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Comparison of Conventional and Miniemulsion Copolymerizations of Acrylic Monomers Using Poly(vinyl alcohol) as the Sole Stabilizer

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ABSTRACT: Particle nucleation and growth mechanisms in conventional emulsion and miniemulsion copolymerizations of *n*-butyl acrylate (BA) and methyl methacrylate (MMA) (50/50 wt %) employing poly(vinyl alcohol) (PVA) as the stabilizer were investigated in terms of the evolution of the particle size and the number of particles using capillary hydrodynamic fractionation (CHDF). All results strongly indicate the continuous nucleation and limited aggregation mechanism for conventional emulsion polymerizations and primarily droplet nucleation mechanism for miniemulsion polymerizations. Colloidal instability in conventional emulsion polymerizations was investigated and compared with the corresponding miniemulsion polymerizations in terms of the amounts of grafted and serum PVA and the molecular weight of the serum PVA. Unexpectedly, there was no direct correspondence between the amount of grafted PVA and the colloidal stability in the conventional emulsion polymerizations. Also, the colloidal instability in the latter reactions was studied in terms of the degree of aqueous phase grafting (the decrease in degree of hydrolysis of the serum PVA after polymerization) and the surface properties of the grafted PVA. It was found that the grafted PVA in conventional emulsion polymerizations was more hydrophobic than that produced in similar miniemulsion polymerizations. The colloidal instability during the conventional emulsion polymerizations was considered to be related to this difference in the nature of the grafted PVA.

Introduction

In emulsion polymerization, the surfactant plays important roles in the stability, rheology, and control of the 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 nonwoven materials, water-based inks, paper coatings, and waterborne 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 hydroxyethyl 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 greater 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 takes place at the methine carbon 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 macroradical concentrations via chain transfer. These approaches have been cited in patents and include the addition of water-soluble regulators such as mercaptoacetic acid and cyclohexylamine,[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 using 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 50−500 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 (PVA molecules in this case) 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 0.1−0.2 μm were obtained utilizing 5−20 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

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Table 1. Recipe for the Miniemulsion Polymerizations and Conventional Emulsion Polymerizations of *n*-Butyl Acrylate and Methyl Methacrylate

ingredient	wt (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	160 mM 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.

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

Experimental Section

Materials. *n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were passed twice through inhibitor-removal columns (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), phenolphthalein (Baker), methanol (VWR), sodium lauryl sulfate (SLS, Fisher), 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). DI (deionized) water (treated by reverse osmosis followed by ion exchange) was used throughout.

Procedures. a. Polymerization. The recipe employed in these studies is listed in Table 1. To prepare the miniemulsions, the PVA was first dissolved in DI water (ca. 6 wt % solution) at 90 °C for 3 h, 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 DI 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 min to prepare a crude emulsion. This emulsion was sonified using a Branson Sonifier (model 450) at a 70% duty cycle and a power setting of 8 for 10 min 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 4 h or over 20 h. Conventional emulsion polymerizations were carried out using the corresponding miniemulsion recipe without added costabilizer (hexadecane).

b. Characterization. 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 solubilization method.[19] 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 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 h 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 grafted and/or the adsorbed PVA and stirred for 7 days via magnetic stirring. Afterward, 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 h 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 (3−5 times). The acetonitrile-insoluble polymers that contain both PVA grafted and adsorbed on the particles were dried, weighed, and mixed with DI water. The mixture was heated to 85 °C and stirred for 24 h 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.

