# Poly(vinyl alcohol) stabilization of acrylic emulsion polymers using the miniemulsion approach.

## Citation

Kim, Noma. *Poly(vinyl Alcohol) Stabilization of Acrylic Emulsion Polymers Using the Miniemulsion Approach*. 2003, https://preserve.lehigh.edu/lehigh-scholarship/graduate-publications-theses-dissertations/theses-dissertations/polyvinyl.

# POLY(VINYL ALCOHOL) STABILIZATION OF ACRYLIC EMULSION POLYMERS USING THE MINIEMULSION APPROACH

By

**Noma Kim**

**A Dissertation**
**Presented to the Graduate and Research Committee**
**of Lehigh University**
**in Candidacy for the Degree of**
**Doctor of Philosophy**

**in**

**Polymer Science and Engineering**

**Lehigh University**

**2003**

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# CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

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# ACKNOWLEDGMENTS

I wish to express my sincere gratitude to:

- Professor Mohamed. S. El-Aasser for giving opportunity to work at the EPI and stay at Lehigh for my Ph.D. and for his valuable advice, consistent encouragement, and kindness.
- Professor Andrew. Klein for the interest in this project, valuable suggestions, and serving on the dissertation committee.
- Professor Cesar A. Silebi for his helpful ideas and serving on the dissertation committee.
- Dr. Victoria. L. Dimonie for her endless enthusiasm, curiosity, and valuable discussions for this project.
- Dr. E. David Sudol for his critical comments, rigorous and deep approach to science, and valuable discussions for this project.
- Mr. William E. Lenney for his valuable comments, suggestions, and serving on the dissertation committee.
- Dr. Eric. S. Daniels for his help and Ms. Leanne Adamcik for administrative paperworks.
- Ms. Debra. H. Nyby for making my stay easier at the EPI.
- The Emulsion Polymers Liason Program and all graduate students in EPI.

- Drs. Chan-hong Lee, Jin Yoo, and Dong-ryul Kim for their encouragement to study in Lehigh.
- My parents and my wife's parents for their endless loving and praying.
- My wife, Miyoung, and my son, Chanjoo, for their love, sacrifice, and prayers.

# DEDICATION

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**To my parents and my wife's parents**

**To my wife, Miyoung, and my son, Chanjoo**

**To God**

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# ABSTRACT

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Miniemulsion approach was employed to obtain stable acrylic latexes of *n*-butyl acrylate and methyl methacrylate (50/50 wt%) stabilized with poly(vinyl alcohol) (PVA) and to enhance the grafting reaction between PVA and acrylic monomers at the water/droplet interface. The stability of miniemulsions were studied in terms of the type and concentration of the stabilizer, and the PVA partitioning were determined as a function of the PVA concentration. Using the comparison of PVA partitioning at droplet surface and grafted PVA as a function of concentration, it was suggested that the water/monomer interface is the main grafting site in the miniemulsion polymerization.

Seeded emulsion and miniemulsion copolymerizations initiated with water-soluble (hydrogen peroxide, HPO), partially water-soluble (t-butyl peroxide,TBHP), and oil-soluble (t-butyl peroxyoctoate, TBPO) initiators were carried out to further investigate the oil/water interface as the grafting site for PVA. The interaction between the capillary wall in the CHDF (capillary hydrodynamic fractionation) chromatographic particle sizer and the water-soluble polymers adsorbed on the particle surface was studied using different types of water-soluble polymers and eluants. Different grafting architectures depending on the initiation site were suggested based on the CHDF results.

The amounts of grafted PVA produced in miniemulsion polymers initiated with TBHP and TBPO were substantially less than those in the corresponding seeded emulsion polymerizations. The effect on the internal viscosity at the interface was proposed to

explain the difference in grafting in terms of polymerization methods. Aqueous phase and interface grafting were studied using the measurement of the degree of hydrolysis (DH) of the serum PVA and adsorbed PVA after miniemulsion polymerizations. Based on the results, it was found that aqueous phase and interface grafting occurred in the HPO system; however, interface grafting dominated the TBHP system.

Colloidal instability in conventional emulsion polymerizations was investigated and compared with the corresponding miniemulsion polymerization. It was found that the grafted PVA in conventional emulsion polymerizations was more hydrophobic presumably due to a greater amount of grafted chains than that in similar miniemulsion polymerizations and this could be correlated with the colloidal instability during conventional emulsion polymerizations.

# CHAPTER 1

# INTRODUCTION

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## 1.1 POLY(VINYL ALCOHOL) (PVA)

### 1.1.1 Classification of PVA

Poly(vinyl alcohol) (PVA) is normally classified by the degree of hydrolysis (DH) and degree of polymerization (DP), and structurally the simple water-soluble polymer consisting of the hydroxyl units and the acetate units.[1] In terms of the DH (mole % of the hydroxyl units), there are two major groups; partially hydrolyzed (DH = 87 ~ 89 %) and fully hydrolyzed (DH = 97 ~ 99 %) PVA. The partially hydrolyzed group includes a subgroup with about 80 % DH. Meanwhile, in terms of the DP, there are three major groups; a low viscosity group of approximately 5 cps (DP ~ 500), a medium viscosity group of approximately 20–30 cps (DP ~1700), and high viscosity group of approximately 40–50 cps (DP ~ 2000) based on the viscosity measured of 4 % PVA aqueous solutions at 20 °C.

### 1.1.2 Water Solubility of PVA

The water solubility of PVA depends on its DP and DH, however, the effect of the DH is more significant. The hydroxyl units cause high affinity to water with strong hydrogen bonding between the intra- and intermolecular hydroxyl groups. On the other hand, the residual acetate groups are hydrophobic, and weaken the intra- and the intermolecular hydrogen bonding of the hydroxyl units. However, the presence of an adequate amount of acetate groups increases the water solubility. Sakurada and coworkers,[2,3] Timasheff,[4] and Satake[5] have shown that the critical temperature of the phase separation is lower and the solubility at high temperatures decreases gradually with increasing acetate units. The presence of as little as 2 – 3 mol % of residual acetate groups results in significant change in the water solubility at 40 – 60 °C. Therefore, heating to at least 80 °C is required to dissolve the fully hydrolyzed PVA. At 20 °C, the partially-hydrolyzed PVA (less than 88 % DH) dissolves almost completely in water, however the water solubility shows a significant decrease with increasing DH (Figure 1.1).

### 1.1.3 Viscosity Stability of PVA Solution

The viscosity of fully hydrolyzed PVA aqueous solutions increases with time, and may finally gel. However, the viscosity of 88 % DH PVA is virtually stable with time (Figure 1.2).

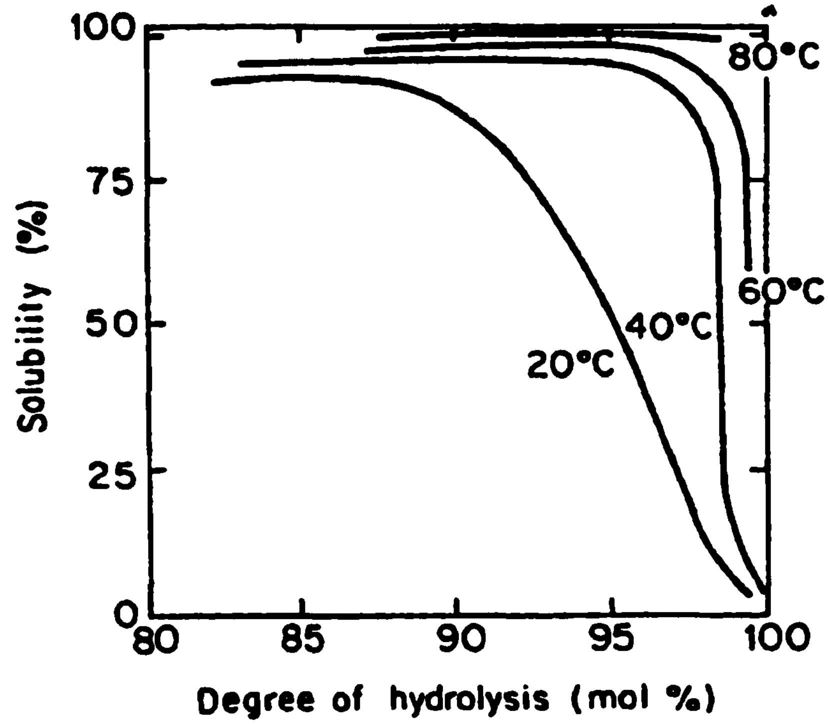

**Figure 1.1:** *Water solubility of PVA as a function of degree of hydrolysis (DH); degree of polymerization (DP) = 1750 (Reprinted from ref. 1)*

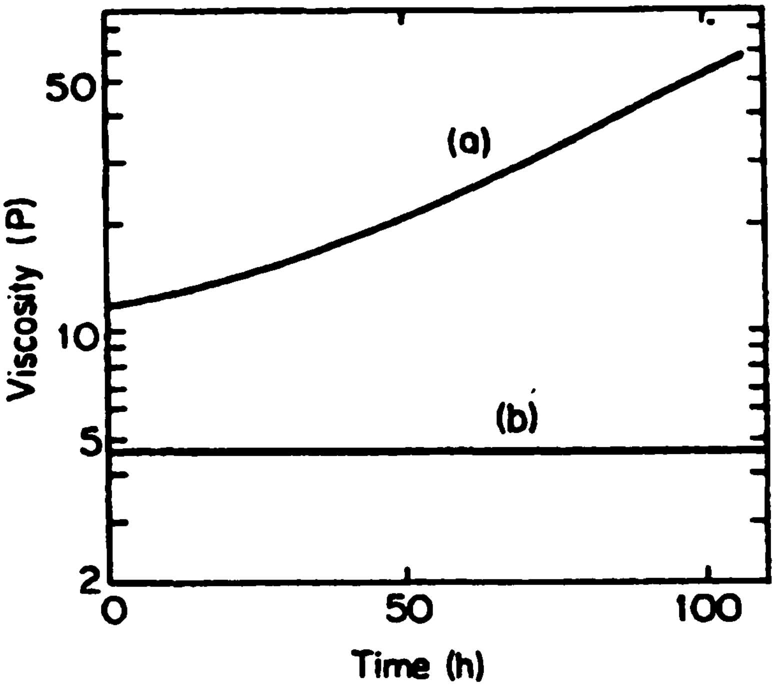

**Figure 1.2:** *Variation of viscosity of PVA aqueous solution with time; (a) DH ~ 98%, DP ~ 1750; (b) DH ~88%, DP ~ 1750; Temperature 5 °C; 8 wt% concentration; measured by Brookfield viscometer (model BL, 60 rpm); (Reprinted from ref. 1)*

However, the introduction of more than 2 mol % acetate groups greatly stabilizes the time dependence of viscosity.[6] This phenomenon may be explained by assuming that the introduction of acetate groups hinders the close packing of fully hydrolyzed PVA molecules and reduces the crystallinity of the molecules. Recently, Nakamae and his co-workers[7] synthesized the modified fully hydrolyzed PVA with hydrophobic groups (dodecyl group) and reported that the viscosity of this modified fully hydrolyzed PVA is stable with time at 5 °C.

### 1.1.4. Surface Activities and Adsorption

The surface activity is important for applications of PVA in suspension and emulsion technology. Mendizabal et al.[8] studied the interfacial tension between styrene and PVA aqueous solutions and reported that the interfacial tension decreased with decreasing DH of PVA. This can be explained by the increasing tendency of PVA adsorption on the interface due to increasing amount of hydrophobic groups (acetate group). Also, they found that the interfacial tension decreased with decreasing molecular weight of partially-hydrolyzed PVA (DH ~ 88 %) and explained this by a faster adsorption of lower molecular weights. Hayashi et al.[9] studied the effects of surface tension and reported that the surface tension at saturation decreased with decreasing DH of PVA. Another factor to affect surface activities is the intramolecular distribution of acetate groups (the sequence distribution of the acetate groups) in the PVA backbone as studied by Hayashi et al.[10] and Budhlall.[11] Hayashi tried to differentiate the different sequence distributions of acetate groups in the PVA backbone using iodine absorption and explained the difference in surface tensions. Meanwhile, Budhlall investigated the sequence distributions of acetate groups using dynamic light scattering and suggested different conformations with different sequence distributions, which may result in different hydrodynamic radii.

Adsorption of PVA on a substrate depends on the DH and molecular weight. Lankveld and Lyklema[12] studied PVA adsorption on paraffin droplets as a function of the DH and molecular weight. They compared the area ($a_o$) occupied per PVA molecule and the projected area ($\pi r_o^2$) of the conformation using the following equation[13]

$$r_g = 4.09(DP/6)^{1/2} \tag{1.1}$$

where $r_g$ is the radius of gyration and DP is the degree of polymerization. In all cases, $a_o$ is less than $\pi r_o^2$ and the ratio of $a_o/\pi r_o^2$ becomes smaller as the molecular weight or the DH of the PVA decreases. The lateral compression is likely to result in a thicker layer, therefore, the thickness of the adsorbed layer increases with increasing molecular weight and with decreasing DH. Also, the surface characteristics of substrate greatly affect the adsorption of PVA. Yuki et al.[14] and Almog and Levy[15] studied the adsorption of PVA on hydrophobic polymer particles such as poly(styrene), poly(*n*-butyl acrylate), and poly(*n*-butyl methacrylate) and hydrophilic polymer particles such as poly(vinyl acetate) and poly(methyl methacrylate). The specific amount of adsorbed PVA on the particles surface did significantly differ depending on the hydrophilicity of the surface.

## 1.2 CONVENTIONAL EMULSION POLYMERIZATIONS USING PVA AS STABILIZER

Emulsion polymerization is a radical chain polymerization in which a monomer or mixture of monomers is polymerized in the presence of surfactants (stabilizers), initiators, some additives such as molecular weight regulators and salts, and water. Its final form is a colloidal dispersion of polymer particles, known as a latex. In emulsion polymerization, the surfactants (stabilizer) are important because they control the polymerization rate, the particle size and its distribution, the stability during the polymerization, and the physical properties of resulting products. Surfactants are amphiphilic molecules. They comprise a hydrophobic tail and hydrophilic head. Depending on the charge of the hydrophilic head, surfactants are classified as anionic, cationic, nonionic, and amphoteric. Typical examples are carboxylates, sulfates, sulfonates, and phosphates for anionics, quaternary nitrogen bases, amines, and nitiriles for cationics, alkyl poly(ethylene oxide), alkylaryl poly(ethylene oxide), and block copolymers for nonionics. Amphoteric surfactants contain both amino and carboxylic acid groups.

A drawback to surfactants is that they must be used in order to obtain shear stable latexes, which are often not economical and may have adverse side effects. For example, the presence of surfactants in a latex system can have a negative effect on water-sensitivity and cause foaming of the final products. In addition, at conventional use levels, surfactants do not impart sufficient mechanical stability to the final products. One possible approach to overcome these shortcomings of conventional surfactants is to use the protective colloids such as hydroxyl ethyl cellulose (HEC) or PVA. The presence of protective colloids provides improved rheology, shear stability, and performance characteristics such as superior primary tackiness.

### 1.2.1 Preparation of Poly(vinyl acetate) (PVAc) Latexes Using PVA As Stabilizer

Most typical examples of the application of PVA as a protective colloid are vinyl acetate and vinyl acetate-ethylene emulsion polymerizations. These latexes are commercially available and their preparation is discussed in reviews.[16,17] When PVA is used as the sole stabilizing agent in an emulsion polymerization, it performs the dual function of providing sites for particle nucleation, as well as providing colloidal stability to the growing particles as a result of their adsorption at the particle-water surface.[18] The hydrophobic acetate units provide the primary anchoring segments and the hydrophilic hydroxyl units project into the aqueous phase as stabilizing moieties. Extensive evidence supports grafting as a primary method of attachment of PVA molecules to PVAc particles,[19,20] but adsorption may also be significant.[17] The extent of the grafting reaction has been shown to be dependent on the degree of hydrolysis of the PVA, molecular weight of the PVA, and the sequence distribution of acetate groups in partially-hydrolyzed PVA.[11] These grafting reactions between the PVA and vinyl acetate can affect the kinetic characteristics of the polymerization process as well as the surface, colloidal, and bulk properties of the resulting latex. Normally the resulting latexes have rather large particles (0.5 to several microns) and wide particle size distributions and this combination was found to produce paints having quite acceptable applications and performance characteristics. The application of fully-hydrolyzed PVA as a stabilizer is limited because the resulting latexes have a fairly large particle diameter and produce a gelation of the latexes at lower temperatures (~ 5 °C), even though they show pseudo-Newtonian flow, higher water resistance, and higher heat resistant films due to higher crystallinity of fully-hydrolyzed PVA. Recently, Nakamae et al.[7,21,22] reported a modified fully-hydrolyzed PVA by incorporating hydrophobic end groups and prepared stable latexes in terms of viscosity at lower temperatures.

### 1.2.2 Preparation of Acrylic Latexes Using PVA As Stabilizer

As discussed previously, PVA has been widely used as a protective colloid in emulsion polymerizations for preparing VAc homopolymers or copolymers. However, the extended applications of PVA as a stabilizer in acrylic or styrene emulsion polymerizations have been limited due to the colloidal instability during the polymerization.

Grafting occurs mainly via the propagation of PVA macro-radicals in aqueous phase.[11,23-25] Therefore, the formation mechanism of PVA macro-radicals is quite important. The initial formation of a PVA macro-radical occurs via hydrogen abstraction by primary radicals or oligomeric radicals mainly, where the hydrogen of the methine carbon is predominantly abstracted.[26] The chain transfer constant of a vinyl acetate radical is quite high from bulk, solution, or suspension polymerization compared with acrylic monomer radicals such as methyl methacrylate radical.[27,28] Also, its chain transfer constant to PVA is about 23 times higher than that to PVAc polymers.[29] Based on those observations, the colloidal stability in vinyl acetate system using PVA as stabilizer has been explained by the favorable grafting tendency of vinyl acetate radical via chain transfer. In other words, the colloidal instability in acrylic systems has been explained by the low chain transfer tendency of acrylic monomer radicals, which results in a lack of grafting. However, the growing oligomeric radicals can easily be captured by the pre-existing particles, and then there exists segregation between PVA molecules in aqueous phase and the growing oligomeric radicals on the particle surface, implying that there is little or no hydrogen abstraction by oligomeric radicals.

Craig [30-32]studied the vinyl acetate/acrylic and acrylic emulsion polymerization in the presence of hydroxy methyl cellulose (HEC) and found that the more extensive grafting occurred in the acrylic emulsion polymerizations, which is not consistent with the above explanation. By adding some water-soluble molecular weight regulator such as triethanol amine, he obtained relatively shear-stable, low-viscosity acrylic latexes. He concluded that the colloidal instability resulted from the more extensive grafting of acrylic monomers with HEC due to their higher monomer reactivity and suggested that the grafting of HEC in acrylic systems should be controlled to obtain stable latexes by adding some molecular weight regulator in the aqueous phase. Recently, Okaya et al.[33,34] studied the emulsion polymerization of methyl methacrylate stabilized with PVA and reported a significant amount of grafted PVA. Also, the decrease of PVA concentration resulted in increased grafted PVA based on the total PVA in the recipe and the increasing particle size as a function of conversion, implying colloidal instability during the polymerization.

A question is why the extensive grafting results in the colloidal instability? One possible explanation is to consider the architecture of grafting. Grafted PVA acts as a polymeric stabilizer on the particle surface. The most effective polymeric stabilizers are considered to be amphipathic block or graft copolymers. The hydrophobic vinyl acetate blocks (or grafts) on the PVA backbone provide the primary anchoring segments, and the hydrophilic vinyl alcohol blocks project out into the aqueous phase as stabilizing moieties. In this stabilization mechanism, the grafting architecture seems to be important because surface activity of polymeric stabilizers is most pronounced when hydrophobic or hydrophilic units are well segregated in the molecule (as in block copolymers, for example). If the grafted chains are randomly dispersed along the PVA backbone during the polymerization, the stabilization will be poor because there is no clear segregation between hydrophilic and hydrophobic blocks. The grafting architecture for maximum stabilization seems to be in the form of block copolymers and these can be ideally achieved using functional end groups, which can easily generate radicals by abstracting hydrogen using primary radicals (e.g., hydrogen of –SH end group).[35,36]

To obtain stable acrylic latexes stabilized by PVA, several patents have been issued. These patents include the addition of water-soluble regulators such as mercaptoacetic acid and cyclohexyl amine[37], the addition of water soluble amino alcohol,[38] the combination of water-soluble and oil-soluble initiators such as persulfate initiator and azo type initiators,[39] the modification of PVA with a thiol-terminated group[35,40] and the addition of alcohol such as methanol.[41,42] Basically, these modifications are based on the suppression of aqueous phase grafting using chain transfer agents. So far, to our knowledge, no acrylic emulsion polymers stabilized with PVA have been commercialized yet, despite many patents being issued.

## 1.3 MINIEMULSION POLYMERIZATIONS USING PVA AS A STABILIZER

Miniemulsions are dispersions of monomer droplets, having diameters in the range of 50 to 500 nm. Formation of sub-micron monomer droplets is brought about by the application of energy through homogenation or microfludization. The diameter of the miniemulsion droplets is mainly controlled by the surfactant concentration. The droplets also contain a low molecular weight, water-insoluble costabilizer, which is necessary to reduce the extent of droplet degradation by Ostwald ripening, such as cetyl alcohol (CA) or hexadecane (HD).[43] In a conventional emulsions, the majority of the surfactant resides in the aqueous phase, as micelles and free surfactant. The monomer droplets are large (≥ 1 μm), and have relatively little interfacial area to adsorb surfactant. By contrast, in minimeulsions, the monomer droplets are small, and the interfacial area is large, so that most of the surfactant resides on the droplet surface, and relatively little is present in the aqueous phase. Anderson et al.[44] showed that more than 80 % of sodium lauryl sulfate (SLS) was present at the water/droplet interface in the styrene miniemulsion systems by determining the aqueous phase SLS concentration by measuring the surface tension using the maximum bubble pressure method. Chang et al.[45] determined the critical micelle concentration (cmc) of styrene miniemulsions and macroemulsions stabilized with SLS using a conductance technique and found that the cmc of the macroemulsion is only 10 % greater than that of SLS aqueous solution, whereas the cmc of the miniemulsion is about

5 times that of SLS aqueous solution. Therefore, the miniemulsion technique is an excellent technique to confine the stabilizer at the water/droplet interface.

Most minimeulsion polymers have been prepared using anionic surfactants such as sodium lauryl sulfate or sodium hexadecyl sulfate.[43] The application of nonionic surfactants provides colloidal stabilization via steric effects and decreases the sensitivity of the resulting latexes to the pH or ionic strength in the aqueous solution. In addition, they provide freeze-thaw stability. Because of these advantages, there have been many attempts to prepare miniemulsion polymers stabilized with nonionic surfactants. The initial work applying nonionic surfactants (more specifically water-soluble polymers, PVA) to stabilize the miniemulsion droplets was done by Wang and Schork.[46] Their main objectives were to stabilize vinyl acetate miniemulsion droplets using PVA and to study the feasibility of using polymers as a costabilizer instead of cetyl alcohol or hexadecane. Unfortunately, there was no detailed analyses for the PVA partitioning and extension to acrylic miniemulsions. Chern and Liou[47] studied the influence of the mixed SLS/NP-40 surfactants on the miniemulsion polymerization of styrene. Landfester et al.[48] studied the styrene miniemulsion polymerization using polyoxyethylene (50) hexadecyl ether. Chern and Chen[49] used NP-40 (nonylphenol polyoxyethylene (40) ether) coupled with different hydrophobes as costabilizers to observe the Oswald ripening in the styrene miniemulsion systems. Wu and Schork[50] studied the kinetics of miniemulsion polymerization of vinyl acetate stabilized with Brij 35 (polyoxyethylene (23) lauryl ether). de Brouwer et al.[51] applied nonionic surfactant such as Brij 98 (polyoxyethylene (20) oleyl ether) to overcome the stability problem of miniemulsions in living radical polymerization.

## 1.4 PROJECT OBJECTIVES

As discussed previously, to obtain stable acrylic emulsion polymers stabilized with PVA, the aqueous phase grafting should be suppressed and the proper grafting architecture should be maintained. Using the miniemulsion approach, the partitioning of PVA in aqueous phase can be minimized, resulting in the suppression of the aqueous phase grafting. Also, it is expected that the main grafting site will be water/droplet interface, resulting in the enhancement of grafting at the interface. Meanwhile, the grafting architecture in miniemulsion polymerization may differ from that in conventional emulsion polymerization because of interfacial grafting of PVA.

The objectives of this research are:

1. To study the feasibility of preparing acrylic miniemulsion polymers stabilized with poly(vinyl alcohol) (Chapter 2).
2. To investigate the main grafting mechanism in miniemulsion polymerizations (Chapter 2).
3. To further investigate the grafting site using seeded emulsion polymerizations and the corresponding miniemulsion polymerizations using various peroxide initiators in terms of water-solubility (Chapter 3 and 4).
4. To compare the conventional and miniemulsion polymerizations in terms of grafting of PVA (Chapter 5).

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# CHAPTER 2

# PREPARATION OF ACRYLIC EMULSION POLYMERS STABILIZED WITH POLY(VINYL ALCOHOL) USING THE MINIEMULSION APPROACH

## 2.1 INTRODUCTION

The stabilizers used in preparing latexes have a strong influence not only on the colloidal properties of the latex but also the physical properties of the resulting films. Poly(vinyl alcohol) (PVA) stabilized latexes show better emulsion fluidity such as Newtonian flow, superior wet primary tackiness as adhesives, good mechanical film properties such as higher tensile strength and creep resistance, excellent mechanical stability, and higher freeze-thaw stability compared to latexes stabilized with low molecular weight surfactants. Nonetheless, the utilization of PVA as a stabilizer in emulsion polymerization has been limited to vinyl acetate systems because it seems to be difficult to graft PVA with monomers such as styrene, butadiene, and acrylic esters.

Generally, there are several routes to obtain grafted PVA. First, grafting can occur by the propagation of PVA macro-radicals that are generated by hydrogen abstraction using an initiator. In this reaction scheme, the initiator radical should have the capability of abstracting a hydrogen and this capability depends on the type of initiator. For example, persulfate initiators such as ammonium persulfate can easily abstract a hydrogen from PVA molecules[1]and the sites for hydrogen abstraction have been studied using NMR.[2] Okamura and Motoyama studied the effect of initiator type and observed that only 14 % of 2,2'-azobis(isobutyronitrile) (AIBN) radicals reacted with PVA, while 97 % of ammonium persulfate radicals did.[3] This is probably due to the easier hydrogen abstraction by the sulfate ion free radicals. Meanwhile, after the generation of PVA macro-radicals, these radicals should be confined with the monomers in the same location for the grafting reaction to be efficient.

In a second route, grafting can occur by the propagation of PVA macro-radicals that are generated by hydrogen abstraction by oligomeric radicals. However, usually carbon-centered radicals have little tendency for hydrogen abstraction because of their low reactivity. Exceptions are vinyl acetate and vinyl chloride radicals.[4,5] Third, grafting can take place through the termination of the generated PVA macro-radicals with the oligomeric radicals. This grafting reaction is limited by the water solubility of the oligomeric radicals. Gilbert described the critical chain length of oligomeric radicals in the aqueous phase for several monomers.[6] If the oligomeric radical surpasses this critical chain length, it will be adsorbed on the pre-existing particles or precipitate. This results in a low probability of terminating with PVA macro-radicals. From these considerations, the most plausible way to obtain the grafted PVA in acrylic emulsion polymerization seems to be the first approach cited above.

Grafted PVA acts as a polymeric stabilizer on the particle surface. The most effective polymeric stabilizers are considered to be amphipathic block or graft copolymers. The hydrophobic vinyl acetate blocks (or grafts) on the PVA backbone provide the primary anchoring segments, and the hydrophilic vinyl alcohol blocks project out into the aqueous phase as stabilizing moieties. In this stabilization mechanism, the grafting architecture seems to be important because the surface activity of polymeric stabilizers is most pronounced when hydrophobic or hydrophilic units are well segregated in the molecule. If the grafted chains are randomly dispersed along the PVA backbone during the polymerization, the stabilization will be poor because there is no clear segregation between hydrophilic and hydrophobic blocks. The grafting architecture for maximum stabilization seems to be in the form of block copolymers and these can be ideally achieved using functional end groups, which can easily generate radicals by abstracting hydrogen using primary radicals (e.g., hydrogen of –SH end group).

Several researchers have proved that the grafting site is the aqueous phase in conventional emulsion polymerizations[2,7,8] and hydrogen abstraction mainly take places at the methine carbons of the PVA. [1,9] In aqueous phase grafting, the hydrogen abstraction by primary radicals on the PVA occurs randomly along the whole chain, and is followed by grafting, which may result in a decrease in the stabilization power owing to loss of the boundary of segregation between hydrophobic and hydrophilic portions. To maintain the segregation between hydrophobic and hydrophilic portions of the molecules, the average amount of grafted polymer per PVA molecule should be controlled or the grafted PVA should have a proper grafting architecture such as block copolymers

Craig studied the grafting of hydroxyl ethyl cellulose (HEC) in acrylate emulsion polymerizations and concluded that acrylate monomers (*n*-butyl acrylate was studied) had a higher propensity for grafting to PVA than vinyl acetate because of their higher reactivity, implying that colloidal instability of acrylic emulsion polymer systems stabilized with water-soluble polymers such as HEC and PVA might result from the excessive grafting of the water-soluble polymers (probably a higher amount of grafted polymers per PVA molecule).[10,11] Based on this explanation, to maintain the segregation between the hydrophobic and hydrophilic portions by suppressing excessive grafting on the PVA chain in the aqueous phase (actually decreasing the amount of grafted polymer per PVA molecule), several patents have been issued. These patents include the addition of water-soluble regulators such as mercaptoacetic acid and cyclohexyl amine,[12] the addition of water-soluble amino alcohol,[13] the combination of water-soluble and oil-soluble initiators such as persulfate initiator and azo type initiators,[14] the modification of PVA with a thiol-terminated group with a specific initiator such as potassium bromate,[15,16] and the addition of alcohol such as methanol.[17,18] Basically, these modifications are based on the suppression of aqueous phase grafting using chain transfer agents, which may result in adverse effects on the reaction kinetics and difficulties in reaction rate control because the addition of water soluble agents may also affect the concentration of primary radicals. Also, the final particle size was larger (> 0.5 μm in most cases) and the distribution broader.

Okaya et al. studied the grafting of PVA in MMA emulsion polymerizations.[19,20] To simulate the early stages of the emulsion polymerization, the monomer concentration was diluted to 1mL/100 g of water and 1 g of PVA (DP=580, DH~88%) was added with various initiator systems such as ammonium persulfate and azo initiators. They found that 90 % of the MMA and 60% of the PVA were grafted without any flocculation. Meanwhile, decreasing the PVA to 0.1 g resulted in the formation of coagulum, indicating that the higher amount of PVA is required to stabilize the latex in conventional emulsion polymerization. The amount of grafted PMMA was decreased by adding an alcohol such as isopropyl alcohol, implying that the addition of alcohol actually suppresses the grafting of acrylic monomer on the PVA backbone by decreasing the hydrogen abstraction from PVA by the sulfate radical, because of the competing hydrogen abstraction on the alcohol presumably. Also, it was observed that the particle size became larger with decreasing amount of grafted PMMA by adding alcohol, implying that the system may become unstable. However, there was no information reported on the amount of grafted PVA with added alcohol. Therefore, it is not clear whether the addition of alcohol affects only the amount of grafted PMMA.

Miniemulsions are aqueous dispersions of relatively stable oil droplets with sizes in the 50-500 nm region prepared by shearing a system containing monomer, water, surfactant (stabilizer), and costabilizer, which is added to suppress Ostwald ripening of the droplets.[21] During the formation of a miniemulsion, a large oil/water interface is created and there will be a large driving force for the adsorption of stabilizer on the monomer droplets Anderson et al.[22] showed that more than 80 % of the sodium lauryl sulfate (SLS) stabilizer was present at the water/droplet interface in the styrene miniemulsion systems by determining the aqueous phase SLS concentration via the surface tension using the maximum bubble pressure method. Chang et al.[23] determined the critical micelle concentration (cmc) of styrene miniemulsions and macroemulsions stabilized with SLS using a conductance technique. They found that only 10 % of the SLS are present at the water/droplet interface in macroemulsions at the cmc, whereas 80 % of the SLS are present at the water/droplet interface in miniemulsions at the cmc.

Therefore, the miniemulsion technique is an excellent technique to confine the stabilizer at the water/droplet interface. Using the miniemulsion approach, aqueous phase grafting (random grafting presumably) can be minimized, while grafting at the water/monomer interface may still maintain the segregated structure of the stabilizer.

In this chapter, we study the use of poly(vinyl alcohol) as stabilizer in the preparation of acrylic miniemulsions, followed by polymerizations to obtain stable latexes. This chapter focuses on the study of miniemulsions stabilized with PVA in terms of the type of costabilizer and the concentration of the PVA, and then the grafting of PVA in miniemulsion polymerizations as a function of the PVA concentration.

## 2.2 EXPERIMENTAL

### 2.2.1 Materials

*n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were passed twice through an inhibitor-removal column (Sigma-Aldrich). Hexadecane (HD, costabilizer, Sigma-Aldrich), cetyl alcohol (CA, costabilizer, Sigma-Aldrich), sodium bicarbonate ($NaHCO_3$, Fisher), and ammonium persulfate (APS, 99+ %, ACS Grade, Sigma-Aldrich) were used as supplied. Poly(vinyl alcohol) (PVA) was obtained as a commercial product (Poval 205, degree of hydrolysis (DH)=87~89%, degree of polymerization (DP)= 500, Kuraray Co. Ltd., Japan).

### 2.2.2 Miniemulsion Preparation and Polymerization

The recipe used to prepare the various miniemulsions comprising several different formulation components is shown in Table 2.1. PVA was dissolved by heating at 90 °C for 3 hrs in deionized water (c.a. 6 wt%) and the solution was filtered using a 200 mesh screen. The solids content of the PVA solution was determined gravimetrically and adjusted to 5.9 wt% by adding deionized water.

***Miniemulsions stabilized with HD:*** A specific amount of HD was mixed with the monomers (BA and MMA). An aqueous PVA solution and DI water were then added to the monomer mixture and stirred for 10 minutes to prepare a crude emulsion for 10 minutes prior to subjecting the system to high shear.

***Miniemulsion stabilized with CA:*** A specific amount of CA was mixed with the PVA solution and DI water and then stirred for 2 hrs at 70 °C. After cooling, undissolved CA particles were found for the higher amounts of CA (0.833 and 1.744 g). Monomers were added and stirred with a magnetic bar for 24 hrs to completely dissolve the CA particles and to obtain a good crude emulsion.

The crude emulsions were sonified using a Branson Sonifier (Model 450) at a 70 % duty cycle and a power setting of 8 for 10 minutes accompanied by continuous magnetic stirring in an ice bath. All miniemulsion polymerizations were performed in a 500 mL four-neck flask equipped with a reflux condenser, nitrogen gas inlet tube, and Teflon stirrer (~ 200 rpm) for 24 hrs at 60 °C.

**Table 2.1:** Recipe for the Miniemulsion Polymerization of *n*-Butyl Acrylate and Methyl Methacrylate

| Ingredient | Weight (g) | Concentration |
|---|---|---|
| Deionized water | 80.0 | |
| *n*-Butyl acrylate (BA)[a] | 0 – 20.0 | |
| Methyl methacrylate (MMA)[a] | 0 – 20.0 | |
| PVA 205 | 0.5 – 4.0 | 2.5 – 20 wt% based on monomer |
| Hexadecane (HD) | 0.726 | 3.6 wt% based on monomer |
| $NaHCO_3$ | 0.007 | 1 mM based on aqueous phase |
| Ammonium persulfate (APS) | 0.018 | 1 mM based on aqueous phase |

[a] The weight ratio of total monomers to water always kept at 20/80.

