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Poly(vinyl alcohol) Grafting in Miniemulsion Polymerization

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ABSTRACT: Poly(vinyl alcohol) (PVOH) can be advantageously used in miniemulsion polymerization as it yields latexes more stable than those produced by conventional emulsion polymerization. Latex stabilization and properties are affected by the extent of grafting of PVOH. The effect of the initiator system and the polymerization process (miniemulsion vs conventional emulsion polymerization) on the extent of grafting of PVOH in the polymerization of vinyl acetate and Veova10 was studied. It was found that the fate of the PVOH was strongly influenced by the initiator system and the process employed. The use of potassium persulfate in miniemulsion polymerization led to the maximum grafting level. The mechanistic reasons of these results were discussed.

Introduction

Miniemulsion polymerization is attracting much attention because the characteristic droplet nucleation mechanism allows obtaining waterborne dispersed polymers with unique properties.[1−3] In addition to the effect of the polymer characteristics, the application properties of these latexes are strongly affected by the surfactants. Thus, the use of PVOH as polymeric stabilizer imparts to latexes better emulsion fluidity, superior wet primary tackiness (adhesives), good mechanical film properties (higher tensile strength), excellent mechanical stability, and higher freeze−thaw stability compared to latexes stabilized with low molecular weight surfactants.[4] This is the reason for the extensive use of PVOH in vinyl acetate latexes, which find applications in paints, paper coatings, adhesives, carpet backing, and additives for construction materials.[5] PVOH can be advantageously used in miniemulsion polymerization. Thus, Kim et al.[6] showed that coagulum free 20 wt % solids content acrylic latexes can be obtained in batch miniemulsion polymerization, whereas a large amount of coagulum was obtained in conventional emulsion polymerization using the same formulation (with the exception of the costabilizer used in the miniemulsion polymerization). High solids content (>50 wt %) PVOH stabilizer coagulum free latexes were prepared by means of batch miniemulsion polymerization, while the maximum solids content that could be obtained by batch conventional emulsion polymerization without coagulation was 30 wt %.[7] The latex is stabilized by both adsorbed and grafted PVOH. PVOH adsorbs on the particle surface with the hydrophobic acetate units providing the anchoring segments and the hydrophilic hydroxyl units being soluble in the aqueous phase as stabilizing moieties. Grafting occurs by hydrogen abstraction at the methine carbons of the PVOH followed by propagation of monomer.[8] The grafted PVOH can efficiently adsorb on the particles.[9,10] Although conflicting results on the effect of the extent of grafting on the particle stability have been reported,[6,11] excessive grafting may lead to a less efficient, too hydrophobic stabilizer. Therefore, the extent of grafting should be controlled.

Kim et al.[6,12,13] studied the grafting of PVOH in the miniemulsion copolymerization of butyl acrylate (BA) and methyl methacrylate (MMA). It was reported that the amount of grafted PVOH depended on the MMA/BA ratio and on the initiator used. H_2O_2/ascorbic acid yielded a high level of grafting (56%), whereas *tert*-butyl hydroperoxide/sulfoxylate dehydrate did not yield any grafting. This is interesting, as both initiator systems yield oxygen centered radicals in the aqueous phase. On the other hand, the effect of the initiator was completely different in miniemulsion polymerization and in conventional emulsion polymerization. In addition, using seeded emulsion polymerizations, the authors showed that grafting decreased as the monomer/polymer ratio increased. This was attributed to the decrease of the internal particle viscosity with the higher monomer concentration, which increases termination reactions between primary radicals and PVOH macroradicals at the interface. Although the relationship between the internal viscosity and the polymerization in the hairy layer of PVOH at the particle surface may be a matter of discussion, these works show that monomer concentration and the initiator used are key variables determining the extent of grafting.

In spite of the fact that PVOH is extensively used to stabilized VAc latexes, this work reports, to the best of our knowledge, the first study on the extent of grafting of PVOH in the miniemulsion polymerization of VAc and VeoVa10.

