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High Solids Vinyl Acetate Polymers from Miniemulsion Polymerization

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ABSTRACT: High solids content (50%) poly(vinyl acetate) latexes have been prepared from miniemulsion polymerization stabilized using SDS (sodium dodecyl sulfate) or a combination of SDS and nonionic surfactant nonylphenol ethoxylate (Triton X 405) and hexadecane as hydrophobe. The conditions for preparing stable monomer miniemulsion in terms of osmotic and Laplace pressures are discussed. Upon polymerization initiated by ammonium persulfate (APS), one observes in about all cases a decrease of the number of polymer particles as compared to the number of monomer droplets. These two numbers are much more close if the solid content is decreased to 20%, so that the discrepancy can be explained from collisions occurring between the polymer particles and the droplets not yet initiated. Conductometric titration of the serum allows to estimate the coverage of the droplets by the surfactants; further, it can be demonstrated that a part of the SDS is desorbed from the polymer particles that are partly stabilized by the charges coming from the initiator.

Introduction

Miniemulsion polymerizations, reviewed by Sudol and El-Aasser,[1] are gaining more and more attention. Three reviews did appear recently.[2−4] In that process, the size of the droplets is very small, typically in the range 100−500 nm, so that these droplets offer a surface area large enough to capture efficiently the oligoradicals coming from the water phase. Further, the monomer droplets can include an oil-soluble initiator, such as benzoyl peroxide (BPO) or azobis(isobutyronitrile) (AIBN). In that case, the nucleation step, always difficult to control in a classical emulsion polymerization, due to the competition between various possibilities (micellar, homogeneous, and coagulative nucleation), may be avoided. The droplets are then transformed into polymer particles as soon as they included a growing polymer chain. This fact is one of the major interests of the process. Another interest is that it is possible to prepare hybrid latexes upon dissolving another polymer in the monomer mixture to be emulsified.

However, up to now, there is not yet any major industrial process based on miniemulsion polymerizations, and most of the academic studies are dealing with the polymerization of styrene or methyl methacrylate (MMA). Furthermore, in these polymerizations the solids content is often limited below 20%.

In this paper, we would like to present a study of the polymerization of vinyl acetate (VA) with a solid contents of 50%. Just a few reports are dealing with copolymerization of VA with other acrylic monomers in miniemulsion.[5,6] Trials for miniemulsion polymerization of VA alone were reported recently,[7−9] using a polymer (poly(vinyl acetate) or polystyrene) as hydrophobe. It was demonstrated first[7] that, in a CSTR reactor, the fluctuations often observed in the number of particles in a regular emulsion polymerization process can be avoided, so producing a more regular product. This feature could be expected since the origin of these fluctuations comes from an oscillatory nucleation regime and that in miniemulsion polymerization the nucleation process takes place through capture of the radicals by the droplets of the miniemulsion. Thus, provided that the flux of radicals is regular, there are no more reasons for the nucleation process to be fluctuating with time. It was observed further[8] that the use a polymer product as the sole hydrophobe cannot guarantee the stability of the miniemulsion if too long a time has elapsed between the preparation (by sonication) of the miniemulsion and its introduction into the reactor. The reason for using a polymer as hydrophobe was the reports according to which the incorporation of small amounts of polymer in the monomer droplets strongly increased the polymerization rate, most probably upon making easier the capture of oligoradicals from the water phase.[10,11] However, it was demonstrated later[12] that the true reason for the rate enhancement was the fact that the stability of the droplets prior or during the polymerization of the monomer was better. In the last paper by Aizpurua et al.,[9] the polymerization of vinyl acetate in high solids up to 60% is studied, both in emulsion and in miniemulsion, as well in batch or in a CSTR reactor. The previous findings about the suppression of the fluctuating nucleation regime through miniemulsion polymerization was confirmed as well as the interest of using polymers as hydrophobe. Further, it was observed that, due to a broader particle size distribution, it was possible to improve the rheology of the high solids latexes using the miniemulsion process.

In the present paper, most often hexadecane is used as hydrophobe, with a surfactant system including SDS and Triton which allows to increase the solids content to 50%. Systematic comparison of the polymer particle size and number with the corresponding initial droplet features is carried out, and the reasons for the discrepancies between the two are discussed.

