi \) is the volume fraction of particles in the suspension, and \( \varphi_m \) is the volume fraction of particles at maximum packing (\( \approx 0.64 \) for random dense packing, compared to \( \pi/\sqrt{18} \) or \( \approx 0.74 \) for a face-centered cubic lattice\(^46\)).

**6.3 Results and Discussion**

**6.3.1 High Solids Limitations of Block Copolymer Stabilizers**

Despite the potential value of polyelectrolyte block copolymers as stabilizers in emulsion polymerization, their usage in systems resembling commercial applications, e.g. high solids emulsion polymerization, have not been reported. Preliminary experiments to use polystyrene-b-poly(acrylic acid) copolymers to stabilize emulsion polymerizations of styrene with high solids content have been unsuccessful, suggesting the lack of published experimental evidence may be due to an inherent limitation of these stabilizers. Accordingly, a small library of polystyrene-b-poly(acrylic acid) copolymers was prepared for testing as stabilizers in high solids (>40wt%) emulsion polymerization of styrene. The block copolymer structures have been designed to
elucidate the effects of both anchor and stabilizing block by varying their lengths; the characteristics of copolymers B1-4 are reported in Table 6.3 and molecular weight distributions are shown in Figure 6.1.

**Table 6.3.** Characterization of polystyrene-b-poly(acrylic acid) block copolymers B1-4.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>DP&lt;sub&gt;PS&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DP&lt;sub&gt;PAA&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>D</th>
<th>mol% AA&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>51</td>
<td>22</td>
<td>7500</td>
<td>1.12</td>
<td>30</td>
</tr>
<tr>
<td>B2</td>
<td>29</td>
<td>22</td>
<td>5100</td>
<td>1.19</td>
<td>43</td>
</tr>
<tr>
<td>B3</td>
<td>29</td>
<td>61</td>
<td>8400</td>
<td>1.33</td>
<td>68</td>
</tr>
<tr>
<td>B4</td>
<td>29</td>
<td>103</td>
<td>12100</td>
<td>1.57</td>
<td>78</td>
</tr>
</tbody>
</table>

<sup>a</sup> Degree of polymerization determined from GPC molecular weight.
<sup>b</sup> Degree of polymerization based on <sup>1</sup>H NMR block copolymer composition.
<sup>c</sup> M<sub>n</sub> for the methylated copolymer, polystyrene-b-poly(methyl acrylate), reported as polystyrene equivalent.
<sup>d</sup> Molar percentage of poly(acrylic acid) in copolymer determined by <sup>1</sup>H NMR.

![Molecular weight distribution](image)

**Figure 6.1.** Molecular weight distribution of polystyrene-b-poly(acrylic acid) copolymers B1-4. Molecular weight distributions of polystyrene macrorinitiators PS1 and PS2 are also shown (dashed lines).
Emulsion polymerizations of styrene were conducted using copolymers B1-4 as stabilizers, and a high solids content (50 wt%) was targeted. In all cases, emulsion polymerizations stabilized by B1-4 became unstable prior to reaching the high solids target. Failure, or destabilization of an emulsion polymerization, was marked by the formation of significant coagulum. The solids content at this point was assumed to be the maximum achievable solids content for a given stabilizer and particle size; in most cases a thin and hard layer of coagulum at the surface of the latex marked this point, with the same coagulum found attached to the stir bar after removal. Figure 6.2 illustrates the destabilization of an emulsion polymerization at a maximum, or critical, solids content.

Figure 6.2. The interparticle distance decreases as the solids content of an emulsion polymerization increases. A critical solids content will be reached at which interparticle distance is no longer sufficient to prevent the coagulation of particles, i.e. the critical IPD.

The critical interparticle distance, i.e. the distance between particles at the point of coagulation, was determined using eq 6.2 and is reported in Table 6.4 for emulsion polymerizations stabilized by block copolymers B1-4. Since IPD has been calculated using the hydrodynamic particle diameter, it represents an overestimate of the IPD between particle cores.
Table 6.4. Characterization of emulsion polymerizations stabilized by block copolymers B1-4 at the limiting solids content. Target solids content in all cases was 50%.

<table>
<thead>
<tr>
<th>EP</th>
<th>[stabilizer] (mM)</th>
<th>wt% BOM(^a)</th>
<th>(D_n) (nm)(^b)</th>
<th>PDI(^c)</th>
<th>Solids Content (%)(^d)</th>
<th>(N_p) (eq 6.1) ((x10^{16} \text{ L}^{-1}))</th>
<th>IPD (nm) (eq 6.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-E1</td>
<td>1.16</td>
<td>1.740</td>
<td>137</td>
<td>0.13</td>
<td>36</td>
<td>25.2</td>
<td>31</td>
</tr>
<tr>
<td>B1-E2</td>
<td>0.363</td>
<td>0.544</td>
<td>224</td>
<td>0.17</td>
<td>38</td>
<td>6.1</td>
<td>46</td>
</tr>
<tr>
<td>B1-E3</td>
<td>0.145</td>
<td>0.218</td>
<td>286</td>
<td>0.03</td>
<td>34</td>
<td>2.7</td>
<td>70</td>
</tr>
<tr>
<td>B1-E4</td>
<td>0.072</td>
<td>0.109</td>
<td>360</td>
<td>0.07</td>
<td>38</td>
<td>1.5</td>
<td>74</td>
</tr>
<tr>
<td>B2-E1</td>
<td>0.04</td>
<td>0.041</td>
<td>259</td>
<td>0.01</td>
<td>38</td>
<td>4.0</td>
<td>53</td>
</tr>
<tr>
<td>B2-E2</td>
<td>0.01</td>
<td>0.010</td>
<td>392</td>
<td>0.04</td>
<td>36</td>
<td>1.1</td>
<td>86</td>
</tr>
<tr>
<td>B2-E3</td>
<td>0.005</td>
<td>0.005</td>
<td>521</td>
<td>0.14</td>
<td>34</td>
<td>0.44</td>
<td>129</td>
</tr>
<tr>
<td>B3-E1</td>
<td>0.04</td>
<td>0.067</td>
<td>144</td>
<td>0.06</td>
<td>31</td>
<td>18.6</td>
<td>42</td>
</tr>
<tr>
<td>B3-E2</td>
<td>0.01</td>
<td>0.017</td>
<td>254</td>
<td>0.17</td>
<td>31</td>
<td>3.4</td>
<td>73</td>
</tr>
<tr>
<td>B3-E3</td>
<td>0.005</td>
<td>0.008</td>
<td>355</td>
<td>0.14</td>
<td>31</td>
<td>1.3</td>
<td>102</td>
</tr>
<tr>
<td>B4-E1</td>
<td>0.04</td>
<td>0.098</td>
<td>133</td>
<td>0.27</td>
<td>24</td>
<td>18.6</td>
<td>53</td>
</tr>
<tr>
<td>B4-E2</td>
<td>0.01</td>
<td>0.025</td>
<td>198</td>
<td>0.03</td>
<td>26</td>
<td>6.1</td>
<td>72</td>
</tr>
<tr>
<td>B4-E3</td>
<td>0.005</td>
<td>0.012</td>
<td>261</td>
<td>0.06</td>
<td>28</td>
<td>2.9</td>
<td>87</td>
</tr>
<tr>
<td>B4-E4</td>
<td>0.002</td>
<td>0.006</td>
<td>378</td>
<td>0.14</td>
<td>30</td>
<td>1.0</td>
<td>117</td>
</tr>
</tbody>
</table>

\(^a\) Weight fraction of a copolymer stabilizer based on monomer

\(^b\) Number-average hydrodynamic diameter calculated by DLS.

\(^c\) Polydispersity Index of particles calculated by DLS.

\(^d\) Weight fraction of solids at end of emulsion polymerization determined gravimetrically.

It is evident from Figure 6.3 that longer stabilizing blocks are associated with a decrease in the maximum achievable solids content and an increase in the critical IPD; it is also evident that the critical IPD increases with particle diameter.
Figure 6.3. The maximum achievable solids content as a function of stabilizing block length (left), and the critical IPD as a function of particle diameter (right; experiments using same stabilizer are grouped together).

Figure 6.3 suggests that polystyrene-b-poly(acrylic acid) stabilizers limit the maximum achievable solids content of emulsion polymerizations through two mechanisms: (i) the hydrodynamic volume of the stabilizing layer increases the volume fraction of particles more than the weight fraction, and will scale with the size of the stabilizing block, and (ii) the fixed number of stabilizer chains per particle will lead to a decrease in particle stability as particles grow larger. Increasing the number of stabilizer chains per particle should increase solids content by improving particle stability, but will not remove the physical limitation placed on solids content by the stabilizing layer. The effect of the stabilizing layer volume on IPD is illustrated in Figure 6.4. Assuming that the solids content of the stabilizing layer is small relative to its volume, a “coronal” stabilizing layer will occupy volume that otherwise could have contributed to increasing solids content, therefore, limiting the maximum achievable solids content.
Figure 6.4. Interparticle distance is calculated as a function of particle weight fraction for 250 nm diameter particles using eq 6.2 and adjusted for varying coronal thicknesses (left). The stabilizing layer causes a greater increase in the particle volume fraction relative to the particle weight fraction; this reduces the interparticle distance, limiting the achievable particle weight fraction.

6.3.2 Block-Random Copolymer Stabilizers

With the limitations of block copolymer stabilizers in high solids emulsion polymerization identified, it is desirable to redesign their structure to overcome these limitations, and since the limiting parameter appears to be the length of the stabilizing block, the most obvious solutions are to either shorten the stabilizing block or alter its rod-like behavior to reduce its extension from the particle surface. Unfortunately, even a stabilizing block length of 22 acrylic acid units (e.g. B1, B2) limited solids content to below 40 wt%, and shorter blocks would require a decreased polystyrene block length to be dispersible in water. Decreasing the overall degree of polymerization would limit the potential for tailoring, e.g. varying block lengths, and would also increase the weight fraction of the nitroxide in the polymer. The nitroxide/alkoxyamine will be an expensive component of the stabilizer synthesis, so for economic practicality, it is best to stabilize an emulsion with a small number of large chains, rather than a large number of small chains; this
will be also true for other synthetic routes for the stabilizer where the mediating agent or catalyst required is proportional to the number of growing chains. Another option is to decrease the volume of the stabilizing layer by decreasing the system pH, thereby protonating enough acrylate anions in the stabilizing block to allow it to collapse; however, protonation and collapse of the stabilizing block will reduce the electrostatic stabilization of particles and may lead to instability.

With the aforementioned design obstacles in mind, we thought an ideal stabilizer structure should exhibit the following properties:

1. A stabilizing block that is tightly bound to the particle surface, reducing the hydrodynamic volume of the stabilizing layer to enable higher solids content.
2. A stabilizing block with a large number of ionic groups to provide a high electrostatic stabilization.
3. A high degree of polymerization to achieve high efficiency (surface area stabilized per chain) and good nitroxide economy.
4. A large anchoring block to improve efficiency, i.e. anchor all chains to particle interface and prevent wasted chains dissolved in the continuous phase.

Current polyelectrolyte block copolymer stabilizers exhibit the last three properties, but not the first; contrastingly, random copolymer stabilizers exhibit the first two properties, but not the last. It intuitively follows that a structure exhibiting all of these properties will be some hybrid of block and random copolymers, e.g. a block-random copolymer as illustrated in Figure 6.5.
Figure 6.5. Illustration of block and random copolymer stabilizers, and the block-random copolymer stabilizer that resembles a hybrid of these two structures.

Following a hybrid design approach, the anchoring blocks (polystyrene macroinitiators) used in block copolymers B1-4 are combined with stabilizing blocks that resemble the composition of commercial poly(styrene-r-acrylic acid) surfactants, i.e. 20-30 mol% acrylic acid. This design is similar to a gradient copolymer, but has distinct block compositions, rather than a composition that varies continuously over the entire chain; for comparison, a gradient copolymer of styrene-acrylic acid (70 mol% acrylic acid) was previously investigated as a stabilizer in emulsion polymerization with good results at high solids content (45 wt%).47 The block-random copolymers synthesized in this work, BR1 and BR2, are characterized in Table 6.5, with molecular weight distributions shown in Figure 6.6.
Table 6.5. Characterization of polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Anchor block</th>
<th>Stabilizing Block</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DP$_{PS}^a$</td>
<td>$M_n$ (g/mol)</td>
<td>$D$</td>
</tr>
<tr>
<td>BR1</td>
<td>29</td>
<td>3300</td>
<td>1.13</td>
</tr>
<tr>
<td>BR2</td>
<td>51</td>
<td>5600</td>
<td>1.10</td>
</tr>
</tbody>
</table>

$^a$ Degree of polymerization determined from GPC molecular weight.

$^b$ Degree of polymerization based on $^1$H NMR block copolymer composition.

$^c$ Molar percentage of poly(acrylic acid) in copolymer determined by $^1$H NMR.

$^d$ $M_n$ for the methylated copolymer, polystyrene-b-poly(methyl acrylate), reported as polystyrene equivalent.

Figure 6.6. Molecular weight distribution of polystyrene-b-[polystyrene-r-poly(acrylic acid)] copolymers BR1 (left) and BR2 (right). Molecular weight distributions of polystyrene macroinitiators PS1 and PS2 are also shown (dashed lines).

6.3.3 Solution Behavior of Block-Random Copolymers

Dispersing copolymers BR1 and BR2 in aqueous media was expected to be challenging due to their low overall molar composition of 15 and 17 mol% acrylic acid, respectively; compare this to polystyrene-b-poly(acrylic acid) block copolymers which typically require at least 50 mol%
acrylic acid to be dispersed in aqueous media at high temperature (90 °C) and over a period of hours.9,11

The initial strategy to disperse BR1 and BR2 into aqueous media was to add a stoichiometric excess of a strong base relative to carboxylic acid units, followed by heating at high temperature (95 °C) in a sealed flask with stirring. Styrene would then be gradually added to provide solvent-assisted dissolution of the hydrophobic portions of the copolymer. In the first attempt to disperse BR1, the copolymer (7 g/L) was added to alkaline solution, sealed, and immersed in a 95 °C oil bath; however, after only a minute, the mixture became unexpectedly turbid, and within 10 minutes had completely clarified into a transparent, colorless dispersion. Noting that significant dispersion occurred before the medium could have reached the bath temperature, and without solvent assistance, subsequent dispersions were made at a lower temperature and with a higher concentration of stabilizer (70 g/L). The unanticipated ease of dispersing copolymer BR1 and BR2 in aqueous media was at first perplexing, but analysis of the dispersion by dynamic light scattering (DLS) suggests an intuitive and simple mechanism: self-folding. The DLS characterization of BR1 and BR2 dispersions is reported in Table 6.6, with both dispersions showing a single number-average hydrodynamic diameter of approximately 3 nm.