The effect of the initiator system was studied first. Potassium persulfate (KPS), *tert*-butyl hydroperoxide (TBHP)/ascorbic acid (AsAc), lauroyl peroxide (LPO), and benzoyl peroxide (BPO) were used. All of them give oxygen-centered radicals to maximize the hydrogen abstraction from the PVOH, but they differ in the phase in which they are produced and in the hydrophilicity. Potassium persulfate yields sulfate ion radicals in the aqueous phase, TBHP/Ac yields hydrophobic terbutoxyl radicals in the aqueous phase, and LPO and BPO yield oxygen centered radicals of different hydrophobicity (more hydrophobic for LPO) within the polymer particles. In the second part of the article, the extent of grafting of PVOH in miniemulsion and conventional emulsion polymerizations was compared. High solids content formulations were used.

Experimental Section

Materials. Technical grade monomers VAc and VeoVa10 (vinyl ester of a highly branched decanoic acid) purchased from Quimidroga were used without purification. A commercial PVOH, kindly supplied by Wacker Chemie, was used (Celvol 205, degree of hydrolysis = 87−89%, degree of polymerization = 350−650, Celanese). The initiators KPS, LPO, BPO, TBHP, and AsAc, all reagent-grade, were purchased from Sigma-Aldrich and used as received. The costabilizer stearyl acrylate (octadecyl acrylate, 97% pure (SA)) and acetonitrile (ACN) HPLC grade were purchased

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from Sigma-Aldrich and used as received. Double-deionized (DDI) water was used throughout the work.

Miniemulsion Stability Measurements. The stability of the freshly prepared miniemulsions was assessed employing the Turbiscan Laboratory^{expert} apparatus. The working principle of the equipment is measuring the light that is transmitted and backscattered from a dispersion that is contained in a glass vial. Previous research works have shown the potential of the equipment for evaluating the stability of dispersions.[14−16] The moving head of the apparatus scans the entire length of a miniemulsion sample contained in a glass vial acquiring transmission and backscattering data at fixed times. As the miniemulsions prepared in this work were very concentrated only the backscattering data were used. For very stable miniemulsions, the backscattering data shows minimum variation with time, because the size of the monomer droplets remains constant. This technique allows detecting in an early stage phenomena like creaming, sedimentation and coalescence. The graphics obtained from stability analysis (measuring the backscattered light along the cell length during 24 h) are not showed here; however, the results measured at 25 °C were summarized as follows: [-] unstable; [+ +] stable enough to perform batch polymerizations (based on reaction time); and [+ + +] very stable.

Miniemulsion Droplet Size Measurement. The Coulter N4 Plus (dynamic light scattering) was used to measure the miniemulsion *z*-average droplet size (d_d). A fraction of the miniemulsion was diluted with DDI water saturated with VAc (to avoid the diffusion of this monomer to the water; Veova10 is almost water insoluble, and hence, it is expected to remain in the droplets). The droplet size was measured after 5 min of sampling and repeated three times to check the reproducibility.

Polymerization. The aqueous phase was prepared dissolving PVOH at 70 °C in DDI water and the solution was filtered using a 200 mesh screen. The solids content of the PVOH solution was checked to determine the possibility of water evaporation to adjust the surfactant concentration. The costabilizer and the oil soluble initiator were dissolved in the monomers. Both the aqueous and the oil phase were mixed with a magnetic stirrer at 1000 rpm for 20 min. Immediately after this step, the coarse dispersion was fed into a Manton-Gaulin Laboratory-60TBS homogenizer (APV), whose first valve was set to 48.2 MPa and the second valve was set to 7.2 MPa. Fifteen cycles were needed to homogenize the coarse dispersion (reaching the smallest droplet diameter attainable under these conditions). In the case of conventional emulsion process, this step was not applied.

The general procedure for the polymerization consisted of charging 350 g of the miniemulsion (or pre-emulsion) into a 500 mL glass reactor. The reactor was heated to 65 °C with a nitrogen flow to purge the reactor. The temperature was controlled with a cascade control system. Five minutes after the stabilization of the temperature, the reaction was started, adding the initiator. In the case of the thermal water soluble initiator, 20 mL of an aqueous solution of KPS (4.4−7 wt %) was shotwise added. In the case of redox initiator, the aqueous solutions of TBHP (70 wt %) and AsAc (10 wt %) were added during 30 min at 0.05 g/min and 0.35 g/min, respectively.

