Particle Coagulation at Semicontinuous Emulsion Polymerization. II. Characterization of Surface Groups

JAROMÍR ŠŇUPÁREK Jr. and ALENA TUŤÁLKOVÁ, *Research Institute for Synthetic Resins and Lacquers, 532 07 Pardubice, Czechoslovakia*

Synopsis

Semicontinuous emulsion polymerization of acrylic monomers with a monomer emulsion feed has been investigated. The amount of coagulum appearing during the polymerization under conditions of insufficient covering of particle surface by emulsifier was studied from the point of view of particle surface charge. Increasing the surface group concentration via copolymerization of butyl acrylate with acrylic acid or sulfoethyl methacrylate caused increased colloid stability of the system and a rapid decrease in coagulum formation. It was established that during the polymerization acid hydrolysis of ester groups took place, which caused an increase in the carboxyl groups concentration at the particle surface. These carboxyl groups contribute to the colloid stability of the polymerizing system.

INTRODUCTION

Emulsion polymerization with continuous monomer emulsion addition (so-called semicontinuous emulsion polymerization) is widely used in technical production of synthetic latices. It was shown in Part I of this study that the ratio between the amount of emulsifier in the initial reactor charge and its amount in the monomer emulsion (R/E distribution ratio) may greatly affect the tendency of the polymerizing system to coagulum formation during the polymerization. This tendency markedly increased with increasing R/E value as well as with increased alkyl length of the alkyl acrylate.

A primary agglomeration—oligomer radical with another oligomer radical or existing particle and a secondary agglomeration (two unstable particles)—supposedly proceeds during the emulsion polymerization of acrylic monomers.[2] Thus, in the case of an insufficient covering of the particle surface by emulsifier, the particle surface area, the amount of adsorbed emulsifier, and the colloid stability of the system may be in equilibrium. In such an equilibrium state after semicontinuous polymerization using an R/E distribution equal to 50/50, however, it was not found that there was any essential difference in the amount of emulsifier adsorbed on different poly(alkyl acrylates) despite a great difference in the amount of coagulum appearing during the polymerization. On the other hand, copolymerization with acrylic acid or sulfoethyl methacrylate was found to be very effective in minimizing the coagulum formation. The particle surface charge was then studied in relation to the colloid stability (coagulum formation) of systems in which the particles were insufficiently covered by emulsifier.

EXPERIMENTAL

Materials used were: ethyl acrylate (Ugilor); butyl acrylate, 2-ethylhexyl acrylate, and acrylic acid (BASF); sulfoethyl methacrylate (Dow); Fenopon EP 120 [ammonium salt of sulfated alkylphenoxypoly(ethyloxy)ethanol] (GAF); ammonium persulfate p.a., sodium metabisulfite p.a., and $FeCl_3$ p.a. (Lachema, ČSSR); and demineralized water.

Polymerizations were carried out in a 2000-ml stirred glass reactor under a nitrogen atmosphere at 70°C; the peripheral speed of the stirrer was about 1 m/sec. Water, 200 g 6-g sodium metabisulfite, and a variable amount of emulsifier were charged into the reactor. After reaching the polymerization temperature, addition of the emulsion consisting of 800-g monomer, 500-g water, 12-g ammonium persulfate, and a variable amount of emulsifier was started. The emulsion was continuously added during 2.5 hr, and the reaction was completed by additional heating of the reaction mixture for 1 hr at 70°C. The total amount of emulsifier Fenopon EP 120 was 2.25 wt.% surface-active matter/polymer in all experiments. In the case of polymerization with the metabisulfite/Fe^{3+} initiation system, 8.5-g $FeCl_3$ was added to the monomer emulsion instead of persulfate. In the case of polymerization with persulfate 6-g persulfate was added initially to the reactor and 12-g persulfate was added with the monomer emulsion; the polymerization was carried out at 80°C.