### 2.2.3 Analysis

Miniemulsion droplet sizes were measured by dynamic light scattering (DLS) (Nicomp, Model 370). The emulsion was diluted with a monomer-saturated water solution containing 0.1 wt % PVA. Latex particle sizes were measured by capillary hydrodynamic fractionation (CHDF, Model 1100, Matec Applied Sciences) and DLS. The molecular weight of PVA 205 was analyzed at 35 °C by gel permeation chromatography (GPC) using a Waters 515 HPLC pump system with two mixed packed columns (TSK gel-GMPWXL-Tosohaas) preceded by a guard column (TSK – Gel PWXL). The mobile phase was a 0.01 N $NaNO_3$ solution. Poly(ethylene oxide) polymers with molecular weights from 960 to 730,000 g/mol (Polymer Laboratories Inc.) were used as the calibration standards. Mark-Houwink constants for poly(ethylene oxide) and

PVA were taken from published values.[24,25] A serum replacement cell was used to determine the partitioning of the PVA between the surface of the miniemulsion droplets and the aqueous phase. Approximately 80 g of a miniemulsion was placed in the cell and confined by a polycarbonate membrane filter having a 0.4 μm pore size. A clear serum phase was withdrawn through the filter. To check the extent of degradation of the monomer droplets during these experiments, the droplet sizes before and after the experiments were compared. The difference between these two values was 2 ~ 7 nm, showing a relatively small degradation of the monomer droplets. To obtain enough serum for gravimetric analysis, the serum extraction time was varied from 4 hrs to 16 hrs depending on the viscosity of the medium.

The amounts of grafted PVA and adsorbed PVA after polymerizations were determined using the selective solubilization process.[26] Separation of the serum from the latex was carried out by ultracentrifugation (Beckman ultracentrifuge, model L8-70M, rotor SW41). Polyallomer (PP copolymer, SETON) centrifuge tubes (9.5 mL) were used with the swinging buckets. Approximately 10 g of original latex (solids contents ~ 20 wt%) was diluted to 10 wt% solids content, stirred for 10 min to achieve a uniform dispersion, and then centrifuged for 12 hrs at 37,000 rpm and 4 °C. The clear serum was carefully decanted. Acetonitrile was added to disperse and dissolve the sedimented polymer particles that include the grafted PVA and/or the adsorbed PVA, and stirred for 7 days via magnetic stirring. Afterwards, the residual water was removed by distillation of the acetonitrile/water azeotrope at 76 °C, and then the mixture of acetonitrile and polymers was centrifuged to remove the acetonitrile-soluble polymers, which do not contain grafted PVA or adsorbed PVA (2 hours at 18,000 rpm and 4 °C). The supernatant was carefully decanted. The centrifigation was repeated after redispersion of the sedimented polymers until no more polymers were solubilized (3 to 5 times). The acetonitrile-insoluble polymers that contain both the grafted PVA and PVA adsorbed on the particles, were dried, weighed, and mixed with DI water. The mixture was heated to 85 °C and stirred for 24 hrs to extract the water-soluble polymers (adsorbed PVA). Again, centrifugation was performed to separate the water-soluble polymers and the water-insoluble polymers. The same procedure was repeated once more. The water-soluble polymers were dried and weighed. The amount of grafted PVA was calculated by a total mass balance (grafted PVA = PVA in recipe – PVA in serum of latex – adsorbed PVA). The error was around ± 5 % for the whole procedure. Any coagulum after polymerizations was screened using a stainless steel mesh (#200) and dried in an oven and weighed.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Miniemulsion Study

#### 2.3.1.1 Effects of Costabilizers and Their Concentration on the Miniemulsion Stability

As discussed previously, a stable miniemulsion using PVA and costabilizers should be obtained to enhance the grafting of PVA at the water/monomer interface. Miniemulsion stability was determined by the droplet size as a function of time and concentration of costabilizers (HD and CA) using DLS. Figure 2.1 shows the effect of HD concentration on the stability of MMA/BA (50/50 wt%) miniemulsions prepared using PVA/HD. The miniemulsion stability was determined by the variation of droplet diameter as a function of time. The initial droplet diameter seemed to be independent of the HD concentration having an average value of ~200 nm. However, upon aging for 13 days, the droplet diameter greatly increased with decreasing HD concentration, implying instability of the miniemulsion. If the HD concentration was kept above 3.4 wt % based on monomer, the miniemulsion was stable for more than 2 weeks.

The stability of various miniemulsions prepared with PVA/CA is shown in Figure 2.2 as a function of time. In contrast to the miniemulsions prepared with PVA/HD, the droplet size increased as soon as sonification was stopped, indicating some instability of the miniemulsions, even with the CA concentration increased to 8.7 wt % based on monomer. Miller reported similar results for the miniemulsions of toluene stabilized with

SLS/CA and suggested that the primary reason for this instability may result from the redistribution of CA due to its finite water solubility (~ $10^{-5}$ g/dm$^3$), where the slower transport of CA occurs through the aqueous phase causing a non-equilibrium condition between droplets of different sizes.[27]

Therefore, the droplets prepared by CA are easily degraded with time, implying that PVA partitioning at the interface will be decreased with time due to coalescence of droplets, resulting in the decrease of interfacial area.

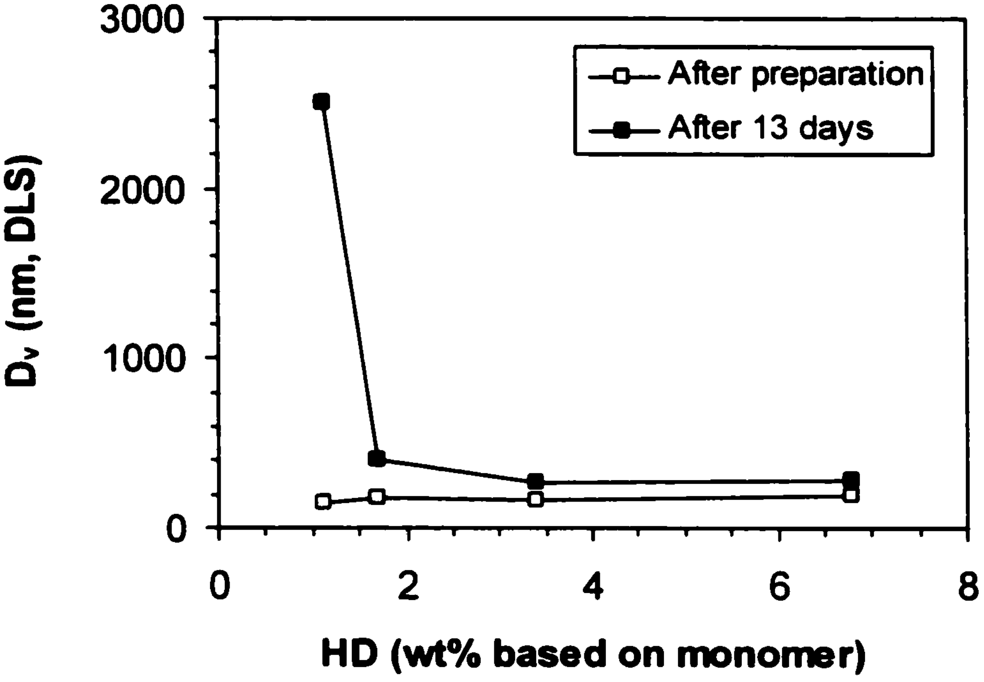

**Figure 2.1:** *Volume-average droplet diameter of miniemulsions measured by DLS as a function of hexadecane concentration (HD); PVA = 10 wt% based on monomer; BA/MMA = 50/50 wt%.*

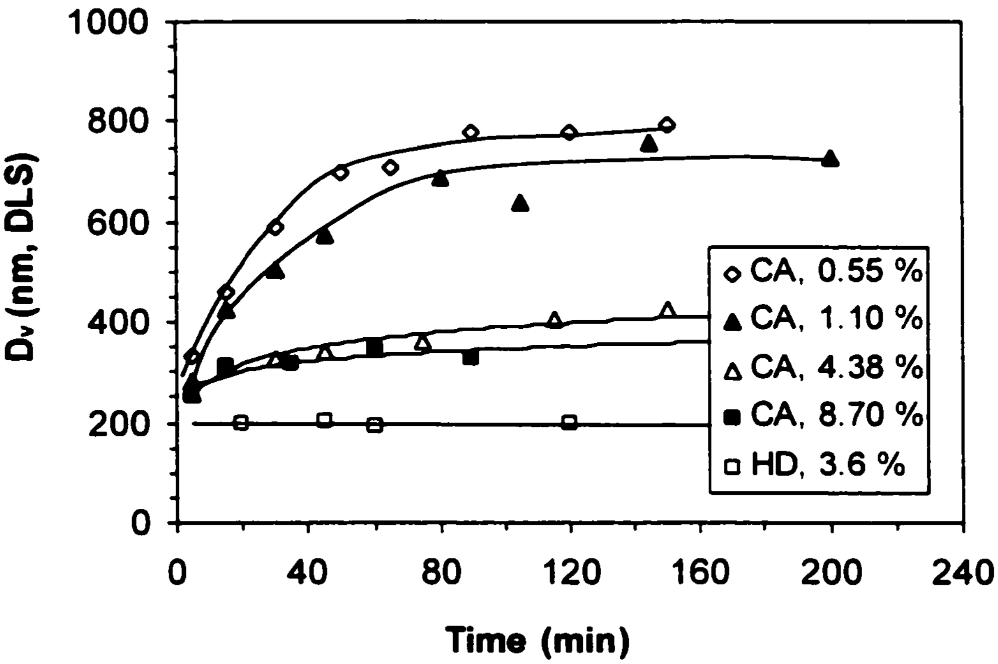

**Figure 2.2**: *Volume-average droplet diameter of miniemulsions measured by DLS as a function of cetyl alcohol (CA) concentration; PVA = 10 wt% based on monomer; BA/MMA = 50/50 wt%; HD = 3.6 wt% based on monomer.*

### 2.3.1.2 Droplet Size and PVA Partitioning as a Function of PVA Concentration

The effect of the PVA concentration on the droplet size (DLS) in miniemulsions prepared using HD (3.6 wt% based on monomer) as costabilizer is shown in Figure 2.3. The droplet size decreased exponentially with the PVA concentration, and then leveled-off, indicating a build-up of PVA molecules in the aqueous phase. To determine the PVA partitioning, the serum PVA of the miniemulsions was collected using a serum replacement cell (Figure 2.4). As expected from the PVA concentration dependence of the droplet size, the fraction of adsorbed PVA decreased sharply after around 10 wt% PVA. Based on the volume-average droplet diameter, the number of adsorbed PVA chains on the droplets increased linearly up to 10 wt% PVA concentration, and then was almost independent of the PVA concentration, showing surface saturation. The adsorption of PVA on the droplets at saturation was around 1.95 mg/m$^2$.

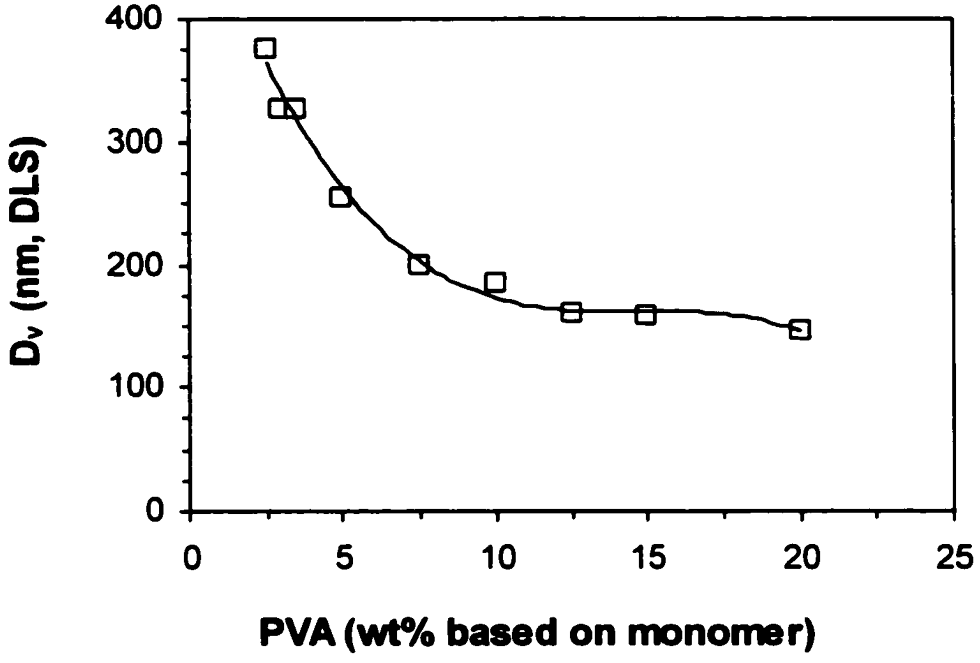

**Figure 2.3:** *Volume-average droplet diameter of miniemulsions measured by DLS as a function of PVA concentration; BA/MMA = 50/50 wt%; HD = 3.6 wt% based on monomer.*

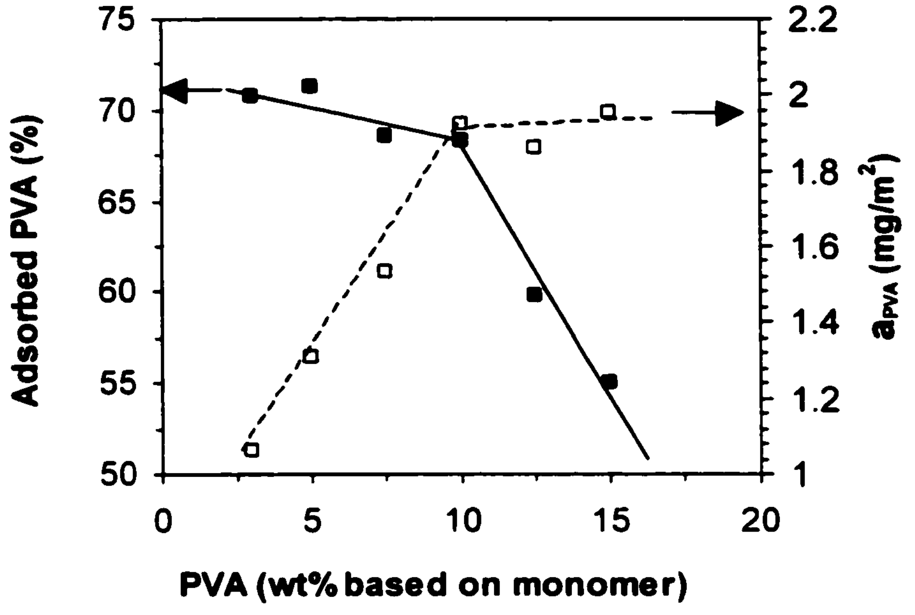

**Figure 2.4:** *Amount of adsorbed PVA on the droplets as a function of PVA concentration; BA/MMA = 50/50 wt%; HD = 3.6 wt% based on monomer; adsorbed PVA per unit area,* $a_{PVA}$*, calculated based on volume-average droplet size.*

Yuki et al. studied the adsorption of PVA on polystyrene (PS) and poly(vinyl acetate) (PVAc) and reported that the amounts of adsorbed PVA at saturation were 3.6 mg/m$^2$ for PS and 0.5 to 1.2 mg/m$^2$ for PVAc and depended on the surface charge density.[15] The difference in the saturation adsorption between MMA/BA miniemulsion droplets (1.95 mg/m$^2$) and PS (3.6 mg/m$^2$) or PVAc (0.5-1.2 mg/m$^2$) can be explained by differences in the hydrophilicity of the surfaces.

From the saturation adsorption (~1.95 mg/m$^2$) and degree of polymerization of PVA (DP=500), the adsorbed area per PVA chain ($a_s$) was estimated to be 18.8 nm$^2$ for MMA/BA miniemulsion droplets. The radius of gyration for PVA can be calculated using eqn (2.1):

$$R_g = 4.09(DP/6)^{1/2} \qquad (2.1)$$

where $R_g$ is the radius of gyration [Å] and DP is the degree of polymerization.[28] For the PVA in this study (DP~ 500, DH ~88 %), the projected area ($a_0=\pi R_g^2$) is about 45.4 nm$^2$ and the $a_s/a_0$ ratio ~ 0.414, indicating that the adsorbed PVA chains protrude into the aqueous phase.

### 2.3.1.3 Molecular Weight of Serum PVA as a Function of PVA Concentration

Initially, the PVA will have a certain molecular weight distribution as it comes from the manufacturer. There are two scenarios for PVA adsorption on the monomer droplets. Before surface saturation, most of the higher molecular weight PVA molecules will be preferentially adsorbed on the droplets. Therefore, it can be expected that the serum PVA has a lower molecular weight and relatively narrower molecular weight distribution compared to the original PVA. After surface saturation, there will be no space for adsorption of the higher molecular weight PVA, resulting in the accumulation of the higher molecular weight PVA in the serum. This is expected to increase and broaden the molecular weight distribution compared to the former case (before surface saturation). Molecular weights and polydispersity indexes ($M_w/M_n$) of the serum PVAs are shown in Figure 2.5 as a function of the initial PVA concentration. Basically, the molecular weight and polydispersity of the serum PVA are lower compared to the original PVA. As expected, the molecular weight in the serum increased sharply and the molecular weight distribution broadened after surface saturation (as previously discussed, surface saturation occurs around 10 wt% PVA).

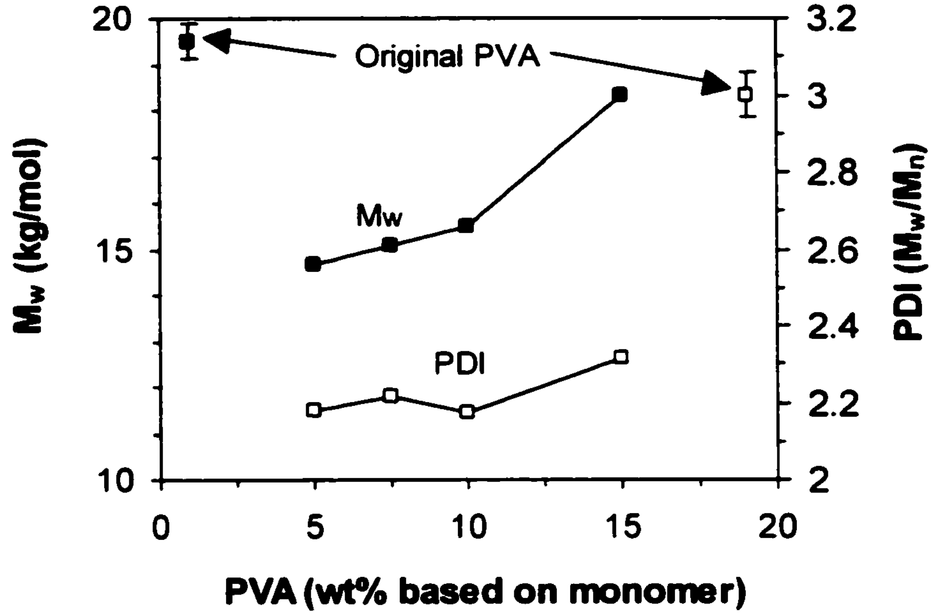

**Figure 2.5:** *Weight-average molecular weight and molecular weight distribution of serum PVA in miniemulsions as a function of PVA concentration: BA/MMA = 50/50 wt%; HD = 3.6 wt% based on monomer.*

#### 2.3.1.4 Droplet Size as a Function of Monomer Composition

So far, all miniemulsions were prepared using a fixed comonomer composition (BA/MMA=50/50 wt%). To further investigate the PVA adsorption on the droplets, the monomer composition was varied for a fixed PVA concentration (10 wt% based on monomer). After the preparation of the miniemulsions, the droplet size at each monomer composition was measured by DLS and then the serum PVA in the miniemulsion was extracted using the serum replacement cell. The amount of PVA adsorbed on the droplets was calculated by the subtraction of the serum PVA from the original PVA concentration in the aqueous phase. Figure 2.6 shows the number of droplets per unit volume and the amount of adsorbed PVA as a function of comonomer composition. The number of droplets per unit volume did not change much up to 75 wt% MMA monomer composition. However, a large increase of the number of droplets occurred beyond 75 wt% MMA. From Figure 2.6, if the cross-sectional area of the PVA molecule adsorbed on the droplets is independent of the comonomer composition, the amount of PVA should increase because the number of droplets per unit volume increased as the MMA composition increased. Therefore, these results show that the cross-sectional area of a PVA molecule greatly depends on the MMA concentration and increases with increasing MMA concentration, especially beyond 75 wt% MMA.

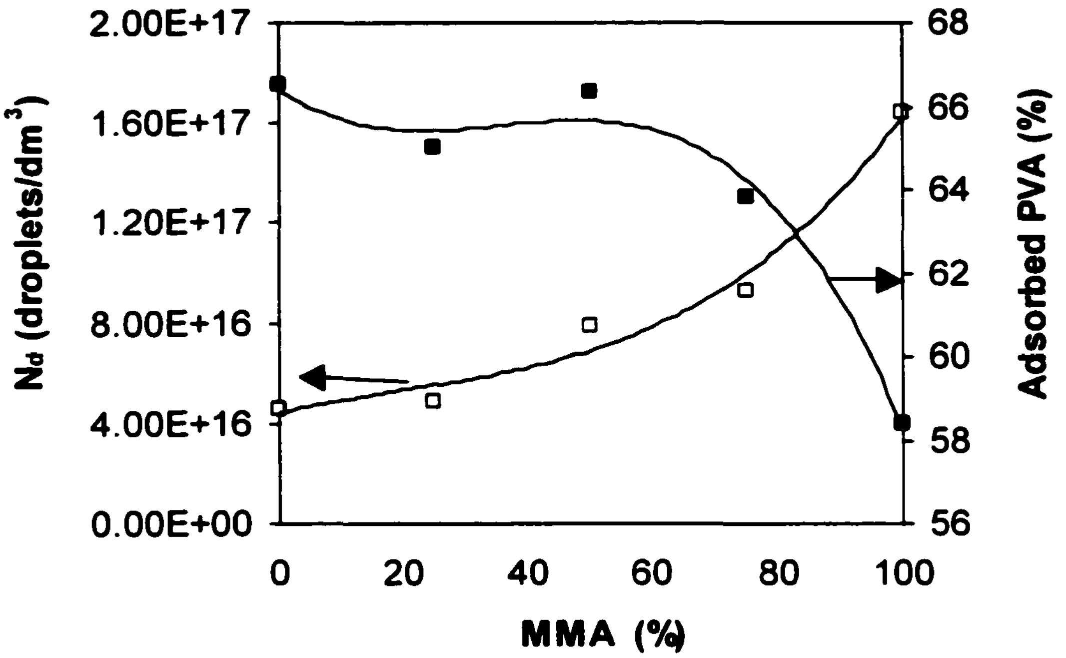

**Figure 2.6:** *Number of droplets per unit volume and the amount of adsorbed PVA on the droplets as a function of comonomer composition: PVA = 10 wt% based on monomer; HD = 3.6 wt% based on monomer.*

### 2.3.2 Polymerization

#### 2.3.2.1 Coagulum

Miniemulsion polymerizations were initiated with APS at 60 °C. After the polymerizations were complete, the amount of coagulum was determined by screening the coagulum using a stainless steel mesh (#200) and used as an indication of stability during the polymerization. The results are shown in Figure 2.7. In general, the amount of coagulum was small and decreased with increasing PVA concentration.

#### 2.3.2.2 Particle Size as a Function of PVA Concentration

Figure 2.8 shows the volume-average droplet diameters measured by DLS and final particle diameters measured by DLS and CHDF. To measure the droplet diameters before injection of APS at 60 °C, a small amount of miniemulsion was withdrawn from the reactor, cooled, and then the droplet size was measured by DLS as a function of the PVA concentration. The final particle diameter measured by CHDF at each PVA concentration was smaller than that measured by DLS, however the PVA concentration dependence of the final particle diameter measured by CHDF was similar to that measured by DLS. The PVA concentration dependence of the final particle diameter measured by DLS was similar to that of the droplet diameter and the final particle diameter is close to the droplet diameter at each PVA concentration, implying that droplet nucleation may be predominant and most of the initial droplets were nucleated.

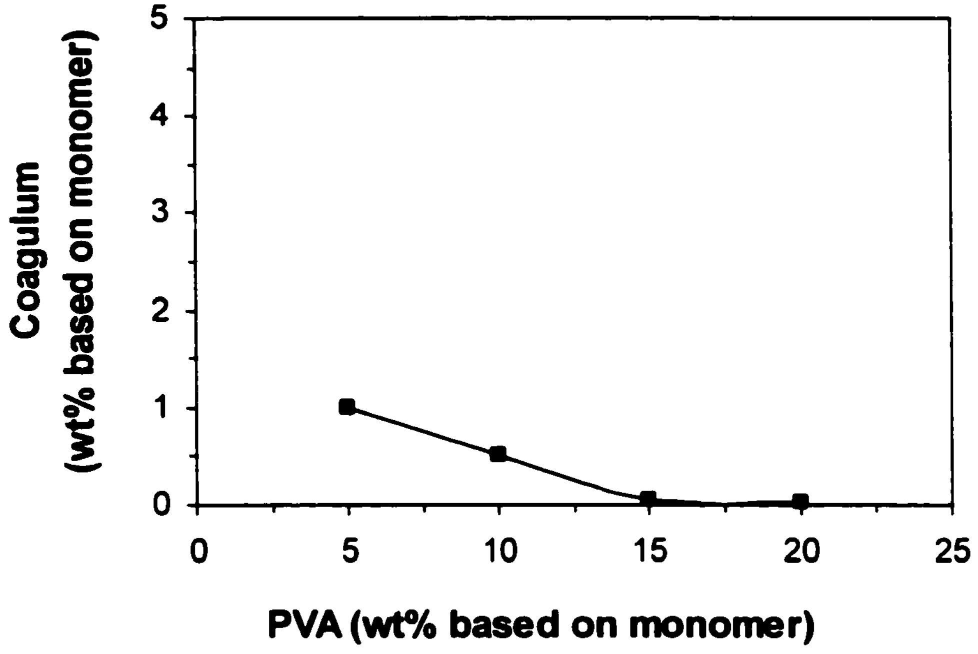

**Figure 2.7**: *Amount of coagulum determined using a stainless steel screen (#200) as a function of PVA concentration; BA/MMA = 50/50 wt%; HD = 3.6 wt% based on monomer; $T_r$ = 60 °C; APS = 1 mM.*

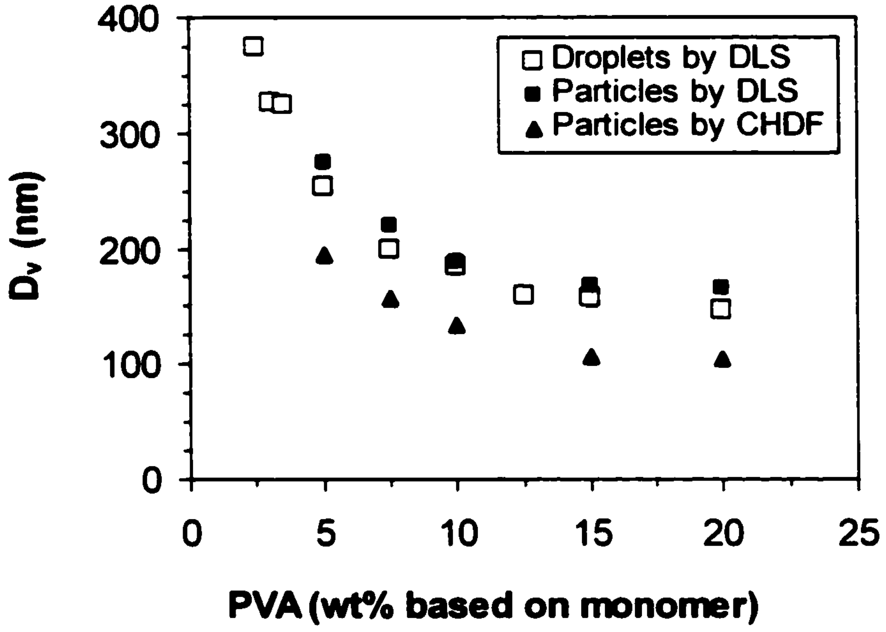

**Figure 2.8:** *Volume-average droplet diameter measured by DLS and final particle diameter measured by DLS and CHDF as a function of PVA concentration; BA/MMA = 50/50 wt%; HD = 3.6 wt% based on monomer.*

#### 2.3.2.3 Grafted and Adsorbed PVA of Latexes as a Function of PVA Concentration

The selective solubilization method was employed to separate the serum, grafted, and adsorbed PVA in the final latex. Figure 2.9 presents the amounts of grafted and adsorbed PVA as a function of PVA concentration based on a unit surface area. The amount of grafted PVA per unit area continuously increased up to 10 wt% PVA, and then became constant, which is consistent with the PVA concentration dependence of adsorbed PVA on the miniemulsion droplets. This strongly supports the hypothesis that the water/monomer interface is the main grafting site in the miniemulsion system.

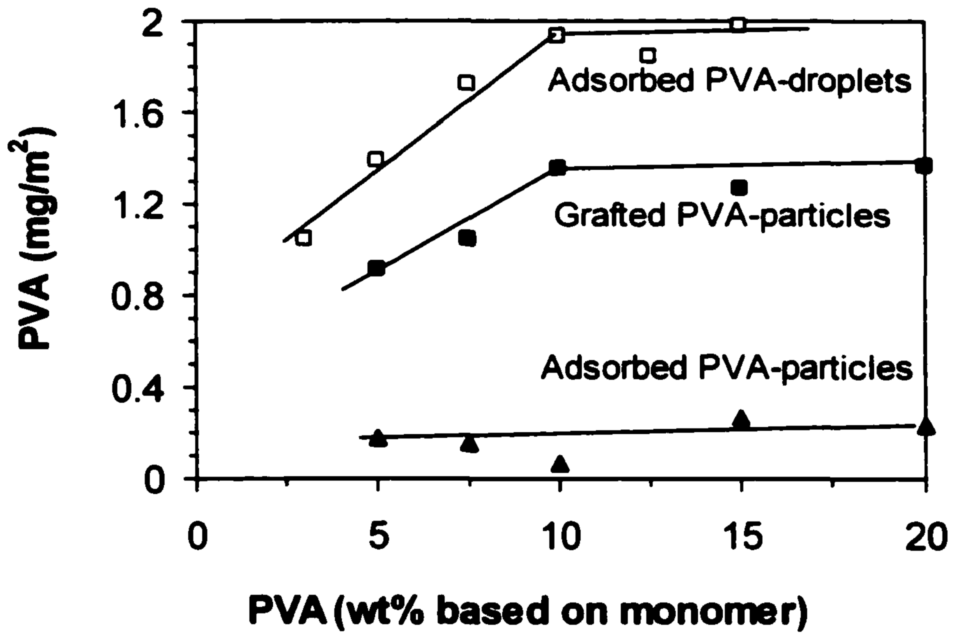

**Figure 2.9:** *Amount of PVA grafted and adsorbed per unit area of the final particles (obtained using the selective solubilization method) and the amount of PVA adsorbed on the droplets as a function of the PVA concentration (obtained via a serum replacement cell); PVA = 10 wt% based on monomer; HD = 3.6 wt% based on monomer; amount PVA of adsorbed on the droplet was estimated based on the volume-average droplet diameter measured by DLS; amounts of PVA grafted and adsorbed on the particles were estimated based on the volume-average particle diameter measured by CHDF.*

### 2.3.2.4 Evolution of Number of Particles ($N_p$) As a Function of Monomer Composition

The preceding polymerizations were performed at a fixed comonomer composition (BA/MMA=50/50 wt%). To further investigate the PVA grafting reaction in terms of monomer composition, the monomer composition was varied for a fixed PVA concentration (10 wt% based on monomer). Basically, all polymerizations carried out were stable for 24 hrs at 60 °C (coagulum < 0.5 wt% based on monomer). Figure 2.10 shows the evolution of the number of particles (calculated from the volume-average particle diameters measured by CHDF) during the polymerization as a function of monomer composition. Particle nucleation seems to cease at around 60% conversion and the nucleation mechanism does not appear to differ much for each composition.

The final number of particles increased with increasing MMA in the comonomer. However, the increase of the final number of particles is larger beyond 75 wt% MMA, which is consistent with the composition dependence of the initial number of monomer droplets, implying that droplet nucleation is mainly operative.

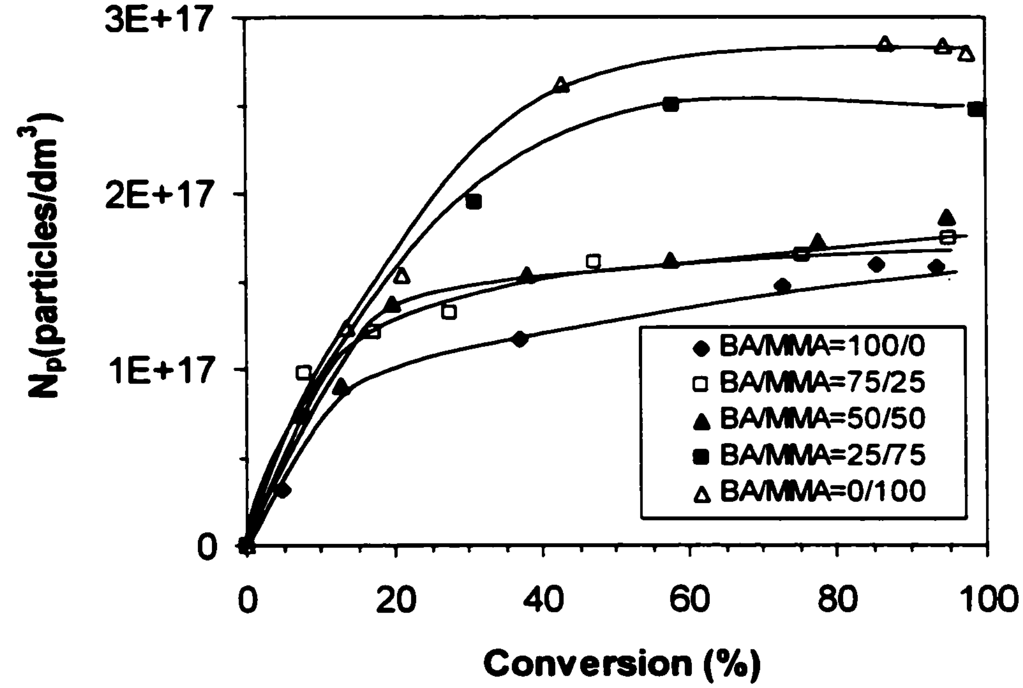

**Figure 2.10:** *Number of particles per unit volume of aqueous phase as a function of MMA comonomer composition and conversion; PVA = 10 wt% based on monomer; HD = 3.6 wt% based on monomer; particle size ($D_v$) was measured by CHDF.*

### 2.3.2.5 Serum of Latexes As a Function of Monomer Composition

The latex serum was extracted by two techniques, filtration (using a serum replacement cell (SRC)) and ultracentrifugation (UC), and compared with the original emulsion serum (Figure 2.11). The original latex was diluted to ~10 wt% solids for an efficient separation of the serum by ultracentrifugation. There was a small difference (~ 2%) in the two methods, however the trend was the same. For homopolymers such as PMMA and PBA or copolymers with low MMA contents (<10 %), the amount of serum PVA in the latexes was similar to that in the emulsions, implying little desorption during the polymerization.