Experimental Section

Materials. All the chemicals—vinyl acetate monomer, ammonium and sodium persulfate (APS, NaPS), benzoyl peroxide (BPO), sodium dodecyl sulfate (SDS), nonylphenol ethoxylate with 40 ethylene oxide units and 70% solids (Triton X 405), dodecyl mercaptan (DM), and hexadecane—were from Aldrich and were used as received. In a few experiments, poly(vinyl acetate) was used as hydrophobe. It was prepared in solution using the following recipe: ethyl acetate 300 g, benzoyl peroxide (BPO) 0.9 g, vinyl acetate 100 g. After 6 h at 70 °C, the conversion was 57%. The polymer without residual mono-

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mer and solvent was obtained upon evaporation. It was characterized by size exclusion chromatography (SEC) as $M_n = 23\,800$ and $M_w = 54\,000$. Deionized water was used in all the experiments.

Miniemulsions. A basic recipe for preparing vinyl acetate miniemulsions includes the following: deionized water 250 g, vinyl acetate 250 g, hexadecane 8−12 g, sodium dodecyl sulfate (SDS) 2−6 g, Triton X 405 (70%) 0−8 g, ammonium persulfate (APS) 0.3 g. The procedure is as follows: the organic phase is dispersed in the water phase under high shear stirring (Ultra Turrax apparatus), 22 000 rpm for 10 min. The resulting droplet size is near 200 nm, and the miniemulsion is stable for several hours. As indicated later on, some change can be made from this basic recipe concerning the stabilizing system or the initiator. The size of the droplets is not larger than the size that can be obtained using a sonifier.

A part only of the surfactant is adsorbed on the droplet surface; the remaining part of the SDS, which is in the serum, is titrated by conductometry (Tacussel TTP 320T), taking into account the contribution of the initiator to the conductivity (which is supposed to remain at a fixed value all along the polymerization process). Such titration allows to estimate how the surface coverage of the paricles is changing.

The interfacial tension between the organic droplets and the continuous water phase was measured using the falling drop method: an automatic buret (Tacussel EBX) is connected to a capillary tube, which goes down in the organic phase (monomer + hexadecane). The buret is filled with the aqueous phase and flows slowly through the capillary as droplets. The volume V of the aqueous phase flowed after a given number of drops from the capillary is noted. The interfacial tension γ is related to this volume through the relationship

$$\gamma = V\Delta\rho gF/r$$

where $\Delta\rho$ is the density difference between the two phases, g is the gravity acceleration, r is the capillary radius (here 0.405 cm), and F is a correction factor given by Lando.[13]

Polymerization. The miniemulsion is transferred into a glass reactor of 1000 mL equipped with a jacket for temperature control, which is maintened at 60 °C; samples are withdrawn from time to time to follow the particle size and to measure by gravimetry the conversion of the monomer.

The particle size is measured by quasi-elastic light scattering (QUELS, Malvern LoCi) and the molecular weight by size exclusion chromatography (SEC, Waters) using polystyrene calibration standards.

Results and Discussion

Some preliminary experiments have been carried out in order to choose the procedure to prepare the miniemulsions. Two apparatus have been tried: either the high-speed Ultraturrax (22 000 rpm) for 10 min or a sonifier (600 W) for 2 min. With the sonifier, one observe a large increase of the viscosity due to the formation of a large amount of very small droplets which disappear within 1 h. For this reason, even if the sonifier was a more powerful disperser, we have chosen the Ultraturrax.

Before studying the miniemulsion polymerizations, it has been decided to look at the stability of the monomer miniemulsions. The criterion used for that was the possibility of dilution with water to be able to measure the droplet size through QUELS. Thus, if the droplet size, which is around 100−250 nm in diameter, does not change by more than 10 nm, the miniemulsion is reputed stable and then can be tested for polymerization. The use of QUELS to measure the droplets size is often criticized by several authors, and certainly, there is no guarantee that there is no change during the dilution needed for the QUELS measurements. However, in his recent review, Asua[2] stated that all the methods already used (staining with OsO_4, cryo-TEM, SANS, soap titration in the serum, surface tension, and QUELS) are not totally safe. The QUELS method is by far the most simple and the more rapid. In addition, it is observed in this paper that further dilution does not cause any further change.

According to Landfester,[4] the stability of a miniemulsion results from an equilibrium between the Laplace pressure, depending on the droplet radius r and of the interfacial tension γ between the droplet—containing both the monomer and the hydrophobe—and the water phase and, on the other hand, the osmotic pressure π, depending on the temperature T, the hydrophobe concentration C, and its molecular weight M.

$$\pi = RTC/M \qquad P = 2\gamma/r$$

Here $R = 8.314$ J mol^{-1} K^{-1}, $T =$ K, $C =$ kg/m^3, $M =$ kg/mol, and γ(interfacial tension) $= S_c\gamma_{sds} + (1 - S_c)\gamma_n$, where S_c is the area covered, $\gamma_{SDS} =$ particle covered with SDS, and $\gamma_n =$ naked particle.