Anionic emulsifier and electrolytes were removed from the products by ion exchangers Ostion KS and Ostion AD (Spolchemie, ČSSR). The samples were purified in two steps using 20-ml ion exchanger mixture (1:1) to 100 ml latex diluted to 10% solids. The samples in each step were stirred for 24 hr, and the purification was followed by conductivity measurements.[3] The ion exchangers of technical grade were specially purified[4] before use.

Conductometric titrations were performed with $0.1N$ or $0.01N$ NaOH using a Radelkis conductometer OK-102/1 at 25°C. The samples were diluted with demineralized water. Carbon dioxide was removed before the analysis by bubbling nitrogen through the sample.

RESULTS AND DISCUSSION

The copolymerization of small amounts of acrylic or methacrylic acid with nonpolar monomers is frequently used to achieve better polymerization. Part of the carboxyl groups are situated at the particle surface,[5] where they increase the surface charge and, consequently, the particle stability. Sulfo groups also act similarly; these may be incorporated on the particle surface by copolymerization with sulfoethyl methacrylate. The relationship between the amount of copolymerized functional monomer and the specific surface charge of BA/AA and BA/SEMA copolymer particles is shown in Figures 1 and 2. This surface charge is defined here as the total charge measured by titration; this is distinguished from the "effective" charge, which is the product of the surface charge and the "apparent degree of dissociation." This effective charge is much smaller than the surface charge.[4] Because of the different dissociation of weak and strong acid groups, the ion-exchanged latex copolymers differed also in their electric conductivity (Table I). Nevertheless, carboxyl groups on the particle surface are very effective in the particle stabilization even in the undissociated state, as shown in Figure 3. The sharp decrease in coagulum formation in sys-
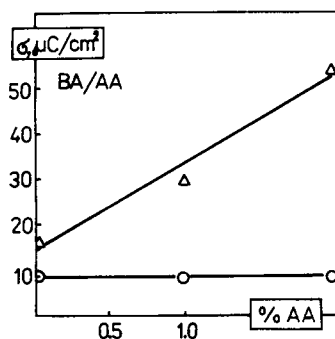
Fig. 1. Particle surface charge (estimated by titration) of butyl acrylate/acrylic acid copolymers in relation to amount of copolymerized acrylic acid: (O) strong; (△) weak; $R/E = 50/50$.
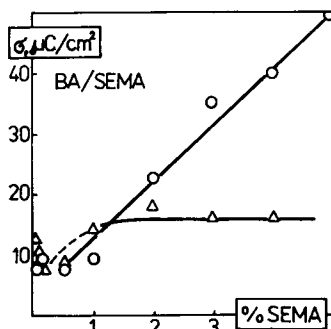

Fig. 2. Particle surface charge (estimated by titration) of butyl acrylate/sulfoethyl methacrylate copolymers in relation to amount of copolymerized sulfoethyl methacrylate: (O) strong; (△) weak; $R/E = 50/50$.

TABLE I
Conductivity of Ion-Exchanged Latices

Copolymer composition, wt. %			Specific conductivity of samples (10 wt. % solids), μS	
BA	SEMA	AA	Original	Ion exchanged
100.0	0	0	5,440	70
99.5	0	0.5	6,250	90
98.0	0	2.0	5,930	110
99.5	0.5	0	5,490	250
98.0	2.0	0	7,700	1,500
96.0	4.0	0	10,500	3,800

tems with specific surface charge over about 30 $\mu C/cm^2$ shows the great influence of this factor.

From this point of view, the initiation system and also its concentration play a great role. Persulfate, which is widely used, aids particle stability by sulfate endgroups; in the persulfate/metabisulfite system, both strong acid sulfate and sulfo endgroups are present on the particle surface.[6] These strong acid groups were found on the surface of deionized particles also in the case of samples in which no sulfoethyl methacrylate was copolymerized. There was a question, however, concerning the generation of weak acid groups (carboxyl), which were estimated at the particle surface even in cases in which no acrylic acid had been
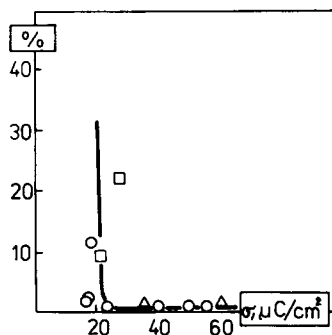
Fig. 3. Coagulum formation during semicontinuous emulsion polymerization of butyl acrylate and its copolymers with acrylic acid and sulfoethyl methacrylate (R/E of Fenopon EP 120 = 50/50) in relation to particle surface charge (estimated by titration): (□) poly(butyl acrylate); (O) BA/SEMA copolymer; (△) BA/AA copolymer.

