Grafting of PVA in Miniemulsion Copolymerizations of *n*-Butyl Acrylate and Methyl Methacrylate Using Water-Soluble, Partially Water-Soluble, and Oil-Soluble Initiators

Noma Kim, E. David Sudol, Victoria L. Dimonie, and Mohamed S. El-Aasser*

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Iacocca Hall, 111 Research Drive, Bethlehem, Pennsylvania 18015

Received August 7, 2003; Revised Manuscript Received February 10, 2004

ABSTRACT: Miniemulsion copolymerizations of methyl methacrylate and *n*-butyl acrylate initiated with water-soluble (hydrogen peroxide, HPO), partially water-soluble (*tert*-butyl peroxide, TBHP), and oil-soluble (*tert*-butyl peroctoate, TBPO) initiators were carried out to study the grafting of poly(vinyl alcohol) (PVA) at the oil/water interface. The amounts of grafted PVA produced in miniemulsion polymerizations initiated with TBHP and TBPO were substantially less than those produced in the corresponding seeded emulsion polymerizations. Differences in the internal viscosities at the respective interfaces were proposed to explain these results. The amount of grafted PVA was determined as a function of the monomer to polymer (M/P) ratio in seeded emulsion polymerizations initiated with TBHP and was found to decrease with increasing M/P ratio. The grafting was followed as a function of conversion in miniemulsion polymerizations initiated with TBPO and where a continuous addition of SFS (sodium formaldehyde sulfoxylate) solution was utilized; the grafting was found to occur mainly in the later stages of the polymerization. Both results strongly support the idea that the different internal viscosities at the interface might affect the termination reactions between primary radicals and PVA macroradicals, thereby resulting in different amounts of grafting. The degree of hydrolysis (DH) of the serum PVA after the miniemulsion polymerizations was determined using FTIR and saponification. On the basis of the results, it was found that aqueous phase and interface grafting occurred in the HPO system; however, interface grafting dominated the TBHP system. In addition, the grafted PVA in the TBHP system was still water-soluble, implying that the grafted chains were short, owing to rapid termination reactions at the interface presumably.

Introduction

Polymeric stabilizers, such as poly(vinyl alcohol) (PVA), are 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 nonwoven 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 PVA will become grafted and/or adsorbed on the latex particles providing stability[4,5] However, using PVA as the stabilizer in emulsion polymerizations of monomers comprising acrylics or styrene, coagulum is formed owing to a lack of mechanical stability presumably, and this might result from extensive grafting of PVA with the acrylic monomers, which have a higher reactivity compared to that of vinyl acetate.[6,7] The instability in conventional emulsion polymerizations compared to similar miniemulsion polymerizations is investigated in some depth in a subsequent paper.[8]

In our previous work, a miniemulsion approach was applied to determine the feasibility of preparing stable acrylic latexes using PVA as stabilizer. It was found that stable latexes could be obtained using 5−20 wt % PVA (based on monomer), and this was despite extensive grafting of the monomers (methyl methacrylate and *n*-butyl acrylate) to the PVA, where 35−55% of the PVA in the recipe was grafted to the surface of the particles.[9] 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 (*tert*-butyl hydroperoxide, TBHP), and oil-soluble (*tert*-butyl peroctoate, TBPO) initiators.[10] 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 loci of radical generation to further clarify the grafting site in miniemulsion polymerizations.This is accomplished by shifting radical production from being predominantly in the water phase using a water-soluble initiator to being predominantly at the oil/water interface using an oil-soluble initiator.

Experimental Section

Materials. *n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were each 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), sodium lauryl sulfate (SLS, Fisher), ascorbic

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* Corresponding author: e-mail mse0@lehigh.edu.

