

Particle Coagulation at Semicontinuous Emulsion Polymerization. I. Some Factors Affecting the Process

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Synopsis

The factors affecting the amount of coagulum appearing during the semicontinuous emulsion polymerization of acrylic monomers were studied. Monomers were added into the polymerization reactor in the form of emulsion. The stability of the polymerization system was greatly affected by the distribution ratio of a constant amount of emulsifier between the initial charge in the polymerization reactor and the monomer emulsion. The amount of arising coagulum was dependent also on the alkyl length of the alkyl acrylate and increased from ethyl acrylate to 2-ethylhexyl acrylate. The amount of appearing coagulum was essentially decreased by copolymerization with acrylic acid and sulfoethyl methacrylate, respectively. In the case of insufficient covering of particle surface by emulsifier, the colloid stability of polymerizing system was greatly increased by the presence of strong as well as weak acid groups chemically bound on the particle surface.

INTRODUCTION

Emulsion polymerization with continuous addition of monomers is a common route used for the preparation of polymer dispersions. This so-called semicontinuous process is advantageous for its easy control of the polymerization heat as well as for very homogeneous composition of products in the case of copolymerization.^{1,2} In this work a semicontinuous emulsion polymerization with the addition of monomers in the form of emulsion was studied. It was shown in the previous work³ that the final particle size and the mechanism of the particle growth may be greatly affected by the distribution of the amount of emulsifier used between the initial reactor charge and the monomer emulsion. At a high concentration of emulsifier in the initial reactor charge, that is, at a high value of the reactor/emulsion (R/E) distribution ratio, a large number of primary particles initially forms, which flocculate during the subsequent polymerization. The extent of the flocculation is controlled by the total amount of emulsifier present in the polymerization system.

Within the region of high R/E distribution ratio values the initial polymerization rate is very high, and an immediate conversion over 90% may be easily reached.^{4,5} The mechanical stability of these latices, however, is as a rule very poor because of insufficient covering of the particle surface by emulsifier. Such highly unsaturated (or equilibrium saturated) colloid systems are practically at the limit of flocculation. Thus, extensive flocculation (coagulation) of particles proceeds under mechanical treatment of the dispersion (i.e., at vigorous stirring, the great peripheral speed of the agitator affects a great shearing stress which causes coagulum formation by localized breaking of the latex). In this work, such extensive flocculation was studied from the point of view of stabilization of

particles by anionic emulsifier and by copolymerization with functional monomers.

EXPERIMENTAL

Materials used were: ethyl acrylate (Ugilor); butyl acrylate, 2-ethylhexyl acrylate, acrylic acid, and acrylonitrile (BASF); sulfoethyl methacrylate (Dow); N-methylolacrylamide (Cyanamid); Fenopon EP 110 and EP 120 [ammonium salts of sulfated alkylphenoxy poly(ethyleneoxy)ethanols differing in their degree of ethoxylation], and Gafac LO 529 and RA 600 (phosphate ester surfactants) (GAF); Etoxon AF 5 [sodium salt of sulfated alkylphenoxy poly(ethyleneoxy)ethanol] (Spolchemie, ČSSR); Texapon K 12 (sodium lauryl sulfate) (Henkel); ammonium persulfate p.a. and sodium metabisulfite p.a. (Lachema, ČSSR); and demineralized water.

Polymerizations were carried out in a 2000-ml stirred glass reactor under nitrogen atmosphere at 70°C (the peripheral speed of the stirrer was about 1 m/sec) with 200 g water, 6-g sodium metabisulfite and a variable amount of emulsifier charged into the reactor. After reaching the polymerization temperature addition of an emulsion consisting of 800-g monomers, 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 the reaction mixture for 1 hr at 70°C. The total amount of emulsifier was 2.25 wt. % active matter/polymer in all experiments.

Particle size was measured by electron microscopy, surface tension was estimated by stalagmometric method.

RESULTS AND DISCUSSION

The relation between the amount of emulsifier in the initial reactor charge and in the monomer emulsion (R/E ratio at the beginning of the emulsion addition) is of fundamental importance for the polymerization. Final particle size and surface tension of butyl acrylate/acrylonitrile/ethylene glycol dimethacrylate/N-methylolacrylamide copolymers prepared using variable R/E ratios of Fenopon EP 120 emulsifier are shown in Figure 1. A variation in R/E ratio causes significant differences in the surface tension development during the polymerization, that is, during the monomer emulsion addition.

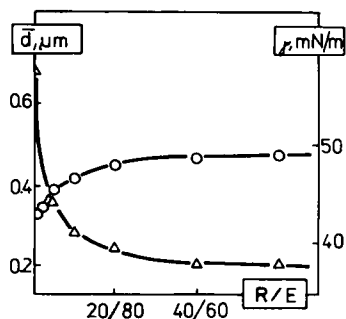


Fig. 1. Final particle size and surface tension of BA/N-methylolacrylamide/AN/EGDMA (83/4/10/3) copolymer latices in relation to the Fenopon EP 120 distribution ratio R/E : (Δ) \bar{d} ; (O) γ .

A schematic representation of three typical cases is given in Figure 2. At a high concentration of emulsifier in the reactor charge, a great number of particles are nucleated soon after the monomer emulsion addition is started. In such a case, the amount of emulsifier added to the polymerization system with the monomer emulsion is as a rule insufficient to cover a great particle-water phase interface. Consequently, this leads to the surface tension increase during the monomer emulsion addition (curve 1). Curve 2 represents the second limiting case, in which no emulsifier was placed into the reactor before the addition of the monomer emulsion. The amount of emulsifier continuously added to the reaction mixture with the monomer emulsion is sufficient to cover a relatively small particle-water phase interface. Then the surface tension of the system decreases rapidly and remains low (close to the value of micellar solution of the emulsifier) during the next course of the polymerization. In this case products with broad particle size distribution are formed. The distribution has frequently two maxima, because new particles appear up to the end of the monomer emulsion addition. Curve 3 represents the case which is important for practical use. In this case only a small amount of emulsifier had been added to the reactor (low value of R/E ratio) before the monomer emulsion addition was started. This enables a rapid initiation of the polymerization reaction at the beginning⁶ but does not lead to an extremely high number of primary particles. The surface tension after initial increase decreases again in consequence to the covering of the particle surface by emulsifier.