copolymerized. Table II shows that weak acid groups appeared in all three cases in which different initiation systems were used—persulfate, persulfate/metabisulfite, and metabisulfite/Fe^{3+}. The highest value of weak acid-to-strong acid group concentration ratio was found in the case of persulfate/metabisulfite-initiated polymer particles. There was also an increase in carboxyl groups concentration at the particle surface after aging of the sample. The data summarized in Table III show an increased amount of surface carboxyl groups as well as an increased concentration of butyl alcohol after aging and heating of poly-(butyl acrylate)/sulfoethyl methacrylate (98/2) latex. This indicates that the acid hydrolysis of ester groups under the polymerization and storage conditions (pH = 2–3) is probably the main source of carboxyl groups at the polyacrylate emulsion particle surface.

The experimental data above indicate the great importance of the chemically bound surface charge bearing groups on the emulsion polymerization process, especially from the point of view of the colloid stability of the systems with low emulsifier level. Ceska[7] suggested in his study on sulfostabilization that, as-

TABLE II
Concentration Ratio of Weak and Strong Acid Groups on Poly(butyl Acrylate) Particle Surface After Polymerization with Various Initiation Systems

Initiation system	C_{weak}/C_{strong}
$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^- + HSO_3^{\cdot}$	2.1
$S_2O_8^{2-} \rightarrow 2\,SO_4^-$	1.3
$HSO_3^- + Fe^{3+} \rightarrow Fe^{2+} + HSO_3^{\cdot}$	1.1

TABLE III
Concentration of Acid Surface Groups and Butyl Alcohol in Sample of Butyl Acrylate/Sulfoethyl Methacrylate (97/3) Copolymer in Relation to Aging and Heating of Sample

Copolymer BA/SEMA (97/3)	Acid groups, meq/g		BuOH, %
	Strong	Weak	
Freshly prepared	0.107	0.049	0.13
Three months/20°C	0.102	0.120	0.46
Three months/20°C + 20 hr/80°C	—	—	0.65
Three months/20°C + 40 hr/80°C	0.094	0.131	—

suming homogeneous particle nucleation, the amount of sulfate groups at the particle surface depends on the monomer polarity and its water solubility. At a low concentration of monomer in the water phase, a side reaction of sulfate radical ions has been proposed:

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^- + \cdot OH$$
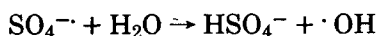
The hydroxy radicals also initiate the polymerization but do not contribute to the electrostatic stabilization. The extent of the side reaction should be greatest during polymerization of water-insoluble monomers. Therefore, a greater concentration of sulfate groups should be found at the poly(ethyl acrylate) than at the poly(2-ethylhexyl acrylate) particles. Acrylic acid can be a primary stabilizer, for it contains carboxyl groups, but it should also posess a secondary or "costabilizer" capacity as a function of its ability to scavenge sulfate radical ions before they can hydrolyze to nonstabilizing hydroxy radicals. Our experimental results, however, did not show any significant difference in strong acid group concentration neither on the particle surfaces of poly(alkyl acrylates) with variable alkyl length nor on butyl acrylate/acrylic acid copolymers. The particle surfaces of various poly(alkyl acrylates), however, differed markedly in the weak acid group concentration, as is shown in Figure 4. The greatest concentration of carboxyl groups was found on poly(ethyl acrylate), the lowest on poly(2-ethylhexyl acrylate) particles. It may be that this difference was caused by a different resistence of those acrylic esters to the acid hydrolysis.