The interfacial tensions are measured through the falling drop method and the particle radius after QELS measurements, while the concentration of SDS in the water phase is obtained from conductometry. Knowing the total amount of SDS added in the recipe, it is easy to deduce from the conductometric measurement how much SDS is covering the surface. We assume that the amount of SDS needed for the full coverage of a droplet is the same than for the corresponding polymer particle, and knowing the total area of the droplets, we can deduce the percent of surface covered as well as the charge density.

In Table 1 are reported the data concerning experiments where the ratios between the hydrophobe (hexadecane) and both the monomer and the SDS have been varied. Stable droplets with diameters between 148 and 216 nm have been prepared, with interfacial tension between 7 and 12 mN/m. The surface coverage does vary by a factor of 7 and the charge density by a factor higher than 10 (from 0.6 and 7.1 μC/cm^2). In these experiments, it is interesting to note that the osmotic pressure is always higher than the Laplace pressure. Then the Ostwald ripening process is forbidden, and the miniemulsion remains stable. This is because the amount of hydrophobe is high enough. Then the miniemulsions are able to resist the dilution needed by the QUELS measurements. The smallest particle size was obtained for a ratio between hexadecane and SDS of 4; this value has been reported as optimum by Delgado et al.[5] We have also observed that if the ratio between P and π is around or lower than 1, or if there is not enough hexadecane compared to the amount of SDS, it is not possible to prepare a stable miniemulsion.

When a miniemulsion of vinyl acetate, stabilized by SDS (8 g/L) and hexadecane, is diluted with water, the conductivity of the serum is increasing, so that a part of the SDS can be desorbed and the surface charge density decreases. When the dilution factor reaches a value of about 10, the charge density drops to a value corresponding approximately to the limit of stability of the corresponding poly(vinyl acetate) latex particle. Increasing the dilution factor causes a progressive decay of the charge density and the increase of free SDS in the serum up to more than 80% for a dilution factor of 40. At this level of dilution, the miniemulsion remains stable.

Table 1. Properties of Vinyl Acetate Miniemulsions Stabilized with SDS and Hexadecane

SDS, g/L	ratio H/VA	ratio H/SDS	D_n, nm	coverage, %	charge density, $\mu C/cm^2$	γ, mN/m	$P \times 10^5$	π, Pa
2	0.033	16.5	161	7	1	11.8	1.47	3.20
	0.053	26.5	171	7	0.97	11.8	1.38	5.00
	0.08	40	216	10	0.6	11.6	1.07	7.30
	0.102	51	213	10	1.4	11.6	1.08	9.10
4	0.033	8.25	198	21	3	10.5	1.06	3.20
	0.053	13.25	190	20	2.9	10.6	1.12	5.00
	0.08	20	201	21	3	10.5	1.05	7.30
	0.102	25.5	188	18	2.6	10.8	1.15	9.10
8	0.033	4.125	130	31	4.5	9.6	1.47	3.20
	0.053	6.625	148	35	5.1	9.2	1.24	5.00
	0.080	10	196	42	6.1	8.5	0.87	7.30
	0.102	12.75	184	38	5.5	8.9	0.97	9.10
20	0.033	1.65	194	48	7.1	7.9	0.82	3.20
	0.053	2.65	193	47	6.9	8	0.83	5.00
	0.080	4	196	45	6.5	8.2	0.84	7.30
	0.102	5.1	169	35	5.2	9.2	1.09	9.10

Table 2. Desorption of SDS and Decrease of the Surface Charge Density of the Droplets Upon Dilution with Either Pure Water or with Triton Aqueous Solution

	dilution with pure water droplet size 111 nm			dilution with Triton solution droplet size 125 nm		
dilution factor	free SDS	surface SDS	$\mu C/cm^2$	free SDS	surface SDS	$\mu C/cm^2$
0	0.031	0.169	3.71	0.028	0.172	4.31
2	0.075	0.125	2.75	0.051	0.149	3.74
4	0.090	0.110	2.42	0.073	0.127	3.18
8	0.113	0.087	1.91	0.111	0.089	2.23
10	0.122	0.078	1.71	0.122	0.078	1.94
12	0.131	0.069	1.52	0.131	0.069	1.73
20	0.156	0.044	0.98	0.153	0.047	1.18
40	0.173	0.027	0.60	0.173	0.047	0.60