10.1021/ma035153w CCC: $27.50

Table 1. Recipe for Miniemulsion Polymerizations with Water-Soluble (HPO), Partially Water-Soluble (TBHP), and Oil-Soluble (TBPO) Initiators[a]

	weight (g)		
ingredient	HPO system	TBHP system	TBPO system
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)[b]	2.0	2.0	2.0
hydrogen peroxide (HPO)	0.0394		
ascorbic acid (AA)	0.0222		
tert-butyl hydroperoxide (TBHP)		0.104	
tert-butyl peroctoate (TBPO)			0.2484
ferrous sulfate (FES)		0.0052	0.0052
sodium formaldehyde sulfoxylate (SFS)		0.052	0.052
ethylenediamine tetracetate (EDTA)		0.052	0.052
deionized water	80.0	80.0	80.0

[a] Peroxide initiator: 58 mM based on monomers. [b] PVA 205: degree of hydrolysis ~ 88%, degree of polymerization ~ 500.

acid (AA, Sigma-Aldrich), hydrogen peroxide (HPO, Sigma-Aldrich), *tert*-butyl hydroperoxide (TBHP, Sigma-Aldrich), *tert*-butyl peroctoate (TBPO, Elf-Atochem), ferrous sulfate (FES, Fisher), sodium formaldehyde sulfoxylate dihydrate (SFS, Acros), disodium ethylenediamine 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). DI (deionized) water (treated by reverse osmosis followed by ion exchange) was used throughout.

Procedures. a. Miniemulsion Polymerization. The recipe used to prepare the various miniemulsions comprising several different formulation components is shown in Table 1. The PVA was dissolved by heating at 90 °C for 3 h in DI water (ca. 6 wt %), and the solution was filtered using a 200 mesh screen. The solids content of the PVA solution was determined gravimetrically. 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 min to prepare a crude emulsion prior to subjecting the system to high shear. This was provided by a Branson sonifier (model 450) operated at a 70% duty cycle and a power setting of 8 for 10 min accompanied by continuous magnetic bar stirring in an ice bath.

Some variations in the procedures were necessary depending on the initiator system. For HPO, the miniemulsion was heated to 60 °C and the HPO was injected, followed by the addition of ascorbic acid solution. For TBHP, the miniemulsion was heated to 60 °C and the TBHP was injected, followed by the addition of SFS solution. For TBPO, it was first mixed with the monomers before preparation of the crude emulsion. After its preparation, the miniemulsion was heated to 60 °C and SFS solution was added.

b. Seeded Polymerizations with Different Monomer to Polymer (M/P) Ratios. Seeded polymerizations with different M/P ratios were carried out (Table 2) using a seed whose preparation is described elsewhere.[10] A solution of PVA (6 wt % aqueous solution) was added to the cleaned seed particles and stirred gently. Monomers were added after 1 h mixing of the seed particles/PVA mixture and then stirred for an additional 2 h. The mixture of seed, PVA, and monomers was heated to 35 °C; the FES/EDTA solution was added first, and then the TBHP was injected, followed by the addition of SFS solution.

c. Continuous Addition of SFS Solution in Miniemulsion Polymerizations. HD and TBPO were mixed with the monomers. Crude emulsions of PVA, FES/EDTA solution, and HD/TBPO/monomers were prepared with 10 min stirring using a magnetic stirrer, and then miniemulsions were prepared by sonifying the crude emulsions as described above. The miniemulsions were heated to 60 °C, and then SFS solution was added via two different modes, namely batch and continuous addition (Table 3). In the continuous addition mode, 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 2. Recipe for Seeded Emulsion Polymerizations with Different Monomer-to-Polymer Ratios

	monomer to polymer weight ratio			
ingredient	1/1	2/1	3/1	4/1
seed latex[a]	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[b]	0.77	1.0	1.3	1.5
TBHP[c]	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

[a] Prepared using two-stage polymerizations from ref 10. [b] The amount of PVA was added to achieve the same amounts of adsorbed PVA per unit area based on particle diameter calculations. [c] Peroxide initiator: 58 mM based on monomers.