However, for the copolymers with high MMA content (>10 wt%), the amount of serum PVA in the latexes was always larger than that in the corresponding miniemulsions, indicating a relatively significant desorption of PVA molecules during the polymerization. As previously discussed, the behavior of the amount of serum PVA in miniemulsions and the number of droplets per unit volume ($N_d$) were similar up to 75 wt% MMA , which means that the droplet surface characteristics do not differ much as a function of MMA up to 75 wt% MMA. In contrast, the addition of a small amount of MMA (10~15 wt%) greatly increased the PVA desorption during the polymerization. However, further additions of MMA did not result in a further increase in PVA desorption, suggesting that the surface characteristics of the final polymer particles abruptly changes beyond 10 to 15 wt% of MMA in the monomer mixture.

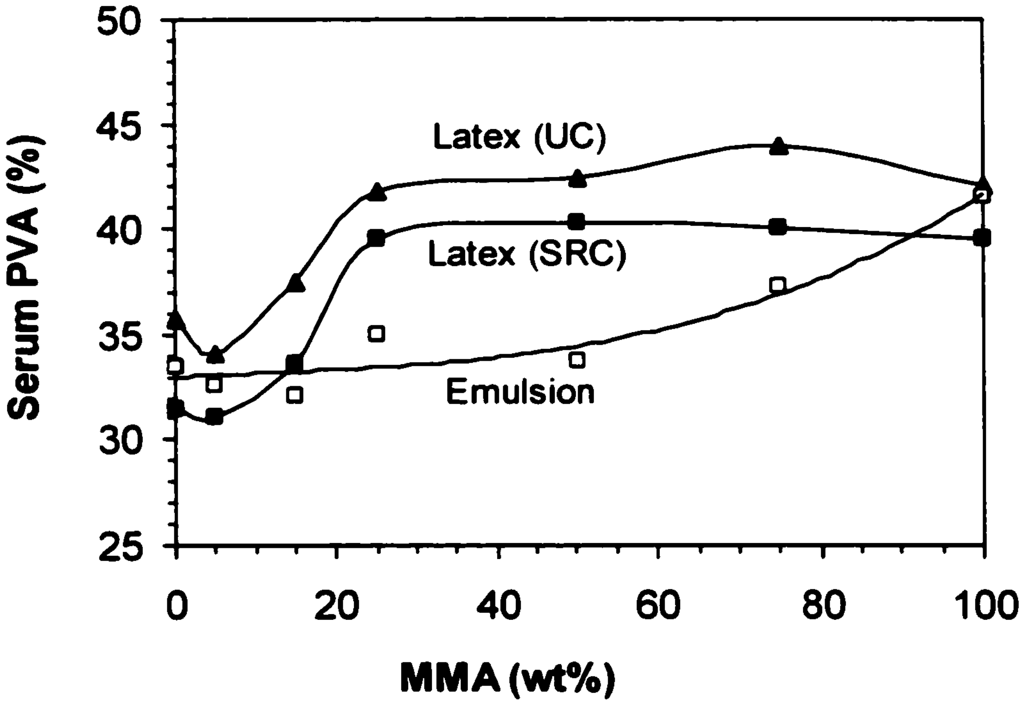

**Figure 2.11:** *Amount of serum PVA in latexes and miniemulsions as a function of monomer composition: UC = ultracentrifugation, diluted to ~10 wt% solids content; SRC = the serum replacement cell, ~20 wt% (original solids content).*

### 2.3.2.6 Grafted PVA As a Function of Monomer Composition

Figure 2.12 shows the amounts of adsorbed and grafted PVA in the final latexes as a function of the monomer composition. The amount of grafted PVA per unit area decreased as the addition of MMA increased from 5 wt% MMA. This might result from the decrease in the adsorbed PVA per unit area during the polymerization due to the changed surface characteristics, indicating again that the grafting depends on the number of adsorbed PVA molecules on the droplets/particles. The addition of a small amount of MMA (5 wt%) greatly increased the grafting and this suggests that some portion of the grafting may actually occur in the aqueous phase.

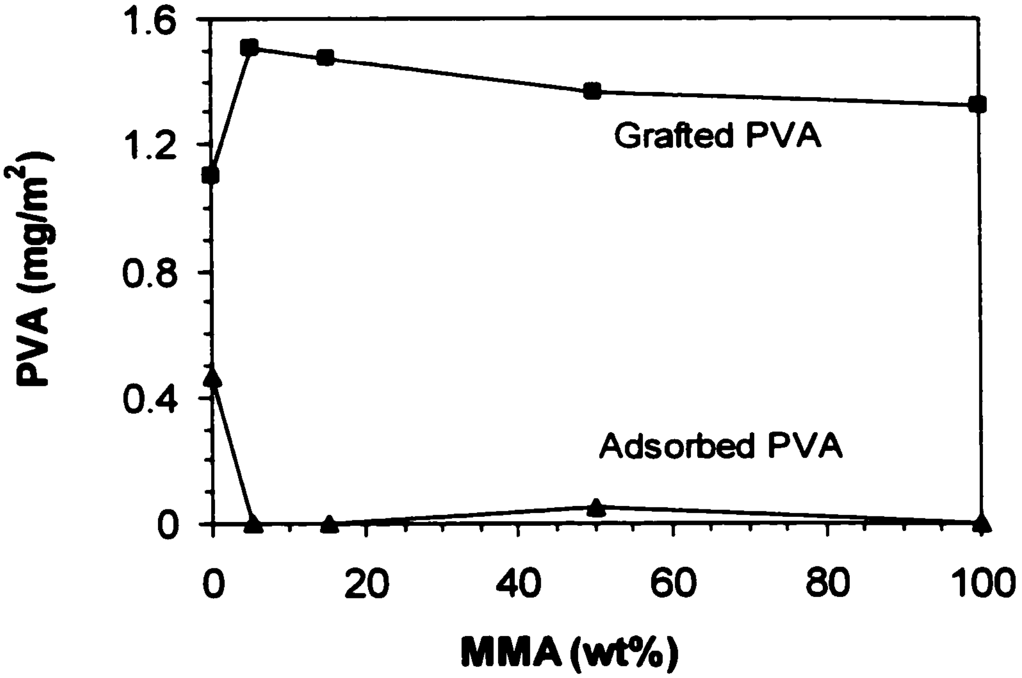

**Figure 2.12:** *Amounts of grafted and adsorbed PVA per unit area of the final particles as a function of MMA concentration obtained using the selective solubilization method: PVA = 10 wt% based on monomer; HD = 3.6 wt% based on monomer; amounts of PVA grafted and adsorbed on the particles were estimated based on the volume-average particle diameters measured by CHDF.*

## 2.4 CONCLUSIONS

Miniemulsions of *n*-butyl acrylate and methyl methacrylate (50/50 wt%) employing poly(vinyl alcohol) (PVA) as the sole stabilizer and hexadecane (HD) as the costabilizer were studied.

HD played a critical role in determining the stability of the miniemulsion droplets and 1.85 ~ 2.78 wt% of HD based on the monomers was required to obtain relatively stable droplets.

The droplet size decreased exponentially as the concentration of PVA was increased, reaching a lower limit. The number of adsorbed PVA chains on the droplets increased as the PVA concentration in the system increased up to around 10 wt%, and then remained almost constant, indicating droplet surface saturation.

A comparison of the number of droplets and the amount of the serum PVA in the miniemulsions showed that the cross-sectional area of the adsorbed PVA molecules on the droplets greatly increased above 75 wt% MMA in monomer composition.

The concentration dependence of grafted PVA was similar to that of the number of PVA molecules adsorbed on the monomer droplets, strongly supporting the hypothesis that the water/monomer interface is the main grafting site in these miniemulsion polymerizations.

Increasing MMA in the monomer composition had a great influence on the surface characteristics of the final particles, which caused a decrease in the amount of adsorbed PVA during the polymerization, and resulted in a decrease in the amount of grafted PVA per unit area.

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# CHAPTER 3

# GRAFTING OF POLY(VINYL ALCOHOL) (PVA) IN SEEDED EMULSION POLYMERIZATION OF ACRYLIC MONOMERS USING WATER-SOLUBLE, PARTIALLY WATER-SOLUBLE, AND OIL-SOLUBLE INITIATORS

## 3.1 INTRODUCTION

Poly(vinyl alcohol) (PVA)-stabilized latexes have some interesting features such as good rheology (Newtonian flow), superior primary tackiness as adhesives, good mechanical film properties such as higher tensile strength and moduli, excellent mechanical stability, and higher freeze-thaw stability compared to latexes stabilized by low molecular weight surfactants. Nonetheless, the utilization of PVA as a stabilizer in emulsion polymerization has been limited to vinyl acetate and its copolymers.

Grafted PVA acts as a polymeric stabilizer on the latex particle surface. The most effective polymeric stabilizers are considered to be amphipathic block or graft copolymers. The hydrophobic vinyl acetate blocks (or grafts) on the PVA backbone provide the primary anchoring segments, and the hydrophilic vinyl alcohol blocks project out into the aqueous phase as stabilizing moieties. In this stabilization mechanism, the grafting architecture seems to be important because the surface activity of polymeric stabilizers is most pronounced when the hydrophobic and hydrophilic units are well segregated in the molecule. If the grafted chains are randomly dispersed on the PVA backbone during the polymerization, the stabilization will be poor because there is no clear segregation between hydrophilic and hydrophobic blocks. The grafting architecture for maximum stabilization seems to be in the form of a block copolymer and this can be ideally achieved using functional groups on the chain end (e.g., hydrogen of –SH end group), which can easily generate radicals by hydrogen abstraction by the primary radicals.

In aqueous phase grafting, hydrogen abstraction on the PVA by primary radicals occurs randomly along the whole chain, and is followed by grafting, which may result in a decrease in the stabilization power owing to loss of the boundary of segregation between hydrophobic and hydrophilic portions. To maintain the segregation between these portions, the average amount of grafted polymer per PVA molecule should be controlled or the grafted PVA should have a proper grafting architecture such as in block copolymers.

Craig studied the grafting of hydroxyl ethyl cellulose (HEC) in acrylate emulsion polymerizations and concluded that acrylate monomers (*n*-butyl acrylate was studied) had a higher propensity for grafting to PVA than vinyl acetate because of their higher reactivity, implying that the colloidal instability of acrylic emulsion polymer systems stabilized with water-soluble polymers such as HEC and PVA might result from the excessive grafting of water soluble polymers (probably higher amounts of grafted polymer per PVA molecule).[1,2]

In our work, a miniemulsion approach was utilized to enhance the grafting of PVA with acrylic monomers such as methyl methacrylate (MMA) and *n*-butyl acrylate (BA), and stable latexes having 100 to 200 nm particle diameters were obtained from 5 to 20 wt% PVA based on monomer.[3] It was suggested that the main grafting site in these miniemulsion systems is the water/monomer interface. This was based on the comparison of the amount of PVA adsorbed per unit area of the miniemulsion droplet surface and the amount of PVA grafted per unit area of the final particle surface as a function of PVA concentration. However, there is still some uncertainty regarding the grafting site in the miniemulsion systems because water-soluble initiator (ammonium persulfate) was used and significant amounts of PVA (30 ~ 40 % of PVA in the recipe) were located in the aqueous phase.

Mechanistically speaking, the first step for grafting of PVA is hydrogen abstraction from the PVA backbone by initiator radicals[2,4] and the formation of PVA macro-radicals depends on the location of the PVA and the initiator. The location of the PVA depends on the emulsion system. In a conventional emulsion system, basically most of the PVA is located in the aqueous phase. In contrast, more than 70 % of the PVA is located at the water/droplet interface in miniemulsion systems.[3]

Seeded emulsion polymerization is a good method to study the interface as a grafting site because the total surface area in the system can be fixed, implying the same amount of PVA adsorbed per unit area of the particle surface. By varying the location of initiation using initiators that have different water solubilities, the site of formation of PVA macro-radicals will be in the aqueous phase and/or at the interface. This chapter investigates the grafting of PVA in seeded emulsion polymerizations as a function of the location of initiation using water-soluble, partially water-soluble, and oil-soluble peroxide initiators with water-soluble activator systems to further clarify the grafting .

## 3.2 EXPERIMENTAL

### 3.2.1 Materials

*n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were passed twice through an inhibitor-removal column (Sigma-Aldrich). Sodium bicarbonate ($NaHCO_3$, Fisher), hexadecane (HD, costabilizer, Sigma-Aldrich), ammonium persulfate (APS, 99+ %, ACS Grade, Sigma-Aldrich), sodium lauryl sulfate (SLS, Fisher), ascorbic acid (AA, Sigma-Aldrich), *t*-butyl hydroperoxide (TBHP, Sigma-Aldrich), *t*-butyl peroxyoctoate (TBPO, Elf-Atochem), ferrous sulfate (FES, Fisher), sodium formaldehyde sulfoxylate dihydrate (SFS, Acros), disodium ethylene diamine tetraacetate, (EDTA, Fisher), sodium chloride (NaCl, Fisher), Brij 35 SP (polyoxyethylene (23) lauryl ether, ICI Americas Inc.), sodium hydroxide (NaOH, Fisher) were used as supplied. Cationic ion exchange resin (AG 50W-X4, Biorad) was washed with deionized water, and anionic groups of anionic ion exchange resin (AG 1-X4, Biorad) was converted to hydroxyl group and washed with deionized water before use. Poly(vinyl alcohol) (PVA) was obtained as a commercial product (Poval 205, degree of hydrolysis (DH)=87~89%, degree of polymerization (DP)= 500, Kuraray Co. Ltd., Japan).

### 3.2.2 Polymerization

Seed latexes were prepared in two stages (Table 3.1). In the first stage, miniemulsion copolymerization of *n*-butyl acrylate and methyl methacrylate was carried out with SLS as a stabilizer and HD as a costabilizer. In the second stage, additional monomers and SLS were added to the first stage latex (miniemulsion copolymer) and stirred for 24 hrs. A buffer was added to the monomer-swollen first stage latex, the mixture was then heated to 60 °C, and APS initiator was injected. At each stage of this process, final conversions were measured using gravimetric analysis and more than 99 % conversion was obtained. The second stage latexes were cleaned using the ion exchange method. Cationic ion exchange resin was extensively washed with deionized water before use. Anionic ion exchange resin was converted from its chloride form to its hydroxide form with 3 N aqueous NaOH solution and then washed with deionized water. After cleaning of each ion exchange resin, the mixed ion exchange resins were prepared using the weight ratio of 51:49 (cationic:anionic). The same weight ratio of the solid polymer (the second stage latex) to the mixed resin was mixed and the mixture was stirred for two hours. The conductance of the latexes was measured after each mixed ion-exchange cycle and the cleaning procedure was repeated until the conductance of the latex reached a constant.

**Table 3.1:** Recipe for the Preparation of Seed Latex

| Ingredient | $1^{st}$ Stage (g) | $2^{nd}$ Stage (g) |
|---|---|---|
| $1^{st}$ Stage Latex (solids) | | 2.5 |
| *n*-Butyl acrylate (BA) | 10.0 | 5.0 |
| Methyl methacrylate (MMA) | 10.0 | 5.0 |
| Hexadecane (HD) | 0.726 | |
| Sodium lauryl sulfate (SLS) | 0.23 (10 mM) | 0.0186 (1.3 mM) |
| Ammonium pesulfate (APS) | 0.0549 (3 mM) | 0.0346 (3 mM) |
| Sodium bicarbonate ($NaHCO_3$) | 0.0201 (3 mM) | 0.0126 (3 mM) |
| Water | 80.0 | 50.0 |
| $T_r$ (° C) | 60 | 60 |
| Reaction Time (hr) | 4 | 4 |
| Remark | Miniemulsion polymerization * | Seeded Polymerization |

*Miniemulsion was prepared using a sonifier at power 8, 70 % duty cycle for 10 min in ice bath.

To carry out seeded polymerizations (Table 3.2), a solution of PVA (6 wt% aqueous solution) was added to the cleaned seed latexes and stirred gently to allow adsorption of the PVA on the particle surfaces. Monomers were added after 1 hr stirring of the seed/PVA mixture and stirred for an additional 2 hrs. The partitioning of PVA was determined by extraction of the serum using a serum replacement cell after 2 hrs mixing of the latex and it was found that 64 % of the PVA in recipe was adsorbed on the surface of the particles. The extension of the mixing time to as long as 24 hrs did not result in much difference in the amount of adsorbed PVA (66%). Seeded polymerizations were initiated using three types of initiators: such as HPO (water-soluble), TBHP (partially water-soluble), and TBPO (oil-soluble) with water-soluble activators.

*Initiation with HPO*: The mixture of seed, PVA, and monomers was heated to 60 °C and HPO was injected, followed by the addition of ascorbic acid solution.

*Initiation with TBHP*: The mixture of seed, PVA, and monomers was heated to 60 °C and the FES/EDTA solution added first, then the TBHP was injected, followed by the addition of SFS solution.

*Initiation with TBPO*: TBPO was mixed with the monomers first and then the mixture of monomer/ TBPO was added to the seed/PVA mixture. The mixture of seed, PVA, monomers, and TBPO was heated to 60 °C and the FES/EDTA solution was added, followed by the addition of SFS solution.

**Table 3.2**: Recipe for Seeded Emulsion Polymerizations with Water-Soluble (HPO), Partially Water-Soluble (TBHP), and Oil-Soluble (TBPO) Initiators

| | HPO (g) | TBHP (g) | TBPO (g) |
|---|---|---|---|
| Cleaned seed latex[1] | 5.0 | 5.0 | 5.0 |
| *n*-Butyl acrylate (BA) | 5.0 | 5.0 | 5.0 |
| Methyl methacrylate (MMA) | 5.0 | 5.0 | 5.0 |
| PVA 205 | 1.0 | 1.0 | 1.0 |
| HPO[2] | 0.01972 | | |
| AA | 0.0114 | | |
| TBHP[2] | | 0.0502 | |
| TBPO[2] | | | 0.125 |
| FES | | 0.0026 | 0.0026 |
| SFS | | 0.026 | 0.026 |
| EDTA | | 0.026 | 0.026 |
| Water | 109.44 | 111.78 | 110.71 |
| Reaction Time (hr) | ~20 | ~20 | ~20 |
| $T_r$ (° C) | 60 | 60 | 60 |

[1] From Table 3.1

[2] Peroxide initiator: 58 mM based on monomers

### 3.2.3 Analysis

Latex particle sizes were measured by capillary hydrodynamic fractionation (CHDF, Model 1100, Matec Applied Sciences) and dynamic light scattering (DLS) (Nicomp Model 370, Particle Sizing Systems). The eluant in CHDF was prepared using a mixture of SLS (0.1 mM) and an unknown nonionic surfactant (0.1 wt%) provided by Matec Applied Sciences, and the conductance of the eluant was 6 to 9 μS. The relative visocosity was determined by dilute solution viscometry using an Ubbelode viscometer with a flow time of 240 s for water at 25 °C. The amounts of PVA grafted and adsorbed at the end of polymerizations were determined using a selective solubilization process[5] and the amount of serum PVA was determined by serum extraction. Any coagulum formed during the polymerizations was screened using a stainless steel mesh (#200).

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 Particle Size and Distribution As a Function of Conversion

Figure 3.1 shows the seeded polymerization kinetics obtained using the different types of initiator. HPO and TBHP exhibited similar kinetics, while TBPO resulted in slower kinetics, implying a lower radical generation rate. The particle size distributions of the final latexes resulting from the seeded polymerizations, including the seed latex, are shown in Figure 3.2 as measured by CHDF. No secondary nucleation was noted for any reaction. However, the average final particle sizes after seeded polymerizations differed depending on the initiator, even though the same seed particles were used.

To further confirm this phenomenon, the particle size as a function of conversion using the different initiators was measured by CHDF (Figure 3.3). PVA was replaced with sodium lauryl sulfate (SLS) to prepare a standard sample (SLS/HPO system). The particle diameter as a function of conversion in the SLS/HPO system was similar to the estimated particle diameter based on the seed particle diameter at each conversion. Interestingly, the addition of PVA to the seed latexes (0 % conversion) resulted in a decrease in the particle diameter in CHDF. The difference in particle diameters between the standard sample (SLS/HPO) and each initiation system with PVA increased with conversion and depended on the initiation system.

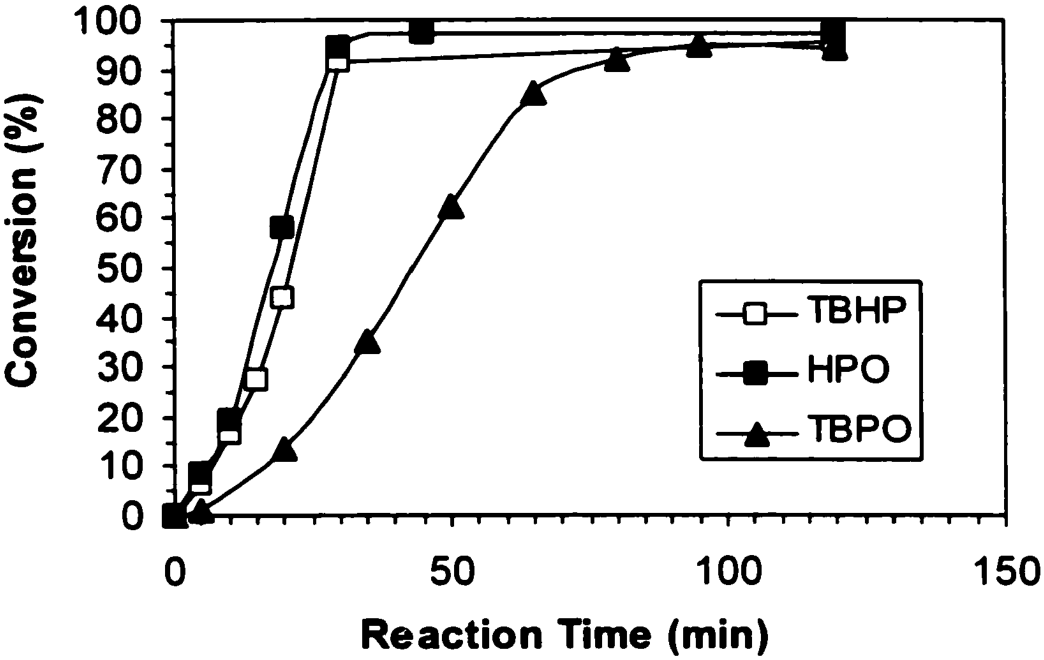

**Figure 3.1:** *Conversion as a function of time in the seeded emulsion polymerizations of MMA/BA (the weight ratio of monomer to seed = 2/1) using PVA as a stabilizer with varying initiator type;* $T_r$ *= 60 °C.*

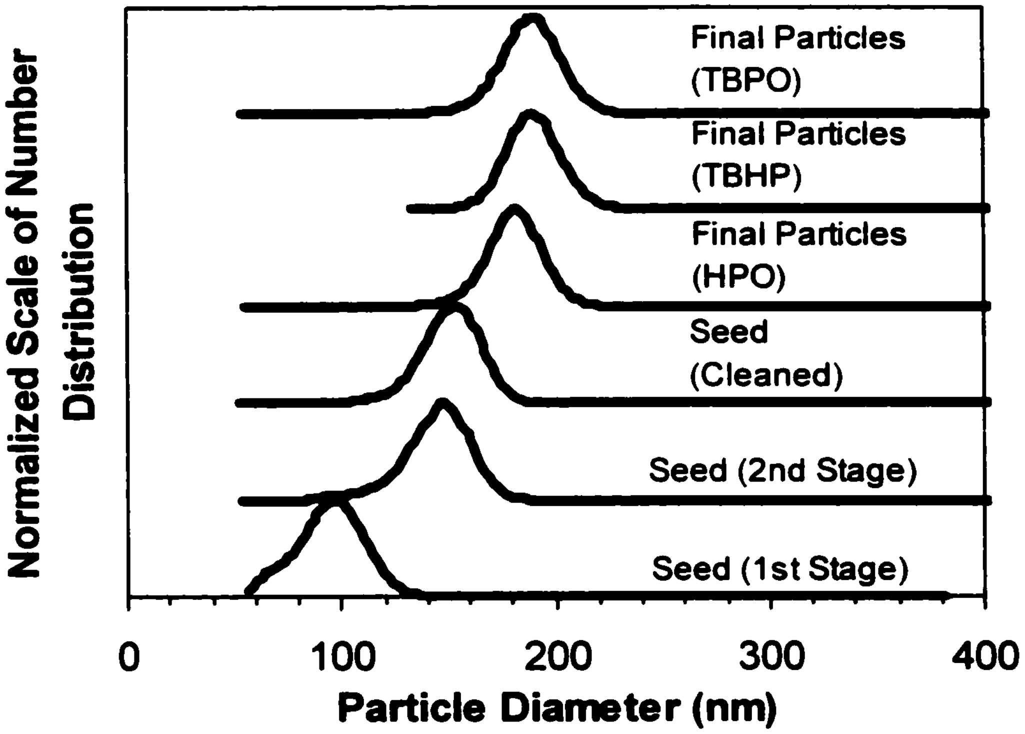

**Figure 3.2:** *Particle size number distributions of seed latexes and latexes resulting from the seeded emulsion polymerizations with varying initiator systems as measured by CHDF.*

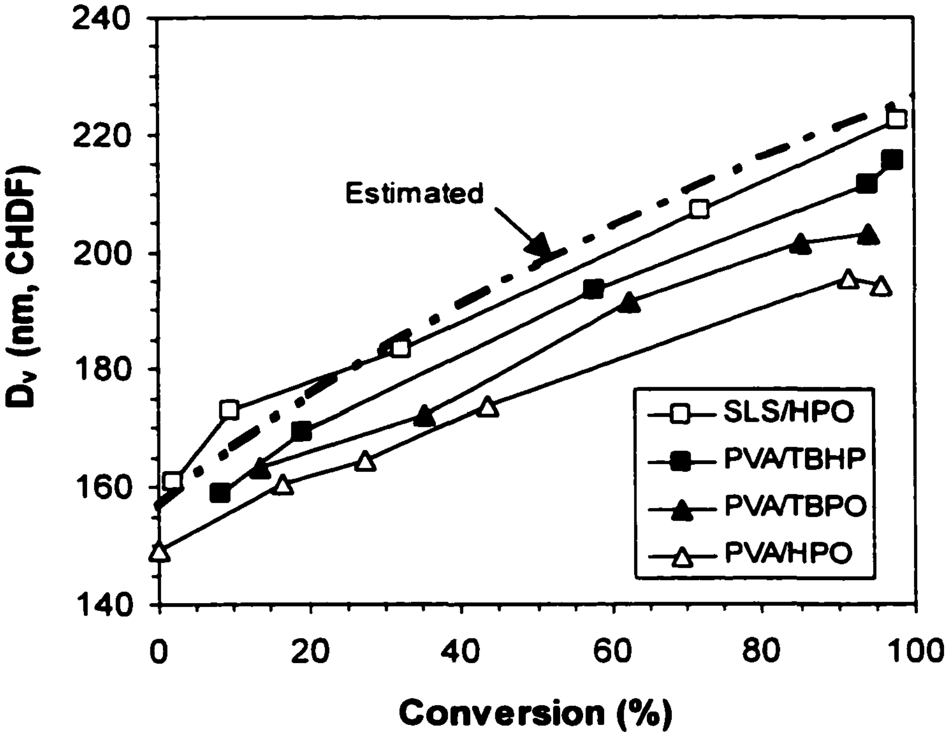

**Figure 3.3**: *Volume-average particle diameter as a function of conversion for the seeded emulsion polymerizations carried out with different initiation systems and stabilizers;* $T_r = 60$ *°C*

Dynamic light scattering (DLS) was employed for comparison with the CHDF results of the seed and final particles (Table 3.3). As expected, the addition of PVA to the cleaned latexes resulted in an increase in the particle diameter, indicating an increase in the hydrodynamic volume due to the adsorbed PVA layer. In addition, the trend observed for the final particle diameter as obtained by DLS as a function of the initiation system was significantly different from that measured by CHDF, implying different surface characteristics (probably different grafting architecture) and the existence of an interaction between the capillary wall in CHDF and the particle surface.

**Table 3.3**: Comparison of Particle Diameters Measured by CHDF and DLS for Seed and Final Particles

| | DLS | | | CHDF | | |
|---|---|---|---|---|---|---|
| | $D_n$[d] | $D_v$[e] | $D_I$[f] | $D_n$ | $D_v$ | $D_w$[g] |
| SLS/HPO (Cleaned)[a] | 210.5 ± 3 | 214.7 ± 2 | 216.0 ± 2 | 217.6 | 218.5 | 220.1 |
| SLS/HPO (Cleaned +PVA)[b] | 224.6 ± 2 | 234.9 ± 1.5 | 236.7 ± 2 | 205.7 | 206.7 | 208.8 |
| PVA/HPO | 205.9 ± 10 | 255.5 ± 12 | 256.0 ± 14 | 179.1 ± 2.7 | 179.8 ± 2.5 | 184.8 ± 0.2 |
| PVA/TBHP | 242.1 ± 2 | 243.8 ± 2.5 | 243.4 ± 3.5 | 205.3 ± 0.8 | 206.1 ± 0.8 | 208.1 ± 0.8 |
| PVA/TBPO | 235.8 ± 4 | 238.8 ± 2 | 239.2 ± 1.5 | 195.6 | 196.5 | 198.4 |
| Seed | 150.0 ± 4 | 152.6 ± 1.5 | 154.5 ± 0.4 | 155.5 ± 0.1 | 156.2 ± 0.1 | 157.8 ± 0.1 |
| Seed +PVA[c] | 162.2 | 167.1 | 170.2 | 146.3 | 147.5 | 149.8 |

*±: Deviations of two measurements

[a] Final particles prepared with SLS and HPO initiation system and cleaned with ion exchange resins

[b] Final particles prepared with SLS and HPO initiation system, cleaned with ion exchange resins, and mixed with PVA; the weight ratio of PVA to polymer = 0.333/5

[c] Seed particles mixed with PVA; the weight ratio of PVA to polymer = 0.170/5

[d] Number-average diameter

[e] Volume-average diameter

[f] Intensity-average diameter

[g] Weight-average diameter

### 3.3.2 Interaction Between Particle Surface and Capillary Wall in CHDF

CHDF is a technique of particle separation brought about by laminar flow in a small diameter capillary tube. [6-8] As a simplification of the process, the separation according to size by fluid flow is explained by two effects: (i) the laminar parabolic velocity profile developed by the fluid moving through the capillary tube allowing the particles to move at different speeds, and (ii) the inability of larger particles to sample by Brownian motion the slower streamlines near the capillary wall as do the smaller particles, known as a size exclusion effect. The larger particles, therefore, move at average speeds greater than the average eluant velocity. Recently, Amnuanypanich and Silebi studied the transport of polystyrene (PS) latex particles through a capillary in the presence of water-soluble polymers such as poly(ethylene oxide) (PEO).[9] Basically, steric effects by the polymers adsorbed on the particles were expected, resulting in an increase in the effective particle diameter and the reduction of the effective inner diameter of the capillary. It was found that the effective diameter of the particles was increased with increasing molecular weight of PEO using DLS and the separation factor (the ratio of the average velocity of particles to that of the eluant) was increased in CHDF, indicating a larger particle size (shorter elution time) with adsorption of the higher molecular weight PEO.

In contrast, in this study, the apparent particle sizes of the latexes with adsorbed PVA were smaller than that of the cleaned latex, implying the existence of an interaction between the polymer surface and capillary wall. To further characterize this interaction, four kinds of water-soluble polymers, namely PVA 105 (poly(vinyl alcohol), DP ~ 500, DH ~ 98 %, Kuraray Co. Ltd., Japan), PVA 205 (poly(vinyl alcohol), DP ~ 500, DH ~ 88 %, Kuraray Co. Ltd., Japan), PVA 80 (poly(vinyl alcohol), DP ~ 250, DH ~ 80 %, Sigma-Aldrich), and PEO 100K (poly(ethylene oxide), $M_v$ ~ 100,000 g/mol, Sigma-Aldrich), were selected. Each water-soluble polymer was added to a cleaned seed latex and the mixture was stirred overnight. The particle diameters were measured by DLS as a function of the weight ratio of water-soluble polymer to cleaned seed latex (Figure 3.4). Basically, the particle diameter increased with increasing ratio of water-soluble polymer to cleaned seed latex and then leveled-off. The exception was PVA 105 (fully hydrolyzed PVA) because of the poor adsorption on the particle surface.[10] The relatively smaller particle diameter at saturation for PVA 80 might have resulted from the lower molecular weight compared with PVA 205 even though the degree of hydrolysis of PVA 80 is lower than that of PVA 205. Meanwhile, the particle diameter at saturation for the PEO 100K was similar to PVA 80 even though the molecular weight of PEO 100K is high.

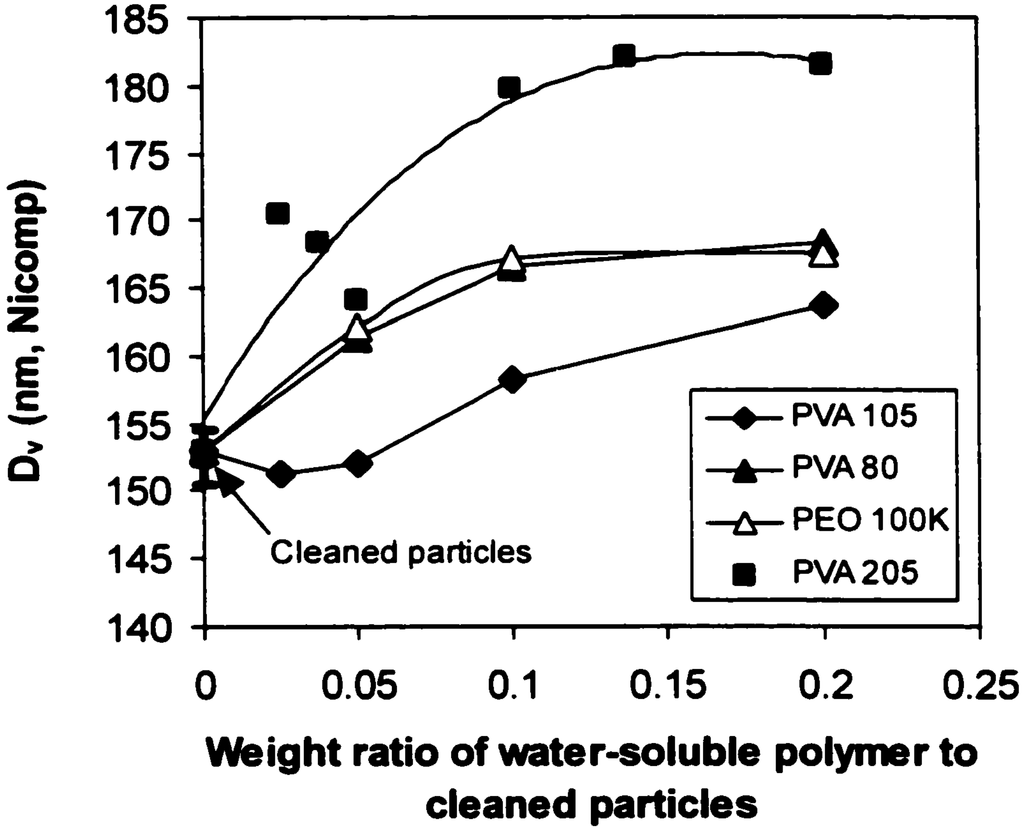

**Figure 3.4:** *Volume-average particle diameter measured by DLS as a function of the weight ratio of water-soluble polymers to cleaned particles based on weight: PVA 105 (poly(vinyl alcohol), DP ~ 500, DH ~ 98 %); PVA 205 (poly(vinyl alcohol), DP ~ 500, DH ~ 88 %); PVA 80 (poly(vinyl alcohol), DP ~ 250, DH ~ 80 %); PEO 100K (poly(ethylene oxide), $M_v$ ~ 100,000 g/mol).*

Based on the DLS results, different ratios of the four water-soluble polymers to cleaned seed latex were prepared to achieve the same apparent particle diameter by DLS (~ 167 nm) and then the particles were measured by both CHDF and DLS (Figure 3.5). Each particle diameter ($D_{v,p}$) was compared to the cleaned seed particle diameter ($D_{v,o}$) ($D_{v,p}/D_{v,o}=1$ means the particle diameter is the same as the seed). For PVA 105, particle diameters obtained by CHDF and DLS were similar to the original clean seed particle diameter, indicating a poor adsorption of PVA 105 on the particle surface, as expected. Meanwhile, for PEO 100K, the particle diameters by DLS and CHDF increased simultaneously, showing the increase of the effective diameter in DLS and the decrease of elution time in CHDF brought about by the adsorbed layer. These results are similar to Amnuaypanich and Silebi's work.