**Table 6.6.** Characterization of 70 g/L dispersions of BR1 and BR2 in alkaline water by dynamic light scattering.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Z-Avg (nm)</th>
<th>PDI</th>
<th>Peaks by Volume (nm)</th>
<th>Peaks by Number (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR1</td>
<td>6</td>
<td>0.3</td>
<td>4 (100%)</td>
<td>3 (100%)</td>
</tr>
<tr>
<td>BR2</td>
<td>12</td>
<td>0.4</td>
<td>4 (98%), 18 (2%)</td>
<td>3 (100%)</td>
</tr>
</tbody>
</table>

The small size of copolymers BR1 and BR2 dispersed in water (3 nm) suggests that these copolymers are dispersed either as very small aggregates containing a few chains each or as single-chain nanoparticles (SCNP) as illustrated in Figure 6.7.
Figure 6.7. Illustration of a block-random polystyrene-b-[polystyrene-r-poly(acrylic acid)] copolymer self-folding into a single-chain nanoparticle under the conditions used in this work. The flexible random copolymer block “wraps” around the insoluble anchoring block, providing stabilization against coagulation with other chains.

To estimate the size of BR1 and BR2 single-chain nanoparticles, one may assume that it will be similar to the size of a single polystyrene chain in water; this is not unreasonable as the copolymers are 83-85% polystyrene on a molar basis. As water is a poor solvent (or non-solvent) for polystyrene, the chain is assumed to be completely collapsed into a sphere with a volume equivalent to the product of the degree of polymerization and the volume of a polystyrene repeat unit ($v_m = 0.167 \text{ nm}^3$). The diameter of this collapsed chain can be calculated by eq 6.3:

$$D_{collapsed, PS} = \frac{\sqrt[3]{2}}{\frac{4\pi}{3}} = \frac{3\sqrt[3]{v_mDP_n}}{4\pi} = 0.683DP_n^{\frac{1}{3}}$$

(6.3)

where $DP_n$ is the degree of polymerization. The diameter of collapsed polystyrene chains, as a function of the degree of polymerization, is calculated using eq 6.3 and shown in Figure 6.8.
Figure 6.8. The diameter of a collapsed polystyrene chain in a poor solvent as a function of the degree of polymerization. Calculated from eq 6.3.

It is found that for block-random copolymers BR1 (DP\textsubscript{n} = 93) and BR2 (DP\textsubscript{n} = 163) the estimated diameters of single-chain nanoparticles from eq 6.3 are 3 and 4 nm, respectively. These diameters are consistent with those measured by DLS, supporting the hypothesis that these block-random copolymers self-fold into single-chain nanoparticles. The self-folding of single synthetic polymer chains is currently an active area of research in polymer science, with many recent articles reviewing the topic\textsuperscript{49,50,51,52,53,54,55} this is an exciting field as it is analogous to the self-folding of polypeptides in nature, and may reveal pathways to the design of higher order polymer architectures like those exhibited by proteins.

6.3.4 Evaluating Block-Random Copolymers as Emulsion Polymerization Stabilizers.

After preparing dispersions of both BR1 and BR2, these dispersions were used to stabilize high solids content emulsion polymerizations of styrene, under the same conditions used to evaluate block copolymers B1-4. Using the same weight fraction of block-random copolymer as block copolymer based on monomer (e.g. <1 wt\%) resulted in unstable emulsions, but increasing
the weight fraction of block-random copolymer to 5 wt% based on monomer led to stable emulsion polymerizations at high solids content, the characteristics of which are reported in Table 6.7.

**Table 6.7.** Characterization of emulsion polymerizations stabilized by block-random copolymers BR1 and BR2. Target solids content was 50%.

<table>
<thead>
<tr>
<th>EP</th>
<th>[stabilizer] (mM)</th>
<th>wt% BOM</th>
<th>D&lt;sub&gt;h,n&lt;/sub&gt; (nm)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Solids Content (%)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>N&lt;sub&gt;p&lt;/sub&gt; (eq 6.1) (x10&lt;sup&gt;16&lt;/sup&gt; L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>IPD (nm) (eq 6.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR1-E1</td>
<td>2.8</td>
<td>5</td>
<td>214</td>
<td>0.06</td>
<td>48</td>
<td>8.9</td>
<td>24</td>
</tr>
<tr>
<td>BR2-E1</td>
<td>1.6</td>
<td>5</td>
<td>227</td>
<td>0.02</td>
<td>50</td>
<td>7.7</td>
<td>23</td>
</tr>
</tbody>
</table>

<sup>a</sup> Weight fraction of a copolymer stabilizer based on monomer

<sup>b</sup> Number-average hydrodynamic diameter calculated by DLS.

<sup>c</sup> Polydispersity Index of particles calculated by DLS.

<sup>d</sup> Weight fraction of solids at end of emulsion polymerization determined gravimetrically.

It is clear that block copolymers are more efficient at stabilizing particle surface area, but to quantitatively compare the efficiencies of block-random copolymers BR1 and BR2 to the block copolymers B1-4, the particle surface areas created per stabilizer chain, gram of stabilizer, and acrylic acid unit were calculated and reported in Table 6.8.

**Table 6.8.** Comparison of block copolymers B1-4 and block-random copolymers BR1 and BR2 based on the efficiency of particle surface area stabilization.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>EP</th>
<th>D&lt;sub&gt;h,n&lt;/sub&gt; (nm)</th>
<th>AA/chain&lt;sup&gt;a&lt;/sup&gt;</th>
<th>SA/stabilizer (m&lt;sup&gt;2&lt;/sup&gt;/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SA/stabilizer (nm&lt;sup&gt;2&lt;/sup&gt;/chain)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>SA/AA (nm&lt;sup&gt;2&lt;/sup&gt;/AA)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>E3</td>
<td>286</td>
<td>22</td>
<td>6300</td>
<td>78</td>
<td>4</td>
</tr>
<tr>
<td>B2</td>
<td>E1</td>
<td>259</td>
<td>22</td>
<td>41100</td>
<td>348</td>
<td>16</td>
</tr>
<tr>
<td>B3</td>
<td>E2</td>
<td>254</td>
<td>61</td>
<td>82800</td>
<td>1200</td>
<td>19</td>
</tr>
<tr>
<td>B4</td>
<td>E3</td>
<td>261</td>
<td>103</td>
<td>100500</td>
<td>2000</td>
<td>20</td>
</tr>
<tr>
<td>BR1</td>
<td>E1</td>
<td>214</td>
<td>16</td>
<td>500</td>
<td>8</td>
<td>0.5</td>
</tr>
<tr>
<td>BR2</td>
<td>E1</td>
<td>227</td>
<td>25</td>
<td>500</td>
<td>13</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Number of acrylic acid units per copolymer chain, determined by <sup>1</sup>H NMR.

<sup>b</sup> Particle surface area per gram of copolymer stabilizer.

<sup>c</sup> Particle surface area per copolymer chain.

<sup>d</sup> Particle surface area per acrylic acid unit in a copolymer chain.
From the results in Table 6.8, it appears that the carboxylate anions in a homopolymer are more efficient at stabilizing particle surface area than the carboxylate anions in a copolymer. Geometrically, a rod-like polyelectrolyte stabilizing block will be anchored at one point to a particle and may “sweep” over a large particle surface area; in comparison, each stabilizing carboxylate unit in a random copolymer stabilizing block will be anchored in place by the flanking hydrophobic regions, localizing the surface stabilization to a small area. This geometric comparison of homopolymer and copolymer stabilizing blocks is illustrated in Figure 6.9. Based on this geometric model, the maximum surface area stabilized by a random copolymer is expected to be proportional to the number of carboxylate units, while the surface area stabilized by a rod-like polyelectrolyte block is expected to be proportional to the square of the number of carboxylate units.

**Figure 6.9.** A homopolymer stabilizing block anchored to a surface at one point (left) is compared to a copolymer stabilizing block anchored to a surface at many points (right). As illustrated, the homopolymer block may have greater freedom of movement, covering a larger surface area than the copolymer.
Unfortunately for block copolymer stabilizers, the rod-like stabilizing block that is responsible for the high surface stabilization efficiency also appears to be responsible for limiting the total particle volume fraction due to effectively decreasing interparticle distances. Ultimately, despite having a lower surface stabilization efficiency compared to a block copolymer, a block-random copolymer will be the better design for applications requiring high particle volume fractions and small interparticle distance.

6.4 Conclusions

This work has shown that the polyelectrolyte blocks of polystyrene-b-poly(acrylic acid) stabilizers limit the achievable solids content in an emulsion polymerization due to the hydrodynamic volume occupied by the stabilizing layer; this is a significant observation as many commercial applications of emulsion polymerization will require a high solids content. It was found that the maximum achievable solids content could be increased by shortening the polyelectrolyte block, but this puts significant restrictions on the design space of these stabilizers, limiting them to low molecular weight copolymers that begin to resemble small molecule surfactants. An improved stabilizer structure has been proposed where the poly(acrylic acid) stabilizing block is replaced by a polystyrene-r-poly(acrylic acid) block, such that the hydrophobic regions of the random copolymer anchor the stabilizing block to the particle surface and allow lower interparticle distances, i.e. higher particle volume fractions. Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers were synthesized with an overall molar acrylic acid composition of less than 20%. Despite a very low molar composition of acrylic acid, the block-random copolymers were dispersed into alkaline water under milder conditions than required for block copolymers and were found to form dispersed nanoparticles consistent with the size of a single self-folded copolymer chain. Dispersion of the block-random copolymers succeeded in
stabilizing high solids content (50 wt% polymer) emulsion polymerizations of styrene, where block copolymer stabilizers had previously failed. While the block-random copolymers had a lower efficiency of particle surface area stabilization compared to block copolymers, they introduce a new structure of emulsion polymerization stabilizer that may be useful in commercial application. Further work will be needed in order to optimize the block-random structure, for example, to determine optimum anchor and stabilizing block lengths, and the effects of stabilizing block composition. Another important observation is that unlike polyelectrolyte block copolymers, the block-random copolymer stabilizers studied do not form large aggregates. Since block copolymer aggregates typically behave as seed particles in emulsion polymerization, it is unclear how single self-folded stabilizer chains will affect the nucleation mechanism; a careful mechanistic study will be needed to understand how the nucleation mechanism is affected by the block-random stabilizers used in this work, and will be the subject of a future publication.

6.5 References


(6) Leemans, L.; Fayt, R.; Teyssie, P.; De Jaeger, N. C. Poly(alkyl Methacrylate-B-Sulfonated


(12) Burguière, C.; Chassenieux, C.; Charleux, B. Characterization of Aqueous Micellar Solutions of Amphiphilic Block Copolymers of Poly(acrylic Acid) and Polystyrene Prepared via ATRP. Toward the Control of the Number of Particles in Emulsion Polymerization. *Polymer (Guildf).* **2003**, *44* (3), 509–518 DOI: 10.1016/S0032-3861(02)00811-X.


Chapter 7
Amphiphilic Block-Random Copolymers: A Thermodynamically Driven Emulsion Polymerization Mechanism?
Abstract

Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers are effective stabilizers for high solids content emulsion polymerization, but exhibit unusual dispersion behavior, self-assembling with low aggregation numbers or possibly self-folding into single-chain nanoparticles. It was observed that emulsion polymerizations stabilized by a block-random copolymer, PS$_{51}$-b-(PS$_{87}$-r-PAA$_{25}$), had a total particle surface area that was directly proportional to the stabilizer concentration and unaffected by kinetically driven processes such as initiation and particle growth rate; this behavior cannot be explained by any known emulsion polymerization mechanism. A “seeded-coagulative” emulsion polymerization mechanism is proposed in which particles grow by polymerization, and continuously coagulate to conserve total surface area. Mathematical equations for this proposed mechanism fit the experimental data well and explain the observed dependence of particle number on stabilizer concentration ($N_p \sim [S]^3$) and solids content ($N_p \sim \tau^2$). This is a novel emulsion polymerization mechanism which is attributed to the unique properties of the stabilizer used. The seeded-coagulative mechanism appears to offer thermodynamic rather than kinetic control of an emulsion polymerization and may offer greater scalability and reproducibility as a result.
7.1 Introduction

The current global demand for emulsion polymers exceeds 10 million metric tons per annum,\(^1\) with large markets in paint, paper coatings, and general-purpose adhesives. The development of new emulsion polymerization formulations can involve significant trial and error if the underlying mechanisms are not well understood. Smith and Ewart,\(^2\) and Harkins\(^3,4\) were pioneers in the development of a theory to describe the micellar nucleation mechanism in emulsion polymerization based on radical compartmentalization. While the Smith-Ewart-Harkins model provided good agreement with conventional emulsion polymerizations of hydrophobic monomers (e.g. styrene), further improvements were made to explain nucleation in the continuous phase, i.e. homogeneous nucleation,\(^5,6,7,8\) the coagulation of homogeneously nucleated particles,\(^9,10,11,12\) and the effect of monomer hydrophobicity on oligomeric radical entry and exit.\(^13,14\) The current mechanistic understanding of emulsion polymerization allows for the knowledge-based design of formulations, and several textbooks have reviewed these design strategies and applications.\(^15,16,17,18\)

Emulsions are thermodynamically unstable, and require a stabilizer to prevent particle agglomeration; the choice of stabilizer affects various facets of colloidal stability (e.g. freeze-thaw stability, shear stability, and stability in the presence of electrolytes), final product properties (e.g. adhesion, gloss, and water resistance of films), and the particle nucleation mechanism. Typical emulsion polymerizations use small molecule surfactants as stabilizers as they are well-understood and cost-effective, but the use of polymeric stabilizers is an attractive alternative due to their highly customizable nature and potential to create new product properties.\(^19,20,21,22\) In the previous chapter, it was found that polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers are effective stabilizers for high solids emulsion polymerization where analogous polystyrene-
poly(acrylic acid) block copolymer stabilizers failed. The block-random copolymers exhibited unusual behavior when dispersed in alkaline media, self-folding into single-chain nanoparticles rather than self-assembling into large aggregates. This behavior differs from other stabilizers which either exchange dynamically between solvated and micellar structures (e.g. small molecule surfactants, random copolymers) or form kinetically frozen aggregates (e.g. block copolymers). It can be predicted that the absence of micelles will rule out a micellar nucleation mechanism, while a large number of single-chain nanoparticles may preclude a homogeneous-coagulative mechanism; however, single-chain seed nanoparticles would contain a single stabilizer chain and be unable to support significant growth as seed particles. Indeed, the mechanism of an emulsion polymerization with this type of stabilizer does not appear to be straightforward, and elucidation of this mechanism is investigated herein.