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 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. (The absorbance of KSCN was kept below 0.1 to maintain the linear relationship between concentration and absorbance.) Films of the samples were then cast onto zinc−selenide (Zn−Se) IR disks (25 × 4 mm). The disks were dried for 24 h at 50 °C and cooled in a desiccator, and then the FT-IR absorbance spectrum for each sample was obtained over a 1 h period. The area ratio of absorbance for the KSCN nitrile group stretch from 2100 to 1950 cm^{-1} and the carbonyl group stretch from 1850 to 1650 cm^{-1} was determined, and the degree of hydrolysis (DH) was calculated on the basis of the original PVA (PVA 205, degree of hydrolysis ~88%) using eq 1:

$$\mathrm{DH} = 100 - \left(\frac{\mathrm{area(carbonyl)/area(nitrile)}}{0.7\,\dfrac{\mathrm{wt(PVA)/wt(KSCN)}}{4.0}} \times 12 \right) \qquad (1)$$

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 at a 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), and 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 on a Japan Industrial Standard (JIS K 6726-1965).[22] However, the actual saponification technique was modified because of the small quantities of the samples. Aqueous 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 4 h minimum. 25 mL of 0.02 N H_2SO_4 was added, and the mixture was

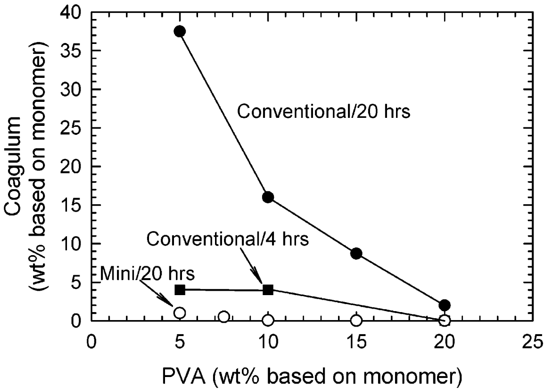

Figure 1. Coagulum as a function of PVA concentration for miniemulsion (Mini) and conventional emulsion polymerizations; BA/MMA = 50/50 wt %; APS = 1 mM; T_r (reaction temperature) = 60 °C; reaction time = 4 and 20 h.

titrated with 0.01 N NaOH solution with 1% phenolphthalein solution in methanol. A blank sample was prepared and titrated simultaneously. The degree of hydrolysis for the unknown samples was calculated on the basis of the original PVA 205 using eq 2:

$$\mathrm{DH} = 100 - \left(\frac{V_1}{V_0 \dfrac{\mathrm{wt(PVA)}}{\mathrm{wt(PVA\ 205)}}} \times 12 \right) \tag{2}$$

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, and 12 is the degree of acetylation of the original PVA 205.

Results and Discussion

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 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 h; however, the formation of coagulum was too high, and it was difficult to analyze the resulting latexes. To suppress the formation of coagulum, the polymerization was stopped after 4 h, and coagulum was collected using the stainless steel screen (200 mesh). The conversion was more than 95% for each polymerization (gravimetric analysis).

Particle Nucleation and Growth Mechanism. The evolution of the particle size and particle size distribution as a function of conversion was investigated using CHDF (Figure 2). In the miniemulsion system, the breadth of the initial particle size distribution becomes only slightly broader with conversion as indicated by the small particle size tail in the distributions. This is indicative of nucleation occurring primarily in the miniemulsion droplets. Meanwhile, in the conventional system, small particles with narrow particle size distributions were generated in the initial stages of the polymerizations, and these particles (~50 nm) were present for conversions greater than 60%, implying continuous nucleation during the polymerization. Budhlall et al.[5] reported similar results for conventional emulsion polymerizations of vinyl acetate.