If the dilution is carried out using a solution of Triton at the cmc (1.6 g/L), the desorption of SDS, as shown by conductometric measurements, follows about the same scheme, with decreasing charge density, at about the same rate as upon dilution by pure water. This is quite surprising because this behavior is very different from the behavior of polymer particles. As reported by Colombie et al.,[14] in the case of polystyrene polymer particles, stabilized by a mixture of Triton and SDS, the SDS is desorbed from the particle surface upon addition of Triton, to a rather large extent. Comparative data about the desorption of SDS and the decrease of the charge density are reported in Table 2. Of course, the stability of the miniemulsion is no more affected by this dilution with the Triton solution than the dilution with pure water.

It was concluded that the optimal conditions for preparing a miniemulsion of vinyl acetate with 50% organic phase were to use a SDS concentration of 8 g/L and a ratio hexadecane/SDS of 4. Then, the osmotic pressure is higher than the Laplace pressure, and the coverage of the droplets with SDS is not too low (30%), while the SDS concentration in the water phase is smaller than the cmc and the charge density at the droplet surface is about 2 times higher than the minimum required for the stability of poly(vinyl acetate) latex particles.

In a first step, a conventional emulsion polymerization was carried out at 20% solid contents, using 2.7 g of SDS, 1.5 g of Triton, and 0.3 g of APS. A large number of particles were initially nucleated (3×10^{17}/L), but because of the rather small amount of surfactant, limited flocculation took place, and the final size was 245 nm (i.e., 2.4×10^{15} particles/L). Correspondingly, the average number of radicals per particle n (estimated from the ratio between the polymerization rate and the product of n and the number of particles at a given time of step II, where the rate remains constant, of the emulsion polymerization) is large, around 50. This is believed to be the result of the flocculation of the particle homogeneously nucleated onto the existing particles and illustrates the difficulty of controlling the nucleation step in vinyl acetate emulsion polymerization. Further, at 80% conversion, the polymerization rate decreases suddenly, possibly after a Tromsdorff effect has been experienced.

Miniemulsion polymerization data are reported in Table 3 with various hydrophobes. The recipe includes in most cases 250 g of vinyl acetate, 250 g of water, and 0.3 g of APS, and the temperature is fixed at 60 °C because the boiling point of the monomer is only 72 °C.

In all cases, the final number of polymer particles is significantly lower than the initial number of droplets, although the monomer miniemulsion seems quite stable upon aging or upon dilution. We think that the explanation of this phenomenon is the merging upon collision of droplets initiated (then already polymer particles swollen with monomer) with other droplets not yet initiated. Such a possible cause of the discrepancy between the two numbers (droplets and polymer particles) was already reported.[15,16] In the first run of this series (entry 1 of Table 3), one observes a continuous decrease of the particle number as the conversion increases; N_p remains stable after more than 90% conversion of the monomer. Figure 1 illustrates these features.

In the presence of mercaptan (entry 2) the polymerization rate is much lower, at least initially, and correspondingly, the decrease of N_p is also much lower, as can be seen in Figure 2. There are two possible causes of merging upon collision: one is the high concentration of the organic phase with a small average distance between monomer droplets and polymer particles, and the second reason is the progressive initiation of the droplets after capture of the oligoradicals coming from the water phase. Indeed, at 60 °C, the rate of radical generation is not very large in the case of APS. The effect of the mercaptan seems to be surprisingly strong. However, it is important to remind that the mercaptan can be used alone as the hydrophobe, as shown by Schork et al.[17] It means that the mercaptan is included inside the particle, but its thiol group, which is hydrophilic in a large pH range, should be located preferentially at the droplet surface; when this group does react