7.2 Experimental

7.2.1 Materials

Styrene (4-tert-butylcatechol as a stabilizer, ≥99%), divinylbenzene (4-tert-butylcatechol as a stabilizer, ≥80%), ammonium persulfate (APS; >98%), and sodium hydroxide (>98%) were purchased from Sigma-Aldrich and used as received. Sulfuric acid (95 %w/w) and hydroquinone (crystalline/laboratory) were purchased from Fisher Scientific and used as received. All water used in this work was in-house distilled water that was further purified (18.2 MΩ-cm) using a Millipore Synergy water purification system equipped with SynergyPak purification cartridges.
7.2.2 Polystyrene-b-[polystyrene-r-poly(acrylic acid)] Stabilizer

The polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymer (BR2) used herein was synthesized and used in the previous chapter. The chemical structure of this stabilizer is shown in Scheme 7.1 and its properties reported in Table 6.5.

**Scheme 7.1.** The structure of polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymer used in this work, as well as the SG1 nitroxide used in synthesis.

Table 7.1. Characterization of polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymer BR2.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Anchor block</th>
<th>Stabilizing Block</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DP_{PS}^{a}</td>
<td>DP_{PS}^{b}</td>
<td>M_{n}</td>
</tr>
<tr>
<td>BR2</td>
<td>51</td>
<td>87</td>
<td>16400</td>
</tr>
<tr>
<td></td>
<td>M_{n}^{b}</td>
<td>M_{n}^{c}</td>
<td>D</td>
</tr>
<tr>
<td>5600</td>
<td>1.10</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>1.10</td>
<td>22</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

- ^{a} Degree of polymerization determined from GPC molecular weight.
- ^{b} Degree of polymerization based on ¹H NMR block copolymer composition.
- ^{c} Molar percentage of poly(acrylic acid) in copolymer determined by ¹H NMR.
- ^{d} M_{n} for the methylated copolymer, polystyrene-b-poly(methyl acrylate), reported as polystyrene equivalent.

7.2.3 Preparation of Aqueous Block-Random Copolymer Dispersions

Block-random copolymer was added to a 20 mL glass vial, to which appropriate amounts of water and a 1 M sodium hydroxide solution were added to produce a specific block-random copolymer concentration (e.g. 70 g/L) with a stoichiometric equivalent of base relative to carboxylic acid units. The vial was then tightly sealed with a plastic cap and heated at 80 °C with magnetic stirring for 30 minutes, during which a colorless transparent dispersion formed. In some
experiments, the effects of the monomer on dispersion properties were studied by adding styrene to a dispersion after cooling to room temperature and stirring for one hour.

### 7.2.4 Emulsion Polymerization Procedure

A standard batch emulsion polymerization of styrene procedure began by adding styrene monomer, deionized water, sodium hydroxide (50 mM), and ammonium persulfate to an aqueous copolymer dispersion. This mixture was then sealed in a 5 mL flask and immersed in an 85 °C bath of silicone oil with magnetic stirring. Emulsion polymerizations were allowed to continue for 4 hours to achieve high conversion of monomer. Stabilizer concentration, initiator concentration, monomer fraction, and stirring were varied as required.

### 7.2.5 Evaluation of Block Copolymer Aggregate and Emulsion Properties

Conversion of emulsion polymerizations was determined gravimetrically by the addition of 100 μL of a 0.1 mol/L hydroquinone solution to 500 μL of the emulsion, followed by drying in an 85 °C vacuum oven. Hydrodynamic diameters of particles were determined with a Malvern Zetasizer Nano ZS at 25°C with non-invasive backscatter optics (173°), using a 4 mW He-Ne (633 nm) laser. All samples were measured in quartz cuvettes. All data was processed using the Malvern Dispersion Technology Software (version 7.11). Block copolymer aggregate dispersions were measured directly, while latex samples were diluted with alkaline (50 mM NaOH) water to obtain an appropriate level of scattering for measurement. Latex samples below full monomer conversion were diluted using alkaline water saturated with styrene to avoid altering the monomer concentration in the latex particles prior to measurement. All reported dynamic light scattering (DLS) measurements are an average of 30 sequential measurements.

The number of latex particles (L⁻¹) was calculated using eq 7.1:
\[ N_p = \frac{6\tau}{\pi \nu_{poly} \rho D_n^3} \]  \hspace{1cm} (7.1)

with \( \tau \) being the polymer content of the latex (g/L) determined by gravimetry, \( \rho \) the density of polystyrene (1.05 g/cm\(^3\)), and \( D_n \) the number-average diameter of the polystyrene core measured by DLS, and \( \nu_{poly} \) the volume fraction of polymer in the particles during size measurement (e.g. 1 for full conversion latex).

The total surface area of latex particles is calculated assuming all particles are spheres:

\[ S_{A_{total}} = N_p 4\pi \left( \frac{D_n}{2} \right)^2 \]  \hspace{1cm} (7.2)

### 7.2.6 Conductometric Titration of Acid Groups in Latex

To determine the number of titratable acid groups in a latex, the latex was diluted with a 5 mM solution of sodium hydroxide to make up 10 mL. The conductivity of the diluted latex was then measured using an S470 SevenExcellence™ pH/Conductivity meter as 5 \( \mu \)L aliquots of 0.5 N sulfuric acid were added.

### 7.2.7 AFM Analysis of Particles

AFM images were made using a Bruker Nanoscope IV multimode scanning probe microscope with ‘E’ scanner (15 \( \mu \)m x 15 \( \mu \)m scan size) in tapping mode with probes from nanoScience Instruments (aluminum reflex coating, 2 nm “super sharp” tip radius, 125 \( \mu \)m cantilever, 40 N/m force constant, 200-300 kHz resonant frequency).
7.3 Results and Discussion

7.3.1 Stabilizer Concentration

Determining the relationship between stabilizer concentration, [S], and the number of particles produced in an emulsion polymerization is perhaps the first logical step when investigating how the particle nucleation mechanism is affected by the stabilizer. The number of particles will be proportional to [S]^{\alpha}, where the exponent \alpha will be indicative of the type of nucleation mechanism; for example, in the theoretical treatment of micellar nucleation proposed by Smith and Ewart the exponent \alpha will be 0.6,\textsuperscript{2} whereas in a seeded mechanism the exponent \alpha will be approximately 1. In this section, emulsion polymerizations of styrene have been conducted using concentrations of the stabilizer BR2 between 0 and 4 mM, while keeping all other concentrations constant. The final number of particles produced in each of these emulsion polymerizations was determined using eq 7.1 and are plotted as a function of BR2 concentration in Figure 7.1.

Figure 7.1. The final number of particles produced in emulsion polymerizations of styrene (20 wt\% monomer, 10 mM APS) as a function of the concentration of block-random copolymer
stabilizer (BR2) concentration. The inset shows data points between 0 and 1.2 mM enlarged scale. Dotted line and equation are a power fit to the data points.

It is immediately apparent from Figure 7.1 that the block-random copolymer stabilizer results in a nucleation mechanism different from either traditional micellar or seeded nucleation mechanisms. For comparison, Figure 7.2 shows the typical relationships between the number of particles and stabilizer concentration in seeded and micellar nucleation mechanisms overlaid with the relationship found in this work.

**Figure 7.2.** The relationship between the number of particles and stabilizer concentration for emulsion polymerizations with a seeded (α = 1) or micellar (α = 0.4-0.8) nucleation mechanism, overlaid with the trend observed in this work (α = 3).

A power fit to the data points in Figure 7.1 results in an α value of approximately 3, which exceeds any value of α published in emulsion polymerization literature. Indeed, values of α greater than 1 are uncommon, and the next highest examples found were α values between 1.7 and 2.1 resulting from the use a poly(vinyl acetate)-b-poly(ethylene oxide) copolymers stabilizers in the emulsion polymerization of styrene;\(^\text{23}\) the authors attributed this result to the nucleation of particles throughout the polymerization, i.e. continuous nucleation. The first hint at understanding the
nucleation mechanism responsible for the abnormally high $\alpha$ value of BR2 comes from converting the number of particles into the total particle surface area, shown in Figure 7.3.

![Figure 7.3](image-url)

**Figure 7.3.** Total surface area of latex particles as a function of block-random copolymer stabilizer (BR2) concentration. Dotted line and equation is a linear fit to the data points.

Figure 7.3 shows a strikingly linear relationship between the total particle surface area and the concentration of block-random copolymer stabilizer used in the emulsion polymerization. In a typical emulsion polymerization the total particle surface area is dependent upon the number and size of particles; in contrast, in emulsion polymerizations stabilized by BR2, it appears that the number and size of particles may be dependent on the total surface area, which is directly proportional to the stabilizer concentration. This relationship between surface area and stabilizer concentration will form the basis of a full theory in a later section.

### 7.3.2 Initiation and Particle Growth Rate

*Ab initio* emulsion polymerization nucleation mechanisms, such as micellar and homogenous-coagulative, are kinetically controlled so that the total number of particles is dependent on kinetic parameters such as the rate of initiation and particle growth; studying the effects of such parameters is, therefore, a good starting place to understanding an unknown nucleation mechanism. In this
section, the effects of both initiation rate and particle volume growth rate on the number of particles are studied. First, the initiation rate was studied by varying the concentration of initiator (7 to 53 mM) to avoid affecting other temperature-sensitive mechanisms such as propagation. The resulting number of particles and total particle surface area are shown in Figure 7.4 as a function of initial initiator concentration.

![Graph showing the relationship between [APS] and Np or Total Particle Surface](image)

**Figure 7.4.** Total number (left) and surface area (right) of particles produced by emulsion polymerization with varying concentrations of APS initiator. The total weight fraction of monomer was 20% monomer, and block-random copolymer stabilizer (BR2) concentration was 0.5 mM stabilizer. Dotted line (left) shows expected number of particles based on the first data point and assuming a Smith-Ewart micellar nucleation model (Np proportional to [APS]0.4).

Figure 7.4 shows that an increase in the initiation rate does not increase the number of particles as expected in a micellar nucleation model, and the total surface area of particles remained relatively constant. The observed trend in Figure 7.4 is instead indicative of a seeded nucleation mechanism, where the rate of initiation does not affect the number of particles.

Next, the effect of particle volume growth rate on particle nucleation was studied at two extremes: monomer flooded and starved. Under flooded conditions, all of the monomer was added to the system and stirred well to ensure particle volume growth was propagation-limited. Under
starved conditions, all of the monomer was added to the system without stirring, resulting in a system where the monomer supply to particles was limited by diffusion across a relatively minuscule surface area. Additionally, a second starved emulsion polymerization was conducted at lower solids content. In both starved cases, stirring was commenced after 30 minutes and the emulsion polymerization allowed to reach full conversion. The characteristics of emulsion polymerizations where the particle volume growth rate was controlled by monomer flooded (stirring) or starved (no stirring) conditions are shown in Table 7.2.

**Table 7.2.** Final characteristics of emulsion polymerizations stabilized by a block-random copolymer (BR2, 0.5 mM) prepared under flooded and starved monomer conditions (10 mM APS initiator).

<table>
<thead>
<tr>
<th>Stirring</th>
<th>Polymer weight fraction (%)</th>
<th>$D_n$ (nm)</th>
<th>$N_p$ ($\times 10^{16}$ L$^{-1}$)</th>
<th>SA ($\times 10^{21}$ nm$^2$/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire reaction</td>
<td>20</td>
<td>288</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Started after 0.5 hr</td>
<td>20</td>
<td>282</td>
<td>1.6</td>
<td>4.0</td>
</tr>
<tr>
<td>Started after 0.5 hr</td>
<td>4</td>
<td>82</td>
<td>20</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Despite a significant period of non-stirring (monomer starved conditions) at the beginning of emulsion polymerizations stabilized by BR2, the total number of particles remained approximately the same. In a micellar nucleation mechanism, it would be expected that starved monomer conditions would lead to a greater number of micelles being nucleated, and therefore a greater final number of particles. Alternatively, in a seeded mechanism, the rate of particle volume growth would not change the number of particles, which is consistent with the results in Table 7.2.

The results in this section demonstrate that the rate of initiation and particle volume growth do not have a significant effect on the number of particles produced in emulsion polymerizations stabilized by the block-random copolymer BR2. These results suggest that the nucleation mechanism may not be kinetically controlled, as expected in seeded emulsion polymerization, but
the previously determined relationship between the number of particles and stabilizer concentration make it clear that it is not a seeded mechanism either. Comparing the total particle surface areas of the emulsion polymerizations in Table 7.2, it can be seen that despite an order of magnitude difference in the number of particles, the total particle surface area was approximately the same. Combined with the linear relationship between total particle surface area and stabilizer concentration presented in the previous section, these observations provide evidence that a thermodynamically controlled mechanism may be responsible.

7.3.3 Swelling Block-Random Copolymer Dispersion with Monomer

Evidence presented in previous sections suggests that a thermodynamic nucleation mechanism exists in emulsion polymerizations stabilized with the block-random copolymer BR2. It is, therefore, interesting to observe the thermodynamic behavior of these systems in the absence of kinetic processes, i.e. polymerization. Styrene monomer was added to dispersions of BR2 and stirred without initiator or increased temperature to avoid polymerization, allowing a thermodynamic equilibrium to be reached. The effect of using different weight fractions of monomer was studied, and the characteristics of these emulsions (not polymerizations) are reported in Table 7.3.
Table 7.3. Characteristics of emulsions prepared by addition of styrene monomer to aqueous dispersions (3 mM) of block-random copolymer BR2. A photograph of each dispersion is shown above the corresponding column (object in bottom of vial is a stir bar).