Table 3. Recipe for Miniemulsion Polymerizations with Different Initiator Concentrations and Modes of Addition of Activator (SFS) Solution

	weight (g)		
ingredient	batch, [I]	continuous, [I]	continuous, 2[I]
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[a]	0.052	0.052	0.104
EDTA	0.052	0.052	0.104
DI Water	102.226	110.726	110.726

[a] Continuous feeding time: 95 min.

d. 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). The amounts of PVA grafted and adsorbed at the end of the polymerizations were determined using a selective solubilization process,[11] and the amount of serum PVA was determined by serum extraction.

FTIR spectroscopy was used to determine the increase in the number of carbonyl groups of the PVA chains present in the aqueous phase serum resulting from the grafting reactions between BA and/or MMA and the PVA stabilizer.[12] The original PVA 205 was compared to the PVA present in the latex serum. Potassium thiocyanate (KSCN) was used as the internal standard for the FTIR spectra. After polymerization, the latex was diluted to about 10 wt % solids content, and the latex serum was separated by ultracentrifugation (Beckman ultracentrifuge, model L8-70 M, rotor SW41, Beckman Instruments) at 37 000 rpm and 4 °C for 8 h. Serum PVA and 0.5 wt % KSCN solution were weighed, and water was added to obtain a proper intensity in the FTIR (absorbance <0.1). 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 FTIR absorbance spectrum for each sample was obtained over a 1 h period. The area ratio of absorbance for the KSCN nitrile group stretch (2100−1950 cm^{-1}) and the carbonyl group stretch (1850−1650 cm^{-1}) was determined, and the degree of hydrolysis was calculated on the basis of the original PVA (PVA 205, degree of hydrolysis ~ 88%) using eq 1:

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

where area(carbonyl) is the area of absorbance of the carbonyl group stretch; area(nitrile) is the area of absorbance of 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 the 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); 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 polymerization. The basic technique was based on Japan Industrial Standard (JIS) K 6726-1965.[13] However, the actual saponification technique was modified because of the small quantity 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 Erlenmeyer flask. 25 mL of 0.02 N NaOH was added to the flask and stirred for a minimum of 4 h. 25 mL of 0.02 N H_2SO_4 was added, and the mixture was titrated using a 0.01 N NaOH solution with 1% phenolphthalein solution in methanol. A blank sample was prepared and titrated simultaneously. The degree of hydrolysis for unknown samples was calculated on the basis of the original PVA 205 using eq 2:

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

where V_1 is the volume of 0.01 N NaOH solution required for the titration of the 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

Kinetics and Particle Size Distribution. Figure 1 shows the conversion−time behaviors of miniemulsion polymerizations as a function of the initiator system. The miniemulsion polymerization initiated with TBHP had the highest polymerization rate resulting 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 Figure 2). The particle size distributions measured by capillary hydrodynamic fractionation (CHDF) for each initiation system are shown in Figure 3 as a function of conversion. No populations of smaller particles are observed, and the particle size distributions of the main peaks shift to larger sizes with increasing conversion. However, some aggregation of the particles occurred using HPO and TBHP after about 30% conversion. Interestingly, the degree of aggregation increased with increasing water solubility of the initiator. The evolution of number of particles per unit volume (N_p) was determined on the basis of CHDF volume-average particle size (D_v) as shown in Figure 2. 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 (based on CHDF) is shown in Figure 4 as a function of conversion while the particle size statistics of the final latexes obtained from dynamic light scattering (DLS) and CHDF are reported in Table 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 if any 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 significant amount of coagulum, indicating that stabilization by the PVA is poor. For the HPO-initiated miniemulsion system, there was some aggregation with little coagulum formed (<0.1 wt %), suggesting that interfacial grafting is still the primary grafting mechanism, while some aqueous phase grafting occurred 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 for the miniemulsion latexes prepared with TBHP and TBPO (see Table 5). However, further characterization of the adsorbed PVA is necessary, which might have some grafted BA and/or MMA units.