The conversion was measured by gravimetry. Latex samples taken at different time intervals were put in preweighed aluminum capsules; immediately thereafter, the reaction was stopped by the addition of a droplet of 1 wt % hydroquinone aqueous solution. The capsule was dried at 60 °C until constant weight was obtained.

Particle Size and Particle Size Distribution (PSD) Measurement. A Disc Centrifuge Photosedimenter (BI-DCP Brookhaven Instruments) was employed to evaluate the particle size (d_p) and the PSD of latexes synthesized. The samples were diluted with 15 g water (until reaching 0.7 wt %) and then 5 mL of methanol were added as well. After this, 0.2 g of the dilution was injected into the disk, which had a spinning fluid, including 15 g of water, 0.2 g of methanol, and 0.1 g of dodecane. The velocity of the disk was varied from 4500−12000 rpm, depending on the mean particle size, and the temperature was 20 °C. The data obtained was transformed to obtain the weight PSD of the latexes.

Table 1. Formulation Used for Studying the Effect of Initiator on PVOH Grafting

component	amount (g)	run	d_d (nm)	stability	initiator (wt %)
VAc	200	B-KPS	268	+ + +	0.5[a]
VeoVa10	50	B-LPO	285	+ + +	0.8[a]
SA	5	B-BPO	279	+ + +	0.8[a]
Celvol 205	20	B-TBHP/AsAc	272	+ + +	0.5[b]
water	230				

[a] Added as a shot at $t = 0$. [b] Fed over 30 min.

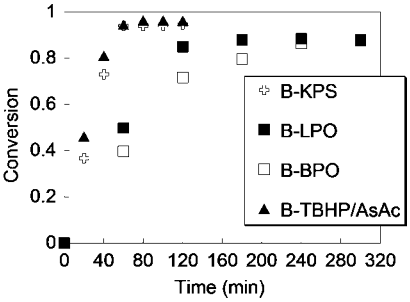

Figure 1. Conversion evolution in the batch miniemulsion polymerizations carried out with different initiators.

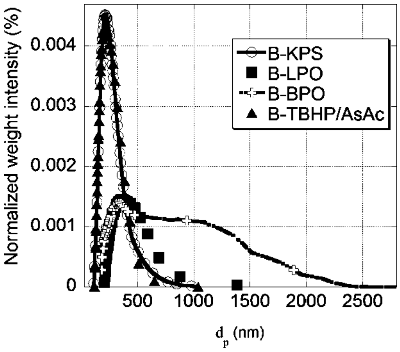

Figure 2. Particle size distribution of the latexes obtained in the batch miniemulsion polymerizations carried out with different initiators.

Measurement of the Amount of the PVOH Grafted and the PVOH Adsorbed. The method developed by the Lehigh group[17] was used to measure the PVOH grafted and the PVOH adsorbed on the particles. It consists of a selective solubilization technique, which employs DDI water and ACN as solvents. The reproducibility of the method was checked by repeating three times every measurement.

Results and Discussion

Effect of the Initiator System on the PVOH Grafting. Table 1 shows the formulation used for the experiments carried out. Figure 1 shows the evolution of conversion of the batch miniemulsion polymerizations. In the case of thermal and redox water-soluble initiators, high values of conversion were reached in 60 min. On the contrary, almost 4 h were needed to reach ~90% of conversion when BPO and LPO were used. The slower generation of radicals, the fact that they were produced in pairs within the particles (enhancing bimolecular termination), and the smaller N_p (Figure 2) led to lower polymerization rates for LPO and BPO as compared with reactions carried out with either KPS or TBHP/AsAc. The redox system gave the fastest process because of the higher rate of radical production.