However, for PVA 205 and PVA 80, the adsorbed layer resulted in a decrease in the particle diameter in CHDF (i.e., increase in elution time) even though these resulted in an increase of the particle diameter by DLS, which means that there might be an interaction between the adsorbed PVA (partially hydrolyzed PVA) and the capillary wall.

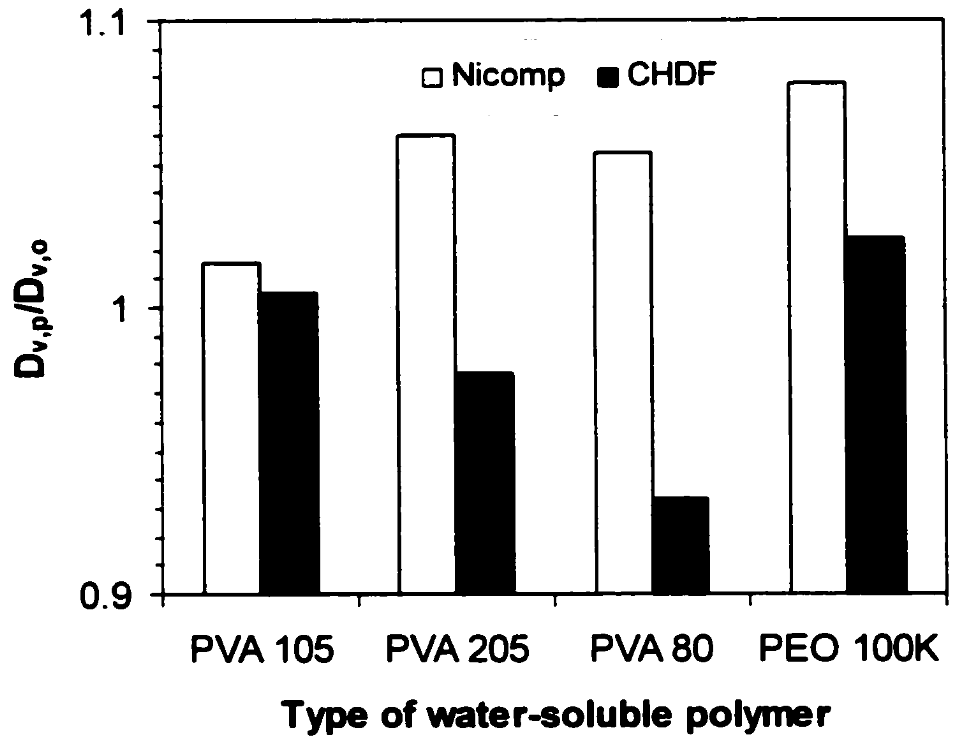

**Figure 3.5:** *Comparison of the ratio of the volume-average diameter of particles having various water-soluble polymers adsorbed on them ($D_{v,p}$) to cleaned seed particles ($D_{v,o}$) as obtained by CHDF and Nicomp; PVA 105 (poly(vinyl alcohol), degree of hydrolysis ~ 98%, degree of polymerization ~ 500), ratio of water-soluble polymer to cleaned seed=0.2/1; PVA 205 (poly (vinyl alcohol), degree of hydrolysis ~ 88%, degree of polymerization ~ 500), ratio of water-soluble polymer to cleaned seed=0.05/1; PVA80 (poly(vinyl alcohol), degree of hydrolysis ~ 80%, degree of polymerization ~ 250), ratio of water-soluble polymer to cleaned seed=0.2/1; PEO 100K (poly(ethylene oxide), $M_v$ ~ 100,000 g/mol), ratio of water-soluble polymer to cleaned seed=0.2/1.*

### 3.3.3 Effects of Eluants in CHDF

The eluant used for a commercial CHDF is a mixture of an anionic surfactant (SLS) and a proprietary nonionic surfactant. Therefore, it is difficult to specify the interaction between the PVA adsorbed on the particle surface and the capillary wall in CHDF. To further investigate the interaction, several types of aqueous eluant solutions, namely 0.4 mM NaCl, an anionic surfactant (sodium lauryl sulfate, SLS, 0.1 mM), a nonionic surfactant (Brij 35 SP (polyethylene oxide (23) lauryl ether) 0.1 wt% and NaCl 0.18 mM), and the mixture of SLS and Brij 35 S (SLS 0.1 mM and Brij 35 S 0.1 wt%) were prepared. As mentioned previously, different ratios of the four water-soluble polymers to cleaned seed latex were prepared to achieve the same apparent particle diameter by DLS (~ 167 nm), and then the apparent particle sizes of latexes having various water-soluble polymers and 109 nm polystyrene standard were measured by CHDF as a function of eluants. NaCl was added to adjust the conductance to be in the recommended range of 8 to 12 μS. Table 3.4 shows the volume-average particle diameter as a function of the water-soluble polymer and eluant composition. The apparent particle sizes differed greatly depending on the composition of the eluant. The accessibility of the particles to the capillary wall (the effective diameter of capillary) can be controlled by the ionic strength (varying the electric double layer thickness) and the steric barrier, which is affected by the adsorption of nonionic species such as nonionic surfactant or water-soluble polymers in the eluant.[11] However, in these systems, the effect of ionic strength seems to be small because the thickness of electric double layer by the difference of ionic strength is similar (several nm difference depending on systems). In the two eluants comprised of 0.4 mM NaCl and 0.1 mM SLS, the effective diameter of the capillary seems to be large because the diameter of the PS standard was smaller than the correct particle diameter (109 nm). In contrast, for the nonionic surfactant (Brij 35 S), the effective diameter of the capillary seems to be small because the diameter of the PS standard was much larger than 109 nm. Meanwhile, the diameter of the PS standard in the mixture of 0.1 mM SLS and 0.1 wt% Brij 35 SP was similar to the original value, implying that this eluant composition is similar to the composition of the standard CHDF eluant.

**Table 3.4:** Volume-Average Particle Diameter Measured by CHDF As a Function of the Eluant Composition

| | NaCl[1] (nm) | SLS[2] (nm) | Brij 35 SP[3] (nm) | SLS + Brij 35 SP[4] (nm) |
|---|---|---|---|---|
| PS-109[5] | 76.3 | 66.6 | 148.7 | 113.9 |
| Cleaned Seed[6] | 90.8 | 79.6 | 188.4 | 159.9 |
| Cleaned Seed + PVA 105[7] | 90.2 | 80.8 | 186.4 | 159.5 |
| Cleaned Seed + PVA 205[8] | 93.3 | 83.0 | 180.5 | 153.1 |
| Cleaned Seed + PVA 80[9] | 89.3 | 78.5 | 178.2 | 149.1 |
| Cleaned Seed + PEO 100K[10] | 94.6 | 84.1 | 189.2 | 165.2 |

[1] 0.4 mM NaCl aqueous solution, conductance 8.6 μS

[2] 0.1 mM Sodium lauryl sulfate, conductance 7.7 μS

[3] 0.1 wt% Brij 35 SP (polyoxyetyhlene(n=23) lauryl ether) + 0.18 mM NaCl, conductance 8.6 μS

[4] 0.1 wt% Brij 35 SP + 0.1 mM SLS

[5] Polystyrene standard 109 nm

[6] Cleaned with mixed ion exchange resin

[7] PVA 105 (poly (vinyl alcohol), degree of hydrolysis ~ 98%, degree of polymerization ~ 500, ratio of water-soluble polymer to cleaned seed=0.2/1

[8] PVA 205 (poly (vinyl alcohol), degree of hydrolysis ~ 88%, degree of polymerization ~ 500), ratio of water-soluble polymer to cleaned seed=0.05/1

[9] PVA 80 (poly (vinyl alcohol), degree of hydrolysis ~ 80%, degree of polymerization ~ 250), ratio of water-soluble polymer to cleaned seed=0.2/1

[10] PEO 100K (poly(ethylene oxide), $M_v$ ~ 100,000 g/mol), ratio of water-soluble polymer to cleaned seed=0.2/1

The results for the relative particle diameters for the cleaned seed latex having the various water-soluble polymers adsorbed on the particle surface as a function of the eluant composition using CHDF are shown in Figure 3.6. For PVA 105, the effect of the eluant composition on the apparent particle diameter seems to be negligible because of the low adsorption of PVA 105 on the particles and perhaps little or no interaction between PVA 105 adsorbed on the particles and the capillary. The apparent diameter of the particles having adsorbed PVA 80 was smaller than that of cleaned latex for all eluants used in this study, even 0.4 mM NaCl solution. One possible explanation for this smaller apparent particle size might be the screening of surface charge by the adsorption of PVA 80 that has a relatively strong hydrophobic character (degree of hydrolysis = 80 %). Only surface sulfate groups resulting from the persulfate initiator, stabilize the cleaned latexes. These create electrostatic repulsion between the particles themselves and between the particles and the capillary wall, which can push the particles into higher velocity streamlines (toward the center of the capillary). However, the adsorption of PVA 80 on the particle surface may result in the screening of the sulfate groups causing a decrease of repulsion, allowing the particles access to the lower velocity streamlines near the wall. The apparent size of particles having adsorbed PVA 205 and PEO 100K were larger than the cleaned particles, which is consistent with the DLS results. Interestingly, the addition of the nonionic surfactant (Brij 35 SP) resulted in a decrease in the apparent size of particles having adsorbed PVA 105, PVA 205, and PEO 100K, implying some retarding effects on the particle moving in the capillary caused by an interaction between the adsorbed water soluble polymers and the Brij 35 S eluant presumably.

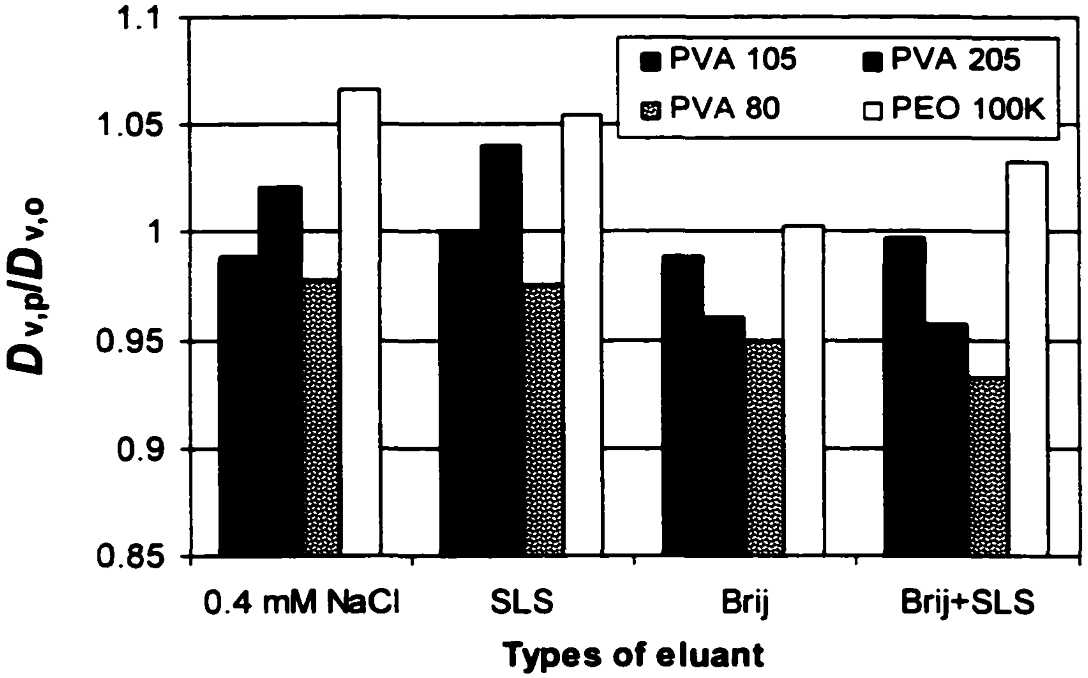

**Figure 3.6:** *$D_{v,p}/D_{v,o}$ as a function of the adsorbed polymer and eluant composition: NaCl 0.4 mM = aqueous 0.4 mM NaCl solution, Conductance = 8.3 μS; SLS = 0.1 mM sodium lauryl sulfate, Conductance = 7.8 μS, Brij = 0.1 wt Brij 35 SP (polyoxyethylene lauryl ether, n=23) with 0.18 mM NaCl, Conductance = 8.6 μS; Brij+SLS = 0.1 wt% Brij 35 SP with 0.1 mM SLS, Conductance = 11.9 μS.*

There have been extensive investigations regarding the interaction of nonionic water-soluble polymers that contain small amounts of a strong hydrophobic group and nonionic surfactants having ethylene oxide units, and this interaction can be explained by the hydrophobic interaction, resulting in the increase of medium viscosity.[12-16] However, it is questionable whether PVA has a hydrophobic interaction with a nonionic surfactant because the size of the hydrophobe in PVA is small (acetate group). Also, there are few reports about the interaction between PVA and nonionic surfactants having ethylene oxide units[17,18] and the interaction has been explained by the hydrophilic interaction.[17] To investigate the interaction between PVA and nonionic surfactant (Brij 35 SP), dilute solution viscometry using an Ubbelode viscometer was carried out to measure the relative viscosity at 25 °C and the results are shown in Figure 3.7. As a standard, an aqueous solution of Brij 35 SP was prepared. The relative viscosity of Brij 35 SP solution as a function of the concentration of Brij 35 SP was measured and increased with increasing concentration of Brij 35 SP. Two kinds of PVA, PVA 105 (98 % DH) and PVA 205 (88 % DH), were added to the Brij 35 SP solution, and then compared with the standard. The addition of PVA 105 did not affect the relative viscosity of the Brij 35 SP, however, the addition of PVA 205 to the Brij 35 SP solution resulted in the increase of the relative viscosity, indicating that there is an interaction between PVA 205 and Brij 35 SP and this is hydrophobic in nature. In addition, the strength of this interaction is quite small because the increase of the relative viscosity is only several percentages higher as compared to the standard Brij 35 SP solution.

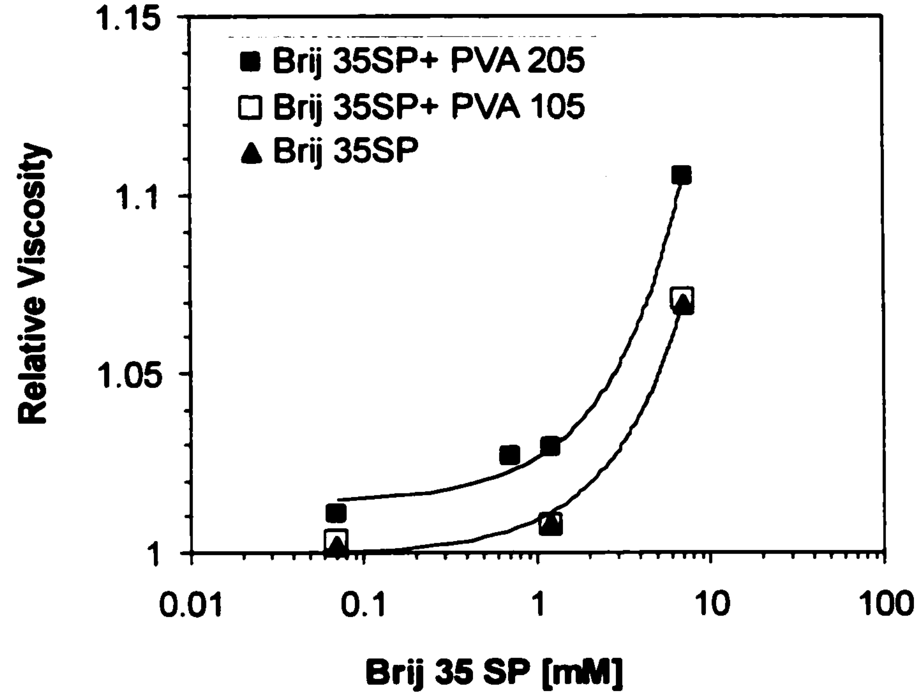

**Figure 3.7**: *Relative viscosity as a function of Brij 35 SP concentration and the addition of PVA; PVA 205, degree of hydrolysis = 88 %; PVA 105, degree of hydrolysis = 98 %.*

So far, it was observed that there is a hydrophobic interaction between partially hydrolyzed PVA such as PVA 205 and Brij 35 SP in solution. Then, how can the interaction of PVA 205 and Brij 35 SP in solution be applied in CHDF? If the interaction between the adsorbed PVA 205 on the particle surface and Brij 35 SP in the aqueous phase exists in CHDF, some particle aggregation is expected, resulting in a decrease of elution times (larger particle size) due to the size exclusion effect compared to the cleaned particles. However, the results were the opposite, implying that any interaction does not occur in the solution but rather between the surface of the capillary and the adsorbed water-soluble polymer on the particles. The capillary is made of fused silica. There have been several reports on the adsorption behavior of nonionic surfactants having ethylene oxide units on silica, where a strong adsorption has been noted.[19,20] Also, Somasundaran et al.[21,22] studied the adsorption behavior of alkylarylethoxylated alcohol nonionic surfactants on silica. They reported that the hydrophobicity of a silica surface can be controlled by the size of ethylene oxide units and suggested that the hydrophobic group of the nonionic surfactant would tend to dangle into the solution after silica surface saturation. A similar phenomenon could have occurred on the wall of capillary. The concentration of Brij 35 SP is quite high (17 times the cmc) and the surface area of the capillary wall is small. Therefore, there will be a lot of dangling hydrophobes (dodecyl groups) on the capillary wall and it is expected that these hydrophobes interact with the adsorbed partially hydrolyzed PVA such as PVA 205 and PVA 80, resulting in longer elution times.

This interaction seemed to be reduced by the addition of SLS to the Brij 35 SP eluant for PEO 100K because the particle size ratio increased by adding SLS. However, the interaction did not decrease for the particles adsorbed with partially hydrolyzed PVA even though SLS was added, suggesting that the interaction between partially hydrolyzed PVA adsorbed on the particles and Brij 35 SP on the capillary wall is relatively strong. In addition, the interaction is apparently proportional to the degree of hydrolysis of the PVA, which might be used to differentiate the surface properties of particles by CHDF.

### 3.3.4 Grafting of PVA

Using the selective solubilization method, the amounts of adsorbed and grafted PVA were determined as a function of the type of initiator (Table 3.5). The amount of grafted PVA formed with TBPO as initiator was very significant and similar to that obtained with HPO, strongly supporting the idea that the interface is a grafting site. However, there is still question whether or not the interface is the main grafting site even when water-soluble initiator is employed as initiator.

**Table 3.5:** Grafted and Adsorbed PVA Obtained from Seeded Emulsion Polymerizations Using Various Initiators

| | Grafted PVA (%) | Adsorbed PVA (%) |
|---|---|---|
| HPO | 59 | 1 |
| TBHP | 29.1 | 24.5 |
| TBPO | 52 | 1.5 |

During the polymerization, approximately 30 ~ 40 % of the PVA exists in the aqueous phase due to its partitioning, implying that there is a high probability for aqueous phase grafting when a water-soluble initiator is used. Therefore, it is difficult to differentiate between aqueous phase grafting and interface grafting in the water-soluble initiator system. To clarify this situation, the serum PVA was removed after adsorption of PVA on the cleaned seed latexes. PVA partitioning was determined after mixing it with the cleaned seed latexes (40 % PVA in aqueous phase and 60 % at interface) and the serum PVA was removed using serum replacement over several days. During the cleaning procedure, the serum PVA was collected with a certain interval, dried, and weighed to determine the PVA partitioning in the aqueous phase. The cleaning was continued until the PVA partitioning in the aqueous phase varied little with time. 95 % of the serum PVA was removed successfully from the seed latexes. To minimize the desorption of PVA from monomer-swollen seed particles due to a temperature increase, the polymerization using the HPO/AA system was carried out at 30 °C (Table 3.6). Using the selective solubilization method, the amount of grafted PVA was determined. About 85 % of the PVA adsorbed on the seed particles before the polymerization became grafted PVA (51% PVA in recipe), indicating that the interface is still a main grafting site even though a water-soluble initiator is employed. Meanwhile, the amount of grafted PVA obtained with TBHP was smaller than that with HPO or even TBPO. Based on the kinetics data (Figure 3.1), the primary reason for the relatively low amount of grafted PVA was assumed to be the extremely fast radical generation rate that may result in mutual termination reactions between the primary radicals or termination between the generated PVA radical and the primary radicals. This issue has been further investigated in chapter 4.

**Table 3.6:** Recipe for Seeded Polymerization with HPO Initiation System after Removing Serum PVA

| Ingredient | Amount (g) |
|---|---|
| Deionized water | 78.3 |
| Seed[a] | 4.7 |
| *n*-Butyl acrylate (BA) | 5.0 |
| Methyl methacrylate (MMA) | 5.0 |
| PVA 205[b] | 0.295 |
| HPO[c] | 0.0197 |
| Ascorbic Acid | 0.0114 |

[a] Serum PVA was removed using a serum replacement cell

[b] Adsorbed PVA

[c] 58 mM based on monomers

### 3.3.5 Grafted PVA vs. Interaction in CHDF

Figure 3.8 shows the final particle diameters as measured by CHDF and DLS as a function of the amount of grafted PVA. Apparently, the increase in the grafting resulted in an apparent decrease in the particle diameter in CHDF, implying a greater interaction between the grafted PVA and the capillary wall with increasing amount of grafted PVA. In contrast, the final particle diameters obtained by DLS showed a slight increase with increasing amount of grafted PVA. The final CHDF particle diameters using TBPO and HPO as initiators were significantly different, even though the amounts of grafted PVA were not much different (52 % versus 59 %, respectively). This implies that there are relatively more grafted chains on the surface of particles prepared by HPO as a initiator, resulting in stronger interaction between particle surface and the capillary wall, compared with the surface of particles prepared by TBPO. Therefore, the architecture of the grafted PVA seems to be different depending on the initiation site.

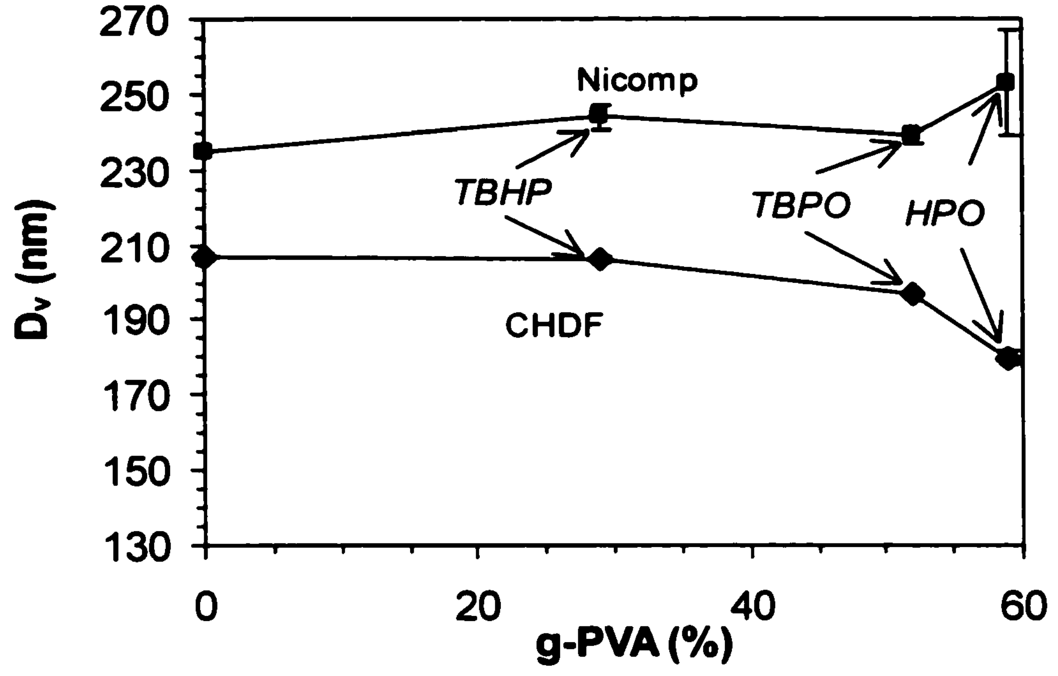

**Figure 3.8:** *Comparison of volume-average particle diameters obtained by CHDF and Nicomp as a function of the amount of PVA grafted in seeded emulsion polymerizations; grafted PVA = 0 % (PVA was adsorbed on clean seed particles.); grafted PVA = 29 % (TBHP initiation system); grafted PVA = 52 % (TBPO initiation system); grafted PVA = 59 % (HPO initiation system).*

## 3.4 CONCLUSIONS

The amounts of grafted PVA were similar in the HPO- and TBPO-initiated seeded emulsion polymerizations, strongly supporting the interface as the main grafting site. Seeded emulsion polymerizations carried out after removing the serum PVA showed that the interface was still the main grafting site even when a water-soluble initiator (HPO) was used.

The adsorption of partially-hydrolyzed PVA on cleaned latexes resulted in an interaction between the nonionic surfactant on the capillary of the CHDF and the PVA adsorbed on the particles, and the interaction was apparently proportional to the degree of hydrolysis of the PVA chains. The apparent final particle sizes of the latexes prepared with TBPO and HPO differed by CHDF, even though the amount of grafted PVA was not much different, implying that the architecture of the grafted PVA in the TBPO system differed from that in the HPO system.

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# CHAPTER 4

# GRAFTING OF POLY(VINYL ALCOHOL) (PVA) IN MINIEMULSION POLYMERIZATION OF ACRYLIC MONOMERS USING WATER-SOLUBLE, PARTIALLY WATER-SOLUBLE, AND OIL-SOLUBLE INITIATORS

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## 4.1 INTRODUCTION

Polymeric stabilizers, such as poly(vinyl alcohol) (PVA), have been widely used industrially in combination with low molecular weight surfactants for the emulsion polymerization of vinyl acetate and vinyl acetate-ethylene comonomer systems.[1] These aqueous dispersions stabilized with poly(vinyl alcohol) are useful in the manufacture of latex paints, binders for non-woven materials, water-based inks, paper coatings, and water-borne adhesives such as pressure sensitive adhesives because of improved rheology, chemical and mechanical stability, primary tackiness, and film performance such as tensile strength and modulus.[2,3] During the polymerization, the grafting and/or the adsorption of polymeric stabilizers are required to obtain stable latexes.[4,5] However, in the emulsion polymerization of monomers comprising acrylics or styrene using PVA as a stabilizer, coagulum forms due to a lack of mechanical stability presumably and this might result from the extensive grafting of PVA with acrylic monomers, compared to vinyl acetate, because of their higher reactivity.[6,7]

In our work, a miniemulsion approach was applied to study the grafting of PVA with acrylic monomers such as methyl methacrylate (MMA) and *n*-butyl acrylate (BA) and stable latexes were obtained using 5 to 20 wt% PVA based on monomer. This was despite the fact that the miniemulsion systems resulted in extensive grafting, where 35 to 55 % of the VA in the recipe was grafted on the particle surfaces.[8] It was suggested that the main grafting site in these miniemulsion systems is the water/monomer interface. This was based on a comparison of the amount of PVA adsorbed per unit area of miniemulsion droplet surface and the amount of PVA grafted per unit area of final particle surface, as a function of the PVA concentration. Also, seeded emulsion polymerizations using PVA as stabilizer were carried out to further clarify the role of the interface as a grafting site using water-soluble (hydrogen peroxide, HPO), partially water-soluble (*t*-butyl hydroperoxide, TBHP), and oil-soluble (*t*-butyl peroctoate, TBPO) initiators.[9] The amount of grafted PVA in the seeded polymerization initiated with HPO was similar to that initiated with TBPO, strongly supporting the hypothesis that the interface is the main grafting site.

Hence, we report further studies of the grafting of PVA as a function of the location of initiation using water-soluble, partially water-soluble, and oil-soluble initiators to further clarify the grafting site in miniemulsion polymerizations.

## 4.2 EXPERIMENTAL

### 4.2.1 Materials

*n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were passed twice through an inhibitor-removal column (Sigma-Aldrich). Sodium bicarbonate ($NaHCO_3$, Fisher), hexadecane (HD, costabilizer, Sigma-Aldrich), ammonium persulfate (APS, 99+ %, ACS Grade, Sigma-Aldrich), sodium lauryl sulfate (SLS, Fisher), ascorbic acid (AA, Sigma-Aldrich), hydrogen peroxide (HPO, Sigma-Aldrich), *t*-butyl hydroperoxide (TBHP, Sigma-Aldrich), *t*-butyl peroxyoctoate (TBPO, Elf-Atochem), ferrous sulfate (FES, Fisher), sodium formaldehyde sulfoxylate dihydrate (SFS, Acros), disodium ethylene diamine tetraacetate (EDTA, Fisher), 0.02 N NaOH (Fisher), 0.1 N $H_2SO_4$ (Sigma-Aldrich), phenolphthalein (Baker), methanol (VWR), and potassium thiocyanate (KSCN, Sigma-Aldrich) were used as supplied. Poly(vinyl alcohol) (PVA) was obtained from a commercial producer (Poval 205, hydrolysis (DH)= 87 ~ 89%, degree of polymerization (DP) = 500, Kuraray Co. Ltd., Japan).

### 4.2.2 Polymerization

#### 4.2.2.1 Miniemulsion Polymerization

The recipe used to prepare the various miniemulsions comprising several different formulation components is shown in Table 4.1. The PVA was dissolved by heating at

90°C for 3 hrs in deionized water (c.a. 6 wt%) and the solution was filtered using a 200 mesh screen. The solids content of PVA solution was determined gravimetrically and adjusted to 5.9 wt% by adding deionized water. A specific amount of HD was mixed with the monomers (BA and MMA). An aqueous PVA solution and DI water were then added to the monomer mixture and stirred for 10 minutes to prepare a crude emulsion for 10 minutes prior to subjecting the system to high shear. The crude emulsions were sonified using a Branson Sonifier (Model 450) at a 70 % duty cycle and a power setting of 8 for 10 minutes accompanied by continuous magnetic stirring in an ice bath.

*Initiation with HPO*: The miniemulsion was heated to 60 °C and HPO was injected, followed by the addition of ascorbic acid solution.

*Initiation with TBHP*: The miniemulsion was heated to 60 °C and TBHP was injected, followed by the addition of SFS solution.

*Initiation with TBPO*: TBPO was mixed with the monomers before preparation of the crude emulsion. The miniemulsion was heated to 60 °C and SFS solution was added.

**Table 4.1:** Recipe for Minemulsion Polymerizations with Water-Soluble (HPO), Partially Water-Soluble (TBHP), and Oil-Soluble (TBPO) Initiators

| Ingredient | HPO system<br>Weight (g) | TBHP system<br>Weight (g) | TBPO system<br>Weight (g) |
|---|---|---|---|
| *n*-Butyl acrylate (BA) | 10.0 | 10.0 | 10.0 |
| Methyl methacrylate (MMA) | 10.0 | 10.0 | 10.0 |
| Hexadecane (HD) | 0.726 | 0.726 | 0.726 |
| Poly(vinyl alcohol) (PVA 205)[1] | 2.0 | 2.0 | 2.0 |
| Hydrogen peroxide (HPO) | 0.0394 | | |
| Ascorbic acid (AA) | 0.0222 | | |
| *t*-Butyl hydroperoxide (TBHP) | | 0.104 | |
| *t*-Butyl peroctoate (TBPO) | | | 0.2484 |
| Ferrous sulfate (FES) | | 0.0052 | 0.0052 |
| Sodium formaldehyde (SFS) | | 0.052 | 0.052 |
| Ethylene diamine tetracetate (EDTA) | | 0.052 | 0.052 |
| Deionized water | 80.0 | 80.0 | 80.0 |

[1] PVA 205: degree of hydrolysis ~ 88%, degree of polymerization ~ 500

*Peroxide initiator: 58 mM based on monomers

#### 4.2.2.2 Seeded Polymerization with Different Monomer to Polymer (M/P) Ratios

Seeded polymerizations with different M/P ratios were carried out (Table 4.2). A solution of PVA was added to the cleaned seed particles and stirred gently. Monomers were added after 1 hr mixing of the seed particles/PVA mixture and stirred for an additional 2 hrs. The mixture of seed, PVA, and monomers was heated to 35 °C and the FES/EDTA solution added first, then the TBHP was injected, followed by the addition of SFS solution.

#### 4.2.2.3 Continuous Addition of SFS Solution in Miniemulsion Polymerization

HD and TBPO were mixed with the monomers. The crude emulsions of PVA, FES/EDTA solution, and HD/TBPO/monomers mixture were prepared with 10 min stirring using a magnetic stirrer and then miniemulsions were prepared by sonifying the crude emulsions as described above. The miniemulsion was heated to 60 °C and then the SFS solution was added in two different modes, namely batch addition and continuous addition (Table 4.3). In the continuous addition mode, the SFS solution was added using a syringe pump (Harvard Apparatus, Model 975) with a flow rate of 0.42 mL/min. The feeding time was 95 min.