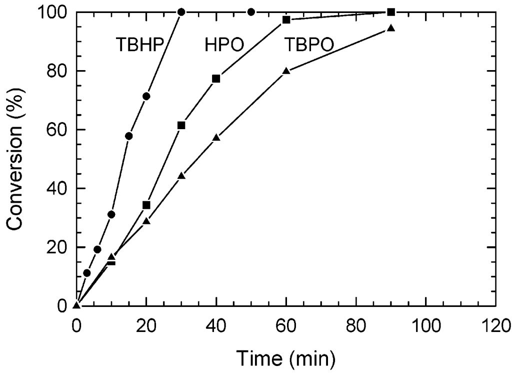

Figure 1. Conversion as a function of time for different initiators in miniemulsion polymerizations of MMA/BA (50/50 wt %). HPO = hydrogen peroxide/ascorbic acid system, TBHP = *tert*-butyl hydroperoxide/SFS system, TBPO = *tert*-butyl peroctoate/SFS system, and PVA 205 = 10 wt % based on monomer; T_r = 60 °C.

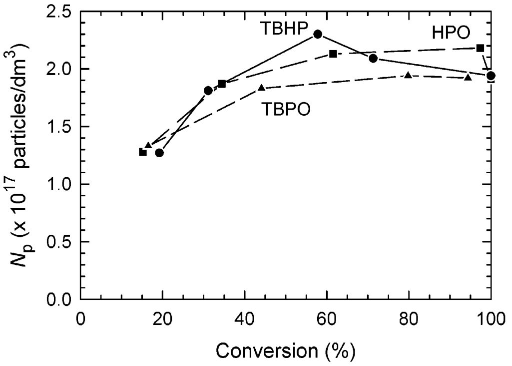

Figure 2. Evolution of the number of particles (N_p) as a function of conversion for HPO-, TBHP-, and TBPO-initiated miniemulsion polymerizations of MMA/BA (50/50 wt %); PVA 205 = 10 wt % based on monomer; T_r = 60 °C.

Grafting of PVA. Table 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 elsewhere.[10] It was found that there is a significant difference in the amounts of grafted PVA on the particles for the oil-soluble and partially oil-soluble initiators, TBPO and TBHP, depending on the polymerization method (seeded emulsion polymerization vs miniemulsion