Figure 2 shows the particle size distribution (PSD) of the latexes produced employing the different initiators. It can be noticed that in the case of B-KPS and B-TBHP/AsAc a high fraction of droplets was nucleated because the mean particle size was similar to that of the droplets (Table 1). Larger particles

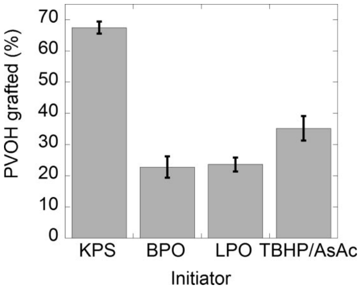

Figure 3. Effect of initiator on the PVOH grafting.

were obtained when oil-soluble initiators were used. It has been reported that the stability of the miniemulsions decrease with the temperature.[18] The stabilities given in Table 1 were measured at 25 °C, therefore, lower stabilities are expected at the reaction temperature (65 °C). Droplet destabilization is a kinetic process, which is more apparent at long process times, namely, at low polymerization rates, that is, for oil-soluble initiators.

Figure 3 presents the effect of the initiator on the amount of PVOH grafted. It can be seen that the amount of PVOH grafted was maximum for KPS followed by TBHP/As/Ac, with those obtained with the oil-soluble initiators being minimum. All of initiators gave oxygen centered radicals, which are very active in hydrogen abstraction. Therefore, the difference in grafting may be due to the rate of radical generation, to the locus of radical formation and/or to the type of radical produced. Let us consider first the initiators giving the higher grafting: KPS and TBHP/AsAc. Under the conditions used to prepare the miniemulsions, it has been shown that most of the PVOH was adsorbed on the monomer droplets.[7] Figures 1 and 2 show that for the same number of particles, the polymerization rate was higher for TBHP/AsAc than for KPS indicating that as expected, the rate of radical generation was higher for the redox system. Therefore, at least with respect to TBHP/AsAc the higher level of grafting found for KPS was not due to a higher radical generation rate. On the other hand, for both KPS and TBHP/AsAc, the radicals are produced in the aqueous phase. Consequently, the difference should be due to the characteristics of the radicals produced.

KPS yields sulfate ion radicals that cannot enter directly into the polymer particles. Therefore, they will stay in the aqueous phase until they react with enough monomer units (mostly, VAc because its water solubility, 2.5 wt %, is much higher than that of the Veova10, 3.61×10^{-3} wt %) to be hydrophobic enough to enter into the organic phase (monomer droplets and polymer particles). While the sulfate ion radicals (and the resulting oligomeric radicals) are in the aqueous phase they may come into contact with either the PVOH dissolved in the aqueous phase or the hairy layer of PVOH surrounding the dispersed organic phase, having the opportunity to abstract a methine hydrogen from the PVOH. The abstraction may also occur during the entry of the oligomeric radical in the polymer particles once they have reached the critical length for entry. It is worth pointing out that the reactivity for hydrogen abstraction of the sulfate ion radicals is higher than that of the oligomeric radicals. On the other hand, as most of the PVOH is adsorbed on the monomer droplets, the contribution of the dissolved PVOH is not expected to be substantial. Monomeric radicals that are produced by chain transfer to monomer in the polymer particles and then desorb to the aqueous phase may also contribute to grafting of the PVOH.

TBHP/AsAc yields terbutoxyl radicals. These radicals are hydrophobic and can enter directly into the dispersed organic phase.[19] Therefore, they are not expected to stay long in the aqueous phase and the opportunity for hydrogen abstraction is when they cross the PVOH hairy layer surrounding the droplets/particles. It is important to point out that the tertbutoxyl radicals are more reactive for hydrogen abstraction than the oligomeric radicals resulting from the KPS. On the other hand, the contribution of the desorbed monomeric radicals should be similar to the case of KPS. According to these ideas, the difference between KPS and TBHP/AsAc is mainly due to the longer time that the sulfate ion radicals and the resulting oligomeric radicals stay in the aqueous phase where they have the opportunity to abstract hydrogens mainly from the adsorbed PVOH.