**Table 4.2:** Recipe for Seeded Emulsion Polymerizations with Different Monomer to Polymer Ratios

| Ingredient | Monomer to Polymer Weight Ratio | | | |
|---|---|---|---|---|
| | 1/1 | 2/1 | 3/1 | 4/1 |
| Seed Latex[1] | 5.0 | 5.0 | 5.0 | 5.0 |
| BA | 2.5 | 5.0 | 7.5 | 10.0 |
| MMA | 2.5 | 5.0 | 7.5 | 10.0 |
| PVA 205[2] | 0.77 | 1.0 | 1.3 | 1.5 |
| TBHP[3] | 0.0251 | 0.0502 | 0.0753 | 0.104 |
| FES | 0.0013 | 0.0026 | 0.0039 | 0.0052 |
| SFS | 0.013 | 0.026 | 0.039 | 0.052 |
| EDTA | 0.013 | 0.026 | 0.039 | 0.052 |
| DI Water | 54.72 | 109.44 | 164.30 | 219.16 |

[1] Prepared using two-stage polymerizations from chapter 3

[2] The amount of PVA was added to achieve the same amounts of adsorbed PVA per unit area based on particle diameter calculations

[3] Peroxide initiator: 58 mM based on monomers

**Table 4.3:** Recipe for Miniemulsion Polymerizations with Different Addition Modes of Activator (SFS) Solution and Initiator Concentrations

| Ingredient | Batch, [I]<br>Weight (g) | Continuous, [I]<br>Weight (g) | Continuous, 2[I]<br>Weight (g) |
|---|---|---|---|
| BA | 5.0 | 5.0 | 5.0 |
| MMA | 5.0 | 5.0 | 5.0 |
| PVA 205 | 2.0 | 2.0 | 2.0 |
| TBPO | 0.2484 | 0.2484 | 0.4968 |
| FES | 0.0052 | 0.0052 | 0.0104 |
| SFS* | 0.052 | 0.052 | 0.104 |
| EDTA | 0.052 | 0.052 | 0.104 |
| DI Water | 102.226 | 110.726 | 110.726 |

*Continuous feeding time: 95 min

### 4.2.3 Analysis

The latex particle sizes were measured by capillary hydrodynamic fractionation (CHDF, Model 1100, Matec Applied Sciences) and dynamic light scattering (DLS) (Nicomp, Model 370). The amounts of PVA grafted and adsorbed at the end of the polymerizations were determined using a selective solubilization process[10] and the amount of serum PVA was determined by serum extraction. FT-IR spectroscopy was used to determine the increase in the number of acetate groups of the PVA chains in the aqueous phase serum resulting from the grafting reactions between BA and/or MMA and PVA.[11] The original PVA 205 was compared to the latex serum. Potassium thiocyanate (KSCN) was used as the internal standard for the FT-IR spectra. After polymerization, the latex was diluted to about 10 wt% solids content and the latex serum was separated by ultracentrifugation (Beckman ultracentrifuge, Model L8-70M, rotor SW41, Beckman Instruments) at 37,000 rpm and 4 °C for 8 hrs. Serum PVA and 0.5 wt% KSCN solution were weighed, and water was added to obtain a proper intensity in the FT-IR (absorbance < 0.1). Films of the samples were then cast onto zinc-selenide (Zn-Se) IR disks (25 x 4 mm). The disks were dried for 24 hrs at 50 °C, cooled in a dessicator, and then the FT-IR absorbance spectrum for each sample was obtained in a 1 hr period. The area ratio of absorbance for the KSCN nitrile group stretch from 2100 $cm^{-1}$ to 1950 $cm^{-1}$ and the carbonyl group stretch from 1850 $cm^{-1}$ to 1650 $cm^{-1}$ was determined and the degree of hydrolysis was calculated based on the original PVA (PVA 205, degree of hydrolysis ~ 88%) using eqn (4.1) :

$$DH = 100 - \left( \frac{\text{Area(Carbonyl)} / \text{Area(Nitrile)}}{0.7 \times \dfrac{\text{Wt(PVA)} / \text{Wt(KSCN)}}{4.0}} \times 12 \right) \qquad (4.1)$$

where Area(Carbonyl) is the area of absorbance from the carbonyl group stretch; Area(Nitrile) is the area of absorbance from the KSCN nitrile group stretch; 0.7 is obtained from the area ratio of absorbance for the KSCN nitrile group stretch and the carbonyl group stretch at the weight ratio of original PVA 205/ KSCN = 4;

Wt(PVA)/Wt(KSCN) is the weight ratio of unknown serum PVA to KSCN (usually Wt(PVA)/Wt(KSCN)=4.0±0.4); 12 is the degree of acetylation of the original PVA 205.

A saponification technique was used to determine the degree of hydrolysis of the serum PVA after polymerization. The basic technique was based on Japan Industrial Standard (JIS K 6726 - 1965).[12] However, the actual saponification technique was modified because of the small quantities of the samples. 0.02 N NaOH and 0.02 N $H_2SO_4$ solutions were prepared. Serum PVA was weighed accurately (about 0.02 g of sample) into a stoppered Ehlenmeyer flask. 25 mL of 0.02 N NaOH was added to the flask and stirred for a minimum 4 hrs. 25 mL of 0.02 N $H_2SO_4$ was added and the mixture was titrated with 0.01 N NaOH solution with 1% phenophthalein solution in methanol. A blank sample was prepared and titrated simultaneously. The degree of hydrolysis of the unknown samples was calculated based on the original PVA 205 using eqn. (4.2):

$$DH = 100 - \left( \frac{V_1}{V_0 \times \dfrac{Wt(PVA)}{Wt(PVA205)}} \times 12 \right) \qquad (4.2)$$

where $V_1$ is the volume of 0.01 N NaOH solution required for the titration of unknown PVA; $V_0$ is the volume of 0.01 N NaOH solution required for the titration of PVA 205; Wt(PVA)/Wt(PVA 205) is the weight ratio of unknown PVA to PVA 205; 12 is the degree of acetylation of the original PVA 205.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Kinetics and Particle Size Distribution

Figure 4.1 shows the conversion-time behavior of miniemulsion polymerizations as a function of the type of the initiator. The polymerization initiated with TBHP had the highest polymerization rate and resulted from the greatest radical flux into the particles. This is inferred from the evolution of the number of particles as a function of conversion for each initiator. which did not differ much (see also Figure 4.3). The particle size distributions measured by capillary hydrodynamic fractionation (CHDF) for each initiation system are shown in Figure 4.2 as a function of conversion. No populations of smaller particles are observed. and the particle size distributions of the main peaks seem to be constant while shifting to larger sizes with increasing conversion. However. some aggregation of the initial particles occurred using HPO and TBHP after about 30 % conversion as noted by the peaks appearing at lager particles sizes in the distributions. Interestingly. the degree of aggregation increased with increasing water solubility of the initiator.

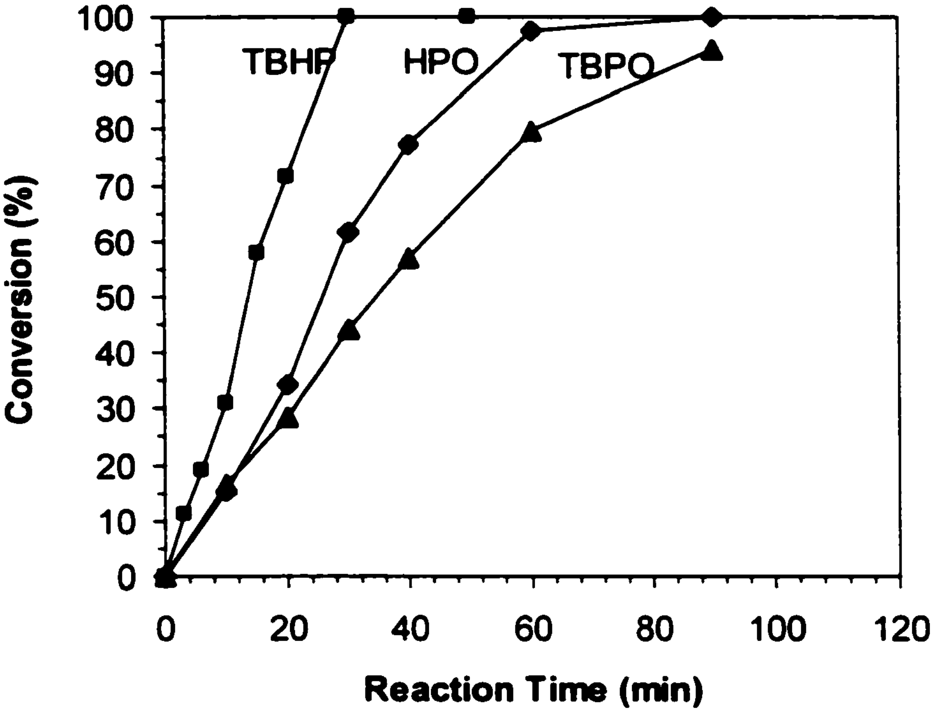

**Figure 4.1:** *Conversion as a function of time for different initiators in miniemulsion polymerizations of MMA/BA (50/50 wt%): HPO, hydrogen peroxide/ascorbic acid system; TBHP, t-butyl hydroperoxide/SFS system; TBPO, t-butyl peroctoate/SFS system; PVA 205 = 10 wt% based on monomer; $T_r$ = 60 °C; reaction time = 20 hrs.*

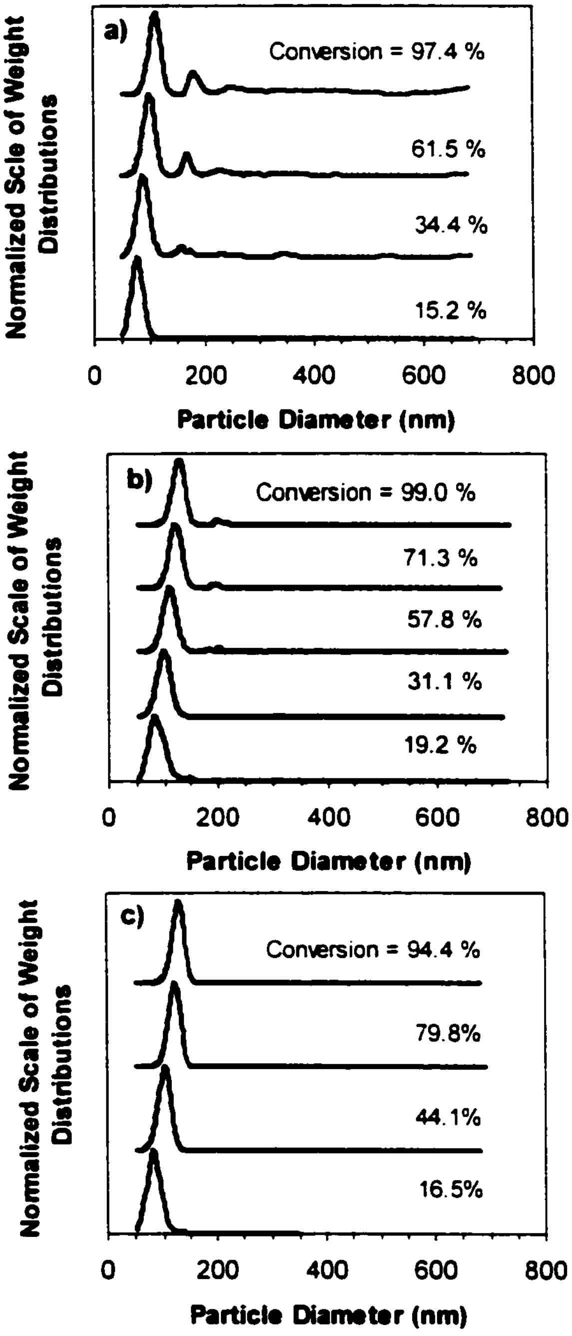

**Figure 4.2:** *Evolution of particle size weight distributions obtained by CHDF as a function of conversion for different initiators in miniemulsion polymerizations of MMA/BA (50/50 wt%); PVA 205 = 10 wt% based on monomer;* $T_r$ *= 60° C; reaction time = 20 hrs; a) HPO system; b) TBHP system; c) TBPO system.*

The evolution of the number of particles per unit volume ($N_p$) was studied based on the CHDF particle size ($D_v$) (Figure 4.3). It is believed that droplet nucleation is mainly operative for each initiation system because the evolution of the number of particles as a function of conversion for each initiation system is quite similar. The evolution of the polydispersity index of the particle size distributions are shown in Figure 4.4 as a function of conversion (based on CHDF), while the particle size statistics of the final latexes obtained from dynamic light scattering (DLS) and CHDF are reported in Table 4.4. Basically, it was expected that the grafting site in miniemulsion polymerization would be the droplet/water interface. If there is only interfacial grafting, the particle size distribution is expected to be relatively narrow for the whole reaction and little coagulum (or limited aggregation) should be obtained, indicating that the polymerizing system is stable. In contrast, if there is only aqueous phase grafting, the particle size distribution should be broad, accompanied by the formation of a large amount of coagulum, indicating that stabilization by PVA is poor. For the HBO-initiated miniemulsion system, there was some aggregation with little coagulum formed (< 0.1 wt%), suggesting that interfacial grafting is still the main grafting mechanism, with some aqueous phase grafting occurring as well. It should be pointed out that the grafting of PVA (formation of water-insoluble PVA) is not always required for colloidal stability as we can see in the example of miniemulsion latexes prepared with TBHP and TBPO (see also Table 4.5), however, we need further characterization of the adsorbed PVA, which might have some grafted BA and/or MMA units.

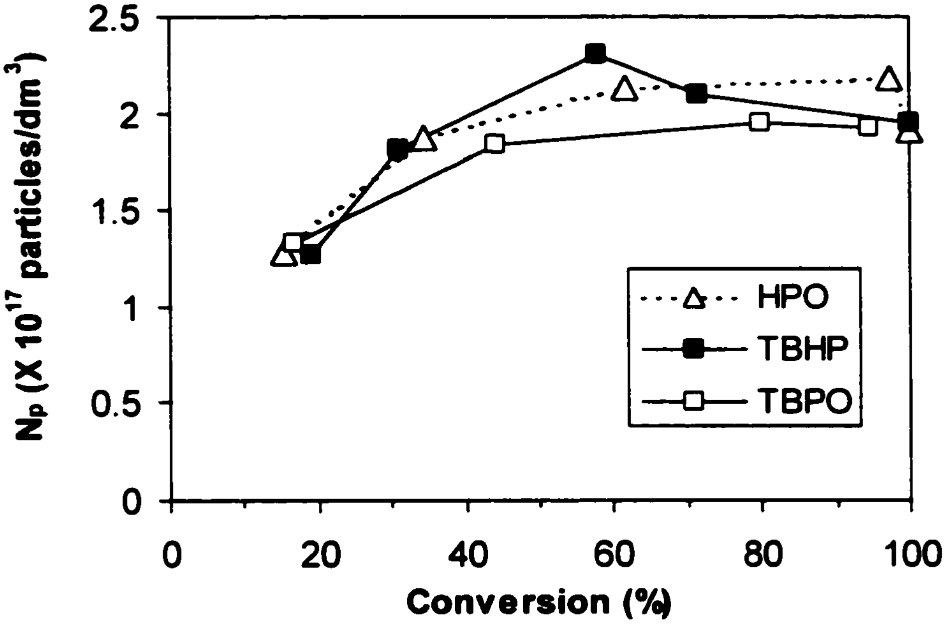

**Figure 4.3:** *Evolution of the number of particles ($N_p$) as a function of conversion for HPO, TBHP, and TBPO-initiated miniemulsion polymerizations of MMA/BA (50/50 wt%); PVA 205 = 10 wt% based on monomer; $T_r$ = 60 °C; reaction time = 20 hrs.*

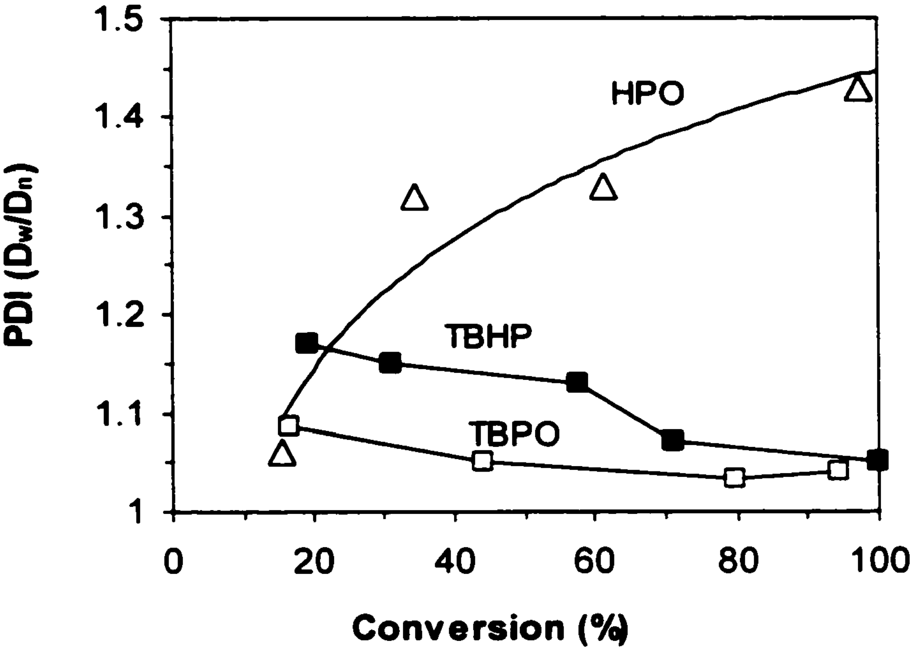

**Figure 4.4:** *Evolution of polydispersity index of particles ($D_w$ $D_n$) as a function of conversion for HPO, TBHP, and TBPO initiated miniemulsion polymerizations of MMA/BA (50/50 wt%); $T_r$ = 60 °C; reaction time = 20 hrs.*

**Table 4.4:** Final Particle Diameter as a Function of the Type of Initiator Used in Miniemulsion Polymerizations

| | CHDF (nm) | | | | DLS (nm) | | | |
|---|---|---|---|---|---|---|---|---|
| | $D_n$ | $D_v$ | $D_w$ | $D_w/D_n$ | $D_n$ | $D_v$ | $D_I$ | $D_I/D_n$ |
| HPO | 121.2 | 129.9 | 168.8 | 1.420 | 89.7 | 161.7 | 200.2 | 1.803 |
| TBHP | 128.9 | 129.5 | 131.3 | 1.050 | 140.5 | 157.1 | 168.2 | 1.118 |
| TBPO | 130.9 | 132.1 | 134.3 | 1.026 | 171.3 | 173.8 | 175.3 | 1.015 |

### 4.3.2 Grafting of PVA

Table 4.5 shows the results obtained for the grafting as a function of the initiator type in miniemulsion polymerizations and the corresponding seeded emulsion polymerizations as reported previously.[9] It was found that there is a significant difference in the amount of grafted PVA on the particles for oil-soluble or partially oil-soluble initiators, such as TBPO and TBHP, depending on the polymerization method (seeded emulsion polymerization vs. miniemulsion polymerization). In contrast, little difference was found for the water-soluble initiator such as HPO, implying that the role of the interface is important for the grafting reaction.

**Table 4.5:** Comparison of Grafted PVA and Adsorbed PVA on the Final Particles as a Function of the Initiation System and Polymerization Method

| | Miniemulsion polymerization | | Seeded emulsion polymerization[1] | |
|---|---|---|---|---|
| | Grafted PVA (%) | Adsorbed PVA (%) | Grafted PVA (%) | Adsorbed PVA (%) |
| HPO | 56.0 | 8.4 | 59.0 | 1.0 |
| TBHP | 0.0 | 52.9 | 29.1 | 24.5 |
| TBPO | 7.5 | 46.6 | 52 | 1.5 |

[1] From Table 3.5, p 88

One of the big differences between seeded emulsion polymerization and miniemulsion polymerization is the monomer concentrations in the particles particularly in the early stages of the polymerizations. In seeded emulsion polymerization, the monomer concentration in the particle is relatively low, implying a higher internal viscosity compared to miniemulsion polymerization. Based on these considerations, it was considered that the differences in grafting might have resulted from the different internal viscosities that may affect the termination reactions between PVA macro-radicals and primary radicals. After generation of PVA macro-radicals, there are several reactions in which these macro-radicals can participate. If these macro-radicals react with monomers, i.e., by a propagation reaction, grafting results. Meanwhile, if termination occurs between a PVA macro-radical and a primary radical, no grafting occurs. In addition, chain transfer from PVA macro-radicals to monomers can be considered. However, chain transfer by carbon-centered radicals is negligible.[13,14] Therefore, the grafting, in this case, is a competitive process between the propagation and termination reactions. As the monomer concentration in the particles increases, a lower viscosity exists at the interface. This lower viscosity will enhance the mobility of primary radicals, which allows increased termination reactions between PVA macro-radicals and primary radicals, resulting in a lack of grafting.

### 4.3.2.1 Monomer to Polymer Ratio (M/P ratio) in Seeded Emulsion Polymerization

To investigate grafting in terms of internal viscosity, the monomer to polymer (M/P) ratio in seeded emulsion polymerizations was varied from 1/1 to 4/1 based on weight (Table 4.2). Seed latexes were prepared and cleaned using the same procedures described previously.[9] Final particle diameters were calculated based on the seed diameter, and the amount of PVA for each M/P ratio in the recipe was varied to maintain the same amount of PVA per total surface area depending on the final particle diameter, implying that the adsorbed PVA per unit area is the same (it was assumed that the adsorption of PVA did not change significantly with M/P ratio).

Figure 4.5 (a) shows the conversion-time behavior as a function of M/P ratio and the corresponding polymerization rates are shown in Figure 4.5 (b). The conversion was determined by gravimetric analysis and the polymerization rate was estimated as the formed polymers per unit time using the conversion. The polymerization rate did not depend strongly on the M/P ratio, although it appeared to be faster at the lower M/P ratio (1/1). The possibility of secondary nucleation at each M/P ratio was examined by observing the evolution of the particle size distributions as a function of conversion using CHDF. No secondary nucleation was evident. A representative example of the evolution of the particle size as a function of conversion for an M/P ratio of 4/1 is shown in Figure 4.6. The amount of grafted PVA and serum PVA after the polymerizations as a function of the M/P ratio were determined using the selective solubilization process. The results are shown in Figure 4.7 as a function of M/P ratio. The serum PVA showed an increasing trend as the M/P ratio increased, implying an increased extent of desorption of PVA during the polymerization or an increase in PVA partitioning in the aqueous phase. Meanwhile, the grafted PVA decreased with increasing M/P ratio, suggesting that a decrease in the internal viscosity results in a decrease in the grafting. This is attributed to increasing termination reactions between primary radicals and PVA macro-radicals at the interface.

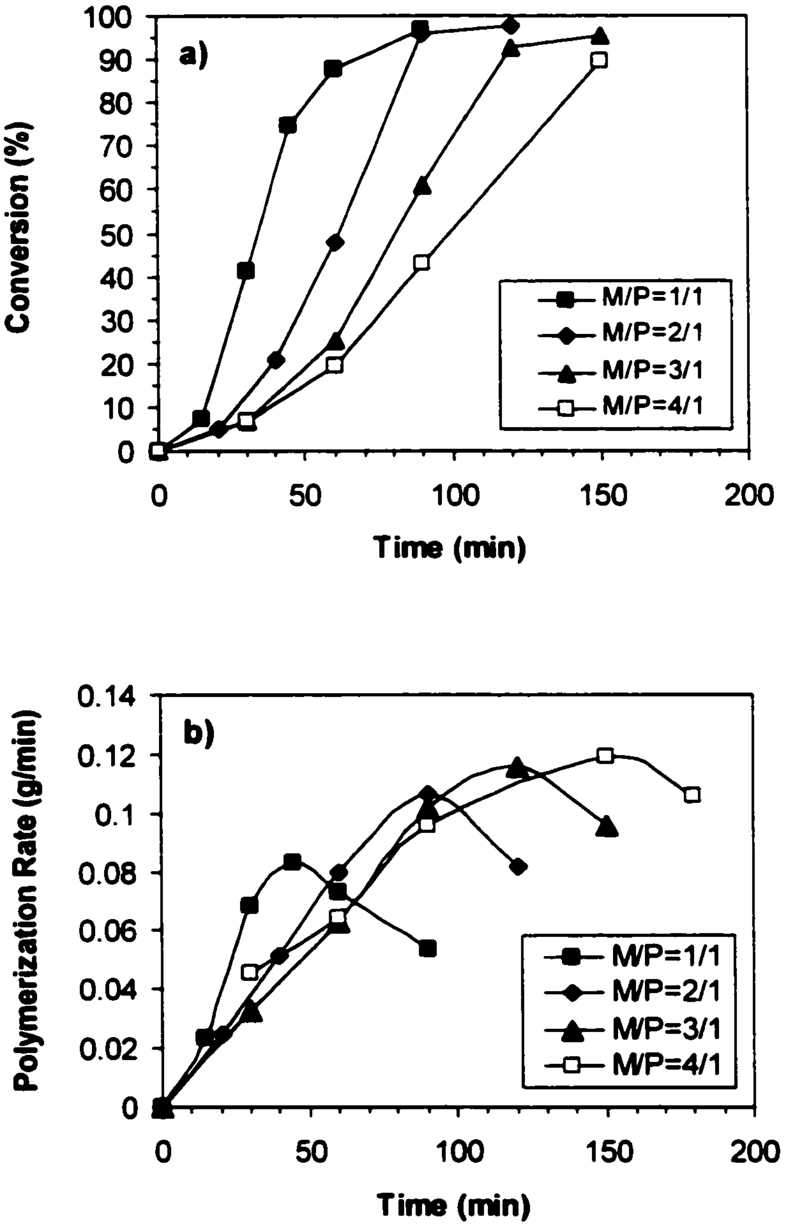

**Figure 4.5:** *Conversion (a) and polymerization rate (b) as a function of time for different monomer to polymer ratios in seeded emulsion polymerizations of MMA/BA (50/50 wt%);* $T_r = 35\,°C$; *initiator (TBHP) = 58 mM based on monomer.*

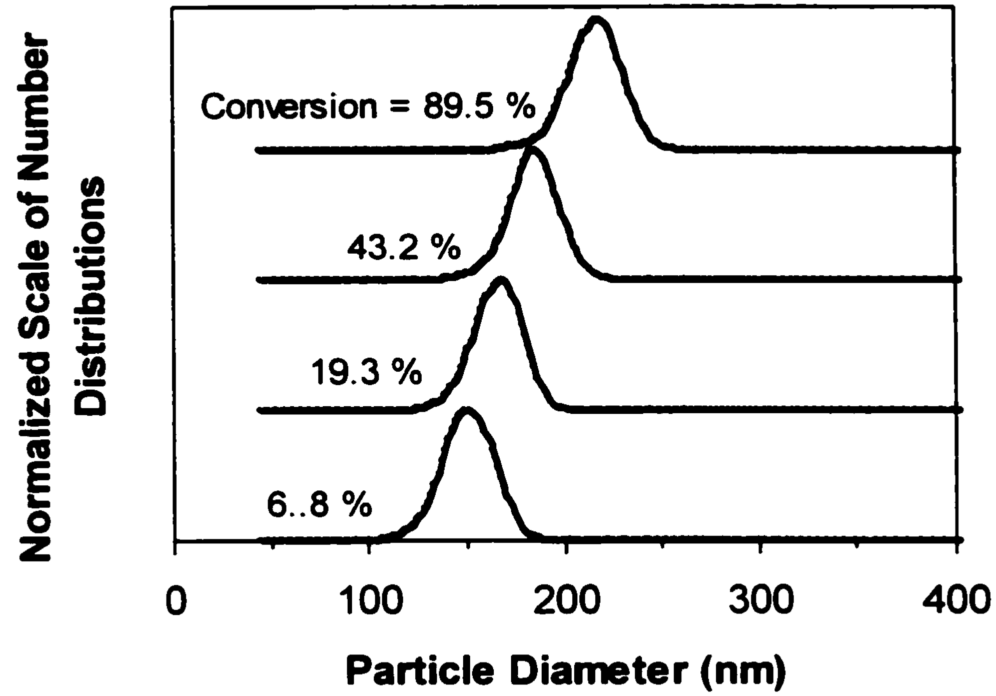

**Figure 4.6:** *Particle size number distributions obtained by CHDF as a function of conversion in a seeded emulsion polymerization of MMA/BA (50/50 wt%); monomer to polymer ratio = 4/1; $T_r$ = 35 °C; initiator (TBHP) = 58 mM based on monomers.*

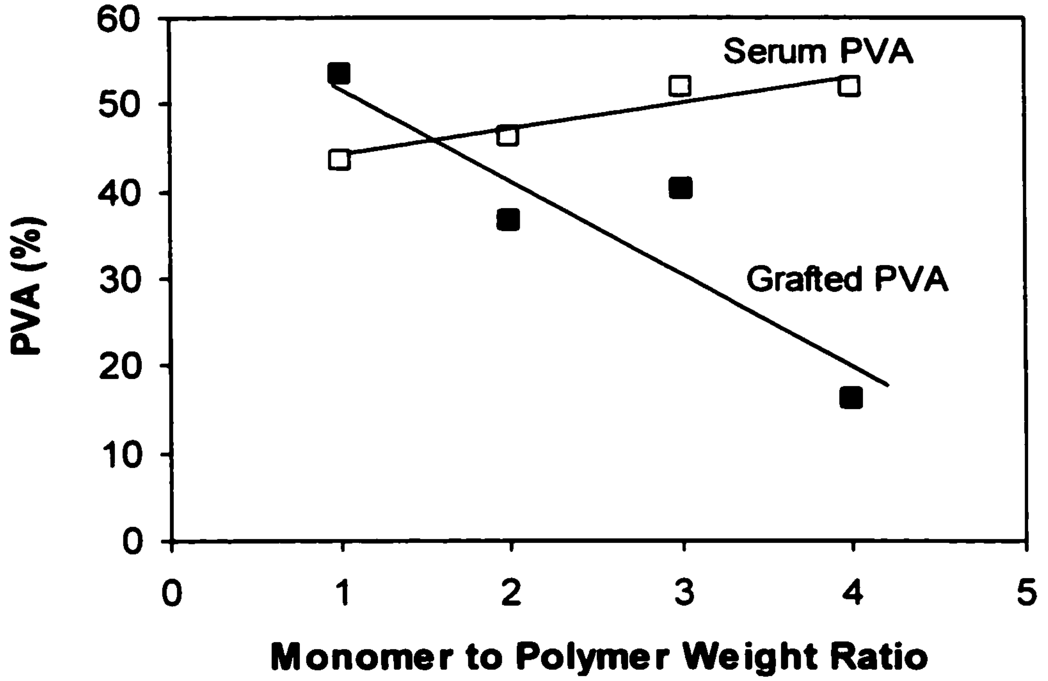

**Figure 4.7:** *Grafted and serum PVA determined by the selective solubilization method as a function of monomer to polymer ratio in seeded polymerizations of MMA/BA (50/50 wt%); $T_r$ = 35 °C; initiator (TBHP) = 58 mM based on monomer.*

### 4.3.2.2 Continuous Addition of SFS Solution in Miniemulsion Polymerization

In the previous section, the monomer to polymer (M/P) weight ratio in seeded emulsion polymerizations was varied to investigate the effect of the internal viscosity on grafting. The results implied that the increase of internal viscosity is an important factor affecting the grafting. However, since the M/P ratio and the primary radical concentrations were varied simultaneously, it is not easy to draw a definitive conclusion. To achieve the same conversion, it took an increasingly longer reaction time with the increasing M/P ratio. This means that the primary radical concentrations in the later stages of the polymerizations decreased with increasing M/P ratio because the activator concentration in the aqueous phase is constant. Therefore, effects of the primary radical concentration on the grafting cannot be excluded.

The amount of grafted PVA as a function of conversion was determined to further investigate the effect of M/P ratio on the grafting during miniemulsion polymerizations. TBPO was used to minimize the aqueous phase grafting and a constant radical generation rate was maintained by the continuous addition of the activator solution (SFS) over 95 min using a syringe pump. In addition, the concentrations of initiator and activator were increased two times to study the effect of the primary radical concentration at the interface on the grafting. Figure 4.8 and Table 4.6 show the kinetics as a function of SFS addition mode and the final particle sizes, respectively. The polymerization rates and final particle size were similar even though the radical generation rates were expected to differ substantially.

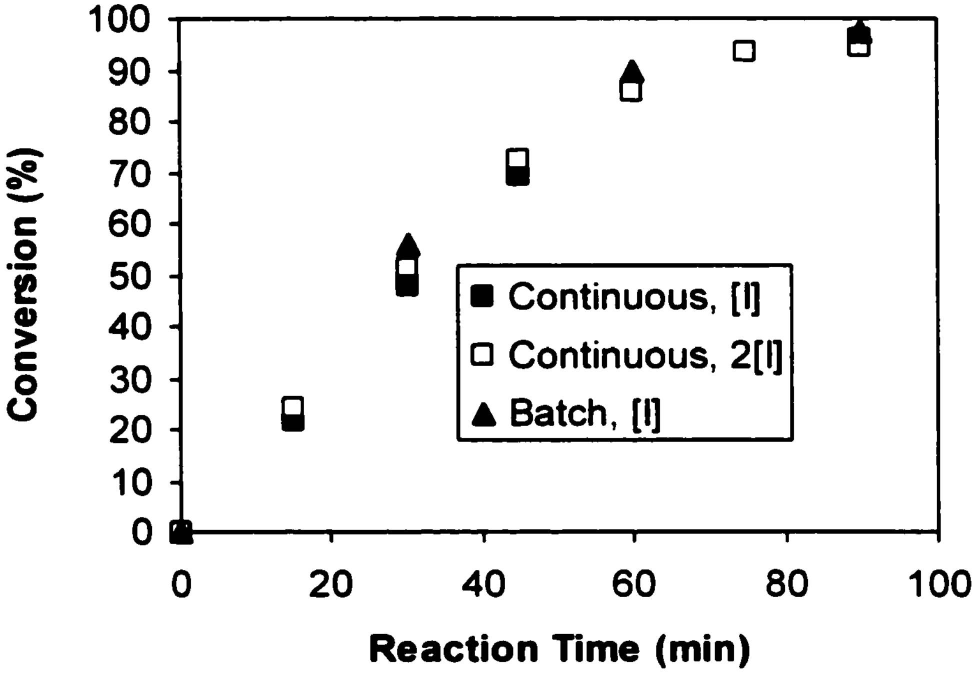

**Figure 4.8:** *Conversion as a function of time for different SFS addition modes and initiator concentrations in miniemulsion polymerizations of MMA/BA (50/50 wt%) initiated with TBPO; PVA 205 = 10 wt% based on monomer; $T_r$ = 60 °C; reaction time = 20 hrs.*

**Table 4.6:** Final Particle Size Measured by CHDF As a Function of SFS Addition Mode and Initiator Concentration in Miniemulsion Polymerizations

| | $D_n$ (nm) | $D_v$ (nm) | $D_w$ (nm) |
|---|---|---|---|
| Continuous, [I] | 122.6 | 123.3 | 124.9 |
| Continuous, 2[I] | 122.5 | 123.3 | 124.8 |
| Batch, [I] | 119.8 | 120.7 | 122.4 |

*[I]=58 mM based on monomer

To confirm the different radical generation rates, the molecular weight and molecular weight distributions of the acetonitrile-soluble polymers obtained from the selective solubilization method were determined. In this system (50/50 wt% of *n*-butyl acrylate and methyl methacrylate), the Mark-Houwink constants for the copolymer are unknown, therefore, the molecular weight and molecular weight distribution were determined relatively against poly(styrene) standards. Figure 4.9 shows the original GPC chromatograms. The molecular weight and molecular weight distributions are summarized in Table 4.7. As expected, the increase in the initiator concentration resulted in lower average molecular weights for the SFS continuous addition experiment. Meanwhile, the batch addition of SFS resulted in the lowest molecular weights. Therefore, the molecular weight results indicate that each system indeed had a different radical generation rate. One conclusion from these findings is that since the particle size and the polymerization rate were similar despite different radical concentrations, this indicates that nucleation takes place entirely in the monomer droplets and virtually all droplets seem to be nucleated.