<table>
<thead>
<tr>
<th>$\tau$ (g/L)$^a$</th>
<th>41</th>
<th>48</th>
<th>53</th>
<th>58</th>
<th>70</th>
<th>78</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_n$ (nm)</td>
<td>9</td>
<td>15</td>
<td>18</td>
<td>20</td>
<td>21</td>
<td>27</td>
</tr>
<tr>
<td>$D_{n,2}$ (nm)$^b$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1018</td>
<td>1312</td>
</tr>
<tr>
<td>PDI</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.35</td>
<td>0.7</td>
<td>0.88</td>
</tr>
<tr>
<td>$N_p$ ($x 10^{19}$/L)</td>
<td>10</td>
<td>2.6</td>
<td>1.6</td>
<td>1.3</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>SA ($x 10^{22}$ nm$^2$/L)$^c$</td>
<td>2.6</td>
<td>1.8</td>
<td>1.7</td>
<td>1.7</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>$v_m$ in droplet$^d$</td>
<td>0.35</td>
<td>0.46</td>
<td>0.51</td>
<td>0.56</td>
<td>0.64</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Only nano-droplets present

Mixture of nano- and micro-droplets

$^a$ $\tau$ is the weight fraction of the dispersed phase (monomer and stabilizer) in the system.

$^b$ $D_{n,2}$ is the second number-average peak detected by DLS, if present.

$^c$ SA is the total surface area of particles.

$^d$ $v_m$ is the volume fraction of monomer based on the block-random copolymer.

As shown in Chapter 6, in the absence of monomer, dispersions of BR2 form very small particles ($\approx$ 4 nm diameter) consistent with the size of single-chain nanoparticles. The results in Table 7.3 demonstrate that the presence of styrene monomer in dispersions of BR2 leads to a rearrangement of the block-random copolymer chains, with greater weight fractions of monomer resulting in larger nanoparticles; recall that there is no initiation or polymerization here, but rather a thermodynamically driven rearrangement. As the volume fraction of monomer (based on BR2) increased from 35 to 56%, the number of particles decreased by an order of magnitude which indicates that block-random copolymer stabilized nanoparticles must be coagulating. The
thermodynamic driving force behind the coagulation of these nanoparticles appears to be the conservation of surface area; the creation of new particle surface area without increasing the amount of stabilizer will incur an energy penalty, so the coagulation of particles to conserve overall surface area will be an exergonic process. Although the total surface area of the nanoparticles was constant relative to the change in the number of nanoparticles, it did decrease as the diameter of the particles increased, suggesting that the surface area stabilized per copolymer chain may be dependent on particle surface curvature. In Table 7.3 there also appears to be a critical volume fraction of monomer where the block-random copolymer is saturated with the monomer (around 0.6 monomer volume fraction) and additional monomer in the system remains as larger micron sized droplets. The monomer saturated nanoparticles will almost certainly be the loci of nucleation in emulsion polymerization due to their large numbers (10^{19} \text{ L}^{-1}), but their large concentration also means that they must coagulate with each other to explain the lower concentration of particles at full conversion. This is very suggestive of a continuously coagulative particle growth mechanism.

7.3.4 A Seeded-Coagulative Emulsion Polymerization

Several conclusions can be made from the experimental observations discussed so far regarding the stabilization of an emulsion polymerization by block-random copolymer BR2:

- The total particle surface area is directly proportional to stabilizer concentration.
- The number of particles is not affected by the kinetic processes of initiation or particle volume growth.
- Swelling of block-random copolymer nanoparticles leads to their coagulation into larger monomer swollen nanoparticles; these nanoparticles are most likely the loci of particle nucleation.
Based on these conclusions, a theoretical emulsion polymerization mechanism is proposed in which an initial population of seed particles grows by both polymerization and coagulation such that the total surface area of particles is conserved. This mechanism is proposed to occur in two stages which are described and illustrated in Figure 7.5.

**Stage 1**

- Stabilizer spontaneously emulsifies a fraction of monomer into nano-droplets, remaining monomer exists as large droplets or as a separate phase.
- Radicals primarily nucleate nano-droplets.
- Nano-droplets grow and coagulate to conserve total surface area.
- Large monomer droplets act as reservoir.

**Stage 2**

- Monomer reservoirs are depleted.
- The number of particles remains constant.
- Increasing particle viscosity decreases termination rate, leading to an increase in polymerization rate ("gel" effect).
- Monomer in particles polymerized until full conversion.

**Figure 7.5.** The two proposed stages of a “seeded-coagulative” emulsion polymerization mechanism.

In a seeded emulsion polymerization, seed particles are present prior to initiation, and each seed particle is nucleated such that the number of particles remains constant. While the mechanism
proposed here also begins with a large population of seed particles, the total surface area of particles, rather than the number of particles, is held constant as a result of continuous particle coagulation. Therefore, “seeded-coagulative” seems like an appropriate name to describe this emulsion polymerization mechanism.

It is curious that the seeded-coagulative mechanism described in Figure 7.5 has not been previously observed, suggesting that it may be unique to the stabilizer used in this work. In order for a stabilizer to result in this type of thermodynamically controlled emulsion polymerization, it must meet two design requirements:

1. Stabilizer must produce seed particles; must be anchored to the dispersed phase rather than readily exchanging through the continuous phase.
2. Initial particles must have insufficient stabilization for further growth; e.g. additional stabilizer must not be added, and stabilizer must not form aggregates with aggregation number large enough to sustain growth.

A stabilizer that only meets requirement 1 will result in a seeded nucleation mechanism, while a stabilizer than only meets requirement 2 will result in a micellar nucleation mechanism, as shown in Table 7.4.

Table 7.4. Comparison of common emulsion polymerization stabilizers based on the requirements satisfied for a seeded-coagulative nucleation mechanism.

<table>
<thead>
<tr>
<th>Seed behavior</th>
<th>Small molecule surfactant</th>
<th>Random copolymer</th>
<th>Block copolymer</th>
<th>Block-random copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seed behavior</td>
<td>No</td>
<td>No</td>
<td>Yes (if sufficient anchoring block)</td>
<td>Yes</td>
</tr>
<tr>
<td>Unstable seed growth</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Nucleation Mechanism</td>
<td>Micellar</td>
<td>Micellar</td>
<td>Seeded</td>
<td>Seeded-coagulative</td>
</tr>
</tbody>
</table>
It follows that both micellar and seeded nucleation mechanisms could be converted into a
seeded-coagulative mechanism under the proper conditions. For example, if additional stabilizer
was not added to a micellar or seeded emulsion polymerization, or the polymerization was
continued indefinitely, the particles would eventually become unstable and coagulate to conserve
surface area, becoming a seeded-coagulative mechanism. Likewise, in a typical micellar
nucleation mechanism, if every micelle were instantaneously nucleated, micelles would behave as
seed particles (i.e. unable to dissociate) and likely follow a seeded-coagulative mechanism.

It is important to note that the conservation of total particle surface area is an experimental
observation and further experiments will be required to understand the fundamental physical
mechanism(s) responsible for this phenomena. It is postulated that the conservation of surface
charge density, in this case the surface density of acrylate anions at the particle/water interface,
may be a driving force in the conservation of surface area.

7.3.5 Instantaneous Equations for Seeded-Coagulative Theory

The previous section has introduced a novel emulsion polymerization mechanism, referred to
here as seeded-coagulative emulsion polymerization. While the fundamental concepts of this
mechanism have been described, mathematical equations describing this mechanism must be
developed in order to test its ability to explain and predict experimental results. The main
assumptions required for this mechanism are as follow:

1. Total particle surface area is equal to the total surface area of stabilizing chains at the
particle/water interface,

\[ a_s[S]_{\text{int}}N_A = N_p 4\pi R^2 \] (7.3)

where \( a_s \) is the surface area covered by a single stabilizer chain (cm\(^2\)), \([S]_{\text{int}}\) is the
concentration of stabilizer chains that exist at a particle/water interface (mol/L), \( N_A \) is
Avogadro’s constant (6.022x10^{23} \text{ mol}^{-1}), N_p is the number of particles (L^{-1}), and R is the number-average particle radius (cm). Here, a_s is assumed to be constant, but is experimentally observed to increase for small particle sizes (e.g. R < 25 nm).

2. Stabilizer chains exist only at the interface (neglect chains that are in the particle or aqueous phase),

\[ [S]_{\text{int}} = [S] \]

where [S] is the total stabilizer concentration in the system (mol/L).

3. Particles will coagulate to conserve total surface area, i.e. total particle surface area is constant.

4. Particles are spherical.

Under these assumptions, instantaneous equations for the number of particles (eq 7.4), particle diameter (eq 7.5), and solids content (eq 7.6) have been derived for Stage 1 of the seeded-coagulative mechanism which ends when monomer droplets have been depleted \( (t = t_d) \); the complete derivations for these equations can be found in Appendix C.

Number of particles (L^{-1}):

\[
N_p(t) = \frac{(a_s[S]N_A)^3}{36\pi \left( \frac{k_p[M]_p\bar{s}M(a_s[S]N_A)^3}{12\pi n_{poly}p_{poly}N_A} \right)^{\frac{2}{3}}} \quad (7.4)
\]

Number-average particle diameter (cm):

\[
D(t) = 2 \left( \frac{9 \left( \frac{k_p[M]_p\bar{s}M(a_s[S]N_A)^3}{12\pi n_{poly}p_{poly}N_A} \right)^{\frac{2}{3}}}{(a_s[S]N_A)^2} \right)^{-\frac{1}{2}} \quad (7.5)
\]

Solids content (g/L):
\[
\tau(t) = v_{\text{poly}} \rho_{\text{poly}} \left( \frac{k_p [M]_p \bar{n} M (a_s S) N_A}{12 \pi v_{\text{poly}} \rho_{\text{poly}} N_A} \right)^{\frac{1}{3}} + \tau_0
\] 

Variables:
- \(t\): time (seconds),
- \(M\): molecular weight of the monomer (104.15 g mol\(^{-1}\)),
- \(\rho_{\text{poly}}\): density of the polymer (1.05 g cm\(^{-3}\)),
- \(\rho_m\): density of the monomer (0.909 g cm\(^{-3}\)),
- \(v_{\text{poly}}\): volume fraction of polymer in a particle,
- \(k_p\): rate constant for chain propagation (L mol\(^{-1}\) s\(^{-1}\)),
- \([M]_p\): monomer concentration in a particle (mol L\(^{-1}\)),
- \(\bar{n}\): average number of radicals in a particle (assumed to be 0.5 for hydrophobic monomers in small particles\(^{15}\)).

Stage 2 of the mechanism has not been modeled in this Chapter but will follow the same kinetics as a typical emulsion polymerization after monomer reservoirs (droplets) have been depleted (Interval III), which has been previously modeled\(^{24,25}\). Modelling of this stage is typically complicated by the fact that a decrease in monomer concentration results in a decreased diffusivity of radicals, and thus a decreased rate of termination; this is the equivalent to the “gel” or Trommsdorff effect in bulk polymerization\(^{26,27}\) and is often referred to as pseudo-bulk kinetics in emulsion polymerization. The average number of radicals in a particle, \(\bar{n}\), increases as the rate of termination in particles decreases, leading to an autoacceleration of the polymerization rate. Due to the complicated relationships between the monomer concentration in particles, the rate of termination, and \(\bar{n}\), modelling of this stage is not reported here, although an example of how it could be done is reported in Appendix C. Although Stage 2 is not modelled, the end points of this stage are either known (e.g. number of particles is constant after Stage 1, final solids content is known) or can be calculated by the analytical solutions for Stage 1 corrected for full conversion.
(e.g. particle diameter). Convenient equations for the final number and diameter of particles, i.e. at the end of Stage 2, are reported below.

Final number of particles (L⁻¹; assuming \( \rho_m \approx \rho_{poly} \), t = tᵢ):

\[
N_p(t_f) = \frac{(a_s[S]N_A)^3}{36\pi \left( \frac{\tau_{tot}}{\rho_{poly}} \right)^2}
\]  

(7.7)

Final particle diameter (cm; t = tᵢ):

\[
D(t_f) = 2 \left( \frac{(1 - v_{poly,t_d})\rho_m + v_{poly,t_d}\rho_{poly}}{\rho_{poly}} \right)^{\frac{1}{3}} \left( \frac{3\tau_{tot}}{(a_s[S]N_A)^2} \right)^\frac{1}{2} \left( \frac{(1 - v_{poly,t_d})\rho_m + v_{poly,t_d}\rho_{poly}}{\rho_{poly}} \right)
\]

(7.8)

7.3.6 Comparison of Model with Experimental Results

Now that mathematical equations have been developed to describe the proposed seeded-coagulative model, these equations will be used in this section to explain and predict the experimental data. First, eq 7.7 has been used to fit the experimentally determined number of particles as a function of stabilizer concentration, using the surface area per stabilizer \( (a_s) \) as the fitting parameter. Figure 7.1 has been re-plotted in Figure 7.6 to show the seeded-coagulative model fit to the experimental data.
Figure 7.6. The final number of particles produced in emulsion polymerizations of styrene (20 wt% monomer, 10 mM APS) as a function of the concentration of block-random copolymer stabilizer (BR2) concentration. Dotted line shows the fit of the seeded-coagulative model (eq 7.7) to the data points (fit using $a_s = 11 \text{ nm}^2$).

As already shown in Figure 7.1, the number of particles is proportional to the stabilizer concentration cubed, and this proportionality is exhibited by the seeded-coagulative model in Figure 7.6. It is also evident from eq 7.7 that the number of particles will be proportional to the inverse-square of the total solids content, $\tau$; to confirm this, several emulsion polymerizations were conducted with varying total solids content while keeping all other parameters constant, and the resulting number of particles was calculated. As shown in Figure 7.7, the number of particles decreases as the total solids content is increased and appears to follow the inverse-square relationship predicted by the seeded-coagulative mechanism.
Figure 7.7. The final number of particles produced in emulsion polymerizations of styrene (2 mM BR2 as stabilizer, 10 mM APS) as a function of the solids content. Dotted line shows the fit of the seeded-coagulative model (eq 7.7) to the data points (fit using $a_s = 8 \text{ nm}^2$). The inset shows data points between 0 and $2 \times 10^{18}$ particles/L with enlarged scale.

While Figure 7.6 and Figure 7.7 show that the seeded-coagulative model predicts the final state of emulsion polymerizations stabilized with BR2, the instantaneous equations for the first stage of the seeded-coagulative model may be used to explain kinetic data obtained by stopping replicate emulsion polymerizations at different times. The conditions used in this kinetic experiment are presented in Table 7.5, along with the parameters used to fit the instantaneous equations.
Table 7.5. Styrene emulsion polymerization conditions used for kinetic study and parameters used to compare with theoretical seeded-coagulative model.