Table 2. Formulation Used in the Experiments in which the Effect of PVOH Concentration on the Level of Grafting was Studied

component	amount (g)	run	PVOH (wt %)[a]	d_d (nm)	stability
VAc	200	B-PVOH1	1	357	+ +
VeoVa10	50	B-PVOH2	2	301	+ + +
SA	3	B-PVOH4	4	276	+ + +
PVOH	5−30	B-PVOH6	6	272	+ + +
KPS	1.25				
water	245−220				

[a] Based on total formulation.

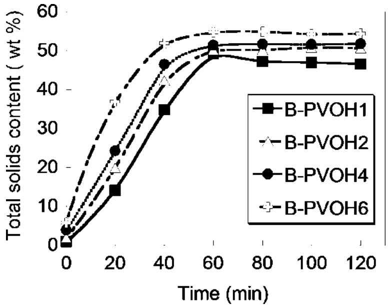

Figure 4. Effect of the PVOH concentration on solids content.

It is interesting pointing out that according to this mechanism, the decrease in PVOH grafting observed by Kim et al.[13] in a seeded emulsion polymerization with the monomer/polymer ratio would be due to a decrease of the sulfate ion radicals/oligomeric radicals ratio, because of the more likely propagation of the sulfate ion radicals and the lower activity of the carbon centered radicals (as compared to oxygen centered radicals) for hydrogen abstraction.

BPO and LPO generated radicals in pairs within the particles/droplets. This led to an extensive termination within the particles. Even though, desorption of these radicals was possible, the desorption rate should be slow and they re-entered rapidly because they are very hydrophobic.[20] Therefore, these radicals can only abstract hydrogen from the PVOH when they cross the hairy layer. Consequently, the level of grafting was low. In those cases, the contribution of the desorbed monomeric radicals may be significant.

Effect of PVOH Concentration on Grafting and Adsorption. The effect of the PVOH concentration on the levels of PVOH grafted and adsorbed was studied in batch miniemulsion polymerizations carried out with the formulation given in Table 2.

Figure 4 shows the evolution of the total solids content in the batch miniemulsions carried out with different PVOH amounts. The total solids content was used instead of the more common monomer conversion because the total solids content includes both the monomer conversion and latex stability. Thus, a decrease of the solids content was observed in run B-PVOH1 as a consequence of the coagulum observed. It can be noticed that as the PVOH increased the polymerization rate increased, mainly due to an increase of the number of particles (N_p; Figure 5).

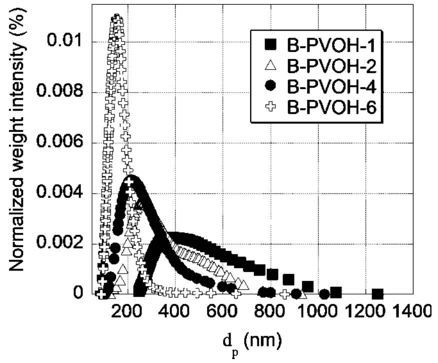

Figure 5. Effect of PVOH concentration on particle size distribution.

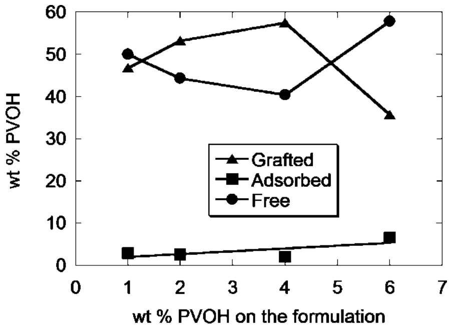

Figure 6. Effect of the PVOH concentration on the fractions of PVOH grafted, adsorbed, and in the aqueous phase (free).

Figure 5 shows that in the case of B-PVOH2 and B-PVOH4 a high fraction of droplets was nucleated as the particles had a size that was similar to that of miniemulsions. The large particles found in B-PVOH1 were a consequence of droplet coalescence due to the low coverage of the particles (estimated coverage ~35%). The narrow PSD with small particles found in B-PVOH6 was a consequence of the nucleation of polymer particles coming from mechanisms characteristic of conventional emulsion polymerization because about 30% of the PVOH was in the aqueous phase (either dissolved or forming aggregates).