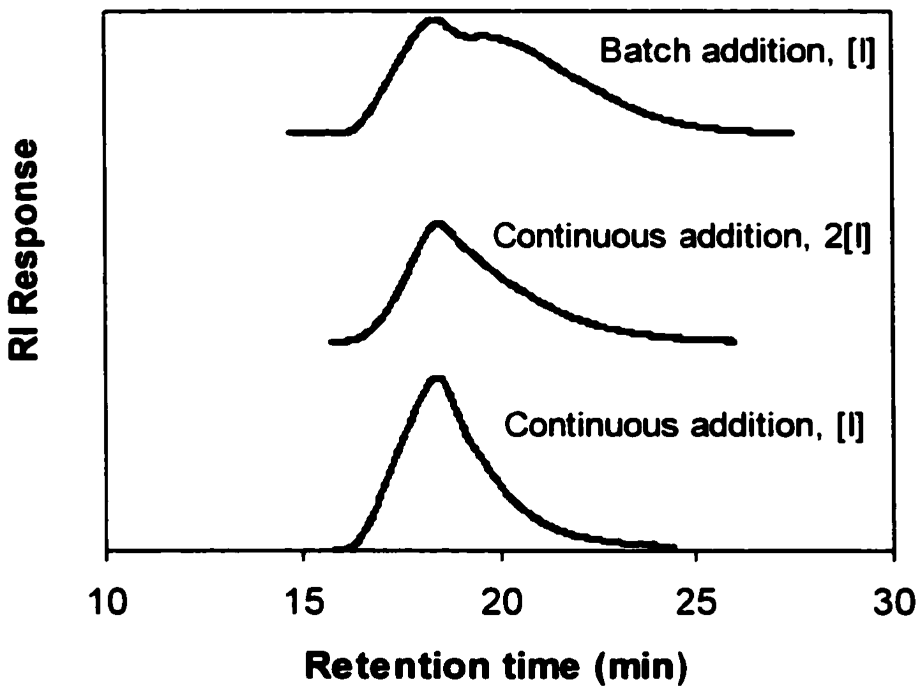

**Figure 4.9:** *GPC chromatographs of acetonitrile-soluble polymers obtained from the selective solubilization method as a function of SFS addition mode and initiator concentrations in miniemulsion polymerizations of MMA/BA (50/50 wt%) initiated with TBPO.*

**Table 4.7:** Molecular Weight and Molecular Weight Distribution As a Function of SFS Addition Mode and Initiator Concentrations in Miniemulsion Polymerizations

| | $M_w$ (g/mol) | $M_n$ (g/mol) | PDI ($M_w/M_n$) |
|---|---|---|---|
| Continuous addition, [I] | 1,349,902 | 329,086 | 4.102 |
| Continuous addition, 2[I] | 870,526 | 182,130 | 4.78 |
| Batch addition, [I] | 853,394 | 103,373 | 8.255 |

*Relative to poly(styrene) standards

**[I]=58 mM based on monomer

Figure 4.10 shows the amount of grafted PVA as a function of conversion in the miniemulsion polymerizations initiated with TBPO. To determine the amount of grafted PVA as a function of conversion, a small amount of sample was withdrawn from the reactor at different conversions, inhibitor solution (hydroquinone, 1 wt% in methanol) added, and the sample was stored at 4 °C. The unreacted monomers in each sample were removed using a rotary evaporator under 60 mmHg at 38 °C and the grafted PVA was determined using the selective solubilization method. When the SFS was added continuously, grafting occurred mainly in the later stages of the miniemulsion polymerization, indicating again that the monomer to polymer ratio in the particles (internal viscosity) is important in determining the grafting of PVA at the interface. At the start of the polymerization, the internal viscosity is low due to a relatively high M/P ratio. Therefore, it is expected that termination reactions between primary radicals and PVA macro-radicals is high because of the high mobility of the primary radicals, which results in little or no grafting. The termination reactions become suppressed as the conversion increases owing to the lower mobility of primary radicals, which results in grafting.

Budhlall et al.[15] reported that the grafting occurred in the early stages of conventional emulsion polymerizations of vinyl acetate because the grafting site was primarily in the aqueous phase. However, as shown here, the grafting mainly occurs near the end of the polymerization if the grafting site is the water/monomer interface because of the suppressed termination reactions at the interface. Meanwhile, the increased initiator concentration in the case where SFS was added continuously resulted in a decrease in the grafting, implying that the termination reaction between the primary radicals and the PVA macro-radicals was increased. However, with batch addition of SFS, the amount of grafted PVA did not differ from the corresponding continuous addition mode even though the overall radical concentration in the batch addition mode was quite high (from molecular weight data). In the latter mode, the primary radical concentration will be high in the early stages of the polymerization while much fewer primary radicals will be available in the later stages of polymerization. As discussed previously, the interface grafting does not occur in the beginning of the polymerization due to the high M/P ratio. Therefore, the available primary radical concentration in the later stages of the polymerization (low M/P ratio) is important in determining the extent of grafting and it seems to be similar for the batch and continuous addition of SFS.

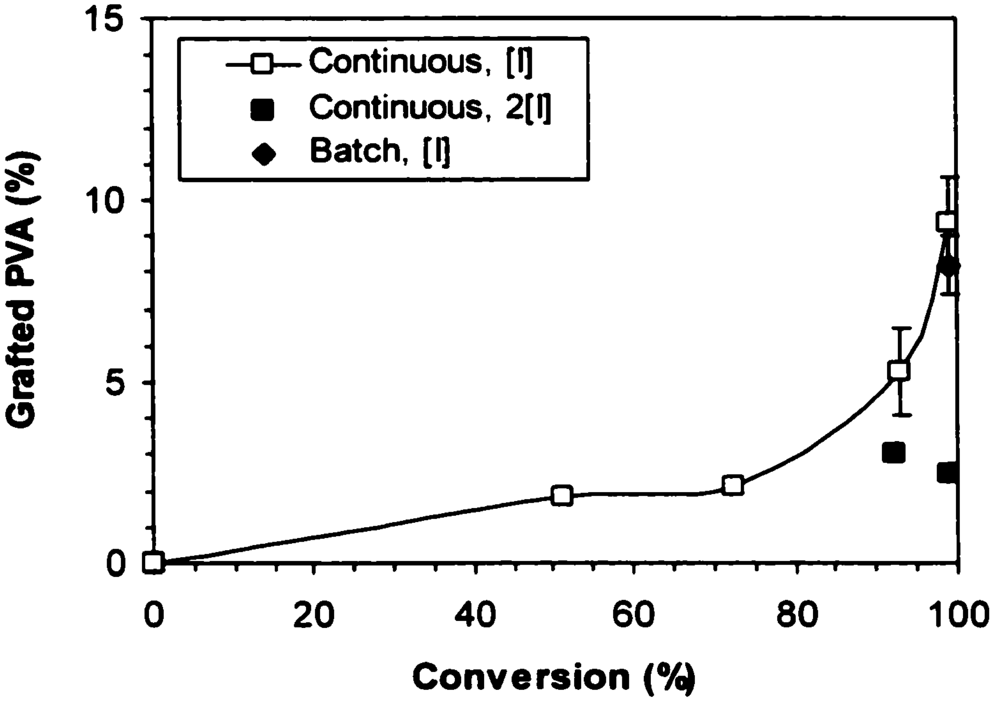

**Figure 4.10:** *Grafted PVA as a function of conversion from different SFS addition modes and initiator concentrations in miniemulsion polymerizations of MMA/BA (50/50 wt%) initiated with TBPO.*

### 4.3.3 Determination of Degree of Hydrolysis (DH) of Serum PVA Using FT-IR and Saponification

So far, this study has focused on the grafted PVA. However, there is approximately 30 ~ 40 % serum PVA present in the initial stages of the polymerization, indicating that the probability of aqueous phase grafting might not be small. Grafting in the aqueous phase was studied using FT-IR and saponification to determine the degree of hydrolysis of the PVA recovered from the serum. FT-IR detects the acetate units from the original PVA and carbonyl units from grafting of MMA and/or BA on the PVA backbone; however, it cannot differentiate between the two functional groups. Meanwhile, saponification can detect only the acetate groups that arise from the original PVA. Therefore, grafting in the aqueous phase can be investigated using the difference between the degree of hydrolysis measured by FT-IR and that determined by saponification. All procedural details were described in the experimental section.

The results for the degree of hydrolysis (DH) of the serum PVA are summarized in Table 4.8. For miniemulsion droplets (last row), the DH of the adsorbed PVA was calculated based on PVA partitioning. Interestingly, the DH of the serum PVA in the miniemulsion showed a value (94.91 % based on FT-IR) higher than the average DH for PVA 205 (88 %). Therefore, relatively low molecular weight[8] and high DH PVA molecules are located in the aqueous phase, implying that a segregation in terms of MW and DH occurs in the miniemulsion. The DH values for serum PVA measured by saponification after the polymerizations show a consistent number for all samples, approximately 91 ~ 92 % DH. Also, the DH values determined by FT-IR are consistent

(94 ~ 95 %) through different from the DH values determined by saponification (91 ~ 92 %), except for the serum PVA in the HPO initiation system, implying that the DH of the serum PVA by FT-IR in the HPO system was actually decreased by grafting of acrylate monomers. The same trend was found for adsorbed PVA in the TBHP system (60 °C). This means that grafting occurred at the interface; however, these grafted PVA are still water-soluble due to the existence of relatively short grafted acrylate chains. Therefore, it seems that even though interface grafting primarily occurs in the TBHP/60 °C system, the grafted chains might be relatively short because of strong termination reactions between the primary radicals and the PVA macro-radicals at the interface. Apparently, there was no grafting in the aqueous phase even though TBHP is a partially water-soluble initiator.

**Table 4.8**: Degree of Hydrolysis Using FT-IR and Saponification in Terms of Initiation System and Reaction Conditions

| | Serum PVA | | | Adsorbed PVA | | | Grafted PVA |
|---|---|---|---|---|---|---|---|
| | % | DH | | % | DH | | % |
| | | FT-IR | Sapo.[7] | | FT-IR | Sapo. | |
| HPO[1] | 35.6 | 90.2 | 91.0 | 8.4 | - | - | 56.0 |
| TBHP[2] | 47.0 | 94.0 | 90.9 | 52.9 | 83.0 | 85.2 | 0.1 |
| TBPO[3] | 46.2 | 94.4 | 90.9 | 46.6 | 86.2 | 86.4 | 7.5 |
| TBHP[4] | 43.3 | 93.5 | 91.7 | 43.9 | 87.7 | 85.5 | 12.8 |
| TBPO/SFS Incre[5] | 51.2 | 94.9 | 92.0 | 28.9 | 86.4 | - | 19.9 |
| Miniemulsion[6] | 33.0 | 94.9 | 92.1 | 67.0 | 84.6[3] | 86.0[3] | |

[1] Batch addition of HPO/Ascorbic acid, $T_r$ = 60 °C

[2] Batch addition of TBHP/SFS, $T_r$ = 60 °C

[3] Batch addition of TBPO/SFS, $T_r$ = 60 °C

[4] Batch addition of TBHP/SFS, $T_r$ = 35 °C

[5] Batch addition of TBPO/Continuous addition of SFS, $T_r$ = 60 °C

[6] Calculated based on PVA partitioning in miniemulsion

[7] Saponification technique

## 4.4 CONCLUSIONS

Some aggregation resulting in an increase in the polydispersity of the particles occurred in the HPO-initiated miniemulsion polymerization, implying that aqueous phase grafting exists in this miniemulsion polymerization system. The amount of grafted PVA on the final particles was significantly decreased for the TBHP- and TBPO-initiated miniemulsion polymerizations compared to the corresponding seeded emulsion polymerizations. The differences in internal viscosities, which might affect the termination reactions between primary radicals and PVA macro-radicals, was suggested to explain the lower grafting in miniemulsion polymerizations. This was confirmed by determining the amount of grafted PVA as a function of monomer to polymer ratio in seeded emulsion polymerizations and the amount of grafted PVA as a function of conversion for a constant radical generation rate in miniemulson polymerizations.

The degree of hydrolysis (DH) of the serum PVA was determined using FT-IR and saponification. Based on the comparison of the DH values using both methods, it was found that aqueous phase grafting resulting in relatively short acrylate chains occurred in the HPO system and interface grafting mainly occurred in the TBHP system, even though TBHP is a partially water-soluble initiator. The grafted chain lengths in the TBHP system seemed to be relatively short because these grafted PVA were still water-soluble; this indicated strong termination reactions at the interface.

## 4.5 REFERENCES

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# CHAPTER 5

# COMPARISON OF ACRYLIC CONVENTIONAL AND MINIEMULSION POLYMERIZATIONS USING POLY(VINYL ALCOHOL) (PVA) AS THE SOLE STABILIZER

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## 5.1 INTRODUCTION

In emulsion polymerization, the surfactant plays important roles in the stability, rheology, and control of particle size of the resulting latexes. In some cases, a polymeric steric stabilizer such as poly(vinyl alcohol) (PVA) can be used either alone or in combination with a surfactant to modify the rheological properties, enhance mechanical stability, and add some performance characteristics in the application of latex paints, binders for non-woven materials, water-based inks, paper coatings, and water-borne adhesives such as pressure sensitive adhesives.[1-2] However, the utilization of PVA as the sole stabilizer in emulsion polymerization has been limited to vinyl acetate or vinyl chloride monomers. In fact, there are difficulties in the preparation of acrylic emulsion polymers and styrene-acrylic emulsion polymers stabilized by PVA via conventional emulsion polymerization, with known processes displaying an extreme rise in viscosity or formation of coagulum during the polymerization.

Craig studied the grafting of hydroxyl ethyl cellulose (HEC) in acrylate emulsion polymerizations and concluded that acrylate monomers (*n*-butyl acrylate was studied) had a higher propensity for grafting to PVA than vinyl acetate because of their higher reactivity, implying that colloidal instability of acrylic emulsion polymer systems stabilized with water soluble polymers such as HEC and PVA might result from the excessive grafting of the water soluble polymers (probably a higher amount of grafted polymer per water-soluble polymer molecule).[3,4]

Several researchers have shown that the main grafting site is the aqueous phase in conventional emulsion polymerizations stabilized with PVA[5-7] and this grafting occurs via hydrogen abstraction, which mainly take places at the methine carbons of the PVA.[8,9] Therefore, the excessive grafting of PVA might be suppressed by a lower hydrogen abstraction rate and the control of PVA macro-radical concentrations via chain transfer. These approaches have been cited in patents and include the addition of water-soluble regulators such as mercaptoacetic acid and cyclohexyl amine,[10] the addition of water soluble amino alcohol,[11] the combination of water-soluble and oil-soluble initiators such as persulfate initiator and azo type initiators,[12] the modification of PVA with a thiol-terminated group with a specific initiator such as potassium bromate,[13,14] and the addition of alcohol such as methanol.[15,16] However, the suppression of grafting in conventional emulsion polymerizations using PVA as a stabilizer is intrinsically difficult because the majority of the PVA molecules are mainly located in the aqueous phase.

Miniemulsions are dispersions of monomer droplets, having diameters in the range of 50 to 500 nm. The droplets normally contain a low molecular weight, water-insoluble costabilizer, which is necessary to reduce the extent of droplet degradation by Ostwald ripening, such as cetyl alcohol (CA) or hexadecane (HD).[17] In miniemulsions, the monomer droplets are small, and the interfacial area is large, so that most of the stabilizer (in this case PVA molecules) resides on the surface of the droplets and this may result in interface grafting, which reduces substantially the aqueous grafting.

In our work, a miniemulsion approach was utilized to enhance the grafting of PVA with acrylic monomers such as methyl methacrylate (MMA) and *n*-butyl acrylate (BA) at the water/monomer interface. Stable latexes having particle diameters of 0.1 to 0.2 μm were obtained utilizing 5 to 20 wt% of PVA based on monomer.[18] It was suggested that the main grafting site in these miniemulsion systems is the water/monomer interface based on a comparison of the amount of adsorbed PVA per unit area of miniemulsion droplet surface and the amount of grafted PVA per unit area of final particle surface as a function of PVA concentration.

This chapter compares conventional acrylic and miniemulsion polymerizations stabilized with PVA in terms of particle nucleation mechanisms, the amount of serum, adsorbed, and grafted PVA on the particles, the aqueous grafting, and the characteristics of the grafted surfaces.

## 5.2 EXPERIMENTAL

### 5.2.1 Materials

*n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were passed twice through an inhibitor-removal column (Sigma-Aldrich). Sodium bicarbonate ($NaHCO_3$, Fisher), hexadecane (HD, costabilizer, Sigma-Aldrich), ammonium persulfate (APS, 99+ %, ACS Grade, Sigma-Aldrich), 0.02 N NaOH (Fisher), 0.1 N $H_2SO_4$ (Sigma-Aldrich), phenolphtalein (Baker), methanol (VWR), and potassium thiocyanate (KSCN, Sigma-Aldrich) were used as supplied. Poly(vinyl alcohol) (PVA) was obtained as a commercial product (Poval 205, hydrolysis (DH)= 87 ~ 89%, degree of polymerization (DP) = 500, Kuraray Co. Ltd., Japan).

### 5.2.2 Polymerization

The recipe employed in these studies is listed in Table 5.1. To prepare the miniemulsions, the PVA was first dissolved in deionized water (c.a. 6 wt % solution) at 90°C for 3 hrs and the solution was filtered using a 200 mesh screen. The solids content of the PVA solution was determined gravimetrically and adjusted to 5.9 wt% by adding deionized water. A specific amount of HD was then mixed with the monomers (BA and MMA). The aqueous PVA solution and DI water were then added to the monomer mixture and stirring was continued for 10 minutes to prepare a crude emulsion. This crude emulsion was sonified using a Branson Sonifier (Model 450) at a 70 % duty cycle and a power setting of 8 for 10 minutes accompanied by continuous magnetic stirring in an ice bath. All polymerizations were performed at 60 °C in a 500 mL four-neck flask equipped with a reflux condenser, nitrogen gas inlet tube, and PTFE stirrer (~200 rpm). Overall polymerization times were either 4 hrs or over 20 hrs. Conventional emulsion polymerizations were carried out using the corresponding miniemulsion recipe without added costabilizer (hexadecane) and no sonification.

**Table 5.1:** Recipe for the Miniemulsion Polymerizations and Conventional Emulsion Polymerizations of *n*-Butyl Acrylate and Methyl Methacrylate

| Ingredient | Weight (g) | Concentration |
|---|---|---|
| Deionized water | 80.0 | |
| *n*-Butyl acrylate (BA)[a] | 10.0 | |
| Methyl methacrylate (MMA)[a] | 10.0 | |
| PVA 205 | 0.6 – 4.0 | 2.5 – 20 wt% based on monomer |
| Hexadecane (HD)[b] | 0.726 | 3.6 wt% based on monomer |
| $NaHCO_3$ | 0.007 | 1 mM based on aqueous phase |
| APS | 0.018 | 1 mM based on aqueous phase |

[a] The weight ratio of total monomers to water was 20/80.

[b] Conventional emulsion polymerizations were carried out without hexadecane.

### 5.2.3 Analysis

The latex particle sizes were measured by capillary hydrodynamic fractionation (CHDF, Model 1100, Matec Applied Sciences) and dynamic light scattering (DLS) (Nicomp, Model 370). Grafted, adsorbed, and serum PVA were determined using the selective solubilzation method.[19] The molecular weight of PVA 205 was analyzed at 35 °C by gel permeation chromatography (GPC) using a Waters 515 HPLC system with two mixed packed columns (TSK gel-GMPWXL-Tosohaas) preceded by a guard column (TSK - Gel PWXL). The mobile phase was a 0.01 N $NaNO_3$ solution. Poly(ethylene oxide) polymers with molecular weights from 960 to 730,000 g/mol (Polymer Laboratories Inc.) were used as calibration standards. Mark-Houwink constants for poly(ethylene oxide) and PVA were taken from published values.[20,21] FT-IR spectroscopy was used to determine the increase in the number of acetate groups of the PVA chains in the aqueous phase serum resulting from the grafting reactions between BA and/or MMA and PVA.[6] The original PVA 205 was compared to the PVA in the latex serum. Potassium thiocyanate (KSCN) was used as the internal standard for the FT-IR spectra. Serum PVA and 0.5 wt% of KSCN solution were weighed, and water was added to obtain a proper intensity in the FT-IR (absorbance < 0.1). Films of the samples were then cast onto zinc-selenide (Zn-Se) IR disks (25 x 4 mm). The disks were dried for 24 hrs at 50 °C, cooled in a dessicator, and then the FT-IR absorbance spectrum for each sample was obtained over a 1 hr period. The area ratio of absorbance for the KSCN nitrile group stretch from 2100 $cm^{-1}$ to 1950 $cm^{-1}$ and the carbonyl group stretch from 1850 $cm^{-1}$ to

1650 cm$^{-1}$ was determined and the degree of hydrolysis (DH) was calculated based on the original PVA (PVA 205, degree of hydrolysis ~ 88%) using eqn. (5.1) :

$$DH = 100 - \left( \frac{\text{Area(Carbonyl)} / \text{Area(Nitrile)}}{0.7 \times \dfrac{\text{Wt(PVA)} / \text{Wt(KSCN)}}{4.0}} \times 12 \right) \qquad (5.1)$$

where Area(Carbonyl) is the area of absorbance from the carbonyl group stretch; Area(Nitrile) is the area of absorbance from the KSCN nitrile group stretch; 0.7 is the area ratio of absorbance for the KSCN nitrile group stretch and the carbonyl group stretch for the weight ratio of PVA 205/ KSCN = 4; Wt(PVA)/Wt(KSCN) is the weight ratio of unknown PVA to KSCN (usually Wt(PVA)/Wt(KSCN)=4.0±0.4); 12 is the degree of acetylation of the original PVA 205.

A saponification technique was used to determine the degree of hydrolysis of the serum PVA after the polymerizations. The basic technique was based in a Japan Industrial Standard (JIS K 6726 – 1965).[22] However, the actual saponification technique was modified because of the small quantities of the samples. 0.02 N NaOH and 0.02 N $H_2SO_4$ solutions were prepared. Serum PVA was weighed accurately (about 0.02 g of sample) into a stoppered Ehlenmeyer flask. 25 mL of 0.02 N NaOH was added to the flask and stirred for 4 hrs minimum. 25 mL of 0.02 N $H_2SO_4$ was added and the mixture was titrated with 0.01 N NaOH solution with 1% phenophtalein solution in methanol. A blank sample was prepared and titrated simultaneously. The degree of hydrolysis for the unknown samples was calculated based on the original PVA 205 using eqn (5.2):

$$DH = 100 - \left( \frac{V_1}{V_0 \times \frac{Wt(PVA)}{Wt(PVA205)}} \times 12 \right) \qquad (5.2)$$

where $V_1$ is the volume of 0.01 N NaOH solution required for the titration of unknown PVA; $V_0$ is the volume of 0.01 N NaOH solution required for the titration of PVA 205; Wt(PVA)/Wt(PVA 205) is the weight ratio of unknown PVA to PVA 205;12 is the degree of acetylation of the original PVA 205.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Coagulum

Conventional emulsion polymerizations and miniemulsion polymerizations were initiated with ammonium persulfate (APS). After the polymerizations were completed, the amounts of coagulum were obtained by screening out the coagulum using a stainless steel screen (#200 mesh); the results are shown in Figure 5.1. In the conventional polymerization systems, the formation of coagulum greatly increased as the PVA concentration decreased; however, only small amounts of coagulum were formed in the corresponding miniemulsion systems. Initially, conventional emulsion polymerizations were carried out for over 20 hrs, however, the formation of coagulum was too high and it was difficult to analyze the resulting latexes. To suppress the formation of coagulum, the polymerizations were stopped after 4 hrs and coagulum was collected using the stainless steel screen (200 mesh). The conversion was more than 95 % for each polymerization (gravimetric analysis).

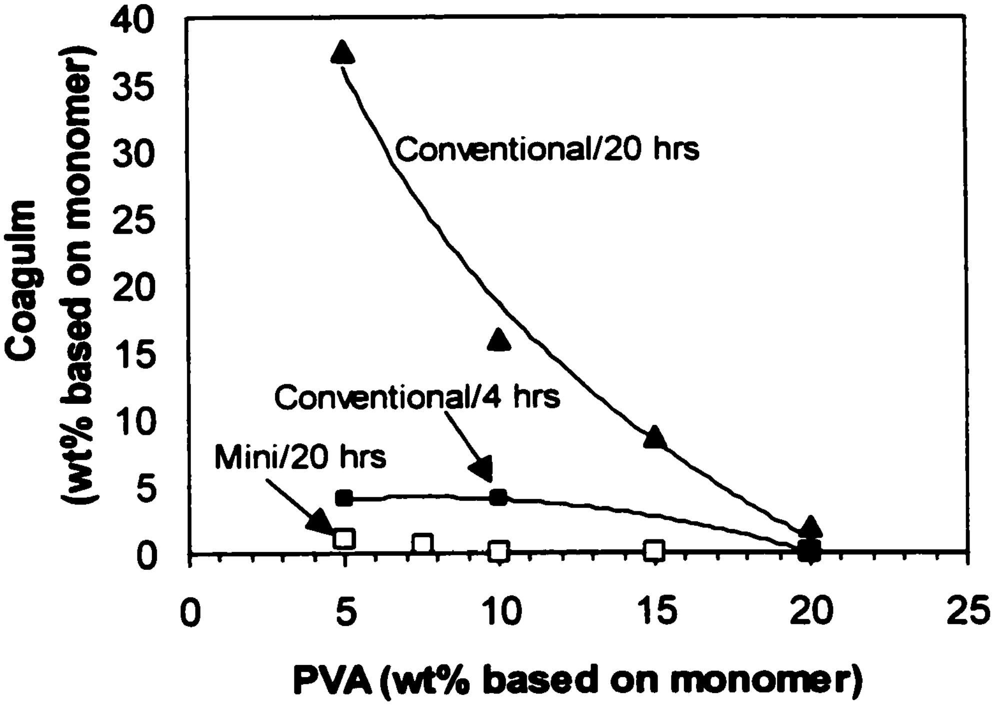

**Figure 5.1:** *Coagulum as a function of PVA concentration for miniemulsion (Mini) and conventional emulsion polymerizations (Conventional): BA/MMA=50/50 wt%; APS = 1 mM; $T_r$ = 60 °C; reaction times of 4 and 20 hrs.*

### 5.3.2 Particle Nucleation and Growth Mechanism

To study and compare the particle nucleation and growth mechanisms for conventional emulsion and miniemulsion systems, the evolution of the particle size and particle size distribution as a function of conversion was investigated using CHDF (Figure 5.2). In the miniemulsion system, the breadth of the initial particle size distribution seemed to be constant during the polymerization, indicating that droplet nucleation dominated. Meanwhile, in the conventional system, small particles with narrow particle size distributions were generated in the initial stages of the polymerizations. The average particle size increased and the size distributions became broader with increasing conversion, indicating limited aggregation. Small particles (~ 60 nm) still existed for conversions greater than 60%, implying continuous nucleation as well. Budhlall et al.[5] reported similar results for conventional emulsion polymerizations of vinyl acetate. Similar phenomena were observed for higher PVA concentrations.

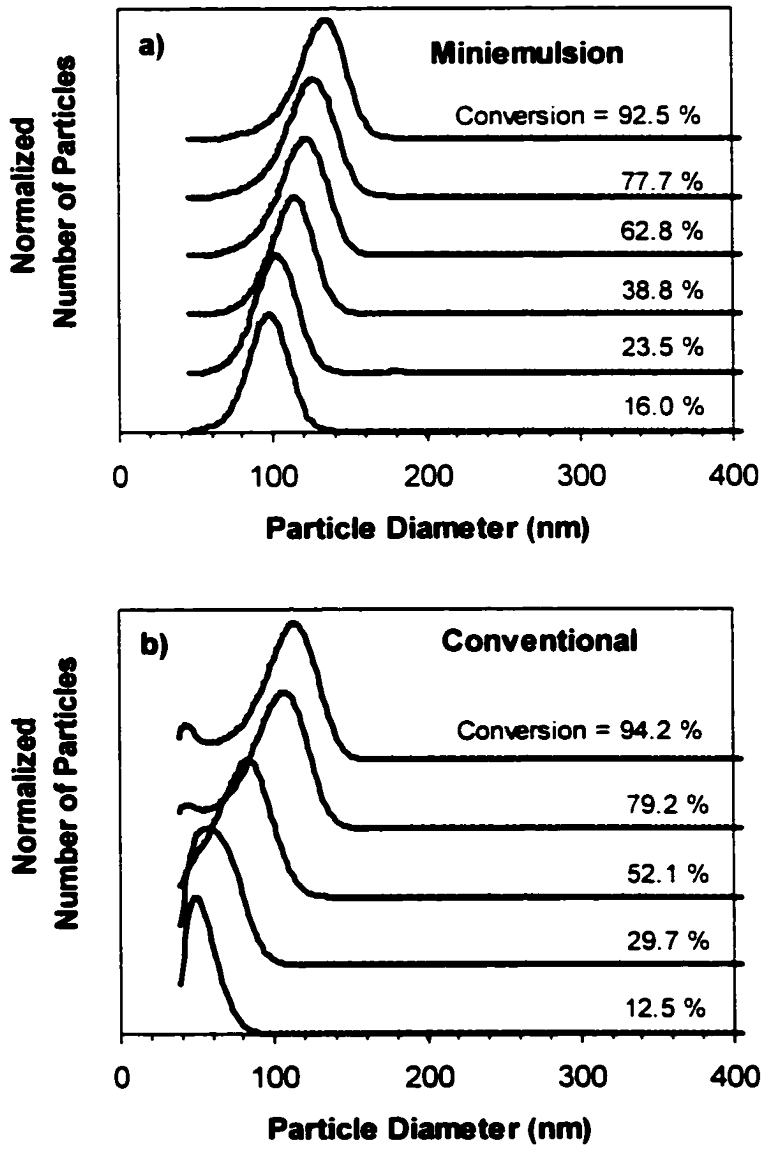

**Figure 5.2:** *Evolution of particle size number distributions measured by CHDF as a function of conversion; The particle sizes below 50 nm were cut-off; a) miniemulsion polymerization; b) conventional emulsion polymerization; BA/MMA=50/50 wt%; PVA = 10 wt%; APS = 1mM; $T_r$ = 60 °C.*

The number of particles per unit volume of water ($N_p$) as a function of PVA concentration was calculated based on the CHDF data ($D_v$) for conventional and miniemulsion polymerizations as shown in Figure 5.3. In the miniemulsion system, $N_p$ increased up to around 60 % conversion and then, was relatively constant for 5 and 10 wt% PVA, indicating that droplet nucleation was dominant. However, at the higher concentrations, 15 and 20 wt% PVA, $N_p$ gradually increased even after 60 % conversion, implying that continuous nucleation exists in these miniemulsion systems, probably owing to the greater PVA partitioning into the aqueous phase.[18] In the conventional system, $N_p$ increased initially and then, decreased after a certain conversion, which indicates that limited aggregation occurred during the polymerizations.

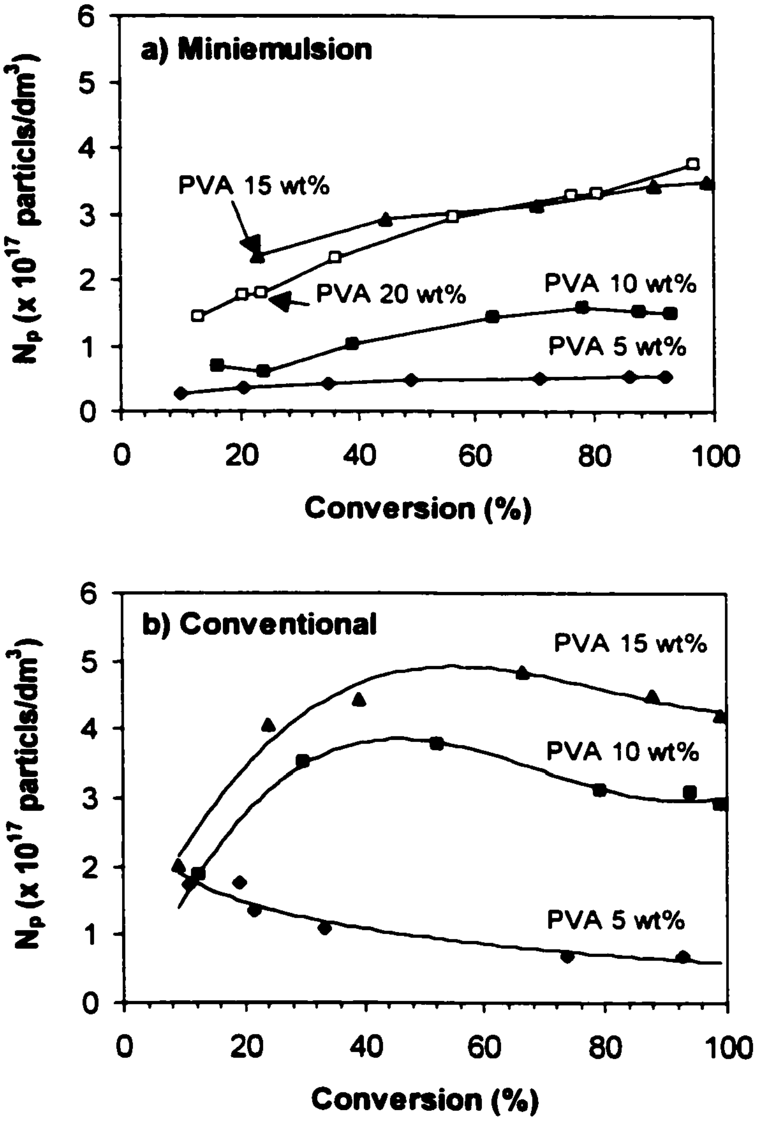

**Figure 5.3:** *Number of particles ($N_p$) based on volume-average particle diameter as a function of conversion at different PVA concentrations: a) miniemulsion polymerization; b) conventional emulsion polymerization; BA/MMA=50/50 wt%; APS = 1mM; $T_r$ = 60 °C.*

### 5.3.3. Amount of Grafted and Adsorbed PVA As a Function of PVA Concentration

Figure 5.4 shows the amounts of PVA adsorbed and grafted on the final particles as a function of the amount of added PVA for both the miniemulsion latex (20 hrs reaction) and the conventional latex (4 hrs reaction). The amount of grafted PVA per unit particle surface area in the miniemulsion polymerization continuously increased up to 10 wt% PVA and then became constant, which strongly supports the hypothesis that the water/monomer interface on the miniemulsion droplets is the main grafting site.[18] Meanwhile, the amount of grafted PVA per unit area in the conventional emulsion polymerization was independent of the PVA concentration and was significantly lower than in the miniemulsion latexes particularly at higher PVA concentrations, which may explain the colloidal instability in the conventional emulsion polymerizations. However, at 5 wt% PVA, the amount of grafted PVA and adsorbed PVA per unit area in the conventional emulsion polymerizations were similar to those obtained in the miniemulsion latex, which implies that the colloidal instability (coagulum) in the conventional system cannot be explained solely on the amount of grafted PVA per unit area. In addition, colloidal stability increased (i.e., decrease in the formation of coagulum) as the amount of adsorbed PVA per unit area increased in the conventional system, indicating that the role of grafted PVA in determining colloidal stability seems to be negligible in the conventional system.