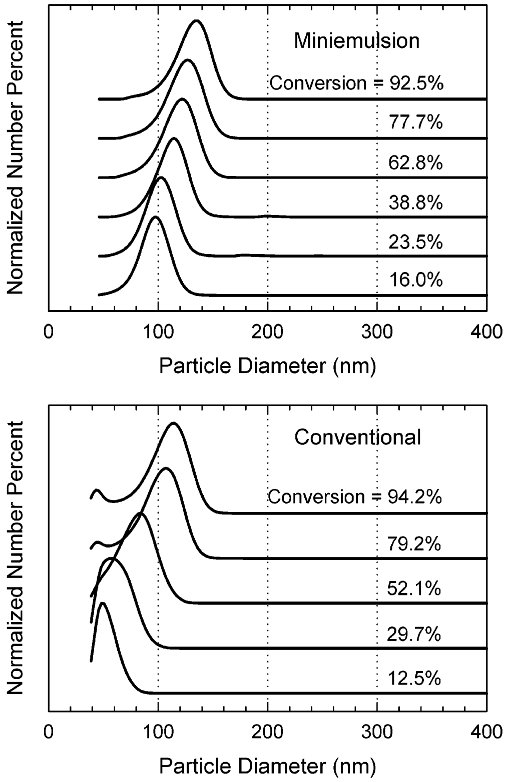

Figure 2. Evolution of particle size number distributions measured by CHDF as a function of conversion: (top) miniemulsion polymerization; (bottom) conventional emulsion polymerization; BA/MMA = 50/50 wt %; PVA = 10 wt %; APS = 1 mM; T_r = 60 °C.

The number of particles per unit volume (N_p) as a function of PVA concentration was calculated on the basis of the CHDF data (D_v) for conventional and miniemulsion polymerizations as shown in Figure 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. This could be explained by an increase in the partitioning of the PVA into the aqueous phase during the formation of miniemulsions at the higher PVA concentrations (32% of PVA in the aqueous phase for 10 wt % PVA vs 45% of PVA in the aqueous phase for 20 wt % PVA).[18] In the conventional system, N_p increased initially and then decreased after a certain conversion, indicating that limited aggregation occurred during these polymerizations.

Amounts of Grafted and Adsorbed PVA as a Function of PVA Concentration. Figure 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 latexes (20 h reaction) and the conventional latexes (4 h reaction). The amount of grafted PVA per unit particle surface area in the miniemulsion polymerizations continuously increased up to 10 wt % PVA and then became constant (saturated), which strongly supports the hypothesis that the water/monomer interface of the miniemulsion droplets is the main grafting site.[18] Meanwhile, the amount of

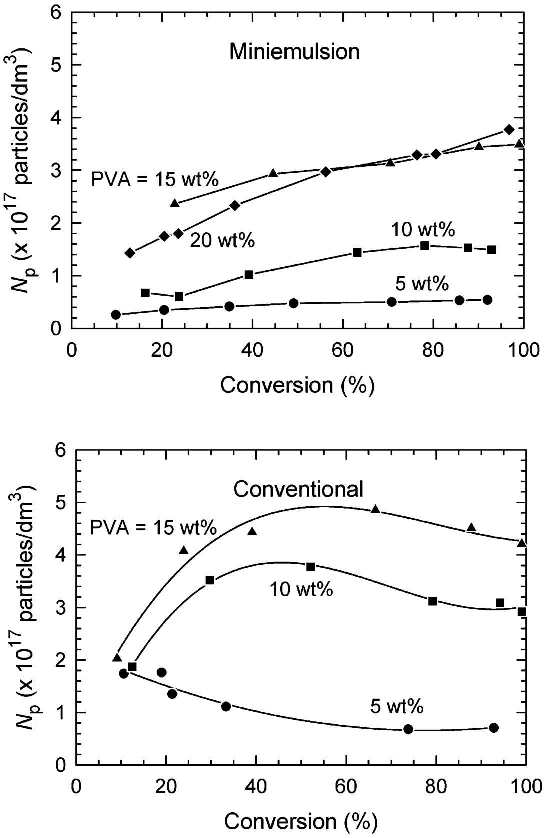

Figure 3. Number of particles (N_p) as a function of conversion at different PVA concentrations: (top) miniemulsion polymerization; (bottom) conventional emulsion polymerization; BA/MMA = 50/50 wt %; APS = 1 mM; T_r = 60 °C; lines drawn for visualization purposes only.