Figure 6 presents the effect of the PVOH concentration on the fractions of PVOH grafted, adsorbed, and in the aqueous phase (free). It can be seen that the fraction of grafting increased with PVOH concentration until 4 wt % and then it decreased for 6 wt % of PVOH. The main difference when the PVOH concentration was increased from 4 wt % to 6 wt % was that the predominant particle nucleation shifted from droplet nucleation to a nucleation mechanism typical of conventional emulsion polymerization. For the polymerization of acrylic monomers Kim et al.[6] reported that, at high PVOH concentrations, the fraction of grafted PVOH was lower for emulsion polymerization than for miniemulsion polymerization, but no reasons for this behavior were given.

Conventional Emulsion versus Miniemulsion Polymerization. Six batch reactions were carried out, three conventional emulsion polymerization (B-Emu) and three miniemulsion (B-Mini) polymerizations, varying the PVOH concentration. A 30 wt % solids content formulation was used because higher solids content resulted in massive coagulum when conventional emulsion polymerization was used. Table 3 shows the formulation and the main characteristics of the miniemulsions and the latexes obtained in these experiments.

Table 3 shows that very stable miniemulsions were obtained and almost complete conversion was reached in all cases. Figure 7 shows that for both the miniemulsion and in the conventional emulsion, the higher the PVOH concentration the higher the number of particles. In the case of the miniemulsion polymerizations, a large fraction of droplets was nucleated as the mean particle size in final latexes was similar to that of the miniemulsions. On the other hand, the homogeneous and heterogeneous nucleation mechanisms present in conventional emulsion polymerization led to a narrower PSD with smaller particles as compared to the miniemulsion polymerizations.

Table 3. Formulation Employed in the Experiments, Comparing Conventional Emulsion versus Miniemulsion Polymerization and Characteristics of the Latexes

component	amount (g)	run	PVOH (wt %)	d_d (nm)	stability	d_p (nm)	conversion (%)
VAc	84	B-Mini1	1.8	281	+ + +	308	94.3
VeoVa10	21	B-Mini2	3.6	240	+ + +	257	94.8
SA	2.1[a]	B-Mini3	5.4	207	+ + +	238	95.3
PVOH	6.3−12.6	B-Emu1	1.8			261	96.9
water	238.7−232.4	B-Emu2	3.6			164	97.8
		B-Emu3	5.4			136	98.2

[a] Only in miniemulsions.

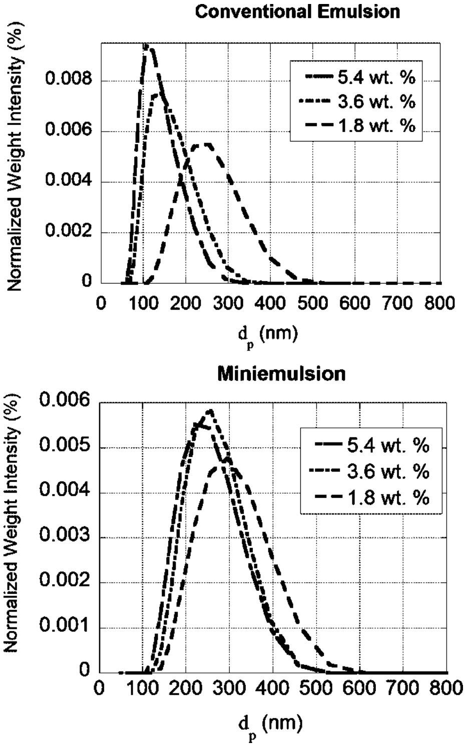

Figure 7. Figure 7. Effect of the PVOH concentration on the PSD in batch miniemulsion and conventional emulsion polymerization.

Figure 8 compares the extent of grafting and adsorption as a function of PVOH concentration in miniemulsion and conventional emulsion polymerization. It can be seen that the fraction of grafted PVOH was always higher in the case of miniemulsion polymerization and that for concentrations of PVOH higher than 3.6 wt % the grafted fraction decreased with the PVOH concentration (although the total amount of grafted PVOH increased with the PVOH concentration).