<table>
<thead>
<tr>
<th>Polymerization Conditions</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, temperature</td>
<td>85</td>
<td>°C</td>
</tr>
<tr>
<td>(\tau), target solids content</td>
<td>126</td>
<td>g L(^{-1})</td>
</tr>
<tr>
<td>[APS], concentration of APS initiator</td>
<td>5x10(^{-3})</td>
<td>mol L(^{-1})</td>
</tr>
<tr>
<td>[S], concentration of stabilizer (BR2) chains(^a)</td>
<td>4x10(^{-4})</td>
<td>mol L(^{-1})</td>
</tr>
</tbody>
</table>

Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>t, time</td>
<td>-</td>
<td>s</td>
</tr>
<tr>
<td>(N_A), Avogadro’s constant</td>
<td>6.022x10(^{23})</td>
<td>mol(^{-1})</td>
</tr>
<tr>
<td>([M]_p), saturation concentration of styrene in particle(^28)</td>
<td>5.8</td>
<td>mol L(^{-1})</td>
</tr>
<tr>
<td>(v_{pol}), volume fraction of polymer in a particle</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>M, molecular weight of the monomer</td>
<td>104.15</td>
<td>g mol(^{-1})</td>
</tr>
<tr>
<td>(k_p), rate constant for chain propagation of styrene(^b)</td>
<td>950</td>
<td>L mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>(\rho_{pol}), density of the polymer</td>
<td>1.05</td>
<td>g cm(^{-3})</td>
</tr>
<tr>
<td>(\rho_m), density of the monomer</td>
<td>0.909</td>
<td>g cm(^{-3})</td>
</tr>
<tr>
<td>(n), average number of radicals in a particle</td>
<td>0.35 (fit)</td>
<td>-</td>
</tr>
<tr>
<td>(a_s), the surface area covered by a single stabilizer chain</td>
<td>1.3x10(^{-13}) (fit)</td>
<td>cm(^2)</td>
</tr>
<tr>
<td>(\tau_o), initial solids content</td>
<td>6</td>
<td>g L(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\)Low stabilizer concentration was chosen to target larger changes in diameter and \(N_p\).

\(^b\)The \(k_p\) for styrene under the reaction conditions (85 °C) was from an activation energy (\(E_a\)) of 33.6 kJ/mol and Arrhenius coefficient (A) of 7.6x10\(^7\) L mol\(^{-1}\) s\(^{-1}\).\(^29\)

Figure 7.8 confirms that the number of particles in an emulsion polymerization stabilized by BR2 decreases as conversion increases, and follows the trend predicted by the seeded-coagulative model (eq 7.4).
Figure 7.8. The experimental number of particles as a function of time calculated using eq 7.1 (with $v_{\text{poly}} = 0.34$). The dashed black line is Stage 1 of the theoretical seeded-coagulative model (eq 7.4) fit using parameters in Table 7.5. The dashed red line shows a constant number of particles in Stage 2 of the model.

Measurement of particle diameter throughout an emulsion polymerization stabilized by BR2 shows that particle size grows rapidly, reaching a final size of $\approx 220$ nm after only half an hour. For comparison, in a typical emulsion polymerization without coagulation the maximum volume growth rate of a particle ($\text{cm}^3/\text{s}$) will be:

$$\frac{dV}{dt} = \frac{k_p [M]_p \bar{n} M}{v_{\text{poly}} P_{\text{poly}} N_A}$$ (7.9)

And the particle diameter as a function of time in this non-coagulative case will be (cm):

$$D(t) = 2 \left( \frac{3k_p [M]_p \bar{n} M}{4\pi v_{\text{poly}} P_{\text{poly}} N_A} t \right)^{\frac{1}{3}}$$ (7.10)

By comparing the instantaneous particle diameters predicted by a typical emulsion polymerization (eq 7.10) and a seeded-coagulative emulsion polymerization (eq 7.5) to the
experimentally measure particle diameters in Figure 7.9, it is obvious that the particle growth rate exceeds what is possible with growth by polymerization only.

**Figure 7.9.** Experimental number-average particle diameter as a function of time measured by DLS. The dashed black line is Stage 1 of the theoretical seeded-coagulative model (eq 7.5) fit using parameters in Table 7.5. Dashed blue ($\bar{n} = 0.5$) and dotted purple ($\bar{n} = 0.35$) lines show the maximum diameter growth rate in the absence of coagulation (i.e. growth by polymerization and monomer swelling only) calculated using eq 7.10 with parameters from Table 7.5.

Finally, the solids content of the emulsion polymerization agreed with the trend expected from a seeded-coagulative emulsion polymerization (Figure 7.10), showing a rapid initial growth rate which then slowed down (Stage 1), followed by an increase in growth rate until reaching full conversion (Stage 2); this trend is similar to the S-shaped curve expected in a typical emulsion polymerization, where autoacceleration of the polymerization rate occurs after monomer droplet depletion.
Figure 7.10. Experimental solids content as a function of time measured gravimetrically. The dashed black line is Stage 1 of the theoretical seeded-coagulative model (eq 7.6) fit using parameters in Table 7.5, and ends after approximately 35 minutes with the depletion of monomer droplets.

The close agreement between the experimental observations and theoretical predictions in this section provide further evidence that a seeded-coagulative mechanism is dominant in emulsion polymerizations stabilized by BR2.

7.3.7 Conservation of Total Surface Area and Surface Acid

While the results presented in previous sections strongly suggest that the conservation of total particle surface area is the driving force behind the seeded-coagulative mechanism, this appears to contradict an observed decrease in total particle surface area as the particle size increases; this effect is shown in both Table 7.3 and Figure 7.11 (experiments from Figure 7.7 re-plotted to show the total particle surface area as a function of particle diameter).
Figure 7.11. The total surface area of particles as a function of their number-average diameter. Same emulsion polymerizations from Figure 7.7 (emulsion polymerizations of styrene with 2 mM BR2 as stabilizer and 10 mM APS). Total surface area appears to remain constant for particle diameters above approximately 50 nm.

According to eq 7.3, a decrease in the total surface area of particles would indicate either a decrease in the concentration of stabilizer at the particle/water interface, or a decrease in the surface area stabilized per stabilizer chain, $a_s$. It was hypothesized that during particle coagulation, some stabilizer chains may become “buried” within particles, and therefore decrease the concentration of stabilizer chains at the particle/water interface. To test this hypothesis, conductometric titration was performed to determine the total number of titratable weak acid groups in a series of latexes stabilized by BR2 with varying solid contents; this is an established technique for the quantification of weak acid groups on the surface of latex particles. The resulting conductometric titration curves are presented in Figure 7.12.
The conductometric titration curves in Figure 7.12 show an initial negative slope due to the replacement of hydroxyl anions with less mobile sulfate anions, followed by a positive slope due to the replacement of immobile weak acid anions (e.g. carboxylates) with sulfate anions. A gradual decrease in the slope of the weak acid region was attributed to a change in measurement conditions due to the destabilization of the polymer particles; the same phenomenon was observed in the titration of a BR2 dispersion. The end of the weak acid titration is marked by a final increase in slope due to excess sulfuric acid. The total amount of titratable weak acid groups in an emulsion polymerization was determined from each respective curve and compared to the particle diameter in Figure 7.13, along with the calculated surface area per stabilizing chain.
As shown in Figure 7.13, the total amount of weak acid in emulsion polymerizations was unaffected by the solids content or particle diameter and suggests that the number of stabilizing chains which are “buried” during coagulation is negligible, with most chains remaining at the particle/water interface throughout an emulsion polymerization. It is, therefore, the conclusion of this section that the surface area stabilized per block-random stabilizer chain, $a_s$, has a dependence on particle diameter which becomes significant when particle diameter is below approximately 50 nm (Figure 7.13); this dependence will limit the predictive capability of the seeded-coagulative model, which assumes constant $a_s$, in this smaller particle size regime.

**7.3.8 Evidence of Particle Coagulation from AFM**

The seeded-coagulative mechanism proposed in this work makes the assumption that particles will coagulate such that the total particle surface area remains constant. The purpose of this section is to provide further evidence that particle coagulation occurs by examining the morphology of these particles. Under certain conditions, the characterization of a latex particle may reveal clues...
to the mechanism responsible for its formation; for example, a particle with a core-shell structure provides evidence of a seeded or stepwise emulsion polymerization. In the case of particles formed by the coagulation and coalescence of smaller particles, the final appearance is expected to be indistinguishable from particles which have grown independently; however, if coalescence is inhibited, it may be possible to alter the final particle morphology such that particles formed by coagulation/coalescence are distinct from particles formed by independent growth. This strategy has been implemented in emulsion polymerizations stabilized by BR2 in two ways: (i) particles were grown under monomer starved conditions, such that particles have a high volume fraction of polymer and viscosity, and (ii) particles were grown in the presence of a cross-linking agent such that the morphology of particles was retained after coagulation. Following each polymerization, particles were analyzed by AFM, and the results of these experiments are shown in Figure 7.14.
<table>
<thead>
<tr>
<th>Batch</th>
<th>Monomer starved</th>
<th>Cross-linked particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 g/L styrene</td>
<td>200 g/L styrene (never stirred, low solids after 4 hours)</td>
<td>200 g/L (80 wt% styrene, 20 wt% divinylbenzene)</td>
</tr>
<tr>
<td>DLS: $D_n = 193$ nm (PDI &lt; 0.1)</td>
<td>DLS: $D_n = 107$ nm (PDI &lt; 0.1)</td>
<td>DLS: too polydisperse</td>
</tr>
</tbody>
</table>

**Figure 7.14.** AFM images of particles produced by emulsion polymerizations stabilized by BR2 (1 mM) under batch (Left), monomer starved (Middle), and cross-linked (Right) conditions. Particle coagulation is evident by the retarded coalescence that appears to a small degree in the monomer-starved case, and to a large degree in the cross-linked case.

From Figure 7.14 it is evident that particles coagulate during emulsion polymerizations stabilized by BR2. The addition of a cross-linking agent to the emulsion polymerization led to both visible coagulum, and the formation of particles with a “cluster” morphology, suggesting coagulation of smaller particles was followed by incomplete coalescence. This effect is illustrated in Figure 7.15.
In the absence of particle coagulation, cross-linking within particles may affect the swelling of those particles with the monomer but is not expected to affect the particle morphology. In the case of monomer starvation, although particle coalescence was likely retarded by the increased viscosity of particles, particles would also have a longer time period to coalesce due to the diffusion-limited polymerization rate; this may be one reason that the effect of inhibited coalescence is less noticeable here compared to the cross-linked case.

7.3.9 Other Observations: Gelation

Occasionally, when conducting emulsion polymerizations stabilized by BR2, the system would quickly form a gel, prematurely ending the emulsion polymerization. These gels were soft white solids that released a liquid (residual water/monomer) when squeezed or manipulated. The
elastic nature of these gels made it possible to remove them completely from the reacting vessel, as shown in Figure 7.16.

![Image](image_url)

**Figure 7.16.** A “latex” after gelation is easily pulled from a vial in which it was formed. Residual monomer/water remains in the vial.

Only batch polymerization systems with a high solids content target (e.g. > 40 wt%) were found to produce these gels, and not reliably; gel formation was never observed at lower solids contents or with the semi-batch addition of monomer. Dabbing gels with a pH indicating strip showed that the gels remained in an alkaline state where particles should be stable. It is hypothesized that this gelation is a result of particle coagulation occurring at a faster rate than particle coalescence. In this case, before two particles have time to coalesce with each other, they may coagulate with a third particle, followed by a fourth, and so on. Thus, rather than individual coagulation events leading to larger discrete particles, a network of coagulated particles may be formed, as illustrated in Figure 7.17.
Coalescence >> Coagulation:

Coalescence << Coagulation:

**Figure 7.17.** Illustration of particle coagulation when the rate of coagulation is slower (top) or faster (bottom) than the rate of coalescence.

This phenomenon appears to be a direct consequence of a seeded-coagulative mechanism, where a large number of coagulation events occur simultaneously during a very short period of time at the beginning of the emulsion polymerization; the number of particles may decrease one or two orders of magnitude in a matter of minutes. As gelation of a latex will be undesirable in most cases, emulsion polymerizations in which a seeded-coagulative mechanism is operative may avoid this problem by limiting the coagulation rate through the polymerization rate, e.g. by the semi-batch feed of monomer to the system or lower temperature. In this manner, coagulated particles should have sufficient time to coalesce with each other between coagulation events. If, however, gelation was desired, it will likely result from the combination of a high initial volume fraction of monomer (e.g. > 40 wt% batch polymerization), a high concentration of stabilizer (i.e. high initial number of particles), and a high polymerization rate (e.g. high temperature, high $k_p$ monomer, etc.).
7.4 Conclusions

As reported in the previous chapter, block-random copolymers with high hydrophobic composition are surprisingly effective stabilizers for high solids emulsion polymerization where block copolymer stabilizers have failed. This new type of stabilizer exhibited unusual dispersion behavior, e.g. self-folding into single-chain nanoparticles, and it was therefore of interest to study the consequences on the emulsion polymerization mechanism. In this work, it was experimentally observed that in an emulsion polymerization stabilized by block-random copolymer PS$_{51}$-b-(PS$_{87}$-r-PAA$_{25}$) the total particle surface area was directly proportional to stabilizer concentration, and the number of particles was not affected by polymerization kinetics. It was also observed that the swelling of block-random copolymer nanoparticles with monomer leads to their coagulation into larger nanoparticles which are likely the loci of particle nucleation. From these observations, a theoretical emulsion polymerization mechanism has been proposed in which a large initial population of monomer swollen seed particles grow by polymerization, and continuously coagulate such that the total surface area of particles is conserved; due to its seeded and coagulative features, this mechanism is referred to as “seeded-coagulative”. This mechanism is proposed to operate under the condition that the stabilizer produces seed particles which have insufficient stabilization for further growth without coagulation.