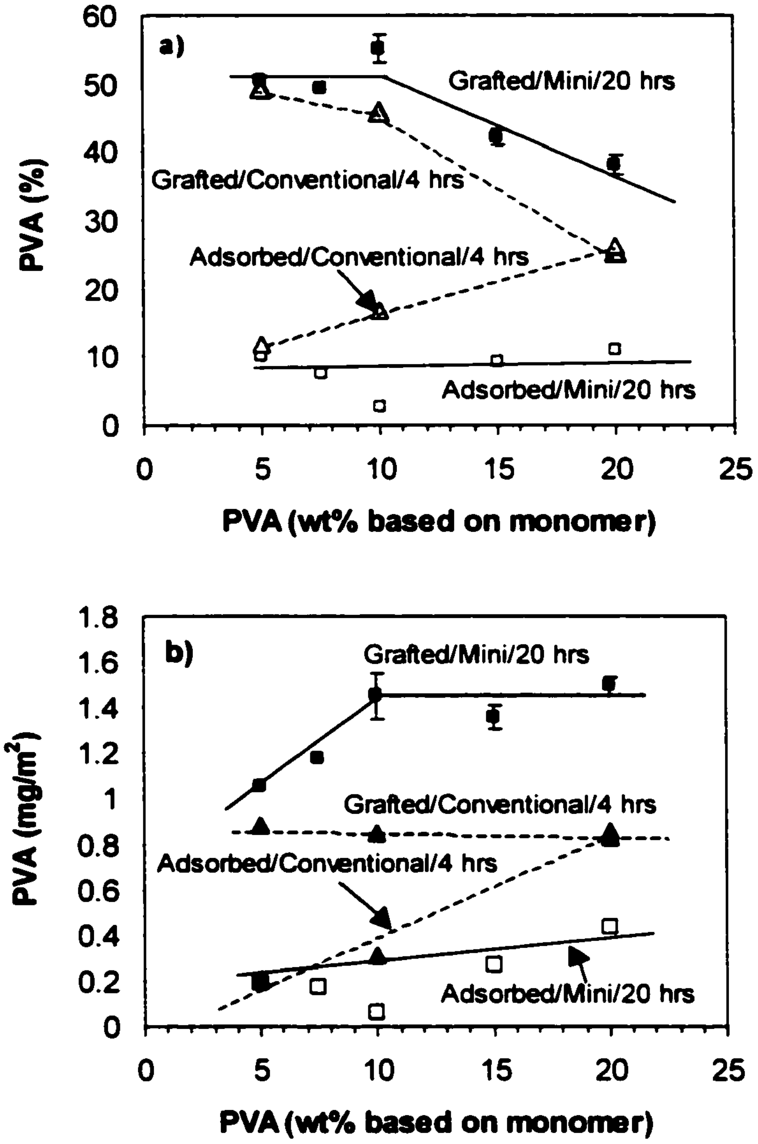

**Figure 5.4:** *Amounts of grafted and adsorbed PVA on the final particles as a function of the amount of added PVA and reaction time for miniemulsion (Mini) and conventional emulsion polymerizations; a) weight basis; b) area basis, specific area (m$^2$/g) was calculated based on volume-average diameter obtained by CHDF.*

### 5.3.4 Possibility of the PVA Desorption from the Particle Surfaces

As mentioned earlier, the colloidal instability of conventional latexes (the amount of coagulum) significantly increased with increasing reaction time. One of reasons for the colloidal instability in the conventional emulsion polymerizations might be the desorption of adsorbed and/or grafted PVA during the longer reaction time (compared to miniemulsion polymerizations), even though it is not clear why the grafted PVA would desorb from the surface of the polymer particles during this stage of the reaction. If there is a significant of PVA desorption depending on the reaction time, the amounts of serum PVA will be increased. Also, the molecular weights of the serum PVA might be increased because relatively higher molecular weight PVAs are located at the particle surfaces. To investigate the possibility of PVA desorption, the serums of the original latexes for each reaction time (4 hrs and 20 hrs) were extracted using the serum replacement cell, and the amounts and the molecular weight of the serum PVA for the different reaction times were determined. Figure 5.5 (a) shows the amount of serum PVA as a function of the amount of added PVA for the conventional emulsion polymerizations (4 hrs and 20 hrs reaction) and the miniemulsion polymerization (20 hrs reaction). Overall, there was no significant difference in the amounts of the serum PVA as function of the reaction time in the conventional system and the amounts of serum PVA in the conventional latexes were similar to the miniemulsion latexes. The weight-average molecular weights of the serum PVA as a function of PVA concentration are shown in Figure 5.5 (b). The molecular weights of the serum PVA of the conventional latexes were close to those of the miniemulsion latexes, and did not vary significantly with the increasing reaction time. Therefore, these results suggest that the desorption of PVA during the reaction is not significant.

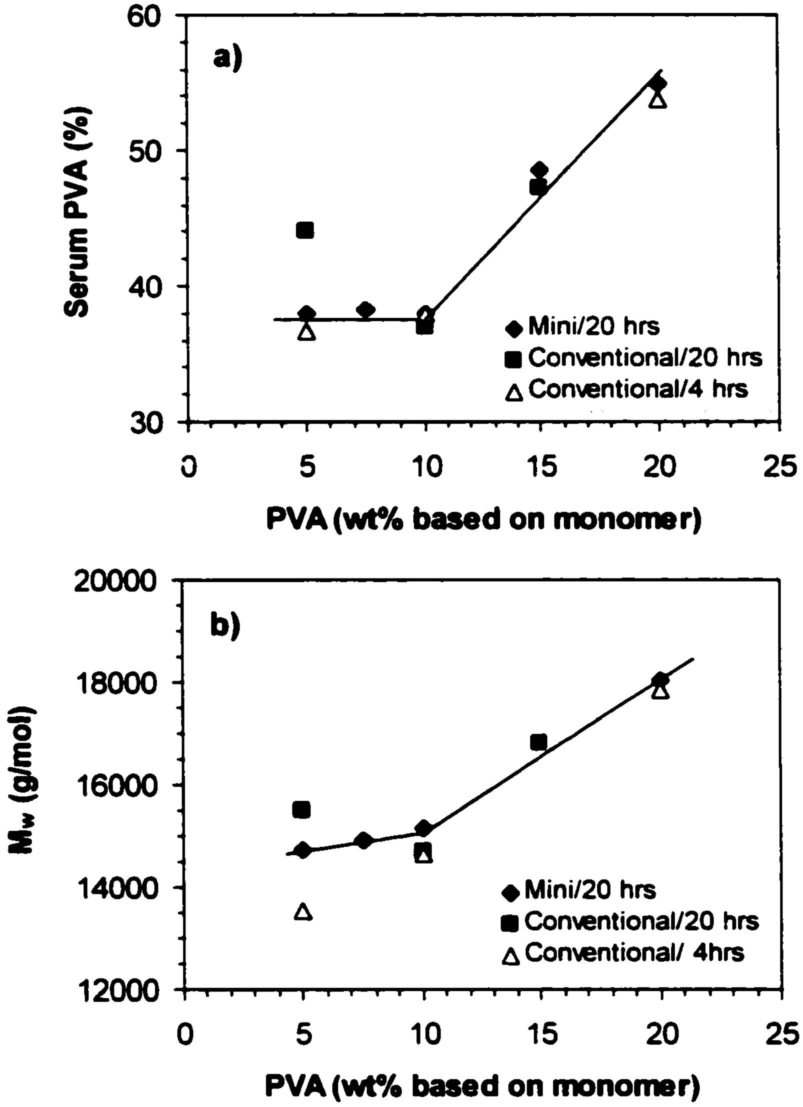

**Figure 5.5:** *Amount of the serum PVA (a) and the weight-average molecular weight of the serum PVA (b) as a function of the amount of added PVA for miniemulsion (Mini) and conventional emulsion polymerizations: BA/MMA=50/50 wt%; APS = 1 mM; $T_r$ = 60 °C ; reaction times of 4 and 20 hrs; solid contents ~ 20 wt%.*

### 5.3.5 Grafting in Aqueous Phase at 5 wt% PVA

So far, attempts to explain the colloidal instability in the conventional emulsion polymerization system were made by studying the amounts of grafted PVA, the desorption of PVA from the surface of the particles in terms of the amounts of the serum PVA and the molecular weights of the serum PVA. However, none of these uncovered any identifiable relationships. Surprisingly, at the 5 wt% PVA concentration, the amounts of adsorbed and grafted PVA on the final particles, the amount of serum PVA, and the molecular weight of the serum PVA obtained by conventional emulsion polymerization were all very similar to those obtained in the miniemulsion polymerizations, which indicates that the physical properties of the conventional emulsion polymers are apparently similar to those of the miniemulsion polymers. However, the resulting stability (coagulum) of the conventional emulsion polymers did differ significantly from that of the miniemulsion polymers. Another point to be noted is that the colloidal stability was not dependent on the amount of grafted PVA, but rather the amount of adsorbed PVA in the conventional system, suggesting that the grafted PVA does not play a dominant role in steric stabilization.

The main grafting site is the aqueous phase in the conventional emulsion polymerizations and at the interface in the miniemulsion polymerizations. Therefore, it is expected that the degree of hydrolysis (DH) of the serum PVA in the conventional latexes should be lower than in the miniemulsion latexes because of a greater amount of aqueous phase grafting. This might be correlated with the colloidal instability in the conventional emulsion polymerizations because more aqueous phase grafting (the increase in the hydrophobicity of the PVA due to grafted acrylate monomer units) can cause flocculation. The DH of serum PVAs extracted from the conventional and miniemulsion latexes after polymerization was determined using FT-IR and the saponification technique. FT-IR detects the acetate units from the original PVA and carbonyl units from grafted MMA and/or BA on the PVA backbone; however, it cannot differentiate between the two functional groups. Meanwhile, saponification can detect only the acetate groups that arise from the original PVA. Therefore, the indication of grafting in the aqueous phase can be investigated using the difference between the degree of hydrolysis measured by FT-IR and that determined by saponification. As a standard, the DH of the serum PVA extracted from a miniemulsion prepared with 10 wt% PVA based on monomer was measured. (The PVA partitioning and molecular weight of the serum PVA for 5 wt% PVA are similar to those for 10 wt% PVA; PVA partitioning in serum = 30 % for 5 wt% PVA and 31.5 % for 10 wt% PVA; $M_w$ of serum PVA = 14,500 g/mol for 5 wt% PVA and 15,500 g/mol for 10 wt% PVA). The results for the degree of hydrolysis (DH) of the serum PVA in the miniemulsion latex and conventional latex at 5 wt% PVA are summarized in Table 5.2.

**Table 5.2**: Comparison of Degree of Hydrolysis (DH) of Serum PVA Obtained from Conventional Emulsion Polymerization and Miniemulsion Polymerization Using FT-IR and Saponification

| | PVA (%) based on monomer | DH of serum-PVA | |
|---|---|---|---|
| | | FT-IR | Saponification |
| Conventional EP (APS)[1] | 5 | 89.6 | 91.4 |
| Mini EP (APS)[2] | 5 | 90.9 | 91.9 |
| Miniemulsion | 10 | 94.9 | 92.1 |

[1] Conventional emulsion polymerization initiated with ammonium persulfate

[2] Miniemulsion polymerization initiated with ammonium persulfate

The DH for serum PVA by saponification shows similar values for all samples, approximately 91 ~ 92 % DH. Except for the serum PVA in the miniemulsion, the DH values by FT-IR are also similar even though there is a difference between DH measured by FT-IR (90 ~ 91 %) and DH determined by saponification (91 ~ 92 %), implying that the DH of the serum PVA determined by FT-IR actually decreased by grafting of the acrylate monomers. However, the DH of the serum PVA obtained from conventional and miniemulsion latexes were close, indicating that the characteristics of the serum PVA in terms of DH are similar and implying that the colloidal instability in conventional latexes can not be correlated with the degree of aqueous phase grafting.

Earhart[6] studied the conventional emulsion copolymerizations of vinyl acetate/*n*-butyl acrylate (50/50 wt%) using two kinds of PVAs, Vinol 205 (DH ~ 88 %, $M_w$ ~ 34,940 g/mol, Air Products and Chemicals) and Vinol 107 (DH ~ 98 %, $M_w$ ~ 26,250 g/mol, Air Products and Chemicals), as the sole stabilizer. He determined the DH of the serum PVA in the final latexes by FT-IR and found that the DH of the serum PVA was almost constant (~82 %) regardless of the DH of the original PVA, which are quite different results compared to this study (~89 %). In miniemulsion polymerizations, PVA molecules are segregated in terms of molecular weight[23] and DH: lower molecular weight ($M_w$ ~ 14,500 g/mol) and higher DH (~95 %) in aqueous phase, higher molecular weight ($M_w$ ~ 22,000 g/mol) and lower DH (~ 84 %) at the droplet surface before the polymerization. Therefore, it is expected that grafting might occur in different ways, that is, aqueous grafting for lower molecular weight and higher DH PVA and interface grafting for higher molecular weight and lower DH PVA. Actually, the amount of serum PVA and its molecular weight after miniemulsion polymerizations were similar to those in the original miniemulsions at each PVA concentration. Comparing these results with Earhart's results in terms of the DH of the serum PVA after polymerization, it might be suggested that lower molecular weight and higher DH PVA has little propensity for aqueous phase grafting and might be suppress the aqueous phase grafting. This should depend on the monomers used, however.

In conventional emulsion polymerizations, there is little possibility for segregated grafting in terms of molecular weight and degree of hydrolysis because most of the PVA are uniformly mixed in aqueous phase initially. However, Budhlall[13] suggested that the conformation may differ from molecular weights of PVA in aqueous phase and this might result in some segregation depending on molecular weights of PVA in aqueous phase. It was found that the DH and molecular weight of the serum PVA obtained from conventional emulsion polymerizations were quite similar to those from miniemulsion polymerizations, implying that the aqueous grafting in conventional emulsion polymerizations might occur selectively and extensively for higher molecular weight and lower DH PVA. Henry and Vito[25] applied a similar concept to obtain acrylic emulsions prepared with fully hydrolyzed (DH > 97 ~ 98 %) and low molecular weight PVA ($M_n$ = 5,000 ~ 13,000 g/mol).

### 5.3.6 Measurement of Particle Size Using Dynamic Light Scattering (DLS) and Capillary Hydrodynamic Fractionation (CHDF) at 5 wt% PVA

The latexes were cleaned using the serum replacement technique and particle diameters were measured by DLS and CHDF. Table 5.3 shows the particle diameter measured by DLS and CHDF after polymerization. By DLS, the volume-average particle diameter of cleaned particles prepared by conventional emulsion polymerization was quite close to that prepared by miniemulsion polymerization. However, by CHDF, the volume-average particle diameter of cleaned particles prepared by conventional emulsion polymerization was smaller that that prepared by minieumlsion polymerization. An apparently smaller particle size in CHDF might indicate a strong interaction between the capillary wall and the grafted surface of the particles owing to a greater amount of grafted chains on the PVA (an increase in the number of hydrophobes).[26] Therefore, the grafted surface of particles prepared by conventional emulsion polymerization might be more hydrophobic, which may result in the poor stability.

**Table 5.3:** Particle Sizes of Conventional and Miniemulsion Latexes Measured by Capillary Hydrodynamic Fractionation (CHDF) and Dynamic Light Scattering (DLS) at 5 wt% PVA

| | | | CHDF | | | DLS | |
|---|---|---|---|---|---|---|---|
| | | $D_n$ | $D_v$<br>(nm) | $D_w$ | $D_n$ | $D_v$<br>(nm) | $D_I$ |
| Conventional | Uncleaned | 186.4 | 190.2 | 200.6 | 154.1 | 268.6 | 271.3 |
| EP[1] | Cleaned[3] | 187.5 | 191.5 | 200.6 | 208.6 | 262.9 | 262.8 |
| Mini-EP[2] | Uncleaned | 200.8 | 202.0 | 205.5 | 254.1 | 261.8 | 261.5 |
| | Cleaned[3] | 197.7 | 198.9 | 203.2 | 253.3 | 260.2 | 260.2 |

[1] Conventional emulsion polymerization, 5 wt% PVA based on monomer

[2] Miniemulsion polymerization, 5 wt% PVA based on monomer

[3] Cleaning via serum replacement

### 5.3.7 Adsorption Isotherm of SLS on Grafted Surfaces at 5 wt% PVA

The adsorption isotherms of SLS on the cleaned particles prepared by conventional emulsion polymerization and miniemulsion polymerization were determined to see if differences in surface properties could be detected. Certain amounts of SLS and cleaned particles were mixed overnight and the serum of the mixture was extracted using a serum replacement cell. The conductance of the serum was measured and the concentration of SLS in the serum was calculated based on an SLS-conductance calibration. Figure 5.6 shows the adsorption isotherms of SLS and surface area occupied by SLS molecule on the particles prepared by conventional emulsion polymerization and miniemulsion polymerization. These results clearly indicate that the particles prepared by conventional emulsion polymerization are more hydrophobic than the particles prepared by miniemulsion polymerization, implying that the architecture of grafted PVA in the conventional latexes differs from that in the miniemulsion latexes.

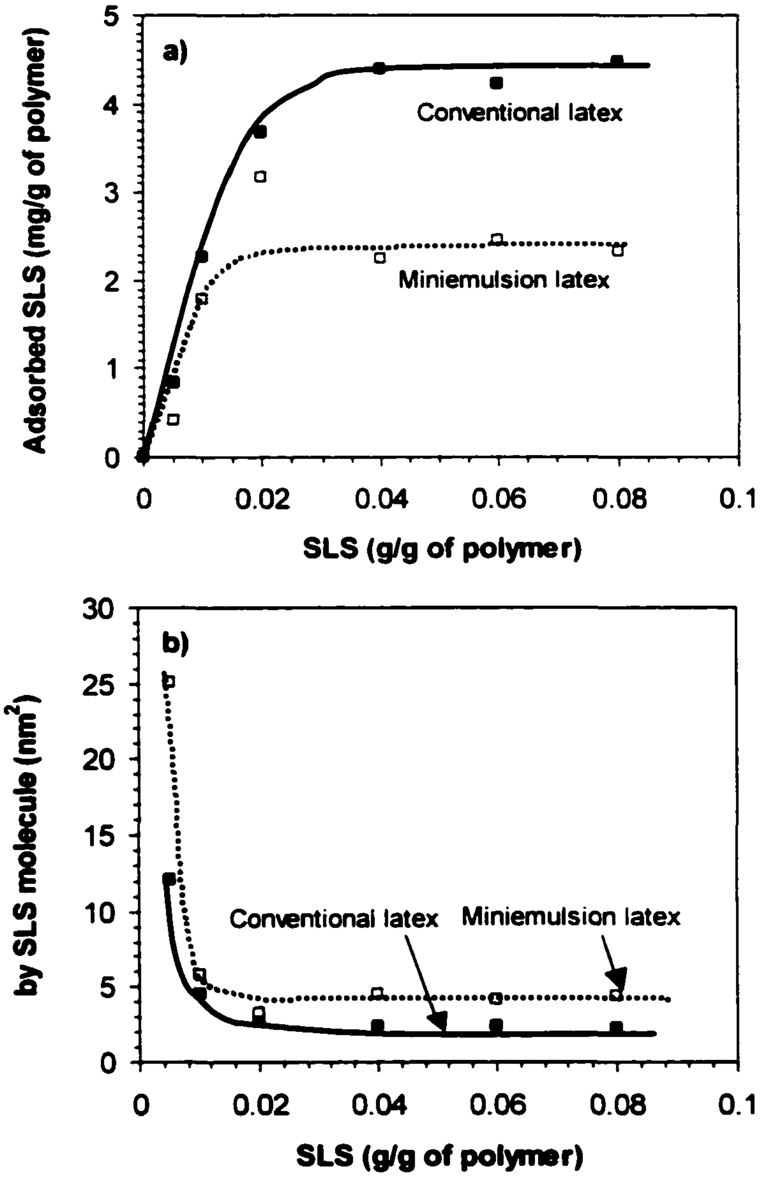

**Figure 5.6:** *Adsorption isotherms of SLS (a) and the surface area occupied by SLS molecule on the cleaned particles prepared by conventional emulsion polymerization and miniemulsion polymerization: BA/MMA=50/50 wt%; PVA = 5 wt%; APS = 1 mM; $T_r$ = 60 °C; reaction time 4 hrs for conventional emulsion polymerization and 20 hrs for miniemulsion polymerization.*

## 5.4 CONCLUSIONS

The miniemulsion technique greatly reduced the formation of coagulum during emulsion polymerizations employing PVA as the sole stabilizer. Limited aggregation and continuous nucleation occurred in conventional emulsion polymerizations, while droplet nucleation was primarily operative in miniemulsion polymerizations.

The colloidal instability in conventional emulsion polymerizations was not closely related to the amount of grafted PVA on the particles and the desorption of PVA. The degrees of hydrolysis of the serum PVA obtained from the conventional and miniemulsion latexes were similar, implying that aqueous phase grafting cannot be correlated with the colloidal instability during the conventional emulsion polymerization.

The surface area occupied per SLS molecule for particles prepared by conventional emulsion polymerization was significantly smaller than that prepared by the corresponding miniemulsion polymerization, indicating that the surface of the particles prepared by conventional emulsion polymerization was more hydrophobic owing to a higher number of grafted chains per PVA molecule or some PVA inclusion into particles presumably. Colloidal instability during the conventional acrylic emulsion polymerization stabilized with PVA might be closely correlated with this hydrophobic surface (different architecture of grafting).

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# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6.1 CONCLUSIONS

The primary conclusions obtained from this work are that the stable acrylic (MMA/BA) emulsions and latexes stabilized with poly(vinyl alcohol) were prepared using the miniemulsion approach and the main grafting site during polymerization was the water/monomer interface. The following observations and conclusions can be drawn from the dissertation work.

1. HD played a critical role in determining the stability of the miniemulsion droplets and 1.85 ~ 2.78 wt% of HD based on the monomers was required to obtain relatively stable droplets.

2. The droplet size decreased exponentially as the concentration of PVA was increased, reaching a lower limit. The number of adsorbed PVA chains on the droplets

increased as the PVA concentration in the system increased up to around 10 wt%, and then remained almost constant, indicating droplet surface saturation.

3. The comparison of the number of droplets and the amount of the serum PVA in the miniemulsions showed that the cross-sectional area of the adsorbed PVA molecules on the droplets greatly increased above 75 wt% MMA in monomer composition.

4. The concentration dependence of grafted PVA was similar to that of the number of PVA molecules adsorbed on the monomer droplets, strongly supporting the hypothesis that the water/monomer interface is the main grafting site in these miniemulsion polymerizations.

5. Increasing MMA in miniemulsion copolymerizations of *n*-butyl acrylate and methyl methacrylate had a great influence on the surface characteristics of the final particles, which caused a decrease in the amount of adsorbed PVA during the polymerization because of increased cross-sectional area of adsorbed PVA on the hydrophilic surface, and resulted in a decrease in the amount of grafted PVA per unit area.

6. The amounts of grafted PVA were similar in the HPO- and TBPO-initiated seeded emulsion polymerizations, strongly supporting the interface as the main grafting site. Seeded emulsion polymerizations carried out after removing the serum PVA showed that the interface was still the main grafting site even when a water-soluble initiator (HPO) was used.

7. The adsorption of partially-hydrolyzed PVA on cleaned latexes resulted in the interaction between the nonionic surfactant on the capillary of the CHDF and the PVA adsorbed on the particles, and this interaction was apparently proportional to the degree of hydrolysis of the PVA chains. The apparent final particle sizes of the latexes prepared with TBPO and HPO differed by CHDF, even though the amount of grafted PVA was not much different, implying that the architecture of the grafted PVA in the TBPO system differed from that in the HPO system.

8. Some aggregation, resulting in an increase in the polydispersity of the particles, occurred in the HPO-initiated miniemulsion polymerization, implying that aqueous phase grafting exists in this miniemulsion polymerization system.

9. The amount of grafted PVA on the final particles was significantly decreased for the TBHP- and TBPO-initiated miniemulsion polymerizations compared to the corresponding seeded emulsion polymerizations.

10. The differences in internal viscosities, which might affect the termination reactions between primary radicals and PVA macro-radicals, were suggested to explain the lower grafting in miniemulsion polymerizations. This was confirmed by determining the amount of grafted PVA as a function of monomer to polymer ratio in seeded emulsion polymerizations and the amount of grafted PVA as a function of conversion for a constant radical generation rate in miniemulson polymerizations.

11. The degree of hydrolysis (DH) of the serum PVA was determined using FT-IR and saponification. Based on the comparison of the DH values using both methods, it was found that aqueous phase grafting resulting in relatively short acrylate chains occurred in the HPO system and interface grafting mainly occurred in the TBHP system, even though TBHP is a partially water-soluble initiator. The grafted chain lengths in the TBHP system seemed to be relatively short because these grafted PVA were still water-soluble; this indicated strong termination reactions at the interface.

12. The miniemulsion technique greatly reduced the formation of coagulum during emulsion polymerizations employing PVA as the stabilizer. Limited aggregation and continuous nucleation occurred in conventional emulsion polymerizations, while droplet nucleation were primarily operative in miniemulsion polymerizations.

13. The colloidal instability in conventional emulsion polymerizations could not be closely correlated to the amount of grafted PVA on the particles, the desorption of PVA, and the molecular weight of the serum PVA.

14. The degrees of hydrolysis of the serum PVA obtained from conventional emulsion latexes and miniemulsion latexes were similar, implying that aqueous phase grafting cannot be correlated with the colloidal instability during the conventional emulsion polymerization.

15. The surface area occupied per SLS molecule for particles prepared by conventional emulsion polymerization was significantly smaller than that prepared by the corresponding miniemulsion polymerization, indicating that the surface of the particles prepared by conventional emulsion polymerization was more hydrophobic owing to a higher number of grafted chains per PVA molecule or some PVA inclusion into particles presumably. Colloidal instability during the conventional acrylic emulsion polymerization stabilized with PVA might be closely correlated with this hydrophobic surface (different architecture of grafting).

## 6.2 RECOMMENDATIONS

Some additional work would bring more insights in this area.

1) In this study, the molecular weight distribution of poly(vinyl alcohol) is broad ($M_w/M_n \sim 3$). Therefore, it is difficult to study the grafting in terms of molecular weight. The use of PVAs having narrow molecular weight distributions will benefit the further understanding of grafting in the aqueous phase and at the interface.

2) This work has shown that the surface properties of grafted PVA in miniemulsion polymers differ from those in conventional emulsion polymers due to different grafting architectures presumably (in chapter 5). To further investigate the different surface properties, films were prepared by latexes that were cleaned using the serum replacement cell. The static contact angle measurement was employed to study the surface properties,

however, similar contact angles (~ 90°) were obtained for each film, implying that the migration of PVA to the film surface is little and the contact angle is not sensitive to the grafting architecture. One possible characterization of the grafting architecture can be done with the dynamic mechanical analyzer. Depending on the architecture of grafting such as the amounts of grafted polymers and graft chain lengths, the $T_g$ (~ 80 °C) and tanδ will vary. Also, study of the latex viscosity (rheology) could help to characterize the different grafting architecture.

4) As discussed in the appendix, the application of cetyl alcohol as a costabilizer in miniemulsion polymerization is not recommended in terms of miniemulsion stability in this study compared to hexadecane. However, the functional group (–OH) in cetyl alcohol can affect the grafting, especially for interface grafting. Therefore, the combination of hexadecane and cetyl alchol as a costabilizer systems can be considered to investigate the effect of –OH on the grafting at the interface. Also, the application of a modified PVA such as thiol terminated PVA (SH-PVA) can be considered to study the effect of –SH at the interface. In both cases, different grafting architectures are expected.

5) The application of fully hydrolyzed PVA as a stabilizer in miniemulsion polymerization is difficult due to its poor adsorption on the droplet surface. The preparation of miniemulsions using modified fully hydrolyzed PVA with terminal dodecyl group (R-PVA) is feasible. However, it is questionable whether the grafting would occur at the droplet surface of the miniemulsion because it seems that a terminal

dodecyl group would only attach to the surface, and not be available for hydrogen abstraction.

6) It was shown that there is an interaction between partially hydrolyzed PVA adsorbed on the particle surface and the capillary wall in CHDF due to a hydrophobic interaction and this interaction seems to be dependent on the grafting architecture. The characterization of PVA in terms of molecular architecture such as blockiness is important because blockiness can affect the reaction rate, particle nucleation and growth mechanisms, and grafting. The molecular architecture of PVA such as blockiness might be characterized using the CHDF.

# APPENDIX

## I. The Choice of Shear Instrument

Miniemulsions are dispersions of monomer droplets, having diameters in the range of 50 to 500 nm. Formation of sub-micron monomer droplets is brought about by the application of energy through homogenation or microfluidization. Initially, acrylic miniemulsions stabilized with PVA were prepared by sonification (Branson, Model 450) alone or sonification followed by microfluidization (Microfluidics, Model 110T) (similar recipe to Table 2.1). The application of microfluidization imparts higher shear energy to the emulsion, resulting in smaller miniemulsion droplets.[1] However, in our case, the average droplet size prepared by sonification was smaller than that by microfluidization (Figure A.1). Also, the lines in the Microfluidizer were often clogged, implying that some portions of the PVA were solidified in the lines. Due to line clogging and unexpected larger droplet sizes, the sonifier was chosen as the principal shear instrument.

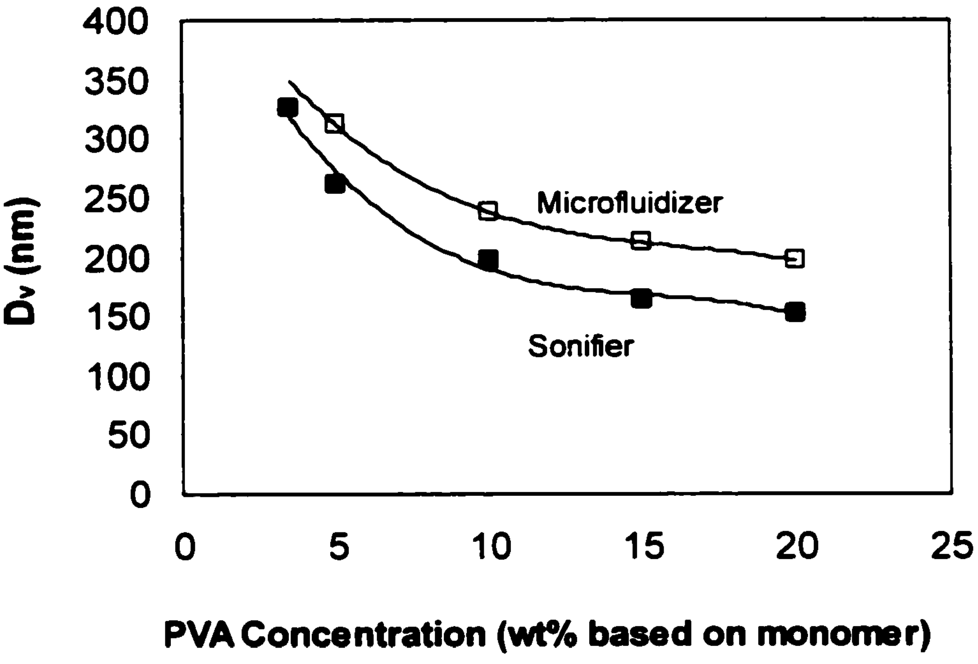


**Figure A.1**: *Volume-average droplet diameter measured by dynamic light scattering (DLS) as a function of PVA concentration in terms of shear instruments: Sonifier, 70 % duty cycle, Power 8, and 10 min sonification; Microfluidizer, 50 % duty cycle, power 6, and 1 min sonification and followed by 10 passes through Microfluidizer; n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 10 wt% based on monomer; hexadecane (HD) = 3.6 wt % based on monomer; solids content ~ 20 %.*

## II. Choice of Costabilizer and the Possibility of High Solids

In the preparation of a miniemulsion, the costabilizer is necessary to prevent the degradation of droplets via Ostwald ripening. In most cases, low molecular weight cosatbilizers, such as cetyl alcohol (CA) or hexadecane (HD), have been utilized, even though there were some approaches to replace CA or HD with polymers[2] and chain transfer agents.[3,4] Initially, the miniemulsions were prepared using CA or HD as a costabilizer (Table A.1) and polymerizations were carried out in a four-neck flask. The droplet size after preparation of the miniemulsion and the final particle size were measured by dynamic light scattering (DLS). In the miniemulsion prepared with HD, the solid contents was increased to 40 wt%.

Some physical properties of the miniemulsions and final latexes are summarized in Table A.2. The preparation of the miniemulsion with CA was not efficient compared to that by HD in terms of droplet size. Also, as discussed in chapter 2, the droplets prepared using CA easily degraded with time, implying that PVA partitioning at the interface decreases with time due to coalescence of droplets, resulting in the decrease of the interfacial area. The final particles from the miniemulsion prepared using CA showed larger diameters and a broader particle size distribution, indicating that the application of CA as a costabilizer is not suitable in this project. Therefore, miniemulsion stability is a critical factor to obtain stable acrylic latexes stabilized with PVA. The possibility of high solids content latexes was investigated using HD system by reducing water in recipe. The high viscosity of the miniemulsion was observed after sonification. After polymerization, the final particle size was similar to that obtained at low solids content (~ 20 %) and coagulum was not observed. The final latexes showed iridescence, indicating a narrow particle size distribution.

**Table A.1:** Recipe for the polymerizations as a function of costabilizer and solids content

| Ingredient | Cetyl alcohol[a] | Hexadecane[b] | Hexadecane/High solids[c] |
|---|---|---|---|
| Deionized water | 80.0 | 80.0 | 30.0 |
| *n*-Butyl acrylate (BA)[a] | 10.0 | 10.0 | 10.0 |
| Methyl methacrylate (MMA)[a] | 10.0 | 10.0 | 10.0 |
| PVA 205 | 2.0 | 2.0 | 2.0 |
| Hexadecane (HD) | | 0.726 | 0.726 |
| Cetyl alcohol (CA) | 0.776 | | |
| $NaHCO_3$ | 0.03 | 0.03 | 0.03 |
| Ammonium persulfate (APS) | 0.06 | 0.06 | 0.06 |

[a,b] sonified at 70 % duty cycle, power 8, and 4 min

[c] sonified at 70 % duty cycle, power 8, and 10 min

*$T_r$: 60 °C for 2 hrs and then raised to 70 °C, total reaction time = 4 hrs

**Table A.2:** Physical properties of miniemulsions and the resulting latexes as function of costabilizer and solids content

| | | Cetyl alcohol | Hexadecane | Hexadecane/High solids |
|---|---|---|---|---|
| Miniemulsion | $D_v$ | 272.9 | 180.4 | - |
| Droplets[a] | $D_I$ | 269.7 | 201.1 | - |
| | $D_n$ | 221.4 | 141.4 | - |
| Conversion (%) | | 96.9 | 96.9 | 95.3 |
| Solids content (%) | | 20.5 | 20.5 | 40.6 |
| Particles[a] | $D_v$ | 1570.6 | 272.0 | 284.0 |
| | $D_I$ | 752.3 | 269.0 | 280.2 |
| | $D_n$ | 91.3 | 247.5 | 265.9 |
| Sedimentation (days) | | <10 | >60 | >60 |

[a] measured by DLS

### III. Choice of PVA in Terms of Molecular Weight

Two kind of PVA in terms of molecular weight were considered in this project, PVA 205 (degree of hydrolysis (DH) ~ 88%, degree of polymerization (DP) ~ 500) and PVA 217 (degree of hydrolysis (DH) ~ 88%, degree of polymerization (DP) ~ 1750). Miniemulsions were prepared using PVA 205 and PVA 217 (Table A.3). Miniemulsion polymerizations were carried out using the bottle polymerizer (~ 40 rpm with end-over-end rotation). Figure A.2 shows the effect of the PVA concentration and the molecular weight on the droplet size. The droplet size exponentially decreased as the concentration of PVA increased, and then leveled off despite the increased amount PVA. This lower limit of the droplet size was larger, and was attained at a lower PVA concentration as the molecular weight of the PVA increased. This implies that the higher molecular weight PVA is less efficient in reducing the droplet size, i.e., less surface active. Mendizabal et al.[5] studied the interfacial tension between styrene and PVA aqueous solutions and found that the surface activity increased with decreasing molecular weight, i.e., lower interfacial tensions for low molecular weight) and decreasing degree of hydrolysis of the PVA . Lankveld and Lykleman[6] also studied the adsorption of PVA on emulsified paraffin droplets in water and calculated the adsorption area per PVA molecule, $a_0$, by measuring the droplet size and the ratio of $a_0$ to the projected area ($\pi R_g^2$, where $R_g$ is the radius of gyration). The ratio of $a_0$ to $\pi R_g^2$ was found to decrease as the molecular weight of the PVA was increased. This also indicates that a relatively small fraction of the polymer chains in the high molecular weight PVA is adsorbed on the paraffin droplets and why the surface activity decreased as the molecular weight is increased.