Table 3. Data of Vinyl Acetate Miniemulsion Polymerizations Initial and Final State[a]

run	hydrophobe, g		SDS, g	Triton, g	N_d/L × 10^{16}	free SDS, g	final N_p/L × 10^{16}	N_d/N_p	SDS serum, g	charge density, μC/cm^2
1	H	8.25	2	0	19.1	0.42	2.81	7.2	0.61	8.8
2	H +DM	8.1 7.3	2	0	8.16	0.54	2.88	2.48	1.22	4.8
3	H +DM	13.5 8.5	2	0	11.7	0.63	3.6	3.2	1.62	2.05
4	H	8.2	2	4.25	12.3	0.52	1.28	9.6	1.20	6.4
5	H	8.7	2	4.85	16.2	0.28	2.75	6	0.71	8.0
6	H	16.1	4	7.7	32	1.56	5.1	6.3	3.50	2.45
7	PVAc +DM	10.2 6	2	0	11.3	0.52	4.6	2.48	1.40	3.18
8	PVAc +DM	8.2 6.3	2	0	18.1	0.48	4.25	3.8	1.42	3.16
9	H +BPO	8.6 2	2	0	18.3	0.48	3.15	5.8	1.28	4.36
10	H +BPO	14.6 2	4.8	9	21.8	2.10	5.4	4	3.08	8.48
11	H	8.2	2	0	7.9	0.58	3.56	3.3	1.98	0.13
12	H +DM	8.35 7.4	2	0	11.9	0.93	3.63	3.2	2.08	-0.43
13	H	8.2	4	0	10.5	1.02	2.98	3.5	3.51	3.16
14	H + DM	8.3 7.35	4	0	6.7	2.28	2.92	2.3	3.10	5.46
15	H	16.1	4	0	7.9	1.98	3.02	2.6	2.63	8.02

[a] H = hexadecane, DM = dodecylmercaptan, BPO = benzoyl peroxide, and PVAc = poly(vinyl acetate). In all cases, the recipe includes 250 g of vinyl acetate, 250 g of water, and 0.3 g of APS (except in runs 11 and 12, where it is 1.2 g), and the temperature is fixed at 60 °C.

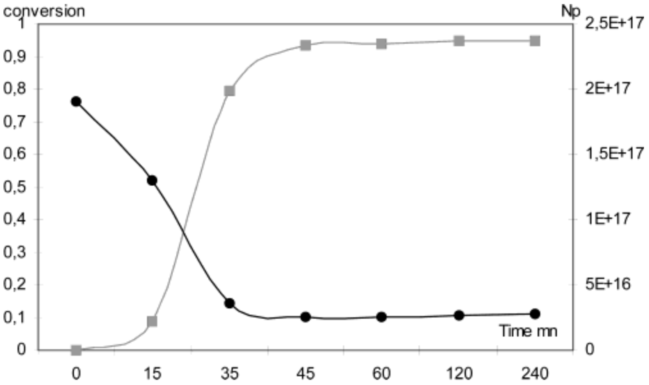

Figure 1. Polymerization kinetics in run 1 and evolution of the particle number.

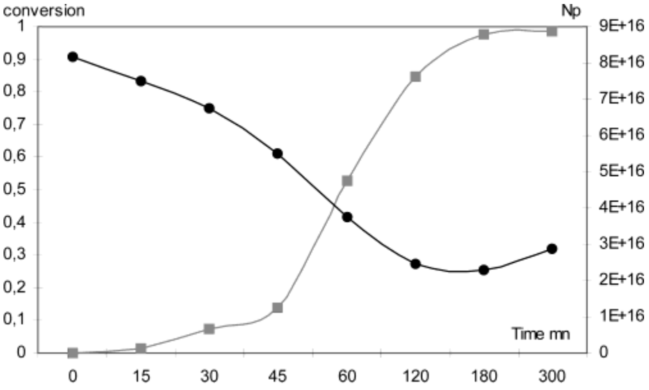

Figure 2. Polymerization kinetics in run 2 and evolution of the particle number.

with the oligomeric radical coming from the water phase where they are generated, some retardation of the nucleation process might occur, as can be observed in Figure 2, where the nucleation period seems to be as long as 45 min. However, a strong acceleration of the polymerization rate is observed later, which could be due to some enhancement of the rate of decomposition of the APS. A rather similar behavior (initial retardation followed by a high polymerization rate) is observed in another run (entry 3 of Table 3) where the amount of hexadecane has been increased, without changing significantly the amount of mercaptan.

When the recipe does contain a nonionic surfactant (Triton) in addition to SDS (entries 4−6), the behavior does not change drastically: the particle number decreases in the same way that the conversion increases.