Mathematical equations have been developed to describe the proposed seeded-coagulative model, and are in good agreement with the experimental data; the seeded-coagulative model explains the observed dependence of emulsion properties on stabilizer concentration and solids content, and also explains the time evolution of the number of particles, particle diameter, and solids content. AFM analysis has confirmed the coagulation of particles by the observation of incomplete coalescence of particles in the presence of a cross-linking agent. A seeded-coagulative
emulsion polymerization mechanism has not been reported previously, which is likely due to the unique properties of the stabilizer required. Further studies will be needed to determine the range of block-random copolymer structures responsible for this mechanism, the potential obstacles inherent to the mechanism (e.g. gelation), and the robustness of the mechanism. The development and reproducibility of conventional emulsion polymerizations are often hindered by a dependence on kinetic processes (e.g. heat exchange, stirring, feed rates, propagation rate constants, initiator decomposition and efficiency); a thermodynamically driven seeded-coagulative mechanism which eliminates these kinetic dependencies has the potential to be a powerful new tool in the development of robust and readily scalable emulsion polymerization processes.

7.5 References


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(17) Lovell, P. A.; El-Aasser, M. S. Emulsion Polymerization and Emulsion Polymers; John Wiley and Sons Ltd., 1997.


Chapter 8
Conclusions and Recommendations

8.1 Conclusions

Achieving greater facility and economy in block copolymer synthesis may have the consequences of increased molecular weight dispersity and homopolymer impurity; the main objective of this work was to determine how these consequences would affect the performance of a block copolymer used to stabilize an emulsion polymerization. Chapters 3, 4, and 5 have shown that while greater molecular weight dispersity and homopolymer impurity did affect the solution behavior of a polystyrene-b-poly(acrylic acid) block copolymer stabilizer, there was no negative effect on the particle stability or particle size dispersity of emulsion polymerizations stabilized by the block copolymers. It is concluded that neither high molecular weight dispersity nor homopolymer impurity preclude the use of block copolymers as stabilizers in emulsion polymerization, but are rather parameters to be tuned by the polymer chemist.

While this work has improved the economic outlook of block copolymer stabilizers by demonstrating their tolerance to more economical synthetic routes, it has also identified limitations to their stabilization of emulsion polymerization. It was found that a polyelectrolyte stabilizing block can cause two problems: (i) a polyelectrolyte stabilizing block at less than complete neutralization may inhibit radical entry into seed aggregates and result in high particle size dispersity, and (ii) rod-like polyelectrolyte blocks produce a hydrodynamic corona around particles, increasing the volume fraction of particles without increasing the weight fraction, and limiting the achievable solids content in an emulsion polymerization as a result. It was clear from
Chapter 6 that a polyelectrolyte stabilizing block could severely limit the solids content of a block copolymer stabilized emulsion polymerization. By understanding the problems inherent to a polyelectrolyte stabilizing block, a new stabilizer structure was designed to solve these problems; this new structure replaced the poly(acrylic acid) stabilizing block with a polystyrene-r-poly(acrylic acid) block, based on the idea that a random copolymer would be hydrophobically bound to the particle surface rather than extended into the continuous phase. Indeed, it was found that emulsion polymerizations stabilized with these novel polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers could yield colloidally stable latexes with lower interparticle distances and solid contents up to at least 50 weight percent.

In addition to stabilizing high solids content emulsion polymerizations, the polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers were found to have an unusual solution behavior. Block-random copolymers with an overall polystyrene composition greater than 80 molar percent were readily dispersed in alkaline media, forming dispersed nanoparticles that were consistent with the size of a single self-folded copolymer chain. This prompted the investigation in Chapter 7 to determine how the emulsion polymerization mechanism is affected by this unusual stabilizer behavior. It was observed that emulsion polymerizations stabilized by a block-random copolymer had a total particle surface area which was directly proportional to the stabilizer concentration and unaffected by polymerization kinetics. This work proposes a “seeded-coagulative” emulsion polymerization mechanism where particle growth occurs both by polymerization and continuous coagulation such that the total particle surface area is conserved; in this mechanism, the number of particles is determined by the thermodynamically controlled coagulation of particles rather than kinetic factors such as initiation or polymerization rate. Mathematical equations derived for a seeded-coagulative mechanism explained the observed
dependence of the number of particles, $N_p$, on stabilizer concentration ($N_p \sim [S]^3$) and solids content ($N_p \sim \tau^2$), which could not be explained by any other known emulsion polymerization mechanism.

As is the nature of research, for every question answered by this work, another question has been created. While it has been demonstrated that block copolymer stabilizers are useful despite dispersity and impurity, this begets the questions of where else this may hold true. Likewise, the introduction of an improved stabilizer structure and novel emulsion polymerization mechanism will open new research opportunities, some of which are discussed in the following section.

8.2 Recommendations for Future Work

This work shows that when designing block copolymers, specifically those used to stabilize emulsion polymerizations, the most important properties are their topology and composition, not their molecular weight dispersity. In other words, the production of blocks using living polymerization is far more important than controlling the molecular weight dispersity of the blocks. Accordingly, the assumption that low molecular weight dispersity is required in a specific application should be challenged experimentally, especially where such an assumption limits economic practicality. A general recommendation based on this work would be that those designing block copolymer materials should consider properties such as high molecular weight dispersity and homopolymer impurity as potential design parameters, as they were shown to be in this work. While low molecular weight dispersity and impurities are good indicators of a controlled and living polymerization, the correlation of these indicators with final polymer properties is often unjustified, and discourages the production or use of polymers in environments where these characteristics are not technically or economically achievable, e.g. an industrial-scale production environment.
Another general recommendation is the continued research of polymeric surfactants. This work has shown that even a small change in an amphiphilic block copolymer can have an enormous impact on properties, and the innumerable possible permutations of copolymers and the resulting properties allow for the precise tailoring of polymeric surfactants to specific applications.

More specific recommendations for future work are related to the novel block-random copolymer stabilizers introduced in this work (Chapters 6 and 7). Although the few block-random copolymers synthesized in this work performed very well, it is unlikely that these structures are optimal. It would be valuable to conduct a further study of these block-random copolymers to optimize their structure based on performance and cost considerations, and also to understand their inherent limitations. Recommended work would include:

- Varying the molecular weight and composition of the stabilizing random copolymer block. Limitations are expected where the copolymer behaves as a polystyrene-b-poly(acrylic acid) copolymer (e.g. high acrylic acid composition), and where the copolymer behaves as a polystyrene homopolymer (e.g. low molecular weight, and low acid composition).
- Varying the molecular weight of the anchor block. Determine if the anchor block length needs to scale proportionally to stabilizing block length, or if some critical length is sufficient for anchoring behavior.
- Varying the chemical structure to use different hydrophobic (e.g. hydrophobic acrylate or methacrylate) and hydrophilic (e.g. cationic, stimuli-responsive, non-ionic) monomers.
- Optimizing and evaluating structures based on solution behavior (e.g. dissolution, insolubility, self-folding, or self-assembly), stabilization efficiency (e.g. particle surface area created per mass of stabilizer), and economy (e.g. particle surface area created per
mass of nitroxide; larger copolymer molecular weight will yield better nitroxide economy).

Beyond the optimization of block-random copolymers, it would be interesting to further investigate their self-folding behavior and its potential usefulness. The self-folding of polymer chains into single-chain nanoparticles is currently an active research topic, and the block-random copolymers in this work present a new approach to achieving this. It would also be worth exploring how the block-random copolymer stabilizers affect the final emulsion polymer properties, e.g. film formation, water resistance, durability, or adhesion.

Finally, the seeded-coagulative emulsion polymerization mechanism has been introduced, but only briefly investigated in this work. It would be worthwhile to reproduce the seeded-coagulative mechanism with monomers other than styrene and different stabilizer structures, and to design experiments to further refine the mechanism; for example, additional experiments are needed to determine how the surface area stabilized per chain, \(a_s\), is related to particle size. It would also be valuable to develop theoretical models to describe the development of the molecular weight and particle size distributions throughout the seeded-coagulative mechanism. Additionally, there are consequences to a seeded-coagulative mechanism that could be of academic or commercial interest, for example:

- Monomer swelling of self-folding chains results in seed particles of very small and controlled diameters (< 20 nm). Particles with such a small size may be used in combination with larger particles (100-200 nm) to produce a bimodal distribution, a common strategy to produce very high solids content emulsion polymerizations.
• The final number of particles is directly proportional to the concentration of stabilizer, so
the effect of conventional dynamic surfactant may have interesting effects, e.g. slowed
coagulation or increased particle number.
• As demonstrated in this work, under certain conditions the rapid coagulation of particles
results in the gelation of the latex. This effect is worth noting in the case that a gel
structure is a desirable product.
• The seeded-coagulative mechanism involves many coagulation events, and interference
with these events may be exploited to produce different particle morphologies or
properties, for example:
  o Cross-linking of particles throughout polymerization to obtain “lumpy” and
    likely unstable clusters of smaller particles.
  o Cross-linking of particles before coagulation to obtain small cross-linked
    particles dispersed in larger particles.
  o Polymerization with incompatible polymers could lead to core/shell or occluded
    morphologies.
• A thermodynamically controlled emulsion polymerization would have greater scalability
and reproducibility compared to current emulsion polymerizations which are dependent
on many kinetic factors (e.g. stirring speed, initiation and polymerization kinetics,
monomer addition rate, etc.).
Appendix A

Effect of Stabilizing Block Dispersity

A.1 Blending Block Copolymers to Decouple $M_n$ and Dispersity

A series of poly(acrylic acid) chain extensions (X1-8) were prepared from the same polystyrene macroinitiator (Table A.1). The molar fractions of X1-8 block copolymers that were blended to produce the library of block copolymers (M1-M8) are shown in Table A.2. These fractions were determined by trial and error by simulating the blending of the molecular weight distributions in a spreadsheet.

Table A.1. Number-average molecular weight and dispersity of each polystyrene-b-poly(acrylic acid) chain extension produced from a single polystyrene macroinitiator.

<table>
<thead>
<tr>
<th>PS-b-PAA Chain Extension</th>
<th>$M_n$ (g/mol)$^a$</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>4200</td>
<td>1.11</td>
</tr>
<tr>
<td>X2</td>
<td>5000</td>
<td>1.33</td>
</tr>
<tr>
<td>X3</td>
<td>5300</td>
<td>1.15</td>
</tr>
<tr>
<td>X4</td>
<td>6600</td>
<td>1.13</td>
</tr>
<tr>
<td>X5</td>
<td>7000</td>
<td>1.13</td>
</tr>
<tr>
<td>X6</td>
<td>8700</td>
<td>1.29</td>
</tr>
<tr>
<td>X7</td>
<td>10100</td>
<td>1.42</td>
</tr>
<tr>
<td>X8</td>
<td>12300</td>
<td>1.55</td>
</tr>
</tbody>
</table>

$^a$ $M_n$ for polystyrene-b-poly(methyl acrylate) reported as polystyrene equivalent. Same macroinitiator used for all block copolymers ($M_n=3396$ g/mol, $D_{PS} = 1.11$).
Table A.2. Molar percentage of each PS-b-PAA chain extension (X1-8) used to produce the library of blend copolymers (M1-8).

<table>
<thead>
<tr>
<th>Blended Copolymer</th>
<th>PS-b-PAA Chain Extension (mol%) in Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X1</td>
</tr>
<tr>
<td>M1</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>15%</td>
</tr>
<tr>
<td>M4</td>
<td>33%</td>
</tr>
<tr>
<td>M5</td>
<td>37%</td>
</tr>
<tr>
<td>M6</td>
<td>15%</td>
</tr>
<tr>
<td>M7</td>
<td>21%</td>
</tr>
<tr>
<td>M8</td>
<td>11%</td>
</tr>
</tbody>
</table>
A.2 Atomic Force Microscopy

Single drops of the block copolymer aggregate (M1 and M8) dispersions and corresponding emulsions were placed on fresh-cleaved mica using a microliter pipette and allowed to dry under ambient conditions. The dried ‘films’ were then characterized by TappingMode™ AFM (MultiMode 8/Nanoscope V, Bruker Nanosurfaces, Santa Barbara, CA). Height and phase images of M1 and M8 particles are shown in Figure A.1 and Figure A.2, respectively.

Figure A.1. AFM height (topography) and phase (viscoelasticity) images of M1 block copolymer aggregates (top), and polystyrene emulsion particles stabilized by M1 (bottom). Block copolymer
aggregates measured 18 – 40 nm in diameter with an average diameter of 20 nm, while particles measured 80 – 115 nm diameter with an average diameter ~95 nm.

**Figure A.2.** AFM height (topography) and phase (viscoelasticity) images of M8 block copolymer aggregates (top), and polystyrene emulsion particles stabilized by M8 (bottom). Block copolymer aggregates measured 20 – 45 nm with average diameter approximately 30 nm, while particles measured 110 – 170 nm with average ~140 nm diameter.
A.3 Static Light Scattering

Weight-average molecular weights of each block copolymer aggregate were determined by static light scattering using Debye plots produced with five concentrations of block copolymer aggregate (0.2, 0.4, 0.6, 0.8, and 1 g/L). The weight-average molecular weight was related to the excess scattering intensity according to eq A.1,

\[
\frac{KC}{R_{\theta}P(\theta)} = \frac{1}{M_w} + 2A_2C
\]  
(A.1)

where \(C\) is the copolymer concentration, \(M_w\) is the weight-average molecular weight of scattering particles, \(A_2\) is the second virial coefficient, and \(K\) is an optical constant defined by eq A.2,

\[
K = \frac{4\pi^2n_0^2}{\lambda^4N_A} \left(\frac{dn}{dC}\right)^2
\]  
(A.2)

where \(n_0\) is the refractive index of the solvent (1.33), \(dn/dC\) is the refractive index increment (0.14 mL/g, Figure A.3), \(\lambda\) is the laser wavelength (633 nm), and \(N_A\) is the Avogadro constant (6.022x10\(^{23}\) mol\(^{-1}\)).

\(R(\theta)\) is the excess Rayleigh ratio defined in eq A.3:

\[
R_{\theta} = R_{tol} \frac{I_A n_0^2}{I_{tol} n_{tol}^2}
\]  
(A.3)

where \(R_{tol}\) is the Rayleigh ratio of toluene (1.35 x 10\(^{-5}\) cm\(^{-1}\)), \(I_A\) is the excess scattering intensity of the analyte, \(I_{tol}\) is the scattering intensity of a toluene standard, and \(n_{tol}\) is the refractive index of toluene (1.496).