**Table A.3:** Recipe for the preparation of miniemulsions as function of PVA molecular weights

| Ingredient | PVA 205[a] | PVA 217[b] |
|---|---|---|
| Deionized water | 80.0 | 80.0 |
| *n*-Butyl acrylate (BA) | 10.0 | 10.0 |
| Methyl methacrylate (MMA) | 10.0 | 10.0 |
| PVA 205[a] | 0.5 – 4.0 | |
| PVA 217[b] | | 0.2 - 1.0 |
| Hexadecane (HD) | 0.776 | 0.776 |

[a] DP = 500, DH = 88%

[b] DP =1750, DH = 88%

As mentioned earlier in the chapter 1, one advantage of applying the miniemulsion technique is the possibility of obtaining high PVA/monomer ratios at the polymerization loci (droplet interface). Figure A.3 compares the particle sizes obtained via miniemulsion polymerizations as a function of PVA concentration and molecular weight. Overall, the resulting particle size (Figure A.3) was larger than the corresponding droplet size (Figure A.2), which suggests that not all droplets are nucleated or that the mixing efficiency of bottle polymerizer is not good. Based on these results, PVA 205 was chosen for this study.

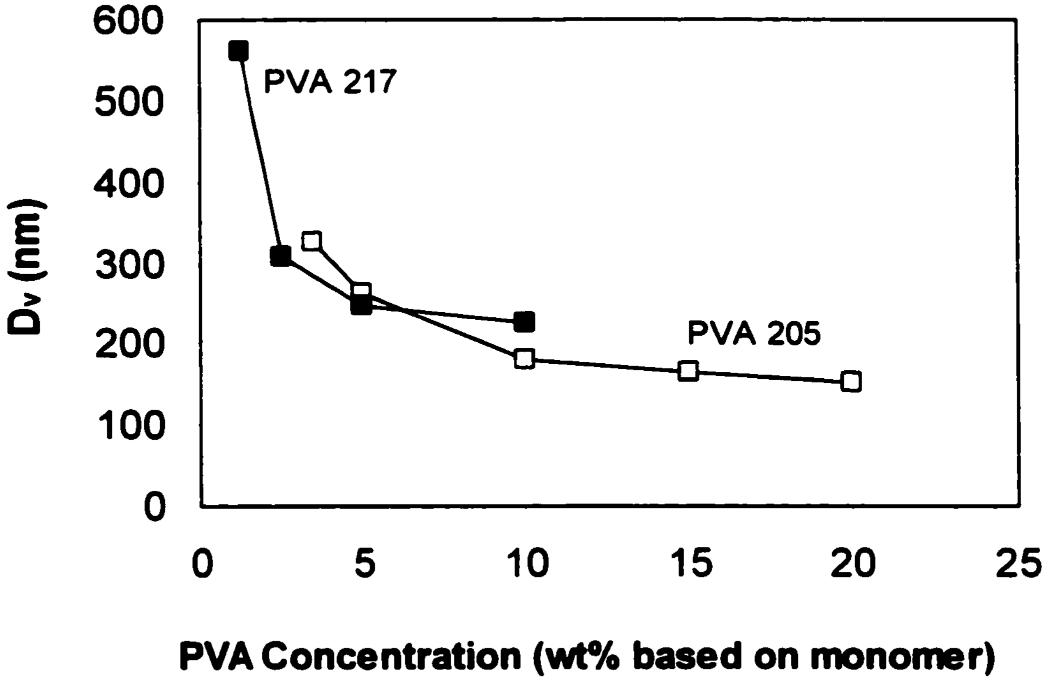


**Figure A.2:** *Volume-average droplet diameter measured by DLS as a function of PVA concentration in terms of PVA molecular weight; sonified at 70 % duty cycle, power 8, and 10 min; n-butyl acrylate/methyl methacrylate = 50/50 wt%; HD, 3.6 wt% based on monomer; PVA 205 (DP = 500, DH = 88%); PVA 217 (DP = 1750, DH = 88%).*

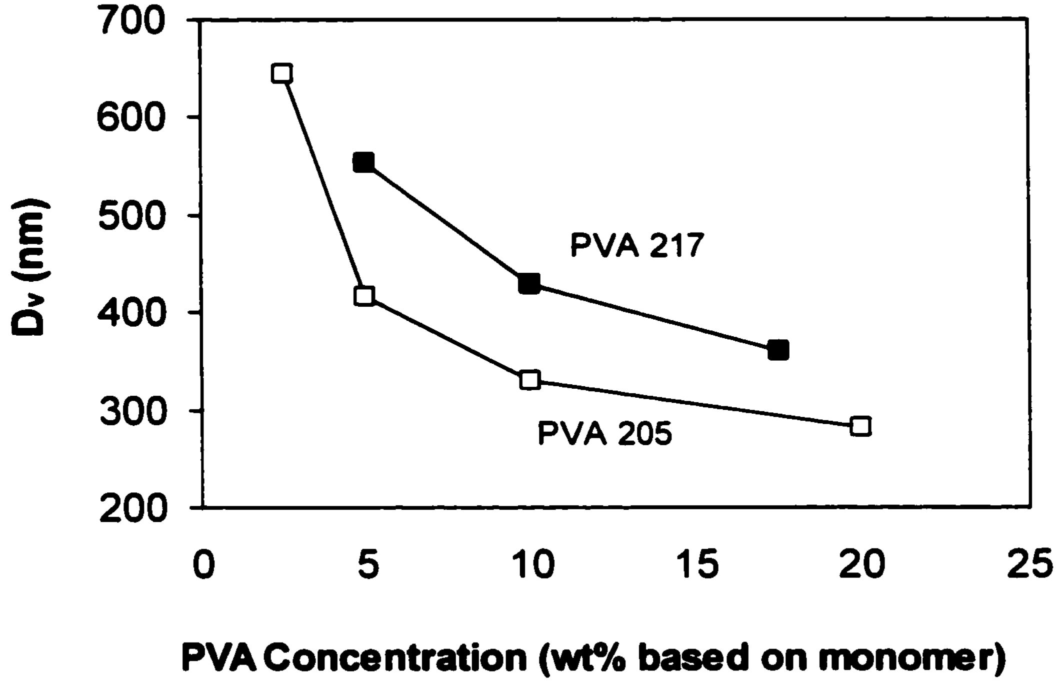


**Figure A.3:** *Volume-average final particles diameter prepared by miniemulsion polymerizations of BA/MMA (50/50 wt%) as a function of PVA concentration in terms of PVA molecular weight; particle sizes were measured by DLS; PVA 205 (DP = 500, DH = 88%); PVA 217 (DP = 1750, DH = 88%).*

## IV. Thermal Stability of Miniemulsion Droplets

As discussed previously, the droplet stability is a critical in determining the stability and final particle size of the resulting latex. If a persulfate initiator is used, a relatively high reaction temperature is required to dissociate the initiator, where the droplet stability is more important. To maintain the initial droplet size at 60 °C, two approaches were studied; an increase in the HD concentration and the addition of a low molecular weight poly(styrene) (PS), ~ 1000 g/mol (Similar recipe to Table 2.1). After the preparation of the miniemulsions, they were kept at 60 °C in a bottle with gentle magnetic stirring. A small amount of miniemulsions was taken, and immediately cooled in an ice bath. The droplet size was measured with time using dynamic light scattering. The results are shown in Table A.4 and Figure A.4. Initial droplet sizes increased with the increasing HD and the addition of oligomeric PS due to the increase of hydrophobicity of the droplets presumably. A typical miniemulsion recipe (HD = 3.6 wt% based on monomer) showed that the initial droplets degraded in 30 min at 60 °C. The increase of HD concentration to 7.2 wt% suppressed the degradation of initial droplets size until 1 hr, meanwhile, the addition of oligomeric PS maintained the original droplet size until 2 hrs. However, the best way to preserve the initial droplet size is to maintain the miniemulsion at a lower temperature (refer to Figure 2.2).

**Table A.4**: Volume-average droplet particle diameter at 60 °C as a function of time in terms of hexadecane (HD) concentration and the addition of oligomeric poly(styrene) (PS)

| Time (min) | [HD][a] | 2[HD] | [HD]+PS[b] |
|---|---|---|---|
| | $D_v$ (nm) | $D_v$ (nm) | $D_v$ (nm) |
| 0 | 180.4 | 198.0 | 199.1 |
| 17 | 201.2 | | |
| 30 | | 205.3 | |
| 47 | 222.0 | | |
| 60 | | | 199.8 |
| 66 | | 207.9 | |
| 91 | 231.0 | | |
| 120 | 229.8 | 228.7 | 199.6 |
| 140 | | | 224.1 |
| 180 | | 230.8 | |
| 200 | 228.3 | | |
| 270 | | | 248.8 |

[a] [HD] = 3.6 wt% based on monomer (160 mM)

[b] PS = 0.5 wt% based on monomer, ~1000 g/mol

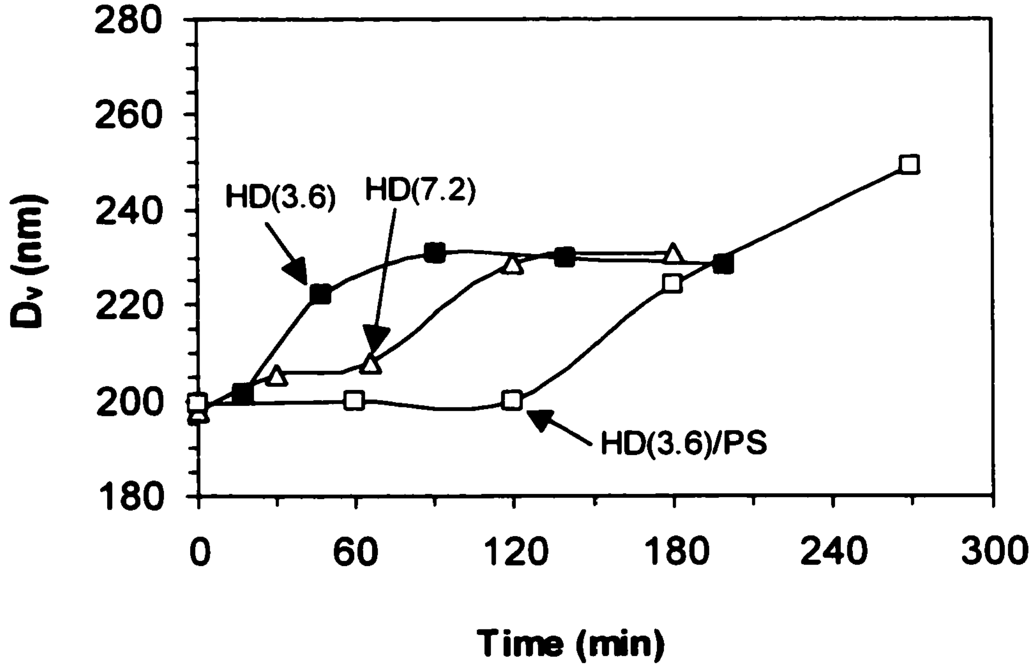


**Figure A.4:** *Volume-average droplet particle diameter at 60 °C as a function of time in terms of hexadecane (HD) concentration and the addition of oligomeric poly(styrene) (PS); n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 (DP = 500, DH = 88%) 10 wt% based on monomer; HD(3.6), HD = 3.6 wt % based on monomer; HD(7.2), HD = 7.2 wt % based on monomer; HD(3.6)/PS, HD = 3.6 wt % based on monomer and the addition of 0.25 wt% PS ($M_w$ ~ 1,000 g/mol) based on monomer.*

## V. Comparison of Miniemulsion Polymerization and Conventional Emulsion Polymerization Initiated with Hydrogen Peroxide/Ascorbic Acid

A comparison of conventional and miniemulsion polymerizations was made using a redox initiation system (hydrogen peroxide/ascorbic acid, HPO/AA). The experimental recipe is shown in Table A.5.

**Table A.5:** Recipe for conventional and miniemulsion polymerizations initiated with hydrogen peroxide(HPO)/ascorbic acid (AA)

| Ingredient | Weight (g) |
|---|---|
| Deionized water | 80.0 |
| *n*-Butyl acrylate (BA) | 10.0 |
| Methyl methacrylate (MMA) | 10.0 |
| PVA 205 | 1.0 and 2.0 |
| Hexadecane (HD) | 0.726 |
| Hydrogen peroxide (HPO) | 0.03 |
| Ascorbic acid (AA) | 0.06 |

*Conventional polymerization was carried out without HD.

**$T_r$ = 30 °C

***Reaction time = 3 hrs

Polymerizations were carried out using the same procedures decribed in chapter 3. The reaction temperature was kept at 30 °C to minimize the degradation of the initial droplet size and the reaction time was 3 hrs. The conventional emulsion polymerization showed faster rates than the miniemulsion polymerization (Figure A.5), implying the higher nucleation rates. Table A.6 shows the final particle diameters and the amounts of coagulum formed as a function of PVA concentration and the polymerization method. As expected from the kinetics, the average particle diameters in the conventional systems were smaller than in the miniemulsion systems. Meanwhile, the formation of coagulum in conventional system was greater than that in miniemulsion system, especially for 5 wt % PVA, indicating that the miniemulsion system is suppressing the formation of coagulum. Figure A.6 shows the final number and weight particle size distributions of the miniemulsion latexes obtained by capillary hydrodynamic fractionation (CHDF) as a function of PVA concentration. There was few small particle (~ 50 nm) population at 10 wt% PVA and no small particle population at 5 wt% PVA, implying that droplet nucleation is dominant. However, there were small populations of larger particles in the number distributions, which are magnified in the weight distributions, indicating some aggregation.

Figure A.7 shows the final number and weight particle size distributions of conventional emulsion polymers obtained by capillary hydrodynamic fractionation (CHDF) as a function of PVA concentration. At 5 wt% PVA, there was a great portion of the populations at small sizes with multi-modal distributions, indicating continuous nucleation and limited aggregation. Increasing the PVA concentration from 5 to 10 wt% greatly suppressed the limited aggregation and it seemed to be a unimodal distribution.

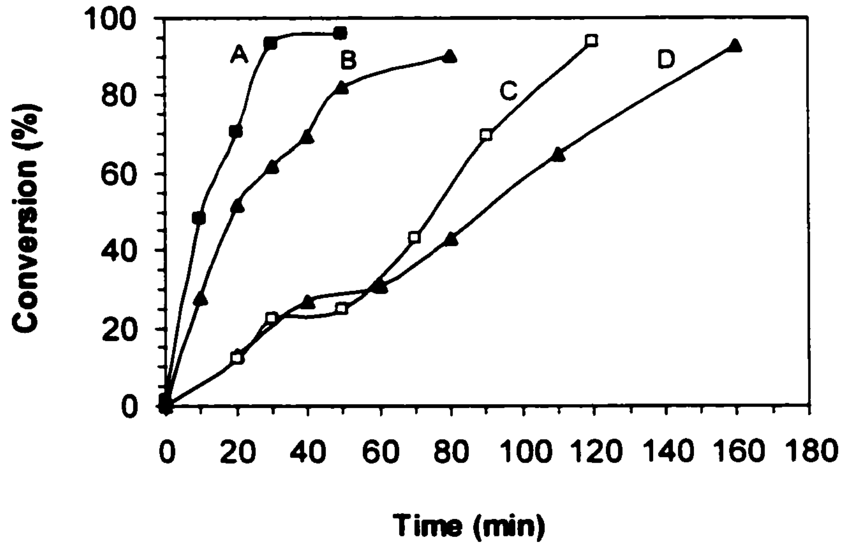


**Figure A.5:** *Conversion as a function of time in terms of polymerization methods and PVA concentration in redox initiated system (HPO/AA); n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 (DP = 500, DH = 88%); A, conventional emulsion polymerization 10 wt% PVA; B, conventional emulsion polymerization 5 wt% PVA based on monomer; C, minemulsion polymerization 10 wt% PVA; D, miniemulsion polymerization 5 wt% PVA.*

**Table A.6:** Final particle diameter and coagulum in terms of polymerization method and PVA concentration initiated with redox system (HPO/AA).

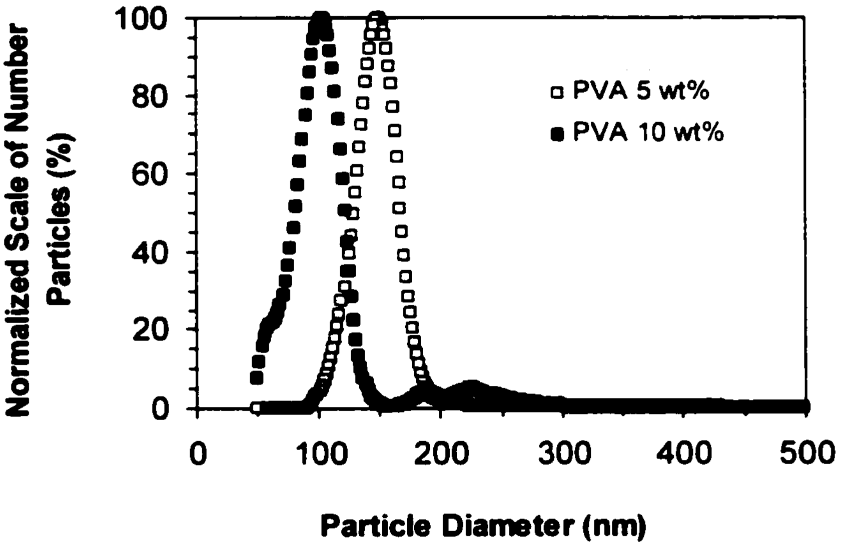
| | PVA (wt%) | Particle diameter (nm)[1] | | | Coagulum[2] (%) |
|---|---|---|---|---|---|
| | | $D_n$ | $D_w$ | $D_w/D_n$ | |
| Miniemulsion polymerizations | 10.0 | 110.5 | 246.3 | 2.24 | 0.031 |
| | 5.0 | 155.3 | 212.4 | 1.37 | 0.748 |
| Conventional emulsion polymerizations | 10.0 | 77.2 | 134.7 | 1.74 | 0.358 |
| | 5.0 | 121.1 | 323.5 | 2.67 | 8.460 |

[1] obtained by CHDF

[2] screened using a stainless steel mesh (#200), wt% based on monomer

This is quite consistent with the significant decrease of coagulum formation and an interesting result compared to the conventional emulsion polymerization initiated with ammonium persulfate (APS) (see chapter 5)

The serum PVA and the adsorbed and grafted PVA on the particles were determined using the selective solubilization method for the miniemulsion latexes and conventional latexes stabilized with 10 wt% PVA and the results are summarized in Table A.7. Basically, the amount of grafted PVA in the conventional latexes were larger than that in the miniemulsion latexes. These results are quite different from the APS system (see also chapter 5).



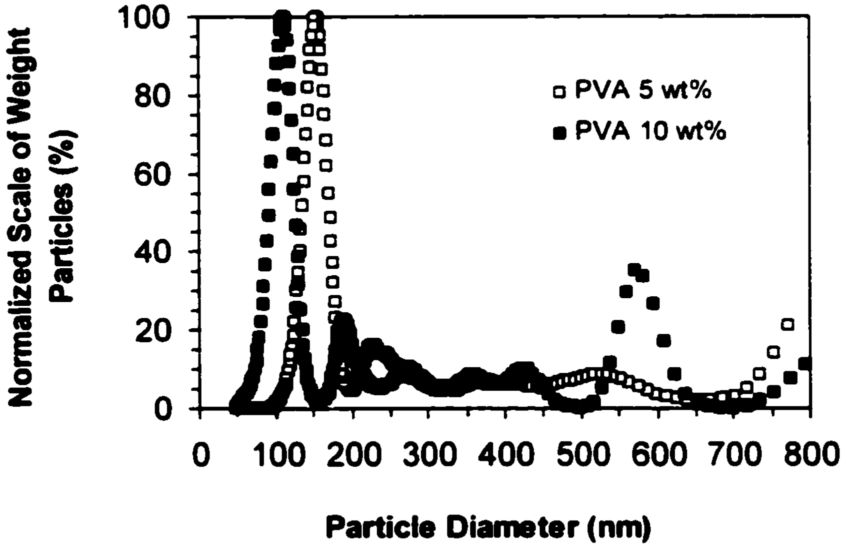
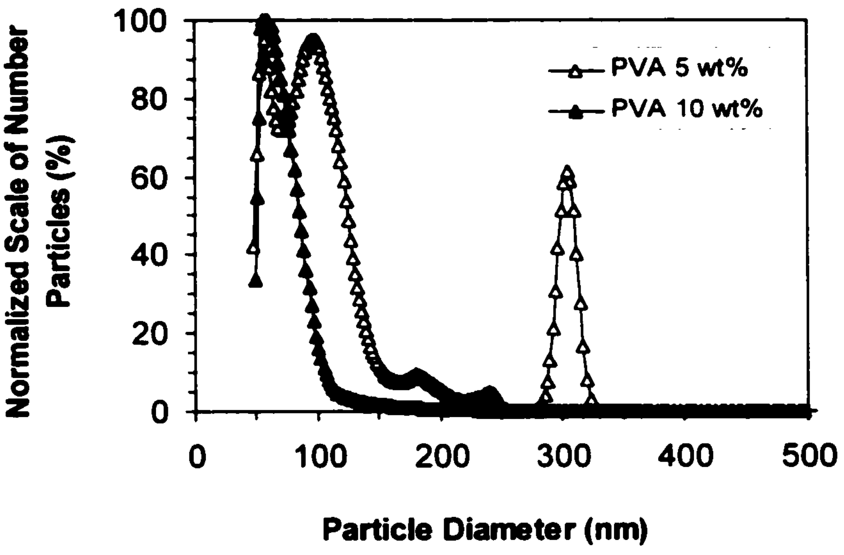


**Figure A.6:** *Number and weight particle size distributions obtained by CHDF as a function of PVA concentration in minemulsion polymerizations initiated by a redox system (HPO/AA): n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 (DP = 500, DH = 88%).*



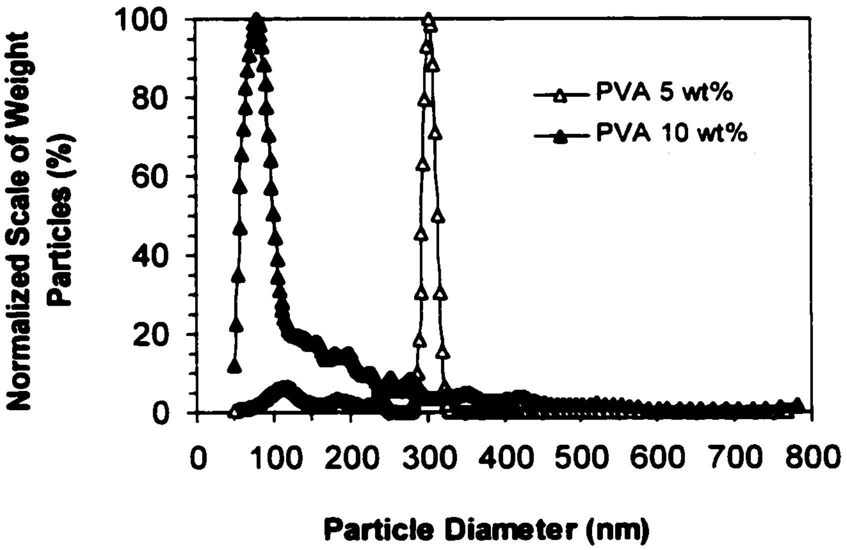


**Figure A.7:** *Number and weight particle size distributions obtained by CHDF as a function of PVA concentration in conventional emulsion polymerization initiated by a redox system (HPO/AA); n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 (DP = 500, DH = 88%).*

**Table A.7:** Amounts of serum PVA, adsorbed, and grafted PVA on the final particles initiated with HPO/AA in conventional and miniemulsion polymerizations at 10 wt% PVA.

| | Serum PVA (%) | Adsorbed PVA (%) | Grafted PVA (%) |
|---|---|---|---|
| Conventional latexes | 28.4 | 6.1 | 65.5 |
| Miniemulsion latexes | 36.5 | 1.1 | 62.4 |

The application of the redox system in conventional acrylic emulsion polymerizations stabilized with PVA may result in stable latexes in terms of coagulum. However, the big difference between the APS system and the redox system is the reaction temperature (60 °C vs. 30 °C) and reaction time (~ 20 hrs vs. 3 hrs). Therefore, the thermal stability of latexes prepared using the redox system was investigated. 70 g of the final latexes prepared by miniemulsion and conventional emulsion polymerizations with 10 wt% PVA were placed in 100 mL glass bottles. Also, 50 g of the final latexes prepared by miniemulsion and conventional emulsion polymerization with 10 wt% PVA were placed in 100 mL glass bottles and 5 g of hydroquinone (2 wt%) was added to prevent any further reaction. Each bottle was rotated using a bottle polymerizer (end-over-end rotation at 40 rpm) for 20 hrs at 60 °C. The formation of coagulum was determined using a stainless steel mesh (#200) and the results are summarized in Table A.8. In the conventional system, a lot of coagulum formed despite the higher amount of grafted PVA, implying that the characteristics of the grafted PVA in the conventional system may differ from that in the miniemulsion system.

**Table A.8:** Thermal stability of latexes prepared by conventional and miniemulsion polymerizations initiated with HPO/AA at 10 wt% PVA.

| Latex code | Coagulum (%)[a] | |
|---|---|---|
| | Without hydroquinone[b] | With hydroquinone[c] |
| Miniemulsion latexes | 3.5 | 1.5 |
| Conventional latexes | 50.7 | 46.5 |

[a] screened with a stainless steel mesh (#200), based on monomer

[b] 70 g of latex in a 100 mL glass bottle and rotated in a bottle polymerizer (end-over-end rotation at 40 rpm)

[c] 50 g of latex and 5 g of hydroquinone (2 wt%) in a 100mLl glass bottle and rotated in a bottle polymerizer

## VI. Preparation of Miniemulsion Using Fully Hydrolyzed PVA

A fully hydrolyzed PVA forms highly water-resistant as well as heat-resistant films due to its high crystallinity (approximately, ~ 25%). However, the viscosity of an aqueous solution increases with time. Also, the application of fully hydrolyzed PVA is difficult because of its low surface activity, resulting in larger droplets and lack of miniemulsion stability. Table A.9 shows the comparison of the droplet size of miniemulsions prepared with fully and partially hydrolyzed PVAs.

**Table A.9:** Comparison of miniemulsion droplet sizes measured by dynamic light scattering in terms of degree of hydrolysis (DH).

| | Droplet diameter (nm)[a] | | |
|---|---|---|---|
| | $D_v$ | $D_I$ | $D_n$ |
| DH = 88 % | 190 ± 10 | 205 ± 8 | 150 ± 10 |
| DH = 98% | 762 | 330 | 81 |

[a] prepared with 10 wt% PVA (DP = 500) based on monomer, *n*-butyl acrylate/methyl methacrylate = 50/50 wt%, 3.6 wt% HD based on monomer, and the ratio of water/monomer = 80/20.

Recently, Nakamae et al.[7] reported a modified fully hydrolyzed PVA by incorporating hydrophobic end groups. They prepared stable conventional vinyl acetate latexes in terms of viscosity at lower temperature. The droplet diameter of miniemulsions as a function of PVA concentration and the droplet stability after 1 day were compared in terms of degree of hydrolysis (Figure A. 8). Basically, the droplet size prepared with the fully hydrolyzed PVA (R-PVA, DP = 300, DH = 98%) was larger than that with the partially hydrolyzed PVA (PVA 205, DP = 500, DH = 88%). Also, the droplet size seemed to be constant after 10 wt% R-PVA, showing a similar trend to PVA 205. The increase in droplet diameter using R-PVA after 1 day was larger than PVA 205, implying that the degradation of the miniemulsions using R-PVA was greater. The partitioning of R-PVA was determined using the serum replacement cell and compared to PVA 205 (Figure A.9). As discussed in chapter 2, the comparison of the droplet size and the partitioning of PVA 205 as a function of concentration showed that the droplet surface was saturated at around 10 wt% PVA. The droplet size using R-PVA leveled–off after 10 wt% PVA, implying that the droplet surface seemed to be saturated with R-PVA molecules. However, the partitioning behavior of R-PVA did differ from that of PVA 205. The partitioning of R-PVA was constant even though the concentration was increased and the droplet size was almost constant, indicating that the number of PVA molecules adsorbed on the constant area droplet surfaces (the same droplet size) increase with increasing concentration, where the configuration of R-PVA at the droplet surface is probably continuously changed.

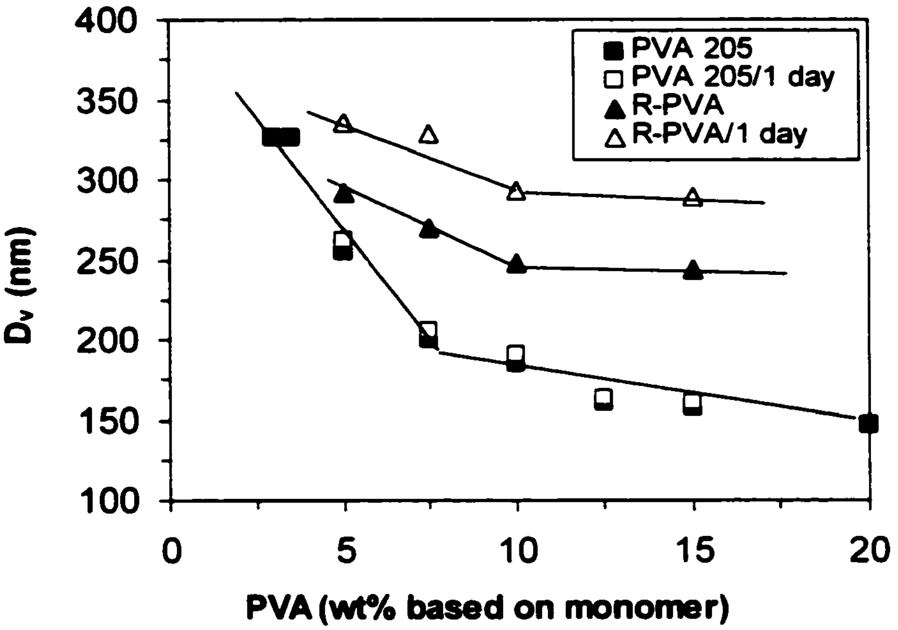


**Figure A.8:** *Volume-average droplet diameter obtained by dynamic light scattering as a function of PVA concentration; n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 (DP = 500, DH = 88%), measured after preparation of minieumlsion; PVA 205/1 day, measured after 1 day; R-PVA (DP = 300, DH = 98%), measured after preparation of miniemulsion; R-PVA/1 day, measured after 1 day.*

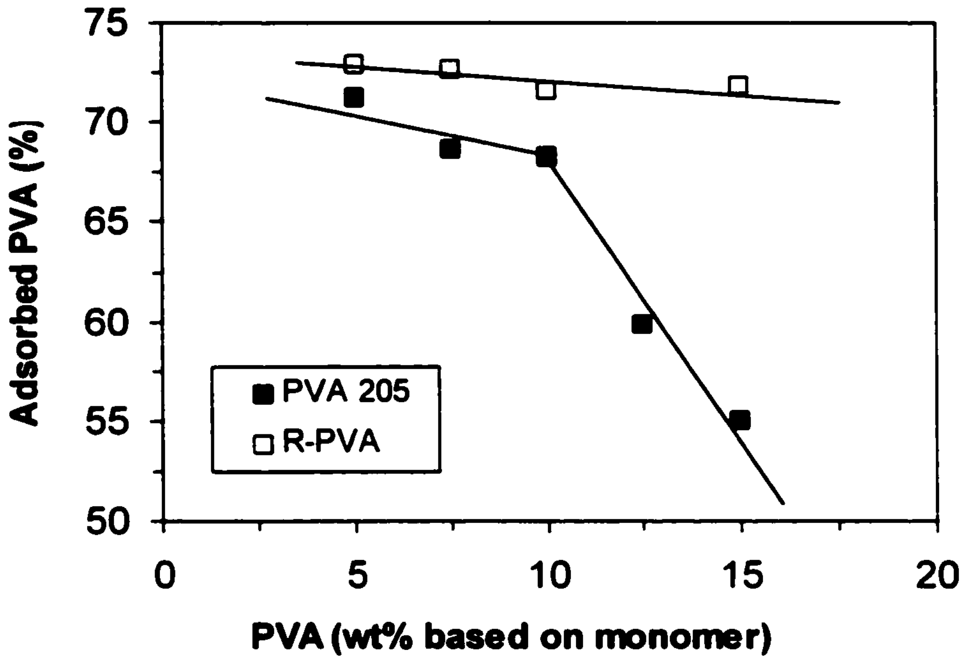


**Figure A.9:** *Amount of PVA adsorbed on the droplet surfaces determined using the serum replacement cell as a function of PVA concentration; n-butyl acrylate/methyl methacrylate = 50/50 wt%; PVA 205 (DP = 500, DH = 88%); R-PVA (DP = 300, DH = 98%).*

## VII. References

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# VITA

Mr. Noma Kim was born as an eldest son on January 4, 1967 in Seoul, the capital city of South Korea, to Myung-chul Kim and Gil-ja Kwak. After graduating Dae-il High School with honors, he was offered admission to the department of Chemical Technology (currently, the School of Chemical Engineering) in Seoul National University, the top engineering school in South Korea. He served as a president of department student council in 1987, probably one of the hardest times in South Korea for democracy, and met a lovely, sincere, and smart girl, Miyoung, his wife at that time. In 1989, he advanced to graduate school and received a scholarship from Han-Kook Tire Manufacturing Company. He studied the material science and surface science of diamond thin films regarding synthesis and the measurement of electrical properties of thin films, under supervised by Professor Ji-wha Lee, and was exposed to colloid science for the first time. After receiving the degree of master of science, he joined the research institute of LG Chemical and started his research career on polymer colloids. His main research areas in LG Chemical were synthesis of rubber latexes such as styrene-butadiene copolymer and poly(butadiene) for impact modification of plastics, preparation of large particle size poly(butadiene) latexes using in-situ agglomeration by acrylic polymer colloids, preparation of amphoteric styrene-butadiene latexes for paper coating applications, and the study of coating colors including amphoteric latexes. He had the opportunity to study at EPI as a visiting scientist in 1996 with the title of the cleaning and characterization of surface-modified styrene-butadiene latexes. During his career in LG Chemical, he commercialized several emulsion polymer products. By these successful research activities, he was the silver medallist of LG Chemical Skill and Technology and the recipient of LG Chemical R&D Award.

Mr. Kim got admission from the chemical engineering department at Lehigh University and joined the EPI on January 2000. While working towards his Ph.D. degree in the Polymer Science and Engineering Program in Lehigh, he received the John Manson Award for his excellence in the qualifying examination in 2000, and the Best Poster Award at the EPI's Annual Review Meeting in 2001, and the TICONA award for outstanding graduate research in 2001. He had the opportunity to present his work at the Gordon Research Conference on Polymer Colloids in Tilton, NH, 2001. He is going to publish several papers by the time of his graduation.