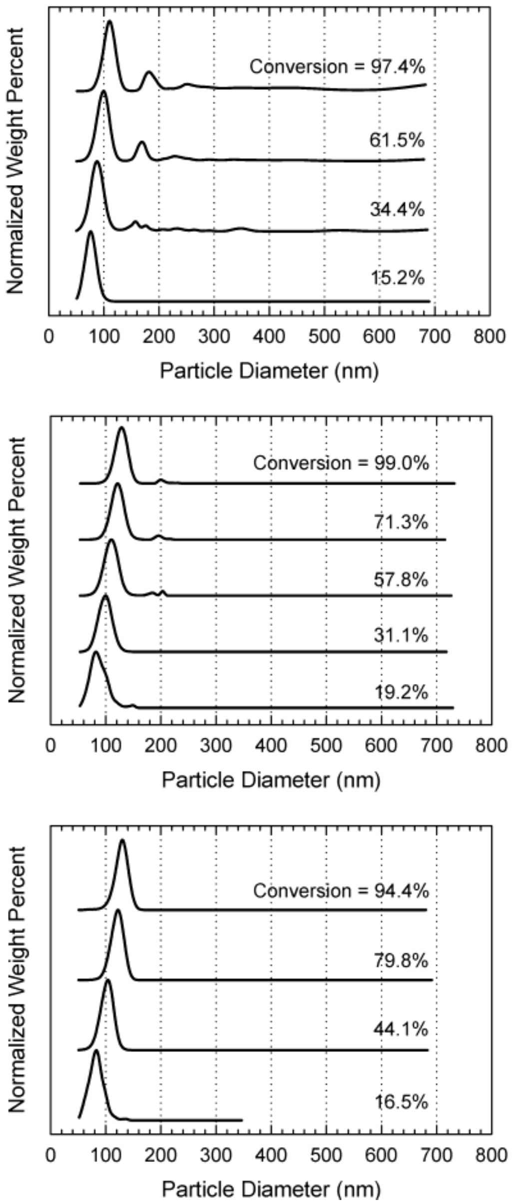

Figure 3. Evolution of particle size weight distributions obtained by CHDF as a function of conversion for different initiators in miniemulsion polymerizations of MMA/BA (50/50 wt %): (top) HPO system, (middle) TBHP system, and (bottom) TBPO system. PVA 205 = 10 wt % based on monomer; $T_r = 60$ °C.

polymerization). In contrast, little difference was found for the water-soluble initiator HPO, implying that the role of the interface is important for the grafting reaction.

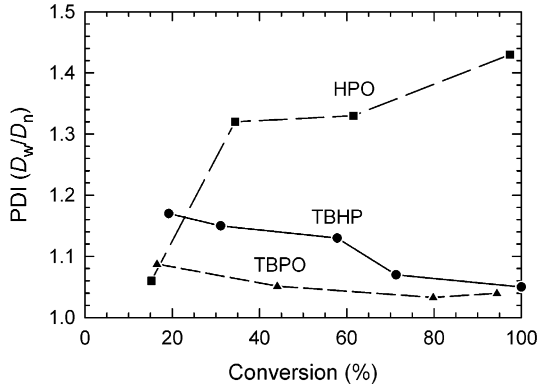

Figure 4. Evolution of particle size polydispersity index (D_w/D_n) as a function of conversion for HPO-, TBHP-, and TBPO-initiated miniemulsion polymerizations of MMA/BA (50/50 wt %); $T_r = 60$ °C.

Table 4. Particle Size Statistics of Final Particles 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

Table 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[a]	
	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	52.0	1.5

[a] From ref 10.

One of the big differences between seeded emulsion polymerization and miniemulsion polymerization is the monomer concentration in the particles, particularly in the early stages of the polymerizations. In the seeded emulsion polymerizations, the monomer concentration in the particles is relatively low, implying a higher internal viscosity compared to those of the miniemulsion polymerizations. On the basis of these considerations, it was assumed that the differences in grafting might have resulted from the different internal viscosities, which can affect the termination reactions between PVA macroradicals and primary radicals. After a PVA macroradical is generated by hydrogen abstraction, there are several reactions in which this macroradical can participate. If it reacts with the monomers (i.e., by propagation), grafting results. Meanwhile, if termination occurs between the PVA macroradical and a primary radical, no grafting occurs. In addition, chain transfer from PVA macroradicals to the monomers could occur; however, this is considered to be negligible.[14,15] Therefore, the grafting, in this case, is a competitive process between the propagation and termination reactions. For particles containing a high monomer concentration, a lower viscosity exists at the interface. This lower viscosity will enhance the mobility of primary radicals, which allows increased termination reactions between PVA macroradicals and primary radicals, resulting in less grafting.

Monomer to Polymer (M/P) Ratio in Seeded Emulsion Polymerizations. 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 2). Seed latexes were prepared and cleaned using the same procedures described elsewhere.[10] Final particle diameters were calculated on the basis of 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 of the particles. (It was assumed that the adsorption of PVA did not change significantly with M/P ratio.)