\(P(\theta)\) is the shape factor for large, non-interacting particles, defined by eq A.4,

\[
P(\theta) = 1 + \left(\frac{16\pi^2n_0^2R_\theta^2}{3L^2}\right)\sin\left(\frac{\theta}{2}\right)
\]  
(A.4)

where \(R_g\) is the radius of gyration, and \(\theta\) is the scattering angle (173°). The Malvern software approximated the radius of gyration (\(R_g\)) from the hydrodynamic radius (\(R_h\)) using a spherical model (\(R_h = \sqrt{3/5} R_g\)).
The $dn/dC$ of a representative block copolymer aggregate (M1) was determined to be 0.14 mL/g using 5 concentrations between 0 and 1 g/L and a Wyatt Optilab rEX with 690 nm LED light source.

![Figure A.3. Plot of differential refractive index against block copolymer aggregate (M1) concentration in 20 mM NaOH at 25 °C.](image)

The $dn/dC$ of this block copolymer aggregate is in agreement with the average $dn/dC$ previously observed (Burguière, C. et al. Polymer. 2003, 44 (3), 509–518) from polystyrene-b-poly(potassium acrylate) block copolymer aggregates, which was 0.14 mL/g at 20 °C. The resultant second virial coefficient, weight-average molecular weight, and aggregation number of each block copolymer aggregate are summarized in Table A.3.
### Table A.3. Second virial coefficient, weight-average molecular weight, and aggregation number of block copolymer aggregates of M1-8 determined by static light scattering.

<table>
<thead>
<tr>
<th>Blended Copolymer</th>
<th>$A_2$ (x 10^4 mL mol^-1 g^-2)</th>
<th>$M_{w,copolymer}$ (Da)$^a$</th>
<th>$M_{w,aggregate}$ (kDa)$^b$</th>
<th>N$_{agg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>1.3</td>
<td>7800</td>
<td>800</td>
<td>107</td>
</tr>
<tr>
<td>M2</td>
<td>1.5</td>
<td>7900</td>
<td>900</td>
<td>116</td>
</tr>
<tr>
<td>M3</td>
<td>2.1</td>
<td>8300</td>
<td>1100</td>
<td>136</td>
</tr>
<tr>
<td>M4</td>
<td>1.4</td>
<td>8800</td>
<td>1200</td>
<td>132</td>
</tr>
<tr>
<td>M5</td>
<td>1.6</td>
<td>9300</td>
<td>1200</td>
<td>128</td>
</tr>
<tr>
<td>M6</td>
<td>2.1</td>
<td>9400</td>
<td>1500</td>
<td>166</td>
</tr>
<tr>
<td>M7</td>
<td>2.4</td>
<td>9800</td>
<td>1500</td>
<td>152</td>
</tr>
<tr>
<td>M8</td>
<td>1.3</td>
<td>10000</td>
<td>2600</td>
<td>260</td>
</tr>
</tbody>
</table>

$^a$Weight-average molecular weight of block copolymers (from gel permeation chromatography).

$^b$Weight-average molecular weight of block copolymer aggregates.
Appendix B

Effect of Anchoring Block Dispersity

B.1 Blending Block Copolymers to Decouple $M_n$ and Dispersity

A series of polystyrene chain extensions (X9-23) were prepared from the same poly(acrylic acid) macroinitiator (Table A.1). The molar fractions of X9-23 block copolymers that were blended to produce the library of block copolymers (M9-M16) are shown in Table B.1.

These fractions were determined by blending of the molecular weight distributions in a spreadsheet.

Table B.1. Number-average molecular weight and dispersity of each poly(acrylic acid)-b-polystyrene chain extension produced from a single poly(acrylic acid) macroinitiator.

<table>
<thead>
<tr>
<th>PAA-b-PS Chain Extension</th>
<th>$M_n$ (g/mol)$^a$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X9</td>
<td>4500</td>
<td>1.22</td>
</tr>
<tr>
<td>X10</td>
<td>4600</td>
<td>1.26</td>
</tr>
<tr>
<td>X11</td>
<td>5100</td>
<td>1.26</td>
</tr>
<tr>
<td>X12</td>
<td>5600</td>
<td>1.27</td>
</tr>
<tr>
<td>X13</td>
<td>6100</td>
<td>1.27</td>
</tr>
<tr>
<td>X14</td>
<td>6600</td>
<td>1.27</td>
</tr>
<tr>
<td>X15</td>
<td>7800</td>
<td>1.27</td>
</tr>
<tr>
<td>X16</td>
<td>8300</td>
<td>1.28</td>
</tr>
<tr>
<td>X17</td>
<td>10600</td>
<td>1.54</td>
</tr>
<tr>
<td>X18</td>
<td>12100</td>
<td>1.48</td>
</tr>
<tr>
<td>X19</td>
<td>13000</td>
<td>1.47</td>
</tr>
<tr>
<td>X20</td>
<td>14100</td>
<td>1.46</td>
</tr>
<tr>
<td>X21</td>
<td>14800</td>
<td>1.44</td>
</tr>
<tr>
<td>X22</td>
<td>15600</td>
<td>1.42</td>
</tr>
<tr>
<td>X23</td>
<td>16300</td>
<td>1.42</td>
</tr>
</tbody>
</table>

$^a$M$_n$ for poly(methyl acrylate)-b-polystyrene reported as polystyrene equivalent. Same macroinitiator used for all block copolymers ($M_n=3814$ g/mol, $D_{PAA}=1.20$).
Table B.2. The molar percentage of each PAA-b-PS chain extension (X9-23) used to produce the library of blend copolymers (M9-16).

<table>
<thead>
<tr>
<th>Blended Copolymer</th>
<th>X9</th>
<th>X10</th>
<th>X11</th>
<th>X12</th>
<th>X13</th>
<th>X14</th>
<th>X15</th>
<th>X16</th>
<th>X17</th>
<th>X18</th>
<th>X19</th>
<th>X20</th>
<th>X21</th>
<th>X22</th>
<th>X23</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M10</td>
<td>9%</td>
<td>6%</td>
<td>56%</td>
<td>28%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M11</td>
<td>5%</td>
<td>6%</td>
<td>41%</td>
<td>21%</td>
<td>11%</td>
<td>11%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M12</td>
<td>11%</td>
<td>4%</td>
<td>27%</td>
<td>18%</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M13</td>
<td>20%</td>
<td>11%</td>
<td>21%</td>
<td>12%</td>
<td>13%</td>
<td>6%</td>
<td>6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M14</td>
<td>36%</td>
<td>12%</td>
<td>6%</td>
<td>12%</td>
<td>15%</td>
<td>4%</td>
<td>4%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M15</td>
<td>47%</td>
<td>7%</td>
<td>5%</td>
<td>2%</td>
<td>10%</td>
<td>6%</td>
<td>3%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M16</td>
<td>68%</td>
<td>1%</td>
<td>2%</td>
<td>2%</td>
<td>4%</td>
<td>6%</td>
<td>3%</td>
<td>5%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
</tbody>
</table>
B.2 Theoretical CAC of Block Copolymer

It is intuitive that as the molecular weight dispersity of the anchoring block increases, the critical aggregation concentration (CAC) should decrease due to the presence of larger anchoring blocks with lower CAC values. Indeed, this can be theoretically predicted by considering the mixed micelle model of Holland and Rubingh (Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* 1983, 87 (11), 1984–1990) which provides the CAC of a mixture of components with different CAC values:

$$
CAC_{mix} = \frac{1}{\sum_i^n \left( \frac{n_i}{f_i C_i} \right)}
$$

(B.1)

where $n_i$, $C_i$, and $f_i$ are the molar fraction, CAC, and activity coefficient of the $i$th component in the mixture, respectively. This model has been extended by Eisenberg and co-workers (Gao, Z.; Eisenberg, A. A. *Macromolecules* 1993, 26 (26), 7353–7360) to describe the CAC of a block copolymer, with the assumption that the CAC of each component is dominated by the anchoring block length:

$$
\log_{10} CAC_i = a D_i^{1/3} + b
$$

(B.2)

where $CAC_i$ is the CAC of a block copolymer with an anchoring block degree of polymerization of $D_i$. The constant $a$ relates the CAC to the length of the anchoring block (i.e. a negative value describing the increasing hydrophobicity of longer anchor blocks), while the constant $b$ describes the log(CAC) of the block copolymer at the limit where anchor block length approaches zero. A Shulz-Zimm distribution was used to approximate $n_i$, the molar fraction of an anchor block of $D_i$:  

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\[ n_i = \Gamma(\alpha)^{-1} DP_i^{\alpha-1} \left( \frac{\alpha}{DP_n} \right)^\alpha e^{\frac{\alpha DP_i}{DP_n}} \]  \hspace{1cm} (B.3)

where \( \Gamma() \) is the gamma function, \( DP_n \) is the number-average degree of polymerization of the anchoring block, and \( \alpha \) is defined as:

\[ \alpha = \frac{1}{D - 1} \]  \hspace{1cm} (B.4)

with \( D \) the molecular weight dispersity of the anchoring block. Combining eqs B.2 and B.3 with eq B.1 gives an equation for the CAC of a block copolymer in terms of the \( D \) and \( DP_n \) of the anchoring block:

\[ CAC_{\text{mix}} = \left\{ \sum_i^n \left( \Gamma(\alpha)^{-1} DP_i^{\alpha-1} \left( \frac{\alpha}{DP_n} \right)^\alpha e^{\frac{\alpha DP_i}{DP_n}} \right) f_i 10^{(\alpha DP_i^{1/3} + b)} \right\}^{-1} \]  \hspace{1cm} (B.5)

The \( CAC_{\text{mix}} \) values for anchoring block \( D \) between 1 and 3 were calculated using eq B.5 for a \( DP_n \) of 32 (same \( DP_{n,PS} \) for M9-M16), and assuming an ideally mixed system (\( f_i = 1 \)). A value of -0.68 was used for \( a \) as previously reported (Gao, Z.; Eisenberg, A. A. Macromolecules 1993, 26 (26), 7353–7360) for polystyrene-b-poly(sodium acrylate) block copolymers with a poly(sodium acrylate) degree of polymerization of 1000, and \( b \) was used to fit the experimental data using a least-squares method (\( b = -3.03 \)).
B.3 Largest Probable Chain in an Aggregate

*Monte Carlo Sampling*

To determine the largest probable chain in a block copolymer aggregate composed of \( n \) chains, a Monte Carlo method was used. In this method, random sampling of the number fraction molecular weight distribution of a block copolymer was used to select \( n \) chains, and the largest chain was recorded. Repeated sampling (10,000/aggregation number) provided a numerical average of the largest probable chain in an aggregate composed of \( n \) chains. The length of the anchoring block in this chain was approximated by subtraction of the number-average molecular weight of the stabilizing block.

![Graph showing the molecular weight of the largest probable chain in an M9-16 block copolymer aggregate as a function of aggregation number.]

**Figure B.1.** The molecular weight of the largest probable chain in an M9-16 block copolymer aggregate as a function of aggregation number.
Characteristic ratio of polystyrene

The characteristic ratio of low molecular weight polystyrene was approximated using the values calculated by Harmandaris and Kremer (reference 36 in article) as a function of the degree of polymerization.

![Graph showing characteristic ratio of polystyrene as a function of the degree of polymerization](image)

**Figure B.2.** The characteristic ratio of polystyrene as a function of the degree of polymerization estimated from the data of Harmandaris and Kremer (reference 36 in article).

Compositional Heterogeneity

The compositional heterogeneity of each block copolymer was approximated by assuming each block follows a Shulz-Zimm distribution such that the probability of a block copolymer having a composition of \( f_A \) can be determined from eq B.6 (Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. *Prog. Polym. Sci.* **2008**, *33* (9), 875–893.):

\[
P(f_A) = \frac{\Gamma(\alpha_A + \alpha_B - 1)}{\Gamma(\alpha_A)\Gamma(\alpha_B)} \left( \frac{\alpha_A}{N_{A,n}} \right)^{\alpha_A} \left( \frac{\alpha_B}{N_{B,n}} \right)^{\alpha_B} \left( \frac{f_A\alpha_A}{N_{A,n}} + \frac{(1-f_A)\alpha_B}{N_{B,n}} \right)^{1-\alpha_A-\alpha_B} f_A^{\alpha_A-1}(1-f_A)^{\alpha_B-1} \quad (B.6)
\]

where \( N_{A,n} \) and \( N_{B,n} \) are the number-average degrees of polymerization of the stabilizing and anchoring blocks, respectively, \( f_A \) is the molar composition of the stabilizing block, \( \Gamma() \) is the gamma function, and \( \alpha \) is defined by eq B.7:
\[ \alpha_i = \frac{1}{D_i - 1} \quad (B.7) \]

with \( D \) the molecular weight dispersity of the \( i \)th block. The degree of polymerization and molecular weight dispersity of each block in copolymers M9-16 can be found in Table B.1. \( P(f_A) \) was normalized such that the area under the curve is equal to unity.

### B.4 Surface Tension as a Function of Anchor Block Length

0.15 mM dispersions of PAA-b-PS chain extensions (Table B.2) X9, 11, 13, 15, 16, 17, 19, and 22 were prepared in the same manner as dispersions of M9-16 (addition of 4x stoichiometric sodium hydroxide and heating to 90 °C), and the surface tension of these dispersions were measured (Figure B.3).

**Figure B.3.** Surface tension of selected poly(sodium acrylate)-b-polystyrene block copolymers (X9, 11, 13, 15, 16, 17, 19, 22) plotted against their anchor block degree of polymerization (Left) and overall poly(sodium acrylate) composition (Right).

A maximum surface activity was observed when the anchoring block had approximately 20 repeat units (70 molar percent acid). Surface activity decreased for chains with very short anchoring blocks (approaching poly(sodium acrylate) homopolymer) and for chains with a larger anchoring block.
Appendix C
Derivation of Seeded-Coagulative Mechanism

C.1 Stage 1: Coagulative Growth

During the seeded-coagulative emulsion polymerization mechanism, the following assumptions are made:

1. Total particle surface area is equal to the total surface area of stabilizing chains at the particle/water interface,

\[ a_s [S]_{int} N_A = N_p 4\pi R^2 \]  

(C.1)

Where \( a_s \) is the surface area covered by a single stabilizer chain (cm\(^2\)), \([S]_{int}\) is the concentration of stabilizer chains that exist at a particle/water interface (mol/L), \( N_A \) is Avogadro’s constant (6.022\( \times 10^{23} \) mol\(^{-1}\)), \( N_p \) is the number of particles (L\(^{-1}\)), and \( R \) is the number-average particle radius (nm).