The smallest reduction factor of the number of polymer particles, as compared with the number of monomer droplets (2.5), is observed when PVAc is used as hydrophobe (entry 7 in Table 3) in the presence of some mercaptan added in order to control the molecular weight. It has been shown earlier[10,11] that one of the important reasons in using a polymer as hydrophobe was to increase the nucleation rate. This statement has been revised when the same group discovered that the cetyl alcohol was not able alone to stabilize the droplets, except if some polymer has been added in the monomer miniemulsion.[12]

Another way to increase the nucleation rate is to add in the recipe an oil-soluble initiator such as BPO to the normal water-soluble APS. This was done for the two runs reported in Table 3 (entries 9 and 10). As compared with run 1, with hexadecane as the sole hydrophobe, the reduction factor is decreased from 6.8 in run 1 to 5.8 and 4.0 when the amount of added BPO was 2.0 g. However, the rate of radical generation of BPO at 60 °C is also rather moderate, and while being hydrophobic, BPO does not increase very much the effect of hexadecane. The difference between runs 9 and 10 is probably caused by the increase of the amount of SDS in run 10 and possibly by the presence of Triton.

In runs 11 and 12, the amount of APS has been increased by a factor of 4. In both cases, the polymerization rate is higher, and no induction period is observed. Correspondingly, the ratio between the final number of particles N_p and the number of droplets N_d is rather low, with again the lowest value for the highest SDS concentration.

The effect of increasing the amount of SDS is shown also in the three last runs in Table 3. A significant reduction of the ratio N_d/N_p is observe upon comparing runs 1 and 13 (from 7.2 to 3.5) or runs 2 and 14 (from 2.48 to 2.3), while the combination of high amounts of hexadecane and SDS with Triton is also efficient in that respect (2.63). The recipes used in runs 6 and 15 were the same, but in run 6 four times more droplets were observed, so that the reduction factor is lower than for run 15.

Another feature reported in Table 3 dealt with the desorption of SDS upon polymerization as shown by conductometric titration of the serum. From that measurement, after correction of the contribution of the amount of the initiator APS introduced in the experiment, it is possible to obtain the contribution of the SDS that is not used for the stabilization of the droplet surface. Upon polymerization, the conductivity increases. Normally we do not expect that such an important increase can be caused by the initiator decomposition: the two charged radicals coming from its decomposition either are captured by the polymer particles which are then initiated or are mutually destroyed, thus not increasing the number of charged mobile molecules. Therefore, it seems safe to conclude that there is desorption of a part of the SDS covering the surface. Furthermore, it is possible to obtain from these data the contribution of the SDS adsorbed onto the surface to the charge density of the polymer particles. The corresponding data are reported in the last column of Table 3. Different parameters in the recipe may have an influence on the SDS desorption. The main parameter, in that respect, is the presence of Triton. It has been shown that the nonionic surfactant does not change the conductivity of the serum, and thus the desorption from the droplets upon dilution, compared with dilution by pure water. The situation is different when the polymerization is carried out. Comparing runs 1 and 4, one can see that the proportion of SDS at the interface decreases from 80 to 70% in run 1 and from 79 to 40% in run 4; this feature could be expected on the basis of the data reported in ref 14, showing that there is a trend for the Triton to replace the SDS in the particle stabilization system.

Following the serum's conductivity all along the polymerization reveals that, in most cases, chiefly in the absence of Triton, the desorption of the SDS does not take place before a high conversion has been reached; in certain cases, most of the apparent desorption took place chiefly after more than 90% conversion. In that situation, the decomposition of the initiator is continuing, and oligoradicals continue to be captured by the particles. Thus, it may be suspected that the SDS desorption is chiefly caused by its replacement by other surface-active species, either Triton or charged moieties coming from the initiator. Data from runs 11 and 12, where the amount of initiator has been increased by a factor of 4, are illustrative in that respect, as shown in Figure 3. In the case of run 12, negative values of the apparent amount of SDS remaining at the interface are then obtained from the conductivity measurement. Obviously, something should be wrong in the assumptions. Most probably, at the end of the polymerization process, the conductivity from initiator residue present in the serum is increasing. The study of styrene polymerization initiated by persulfate salts without emulsifier allowed the group of Rudin[18] to study the various products formed by the persulfate; the authors have observed that only a rather small part (30%) of these products are actually used to initiate polymer chains; the main part are forming oligomers compounds having surface activity, which can be used to increase the particle size in further polymerization steps, and finally about 20% is decomposed in sulfuric acid. The oligomers probably do not change very much the conductivity of the serum because they are carrying two sulfate groups, being formed after a coupling termination reaction; but the part that is decomposed in sulfuric acid certainly increases the conductivity of the water phase. Then a few experiments have been carried out to titrate the charges stabilizing the particles after washing the final latex through ion-exchange resins. The values obtained are 0.67, 0.91, and 0.73 μC/cm^2 respectively for runs 11, 12, and 13. In the case of run 12, this is the major contribution to the surface charge and then to the stabilization of the polymer particles. In the two other cases (runs 11 and 13), the titrations of the latex after the washing process are close together, although the amounts of initiator are very different.