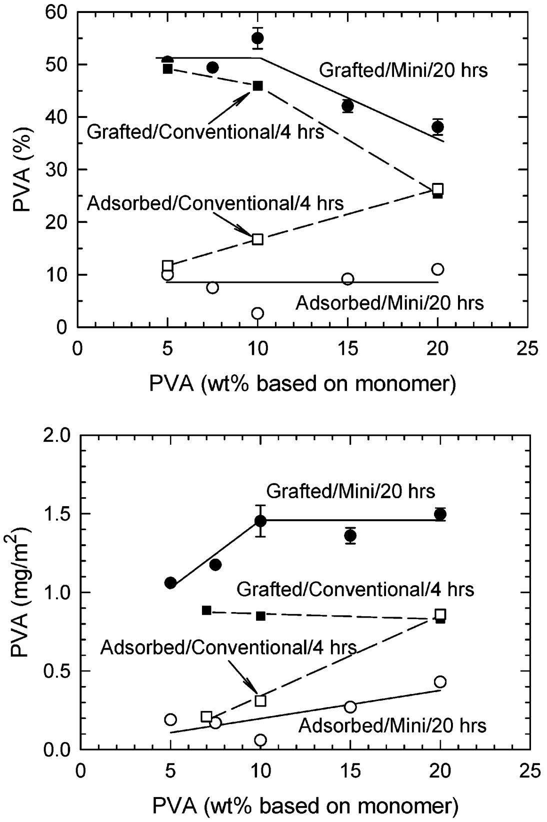

Figure 4. Amounts of grafted and adsorbed PVA on the final particles as a function of the amount of added PVA concentration and reaction time for miniemulsion (Mini) and conventional emulsion polymerizations: (top) weight basis; (bottom) area basis; specific area (m^2/g) was calculated on the basis of volume-average diameter obtained by CHDF.

grafted PVA per unit area in the conventional emulsion polymerizations 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 amounts 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 by the amount of grafted PVA per unit area. In addition, the colloidal stability increased (i.e., decrease in 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.

Possibility of PVA Desorption from the Particle Surface. One of the 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 significant desorption of PVA, the amount of serum PVA will increase. Also, the molecular weights of the serum PVA might be increased because relatively higher molecular weight PVA chains are located at the particle surface. To investigate the possibility of PVA desorption, the serums of the original latexes for each reaction time (4 and 20 h) were extracted using the serum replacement cell, and the amounts and molecular weights of the serum PVAs were determined. Figure 5 (top) shows the relative amount of serum PVA as a function of the amount of added PVA for the conventional emulsion polymerizations (4 and 20 h reaction) and the miniemulsion polymerization (20 h reaction). Overall, the reaction time had no significant effect on the amount of serum PVA 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 are shown in Figure 5 (bottom) as a function of PVA concentration. The molecular weights of the serum PVA of the conventional latexes were close to those in the miniemulsion latexes and did not vary significantly with the increased reaction time. Therefore, these results suggest that the desorption of PVA is not significant.

Grafting in the Aqueous Phase at 5 wt % PVA. At the 5 wt % PVA concentration, the amount 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 very similar to those obtained in the miniemulsion polymerization. This 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