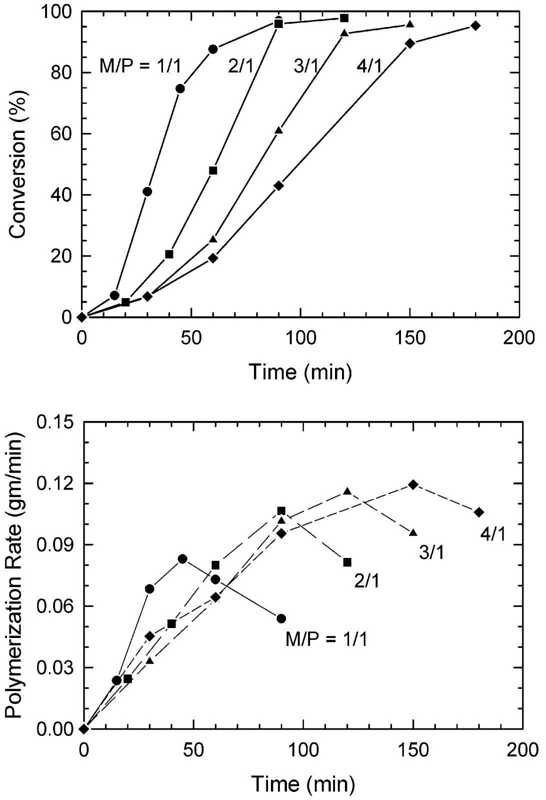

Figure 5. Conversion (top) and polymerization rate (bottom) as a function of time for different monomer-to-polymer ratios in seeded emulsion polymerizations of MMA/BA (50/50 wt %); T_r = 35 °C; [TBHP] = 58 mM based on monomer.

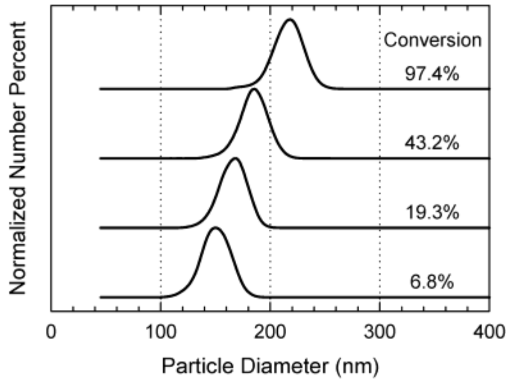

Figure 6. Particle size number distributions obtained by CHDF as a function of conversion in a seeded emulsion polymerization of MMA/BA (50/50 wt %); monomer-to-polymer ratio = 4/1; T_r = 35 °C; TBHP = 58 mM based on monomer.

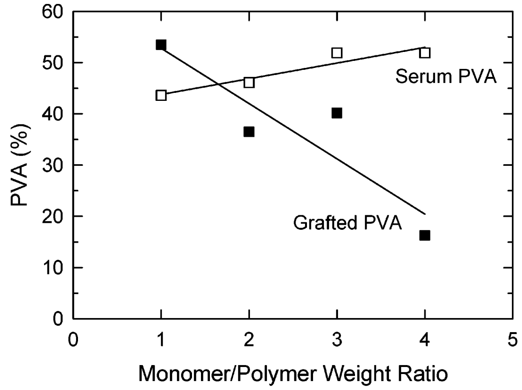

Figure 7. Grafted and serum PVA determined by the selective solubilization method as a function of monomer-to-polymer ratio in seeded polymerizations of MMA/BA (50/50 wt %); T_r = 35 °C; [TBHP] = 58 mM based on monomer; lines represent linear least-squares fit of data.

Table 6. Final Particle Sizes Measured by CHDF as a Function of Initiator Concentration and Mode of SFS Addition in Miniemulsion Polymerizations[a]

	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

[a] [I] = 58 mM based on monomer.

Figure 5 shows the conversion (top) and rate of polymerization (bottom) vs time behaviors as a function of the M/P ratio. The polymerization rate up to the maximum did not depend strongly on the M/P ratio, except at the lowest M/P ratio (1/1), which was significantly faster. 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 distribution as a function of conversion for an M/P ratio of 4/1 is shown in Figure 6. The amounts of grafted and serum PVA after the polymerizations were determined as a function of the M/P ratio using the selective solubilization process. The results in Figure 7 indicate that the fraction of the PVA in the serum increased as the M/P ratio increased, implying an increased extent of desorption of PVA during the polymerization or an increase in PVA partitioning into the aqueous phase. Meanwhile, the fraction of the PVA that was grafted 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 macroradicals at the interface.