The main difference between the miniemulsion and the conventional emulsion is the distribution of the PVOH. In the case of the miniemulsion, most of the PVOH was adsorbed on the monomer droplets, whereas in the case of conventional emulsion polymerization, most of the PVOH was in the aqueous phase (either dissolved or forming aggregates through hydrogen bonding due to its polyhydroxy group). In addition, the PVOH aggregated presents a supermolecular organization with a paracrystalline structure.[21] The formation and presumably the dissolution of these aggregates is a kinetic process that may take relatively long times.

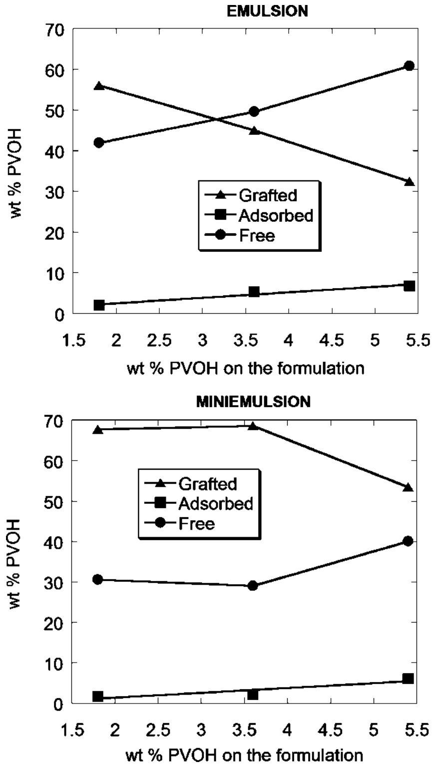

Figure 8. Effect of the PVOH concentration on the fraction of PVOH grafted, adsorbed, and in the aqueous phase (free) for miniemulsion and conventional emulsion polymerization.

For conventional emulsion and miniemulsion polymerization the radicals formed from the KPS (sulfate ion radicals and the oligomeric radicals formed from them) may abstract hydrogens from the PVOH. At least at the beginning of the reaction, the fraction of PVOH in the aqueous phase in conventional emulsion polymerization is larger than in miniemulsion polymerization. Therefore, assuming that all of PVOH of the aqueous phase is accessible, a higher hydrogen abstraction is expected for conventional emulsion. However, a large fraction of the PVOH contained in the aggregates may not be accessible for the aqueous radicals. The fact that the apparent water solubility of vinyl acetate is not affected by the PVOH concentration[22] supports the idea that the interior of the PVOH aggregates is not easily accessible. In this case, the hydrogen abstraction from the PVOH chains may be more likely in the case of miniemulsion polymerization which would justify the higher grafting found for the miniemulsion polymerization.

The differences in PVOH grafting may be also due to the fate of these PVOH radicals, which are not prone to propagate, but may terminate with other radicals. In the case of the conventional emulsion polymerization, the PVOH radical formed will be in the aqueous phase, where there is only a low monomer concentration. Therefore, growing of the relative unreactive PVOH radical to form a graft polymer is not favored and a significant fraction of these radicals may terminate with other radicals. This will reduce the efficiency of the hydrogen abstraction.

In the case of miniemulsion polymerization, the PVOH radicals are formed by hydrogen abstraction from the PVOH forming the hairy layer around the monomer droplet. These radicals have relatively easy access to the monomer (both by monomer diffusion and by rearrangement of the PVOH chains at the surface of the droplet), and hence, propagation yielding a graft polymer is favored.

Later in the polymerization, the surface area of the particles formed by conventional emulsion polymerization was larger than that of the particles obtained in miniemulsion polymerization (Figure 7). Therefore, assuming that adsorption equilibrium was reached, a faster grafting rate would be expected for conventional emulsion polymerization. However, the poor stability of the conventional emulsion polymerization[6,7] strongly suggests that the emulsion particles were not well covered by the PVOH, namely, that adsorption equilibrium was not reached. A reason for this may be that the dissolution of the PVOH aggregates is a slow process. Under these circumstances, the amount of PVOH accessible for the radicals does not increase substantially during the conventional emulsion polymerization.