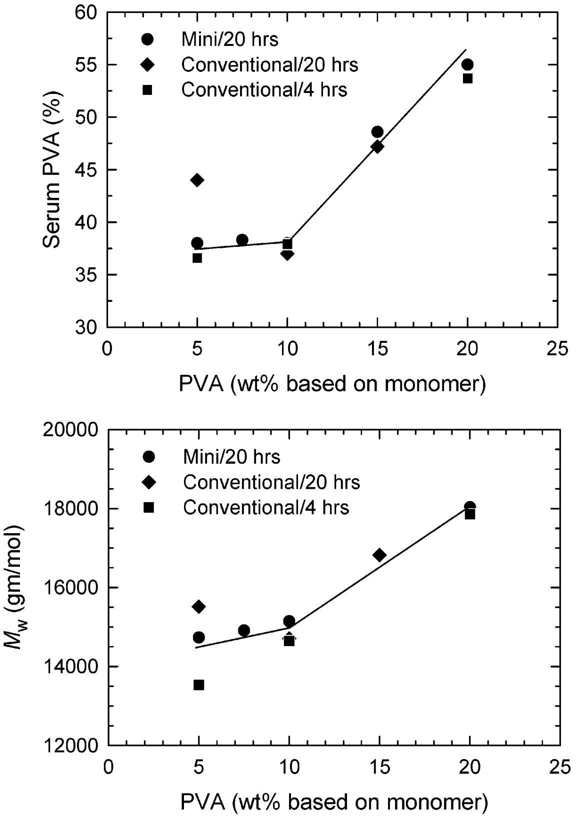

Figure 5. Amount of the serum PVA (top) and the weight-average molecular weight of the serum PVA (bottom) as a function of the amount of added PVA for miniemulsion (Mini) and conventional emulsion polymerizations; BA/MMA = 50/50 wt %; APS = 1 mM; T_r = 60 °C; reaction time = 4 and 20 h; solids contents ~20 wt %.

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 = 30.0% 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.)

Table 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)[a]	5	89.6	91.4
mini EP (APS)[b]	5	90.9	91.9
miniemulsion	10	94.9	92.1

[a] Conventional emulsion polymerization initiated with ammonium persulfate. [b] Miniemulsion polymerization initiated with ammonium persulfate.

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 2. The DH of the 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 the DH measured by FT-IR (90−91%) and the DH determined by saponification (91−92%), implying that the DH of the serum PVA determined by FT-IR actually decreased as a result of grafting of the acrylate monomers. However, the values of DH for the serum PVA obtained from the conventional and miniemulsion latexes were close, indicating that the characteristics of the serum PVA in terms of the DH are similar, implying that the colloidal instability in the conventional latexes cannot be correlated with the degree of aqueous phase grafting.

Earhart[6] studied the conventional emulsion copolymerization of vinyl acetate/*n*-butyl acrylate (50/50 wt %) using two kinds of PVAs, Vinol 205 (DH ~ 88%, M_w ~ 34 940 g/mol) and Vinol 107 (DH ~ 98%, M_w ~ 26 250 g/mol), 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 This differs significantly from our results (~89%). In miniemulsion polymerizations, PVA molecules are segregated in terms of molecular weight[18] and DH:[23] lower molecular weight (M_w ~ 14 500 g/mol) and higher DH (~95%) in the aqueous phase vs 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, namely aqueous phase 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 the lower molecular weight and higher DH PVA has little propensity for aqueous phase grafting and might suppress any grafting there. This should depend on the monomers used, however.

In conventional emulsion polymerizations, there is initially little possibility for segregated grafting in terms of molecular weight and degree of hydrolysis because most of the PVA is uniformly distributed in the aqueous

Table 3. Particle Sizes of Conventional and Miniemulsion Polymers Measured by Capillary Hydrodynamic Fractionation (CHDF) and Dynamic Light Scattering (DLS) at 5 wt % PVA

		CHDF			DLS		
		D_n (nm)	D_v (nm)	D_w (nm)	D_n (nm)	D_v (nm)	D_w (nm)
conventional	uncleaned	186.4	190.2	200.6	154.1	268.6	271.3
latex[a]	cleaned[c]	187.5	191.5	200.6	208.6	262.9	262.8
miniemulsion	uncleaned	200.8	202.0	205.5	254.1	261.8	261.5
latex[b]	cleaned[c]	197.7	198.9	203.2	253.3	260.2	260.2

[a] Conventional emulsion polymerization, 5 wt % PVA based on monomer. [b] Miniemulsion polymerization, 5 wt % PVA based on monomer. [c] Cleaning via serum replacement.

phase. However, Budhlall[24] suggested that the aqueous phase conformation may differ depending on the molecular weight of the PVA, and this might result in some segregation. It was found that the DH and molecular weight of the serum PVA obtained from conventional latexes were quite similar to those from miniemulsion latexes, 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 = 5000−13 000 g/mol).