Continuous Addition of SFS Solution in Miniemulsion Polymerizations. The preceding conclusions are subject to some debate since the M/P ratio and the primary radical concentrations were both varied simultaneously. This occurred because to achieve the same conversion, it took increasingly longer reaction times with the increasing M/P ratio. This means that the primary radical concentrations in the later stages of 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 the miniemulsion polymerizations. TBPO was used as initiator 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 8 and Table 6 show the kinetics as a function of SFS addition mode and the final particle sizes, respectively. The polymerization rates and final particle sizes were similar even though the radical generation rates were expected to differ substantially. To confirm the different radical generation rates, the molecular weight distributions of the

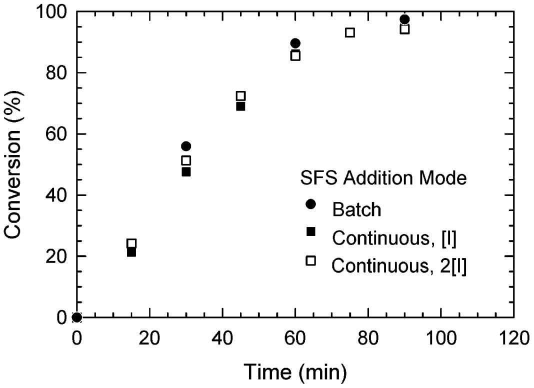

Figure 8. Conversion as a function of time for different SFS addition modes and initiator concentrations in miniemulsion polymerizations of MMA/BA (50/50 wt %) initiated with TBPO; PVA 205 = 10 wt % based on monomer; T_r = 60 °C.

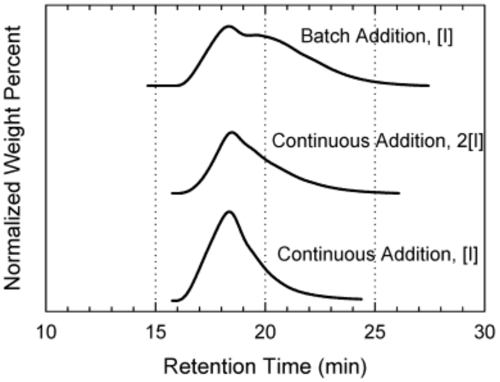

Figure 9. GPC chromatograms of acetonitrile-soluble polymers obtained from the selective solubilization method as a function of SFS addition mode and initiator concentration in miniemulsion polymerizations of MMA/BA (50/50 wt %) initiated with TBPO.

Table 7. Molecular Weights as a Function of Initiator Concentration and Mode of SFS Addition in Miniemulsion Polymerizations[a,b]

	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

[a] Relative to poly(styrene) standards. [b] [I] = 58 mM based on monomer.

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 weights were determined relative to polystyrene standards. Figure 9 shows the original GPC chromatograms. The number- and weight-average molecular weights and polydispersity indexes are reported in Table 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 sizes and the polymerization rates were similar despite different radical concentrations, nucleation must take place entirely in the monomer droplets, and virtually all droplets are nucleated.

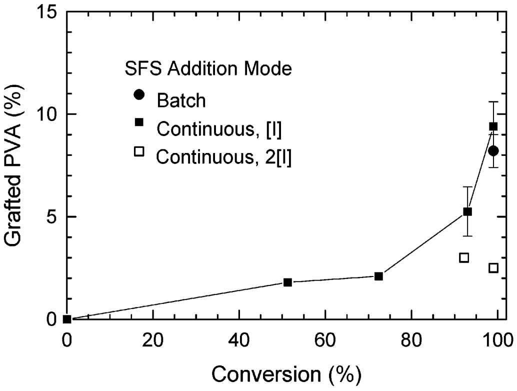

Figure 10. Grafted PVA as a function of conversion for different SFS addition modes and initiator concentrations in miniemulsion polymerizations of MMA/BA (50/50 wt %) initiated with TBPO.