Interesting data are summarized in Table IV, where the amount of coagulum arising during the polymerization of various poly(alkyl acrylates) polymerized in the presence of Fenopon EP 120 using $R/E = 50/50$ is shown in relation to the surface charge of particles; analyzed poly(alkyl acrylates) were prepared at $R/E = 2/98$ to avoid coagulum formation. The surface charge found at poly(ethyl acrylate) particles was as high as the one found at butyl acrylate/acrylic acid (99/1) copolymer particles. In both cases a very low amount of coagulum appeared. It may be that easier acid hydrolysis of ethyl ester groups is an important factor, causing better colloid stability of poly(ethyl acrylate) latex in comparison with the stability of, for example, polybutyl acrylate latex. The data indicate that a "critical" particle surface charge of the studied systems lies somewhere between 30 and 35 $\mu C/cm^2$.
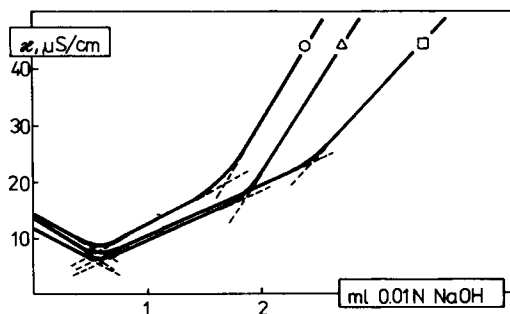

Fig. 4. Conductometric titrations of ion-exchanged poly(alkyl acrylate) latices: (O) poly(2-ethylhexyl acrylate); (△) poly(butyl acrylate); (□) poly(ethyl acrylate).

TABLE IV
Coagulum at Polymerization of Alkyl Acrylates (Distribution of Fenopon EP 120 R/E = 50/50) in Relation to Chemically Bound Surface Groups

Monomer, R/E at polymerization of analyzed polymer	$\bar{d}$, μm	Acid surface groups, meq/g		Surface charge, μC/cm^2			Coagulum at polymerization under R/E = 50/50, %
		Strong	Weak	Strong	Weak	Total	
EA, 2/98	0.29	0.021	0.058	9.8	27.0	36.8	1.4
BA, 2/98	0.29	0.020	0.040	9.3	18.7	28.0	24.4
2-EHA, 2/98	0.29[a]	0.021	0.033	9.8	16.5	26.3	77.0
BA + 1% AA, 50/50	0.22	0.021	0.084	7.4	29.7	37.1	2.4

[a] Approximate value due to difficulties in microscopic estimation.

CONCLUSIONS

The particle surface charge seems to be, under some specific conditions of semicontinuous emulsion polymerization, much more important than the type of emulsifier used. The chemically bound surface charge over about 30 to 35 $\mu C/cm^2$ markedly decreases the coagulum formation even under conditions of insufficient covering of particles by emulsifier. Carboxyl groups at poly(alkyl acrylate) particle surfaces result probably mainly from the acid hydrolysis of ester groups. At poly(ethyl acrylate) particle surfaces, a greater concentration of carboxyl groups was found than at higher poly(alkyl acrylates). This may be the main factor causing better stability of the system and thus minimum coagulum formation during the semicontinuous emulsion polymerization of ethyl acrylate.

References

1. J. Šňupárek, Jr., *J. Appl. Polym. Sci.*, **24**, 909 (1979).
2. N. Sütterlin, H. Kurth, and G. Markert, *Makromol. Chem.*, **177**, 1549 (1976).
3. J. Šňupárek, Jr., Contributed Papers, 3rd Meeting on Surface and Colloid Chemistry, May 24–25, 1977, Chrudim, ČSSR, p. 19.
4. H. J. van den Hul and J. W. Vanderhof, *J. Electroanal. Chem.*, **37**, 161 (1972).
5. J. W. Vanderhof and H. J. van den Hul, *Polym. Prepr.*, **16**(1), 155 (1975).
6. K. L. Barry and J. H. Peterson, *J. Am. Chem. Soc.*, **73**, 5195 (1951).
7. G. W. Ceska, *Polym. Prepr.*, **16**(1), 161 (1975).