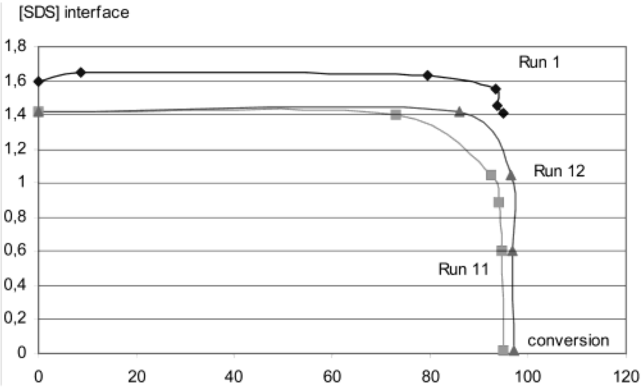

Figure 3. Desorption of SDS in runs 11 and 12 from conductometric measurements.

A new set of experiments have been carried out to obtain these kind of data, in which both the conductivity of the serum and the titration of the sulfate charges coming from the initiator have been carried out. The results of three experiments in which the amount of SDS was constant are reported in Table 4. Because the washing process on ion-exchange resins needs a rather important sample, only a limited number of latexes were studied before the end of the polymerization.

The charge density of the latex surfaces was composed of two parts: the first one comes from the titration of the strong acid SO_4^- groups coming from the persulfate initiator, while the second one comes from the conductometric analysis of the SDS present in the serum, assuming that the contributions of the initiator and of its derivatives did not change during the polymerization process. In the first case (run 21) a maximum of both the contributions can be observed at intermediate conversion. The same is true in the second case (run 22), in which one expects some SDS should be enlarged due to the presence of Triton. The origin of these maxima is not clear. But the most surprising results are obtained in the third case, where there is mercaptan in the recipe. In that case the conductivity of the serum is continuously increasing so that the apparent amount of SDS at the particle surface becomes nul at high conversion. Thus, it was decided to eliminate the

Table 4. Other Data Including Titration of the Sulfate Groups Coming from the Initiator For Runs with 50% Solids

run	SDS, g	Triton, g	DM, g	HD, g	conv, %	D_n, nm	N_p/N_d	SDS free	R cover	μC/cm^2 SDS	μC/cm^2 SO$_4^-$
21	2	0	0	8.2	0	155		0.41	0.33	4.90	0
					23	192	2	0.72	0.35	5.14	2.56
					96	246	5	1.41	0.25	3.59	0.60
22	2	5	0	8.8	0	166		0.05	0.44	6.44	
					52	206	2.1	0.44	0.49	7.18	0.81
					89	223	3	0.88	0.42	6.10	1.09
					94	215	2.7	1.15	0.31	4.53	0.66
23	2	0	7.7	8.6	0	176		0.36	0.40	5.8	
					76	200	1.75	1.74	0.09	1.25	3.18
					81	198	1.7	0	0	0	4.75
					90	207	2.2	0	0	0	1.54
26	4	0	0	16.8	0	151		0.94	0.31	4.61	
					1.6	155	0.90	1.08	0.32	4.52	
					2.5	164	0.80	0.98	0.29	4.96	
					6.1	180	0.60	1.18	0.36	5.13	
					8.3	183	0.55	1.37	0.28	4.89	
					41	217	0.34	2.21	0.29	4.23	
27	4	0	0	18	0	142		0.59	0.34	4.81	
					9	171	0.63	0.66	0.39	5.8	
					53	199	0.33	0.73	0.47	7.27	
					98	221	0.21	1.01	0.49	8.26	
					99	231	0.2	1.19	0.58	8.12	

[a] The initiator is H_2O_2 4 g +1 mL/h ascorbic acid. [b] The initiator is lauryl peroxide 4 g.