2. Stabilizer chains exist only at the interface (neglect chains that are in the particle or aqueous phase),

\[ [S]_{int} = [S] \]

Where \([S]\) is the total stabilizer concentration in the system (mol/L).

3. Particles will readily coagulate and coalesce to conserve total surface area, i.e. rates of surface area growth by polymerization and surface area reduction by coagulation in equilibrium.

4. All particles are spherical. Coagulation leads to coalescence into spherical particles.

Throughout the polymerization, the total volume of particles per volume of system (V; cm\(^3\)/L) will increase with time due to the diffusion of monomer into the particle (as a result of polymerization within the particle) and due to coagulation (to conserve surface area):
\[
\frac{dV}{dt} = \frac{R_pMN_p}{v_{poly} \rho_{poly}}
\]  
(C.2)

with \(M\) the molecular weight of the monomer (104.15 g mol\(^{-1}\)), \(\rho_{poly}\) the density of the polymer (1.05 g cm\(^{-3}\)), \(v_{poly}\) the volume fraction of polymer in a particle, and \(R_p\) the rate of polymerization in a particle (mol s\(^{-1}\)):

\[
R_p = \frac{k_p[M]_p \bar{n}}{N_A}
\]  
(C.3)

with \(k_p\) the rate constant for chain propagation (L mol\(^{-1}\) s\(^{-1}\)), \([M]_p\) the monomer concentration in a particle (mol L\(^{-1}\)), \(\bar{n}\) the average number of radicals in a particle (assumed to be 0.5 for hydrophobic monomers in small particles\(^1\)), and \(N_A\) the Avogadro constant (mol\(^{-1}\)). The \(k_p\) for styrene under the reaction conditions was estimated as 950 L mol\(^{-1}\) s\(^{-1}\) from an activation energy \((E_a)\) of 33.6 kJ/mol and Arrhenius coefficient \((A)\) of 7.6x10\(^7\) L mol\(^{-1}\) s\(^{-1}\).\(^2\) \(v_{poly}\) in eq C.2 accounts for the volume growth of a particle due to monomer swelling and is related to the monomer concentration in particles:

\[
v_{poly} = 1 - v_m = 1 - \frac{[M]_pM}{1000\rho_m}
\]  
(C.4)

With \(\rho_m\) the density of the monomer (0.909 g cm\(^{-3}\)). The rate of total particle volume change is therefore:

\[
\frac{dV}{dt} = \frac{k_p[M]_p \bar{n}M N_p}{v_{poly} \rho_{poly} N_A}
\]  
(C.5)

Substituting the number of particles with eq C.1:

\[
\frac{dV}{dt} = \frac{k_p[M]_p \bar{n}Ma_s[S]_{int}N_A}{v_{poly} \rho_{poly} N_A 4\pi R^2}
\]  
(C.6)

\(R\) is the number-average radius of a particle, and can be expressed in terms of \(V\):

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\[ N_p = \frac{a_s[S]_{int} N_A}{4\pi R^2} = \frac{V}{\frac{4}{3} \pi R^3} \quad \text{(C.7)} \]

\[ R = \frac{3V}{a_s[S]_{int} N_A} \quad \text{(C.8)} \]

Eq C.6 can now be simplified by substitution of equation C.8, followed by integration to find the instantaneous value of \( V \):

\[ \frac{dV}{dt} = \frac{k_p[M]_p \bar{n}M(a_s[S]_{int} N_A)^3}{v_{poly} \rho_{poly} N_A 4\pi \left( \frac{3V}{a_s[S]_{int} N_A} \right)^2} \quad \text{(C.9)} \]

\[ \frac{dV}{dt} = \frac{k_p[M]_p \bar{n}M(a_s[S]_{int} N_A)^3}{v_{poly} \rho_{poly} N_A 36\pi V^2} \quad \text{(C.10)} \]

\[ \int_0^V V^2 dV = \frac{k_p[M]_p \bar{n}M(a_s[S]_{int} N_A)^3}{36\pi v_{poly} \rho_{poly} N_A} \int_0^t dt \quad \text{(C.11)} \]

\[ \frac{1}{3} V(t)^3 + C = \frac{k_p[M]_p \bar{n}M(a_s[S]_{int} N_A)^3}{36\pi v_{poly} \rho_{poly} N_A} t \quad \text{(C.12)} \]

\[ V(t) = \left( \frac{k_p[M]_p \bar{n}M(a_s[S]_{int} N_A)^3}{12\pi v_{poly} \rho_{poly} N_A} t + 3C \right)^{\frac{1}{3}} \quad \text{(C.13)} \]

\[ V(t) = \left( \frac{k_p[M]_p \bar{n}M(a_s[S]_{int} N_A)^3}{12\pi v_{poly} \rho_{poly} N_A} t + V(0)^3 \right)^{\frac{1}{3}} \quad \text{(C.14)} \]

The assumption is made that the initial particle volume will be much less than \( V(t) \), if not zero:
\[ V(t) = \left( \frac{k_p[M]_p \bar{n}M (a_s[S]_{int}N_A)^3}{12\pi v_{poly}\rho_{poly}N_A} \right)^{\frac{1}{3}} t \]  

(C.15)

Next, eq C.15 is used to find the instantaneous number of particles:

\[ N_p(t) = \frac{V(t)}{\frac{4}{3} \pi R(t)^3} \]  

(C.16)

Substituting eq C.8, followed by eq C.15, into C.16:

\[ N_p(t) = \frac{V(t)}{\frac{4}{3} \pi \left( \frac{3V(t)}{a_s[S]_{int}N_A} \right)^3} \]  

(C.17)

\[ N_p(t) = \frac{(a_s[S]_{int}N_A)^3}{36\pi V(t)^2} \]  

(C.18)

\[ N_p(t) = \frac{(a_s[S]_{int}N_A)^3}{36\pi \left( \frac{k_p[M]_p \bar{n}M (a_s[S]_{int}N_A)^3}{12\pi v_{poly}\rho_{poly}N_A} \right)^{\frac{2}{3}}} \]  

(C.19)

Now with an equation for \( V(t) \) and \( N_p(t) \), an equation for \( R(t) \) follows:

\[ N_p(t) = \frac{a_s[S]_{int}N_A}{4\pi R(t)^2} \]  

(C.20)

\[ R(t) = \left( \frac{a_s[S]_{int}N_A}{4\pi N_p(t)} \right)^{\frac{1}{2}} \]  

(C.21)

\[ R(t) = \left( 9 \left( \frac{k_p[M]_p \bar{n}M (a_s[S]_{int}N_A)^3}{12\pi v_{poly}\rho_{poly}N_A} \right)^{\frac{2}{3}} \right)^{\frac{1}{2}} \]  

(C.22)

At the time when all monomer reservoirs are depleted, \( t_d \), the number of particles will remain constant while the monomer concentration in particles begins to decrease until complete
conversion. At this time, the total volume of particles is equal to the total volume of polymer/monomer in the system:

\[ V(t_d) = \frac{\tau_{tot}}{\rho_p} = \frac{\tau_{tot}}{(1 - v_{poly})\rho_m + v_{poly}\rho_{poly}} \]  \hspace{1cm} (C.23)

Where \( \tau_{tot} \) is the total mass content of polymer/monomer in the system (g/L), and \( \rho_p \) is the density of a particle saturated with monomer at \( t_d \).

\[ \tau_{tot} \left(1 - v_{poly}\rho_m + v_{poly}\rho_{poly}\right) = \left(\frac{k_p[M]_p\bar{M}(a_s[S]_{int}N_A)^3}{12\pi v_{poly}\rho_{poly}N_A}t_d\right)^{\frac{1}{3}} \]  \hspace{1cm} (C.24)

Eq C.24 can be rearranged to find \( t_d \),

\[ t_d = \frac{12\pi v_{poly}\rho_{poly}N_A}{k_p[M]_p\bar{M}(a_s[S]_{int}N_A)^3}\left(\frac{\tau_{tot}}{(1 - v_{poly})\rho_m + v_{poly}\rho_{poly}}\right)^{\frac{3}{2}} \]  \hspace{1cm} (C.25)

Substituting \( t_d \) into \( N_p(t) \), the final number of particles is:

\[ N_p(t_d) = \frac{(a_s[S]_{int}N_A)^3}{36\pi \left(\frac{\tau_{tot}}{(1 - v_{poly})\rho_m + v_{poly}\rho_{poly}}\right)^{\frac{3}{2}}} \]  \hspace{1cm} (C.26)

Further simplification is made with the assumption, \( \rho_{poly} \approx \rho_m \):

\[ N_p(t_d) = \frac{(a_s[S]_{int}N_A)^3}{36\pi \left(\frac{\tau_{tot}}{\rho_{poly}}\right)^{\frac{3}{2}}} \]  \hspace{1cm} (C.27)

Likewise, number-average particle radius at \( t_d \) is:

\[ R(t_d) = \left(\frac{3\tau_{tot}}{(1 - v_{poly})\rho_m + v_{poly}\rho_{poly}}\right)^{\frac{1}{2}} \]  \hspace{1cm} (C.28)

It is also useful to develop an equation for the total mass content as a function of time, since this is an easily measured experimental value:
\[ \tau(t) = v_{\text{poly}} \rho_{\text{poly}} V(t) + \tau_0 \]  
(C.29)

\[ \tau(t) = v_{\text{poly}} \rho_{\text{poly}} \left( \frac{k_p [M]_p \bar{n} M(a_s [S]_{\text{int}} N_A)}{12 \pi v_{\text{poly}} \rho_{\text{poly}} N_A} \right)^{\frac{1}{3}} + \tau_0 \]  
(C.30)

Substituting \( t_d \) into eq 30 yields an equation for the solids content at the end of Stage 1:

\[ \tau(t_d) = \frac{v_{\text{poly}} \rho_{\text{poly}} \tau_{\text{tot}}}{(1 - v_{\text{poly}}) \rho_m + v_{\text{poly}} \rho_{\text{poly}}} + \tau_0 \]  
(C.31)

C.2 Stage 2: Monomer Droplet Depletion

Stage 2 of a seeded-coagulative mechanism is assumed to be the same as the final stage of conventional emulsion polymerization, in which all remaining monomer is in the particles, and \([M]_p\) decreases with time. The theoretical treatment of this stage is complicated due to the increasing particle polymer fraction as \([M]_p\) decreases. As \([M]_p\) decreases, termination rate in particles also decreases, and \(\bar{n}\) will gradually increase; this effect on \(\bar{n}\) must be considered otherwise the rate in this stage is greatly underestimated. As the polymer fraction of particles increases, it becomes more difficult for growing radical chains to diffuse and terminate within the particles, where the rate constant of termination, \(k_t\), has been shown to be related to the polymer fraction by a power law, e.g. \(k_t \sim v_{\text{poly}}^b\) (O’Shaughnessy, B.; Yu, J. Phys. Rev. Lett. 1994, 73 (12), 1723–1726). Likewise, it will be assumed that the average number of radicals in a particle will increase with polymer fraction according to a power law:
\[ \bar{n}(t) = -\alpha \left( \left( \frac{v_{poly}(t_{onset})}{v_{poly}(t)} \right)^\beta - 1 \right) + \bar{n}(t_{onset}) \]  
(C.32)

Where \( \alpha \) and \( \beta \) are positive numbers used as fitting parameters.

The rate of change in \( [M]_p \) during Stage 2 can be written as:

\[ \frac{d[M]}{dt} = \frac{k_p[M]\bar{n}(t)N_p(t_d)}{N_A V(t)} \]  
(C.33)

From eq C.33 the time evolution of Stage 2 is then solved numerically, beginning with the calculation of \( [M]_p \) at some small increment \( t_d + \Delta t \), followed by the calculation of polymer volume fraction with the calculated \( [M]_p \):

\[ v_{poly} = 1 - v_m = 1 - \frac{[M]_p M}{1000 \rho_m} \]  
(C.34)

Once the polymer volume fraction is calculated, the total volume and particle radius can be found:

\[ V(t) = \frac{\rho v_{poly}(t_{onset})}{\rho_p} V(t_d) \]  
(C.35)

\[ V(t) = \left( \frac{(1 - v_{poly,t_d})\rho_m + v_{poly,t_d}\rho_{poly}}{(1 - v_{poly}(t))\rho_m + v_{poly}(t)\rho_{poly}} \right) V(t_d) \]  
(C.36)

\[ R(t) = \left( \frac{(1 - v_{poly,t_d})\rho_m + v_{poly,t_d}\rho_{poly}}{(1 - v_{poly}(t))\rho_m + v_{poly}(t)\rho_{poly}} \right)^{\frac{1}{3}} R(t_d) \]  
(C.37)
\[ R(t) = \left( \frac{(1 - v_{poly,t_d}) \rho_m + v_{poly,t_d} \rho_{poly}}{(1 - v_{poly}(t)) \rho_m + v_{poly}(t) \rho_{poly}} \right)^{\frac{1}{3}} \left( \frac{3 \tau_{tot}}{(1 - v_{poly,t_d}) \rho_m + v_{poly,t_d} \rho_{poly}} \right)^{\frac{2}{3}} \]  

(C.38)

The solids content can then be found:

\[ \tau(t) = v_{poly} \rho_{poly} V(t) + \tau_0 \]  

(C.39)

\[ \tau(t) = v_{poly}(t) \rho_{poly} V(t_d) + \tau_0 \]  

(C.40)

And finally, \( \bar{n} \) can be calculated using eq C.32. Using this value of \( \bar{n} \), \( d[M]/dt \) is then recalculated, and the numerically solution continues for the next time increment. In this manner, the solids content and particle diameters have been calculated for Stage 2 using the same parameters for Stage 1 in Chapter 7, and are shown in Figures C.1 and C.2. The \( \alpha \) and \( \beta \) fitting parameters in eq C.32 were 2.5 and 2, respectively.
Figure C.1. Dashed red line shows numerically solved solids content as a function of time during Stage 2, overlaid with experimental solids content (squares) and Stage 1 seeded-coagulative model (dashed black line) from Chapter 7.

Figure C.2. Dashed red line shows numerically solved particle diameter as a function of time during Stage 2, overlaid with experimental particle diameter (squares) and Stage 1 seeded-coagulative model (dashed black line) from Chapter 7.
In loving memory of P. Schmutz