Particle Size of Latexes Prepared with 5 wt % PVA. The latexes were cleaned using the serum replacement technique,[26] and particle diameters were measured by dynamic light scattering (DLS) and capillary hydrodynamic fractionation (CHDF) as reported in Table 3. By DLS, the volume-average particle diameter of the 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 the cleaned particles prepared by conventional emulsion polymerization was smaller than that prepared by miniemulsion 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).[27] Therefore, the grafted surface of particles prepared by conventional emulsion polymerization might be more hydrophobic, which may result in the poor stability.

Adsorption Isotherms of SLS on Grafted Surface of Latex Particles Prepared with 5 wt % PVA. The adsorption isotherms of SLS on the cleaned particles prepared by conventional emulsion and miniemulsion polymerizations were determined to see whether differences in the surface properties could be detected. Varying 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 on the basis of a calibration curve. Figure 6 shows the resulting adsorption isotherms (top) and the surface areas occupied per SLS molecule (bottom). 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 the grafted PVA (number, sites, and chain lengths of grafts) in the conventional latexes differs from that in the miniemulsion latexes. This is considered to be the result of differences in the primary grafting loci in these systems, namely the aqueous phase in the conventional emulsion polymerizations and the droplet surface in the miniemulsion polymerizations.

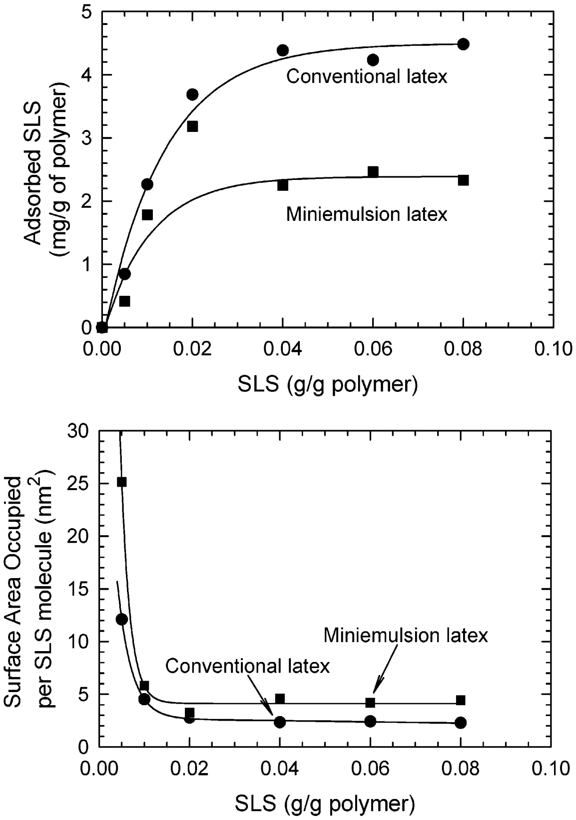

Figure 6. Adsorption isotherms of SLS (top) and the surface area occupied per SLS molecule (bottom) on the cleaned particles prepared by conventional emulsion polymerization and miniemulsion polymerization; BA/MMA = 50/50 wt %; PVA = 5 wt %; APS = 1 mM; T_r = 60 °C; reaction time = 4 h for conventional emulsion polymerization and 20 h for miniemulsion polymerization; lines drawn for visualization purposes only.

Conclusions

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 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 the cause of the colloidal instability during the conventional emulsion polymerization.

The surface area occupied per SLS molecule on particles prepared by conventional emulsion polymerization was significantly smaller than on those prepared by the corresponding miniemulsion polymerization, indicating that the surface of the particles prepared by conventional emulsion polymerization was more hydrophobic. This difference could be attributed to a greater degree of grafting of the PVA molecules or some PVA entrapment in the latex particles. The colloidal instability during the conventional acrylic emulsion polymerizations stabilized with PVA is, therefore, considered to be related to this more hydrophobic surface created by a different grafting architecture.

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