Table 5. Data of Vinyl Acetate Miniemulsion Polymerizations Initial and Final State (Solid Contents 20%)

run		hydrophobe, g	SDS, g	Triton, g	Nd/L $\times 10^{16}$	free SDS	final Np/L $\times 10^{16}$	N_d/N_p	SDS serum	charge density, μC/cm^2
16	H	8.2	2	0	2.25	1.79	1.52	1.5	2.74	−12.79
	H	8.25	2	0	1.29	1.79	1.26	1.0	2.56	−9.8
	+ DM	7.1								
18	PACV	8.2	2	0	1.43	1.64	1.50	0.9	1.77	4
19	H	8.2	2	4.7	1.4	1.3	1.13	1.2	0.96	19.8

Table 6. Other Data Including Titration of the Sulfate Groups Coming from the Initiator For Runs with 20% Solids

run	SDS, g	Triton, g	DM, g	HD, g	conv, %	D_n, nm	N_p/N_d	SDS free	R cover	μC/cm^2 SDS	μC/cm^2 SO$_4^-$
24	4	0	0	16.4	0	86		0.31	0.76	11.1	
					14.8	89	1.1	0.51	0.76	11.1	1.18
					96	108	2.4	3.58	0.13	1.96	0.58
					100	110	2.7	>4	0	0	0.8
25	4.	9.4	14	16	0	137		0.98	1.1	14.4	
					75	144	1.35	1.83	0.87	12.6	0.25
					88	151	1.6	1.87	0.92	11.3	0.36
					96	156	1.8	2.24	0.82	11.9	1.14

contribution of the initiator to the charges of the system and then to use a nonionic initiator. The two last runs (26 and 27) were carried out in these conditions. In the first one (26) a redox system with an initial charge of hydrogen peroxide and a continuous flow of ascorbic acid was used, while in the second (27), an oil-soluble initiator (lauroyl peroxide) was added in the miniemulsion. In the first case the oligoradicals are coming from the water phase and are not charged. The polymerization process is slow, and the particle number is decreasing continuously in a way exactly opposite to the conversion, as in the case of the APS initiation (run 1, Figure 1). The conductivity is continuously increasing, while the apparent charge density goes through a flat maximum. The coverage ratio is also quite constant. In the second case, where the production of radicals is only inside the droplets and polymer particles, the number of particles also decreases as the conversion increases, and the conductivity also increases continuously, but the calculations indicate that most of the SDS stay on the particles surface and the charge density reaches high values up to 8 μC/cm^2.

A few experiments have been carried out, in which the solid contents have been limited to 20%. Corresponding data are reported in Table 5. The most striking result is that the ratio N_d/N_p is now close to 1 in all cases, showing that the droplets are keeping their identity upon polymerization. Another important feature concerns the SDS desorption which seems almost complete. The data from the conductivity of the serum indicate more SDS than the amount initially introduced. This feature obviously indicates that some extra ions have been produced, most probably from the initiator. It is surprising that this observation does not hold when Triton is present.

During the polymerization process, one observes some fluctuations of the particle numbers, with a trend to decrease if the initial polymerization rate is not high enough. On the other hand, it seems that there is a continuous process of homogeneous nucleation of new polymer particles, but their stabilization being not good enough, due to the lack of surfactant to protect against coalescence the newly created surface area, limited flocculation takes place and the number of particles is dependent on the balance between all these processes. Two further experiments have been carried out in which both titration of the sulfate groups coming from the initiator and conductometric analysis of the serum have been effected. The corresponding data are reported in Table 6.

In these experiments, while there is never a large amount of sulfate groups at the surface, the apparent coverage ratio by the SDS is surprisingly high in the presence of both Triton and mercaptan. In the absence of these compounds, SDS desorption takes place at very high conversion. Most probably, the secondary events (homogeneous nucleation, limited coalescence) do occur also at high solid contents, but the main process remains, in this case, the coalescence between polymer particles and droplets not yet initiated.

Conclusion

It is possible to obtain high solids content latexes from miniemulsion polymerization of vinyl acetate in conditions such as the final particle number remaining close to the initial number of droplets. However, when the solid contents is as high as 50%, the particle number tends to be lower than the initial droplets number; the reason for that is believed to be collision between the polymer particles and the monomer droplets not yet initiated, so that the number of particles is decreasing in a manner inversely proportional to the monomer conversion. When the solids content is decreased to about 20%, the number of polymer particles remains stable and closer to the initial number of monomer droplets. Conductometric measurements show that the coverage of the monomer droplets by the SDS is far from complete. Upon polymerization a part of this SDS tends to be desorbed and to be replaced either by the Triton or by charged oligomers formed from the initiator, chiefly at high conversion. If the initiator is not charged, the coverage ratio either remains stable (redox system with hydrogen peroxide−ascorbic acid) or tends to increase, due to the strong decrease of the number of particles (oil-soluble initiator).

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