Conclusions

In the foregoing, the effect of the initiator system and the polymerization process (miniemulsion vs conventional emulsion polymerization) on the extent of grafting of PVOH was studied. Potassium persulfate, *tert*-butyl hydroperoxide/ascorbic acid, lauroyl peroxide, and benzoyl peroxide were used. For miniemulsion polymerization, it was found that the extent of grafting increased as BPO $\approx$ LPO $<$ TBHP/AsAc $<$ KPS. The difference between KPS and TBHP/AsAc was mainly due to the longer time that the sulfate ion radicals (and the oligoradicals formed from them) stay in the aqueous phase, where they have the opportunity to abstract hydrogens, mainly from the adsorbed PVOH.

The fraction of PVOH grafted was always higher for miniemulsion polymerization than for conventional emulsion polymerization and, in both cases, the grafted fraction decreased with the PVOH concentration (although the total amount of grafted PVOH increased with PVOH concentration). The differences between miniemulsion and conventional emulsion polymerization may be due to both the inaccessibility of the large fraction of PVOH contained in the aggregates formed in emulsion polymerization and the difficulties encountered by the PVOH radicals to grow in the aqueous phase due to the low concentration of monomer in this phase.

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References and Notes

(1) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689–757.
(2) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283–1346.
(3) Schork, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butté, A.; Fontenot, K. In *Polymer Particles, Advances in Polymer Science*; Okubo, M., Ed.; Springer-Verlag: Heidelberg, 2005; Vol. *175*, pp 129−256.
(4) Ken, Y.; Masato, N.; Sato, T.; Maruyama, H. *Polym. Int.* **2000**, *49*, 1629–1635.
(5) Vandenzande, G. A.; Smith, O. W.; Bassett, D. R. In *Vinyl Acetate Polymerization, Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley: New York, 1997; pp 563−584.
(6) Kim, N.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Macromolecules* **2003**, *36*, 5573–5579.
(7) Bohórquez, S. J.; Asua, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6407–6415.
(8) Heublein, G.; Meissner, H. *Acta Polym.* **1984**, *35*, 744–747.
(9) Dunn, A. S. In *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W., Eds.; Applied Science Publishers: New York, 1981.
(10) Hartley, F. D. *J. Polym. Sci.* **1959**, *34*, 397–417.
(11) Craig, D. H. *Polym. Mater. Sci. Eng.* **1986**, *54*, 370–374.
(12) Kim, N.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Macromolecules* **2004**, *37*, 2427–2433.
(13) Kim, N.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Macromolecules* **2004**, *37*, 3180–3187.
(14) Mengual, O.; Meunier, G.; Cayré, I.; Puech, K.; Snabre, P. *Talanta* **1999**, *50*, 445–456.

(15) Mengual, O.; Meunier, G.; Cayré, I.; Puech, K.; Snabre, P. *Colloids Surf. A* **1999**, *152*, 111–123.

(16) Lemarchand, C.; Couvreur, P.; Vauthier, C.; Constantini, D.; Gref, R. *Int. J. Pharm.* **2003**, *254*, 77–82.

(17) Egret, H.; Sudol, E. D.; Dimonie, V. L.; Klein, A.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **2001**, *82*, 1739–1747.

(18) Rodríguez, R. *Ph.D. Dissertation*, University of the Basque Country, **2007**.

(19) Da Cunha, L.; Ilundain, P.; Salazar, R.; Barandiaran, M. J.; Asua, J. M. *Polymer* **2000**, *42*, 391–395.

(20) Autran, C.; de la Cal, J. C.; Asua, J. M. *Macromolecules* **2007**, *40*, 6233–6238.

(21) Klein, V, J,; Klenina, O. V.; Kolnibolotchnuk, N. K.; Frenkel, S. Y. *J. Polym. Sci. Symp.* **1973**, *42*, 931–942.

(22) Earhart, N. J. *Ph.D. Dissertation*, Lehigh University, **1989**.

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