Figure 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 (hydroquinone, 1 wt % in methanol) was added, and then the sample was stored at 4 °C. The unreacted monomers in each sample were removed using a rotary evaporator at 60 mmHg and 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 macroradicals are high because of the high mobility of the primary radicals, which results in little or no

Table 8. Degree of Hydrolysis Using FTIR and Saponification in Terms of Initiation System and Reaction Conditions

	serum PVA			adsorbed PVA			grafted PVA
		DH[g]			DH		
	%	FTIR	sapo	%	FTIR	sapo	%
HPO[a]	35.6	90.2	91.0	8.4			56.0
TBHP[b]	47.0	94.0	90.9	52.9	83.0	85.2	0.1
TBPO[c]	46.2	94.4	90.9	46.6	86.2	86.4	7.5
TBHP[d]	43.3	93.5	91.7	43.9	87.7	85.5	12.8
TBPO/SFS incre[e]	51.2	94.9	92.0	28.9	86.4		19.9
miniemulsion[f]	33.0	94.9	92.1	67.0	84.6[c]	86.0[c]	

[a] Batch addition of HPO/Ascorbic acid, T_r = 60 °C. [b] Batch addition of TBHP/SFS, T_r = 60 °C. [c] Batch addition of TBPO/SFS, T_r = 60 °C. [d] Batch addition of TBHP/SFS, T_r = 35 °C. [e] Batch addition of TBPO/continuous addition of SFS, T_r = 60 °C. [f] Calculated based on PVA partitioning in miniemulsion. [g] Errors in DH: ±0.3 by FTIR and ±0.5 by saponification (sapo).

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.[16] 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 between the primary radicals and the PVA macroradicals was increased. However, with the 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 the 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.

Degree of Hydrolysis (DH) of Serum PVA. 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 FTIR and saponification to determine the degree of hydrolysis of the PVA recovered from the serum. FTIR 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 FTIR 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 8. For miniemulsion droplets (last row), the DH of the adsorbed PVA was calculated on the basis of PVA partitioning. Interestingly, the DH of the serum PVA in the miniemulsion showed a value (94.9% based on FTIR) higher than the average DH for PVA 205 (88%). Therefore, relatively low molecular weight[9] and high DH PVA molecules are located in the aqueous phase, implying that a segregation in terms of both 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 FTIR are consistent (94−95%) though different from the DH values determined by saponification (91−92%), except for the serum PVA in the HPO initiator system, implying that the DH of the serum PVA by FTIR 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 rapid termination reactions between primary radicals and the PVA macroradicals at the interface. Apparently, there was no grafting in the aqueous phase even though TBHP is a partially water-soluble initiator.

Conclusions

Some aggregation occurred in the HPO-initiated miniemulsion polymerization resulting in an increase in the polydispersity of the particles, implying that significant aqueous phase grafting exists in this miniemulsion polymerization system. The amount of grafted PVA on the surface of the final latex particles was significantly lower for the TBHP- and TBPO-initiated miniemulsion polymerizations compared to the corresponding seeded emulsion polymerizations. The differences in the internal viscosities of the particles, by which the termination reactions between primary radicals and PVA macroradicals are affected, 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 miniemulsion polymerizations.

The degree of hydrolysis (DH) of the serum PVA was determined using FTIR and saponification. On the basis of a comparison of the DH value 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 rapid termination reactions at the interface.

Acknowledgment. Financial support from the Emulsion Polymers Liaison Program and the PVA supplied by Kuraray Ltd., Japan, are greatly appreciated.

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MA035153W