Electron-microscopic photographs of BA/AN/EGDMA/N-methylolacrylamide copolymers prepared at different R/E ratios are shown in Figure 3. The polymerization at high R/E ratios led to practically monodisperse products, but a tendency of the system to coagulum formation was observed.

Primary and secondary agglomeration^{7,8} proceeds during the emulsion polymerization of acrylic monomers. Its extent depends on the type of alkyl acrylate (monomer polarity), on the type of emulsifier, and, in the case of the studied semicontinuous process, also on the R/E distribution ratio of the emulsifier. The amount of coagulum, appearing during the polymerization due to insufficient stability, is very important from the practical point of view. The coagulum formation under standard conditions of the studied semicontinuous process depends on the R/E distribution ratio as well as on the type of alkyl acrylate, as shown in Figure 4. Fenopon EP 120 was used in the experiments. The differences between the amount of coagulum arising at polymerization of alkyl acry-

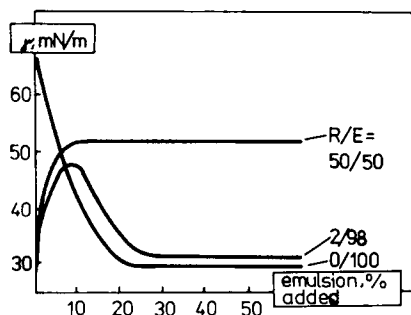


Fig. 2. Schematic representation of surface tension development during addition of monomer emulsion in relation to the emulsifier distribution R/E .

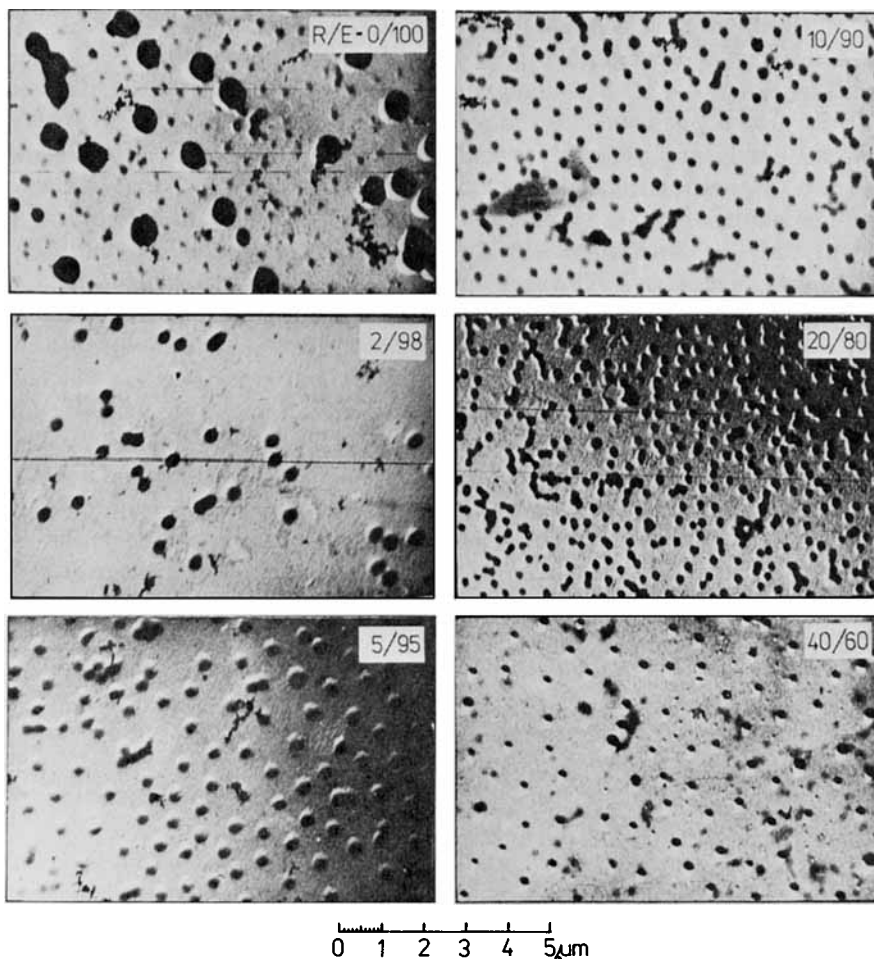


Fig. 3. Electron-microscopic photographs of BA/N-methylolacrylamide/AN/EGDMA (83/4/10/3) copolymer latex particles prepared at different Fenopon EP 120 distribution ratios R/E .

lates with different alkyl length are mainly caused by different stability of the polymer particles (the differences in the particle hardness probably also influence the coagulation process to some extent). Assuming electrostatic stabilization, different stability of the latices may be caused (1) by the character of the anionic emulsifier adsorption on the polymer-water phase interface and (2) by the difference in the stabilization by chemically bound surface groups.

Characteristic properties of poly(alkyl acrylate) latices produced with Fenopon EP 120 at $R/E = 50/50$ are summarized in Table I. The average particle sizes in the samples differ only slightly; thus, the specific particle surfaces do not differ significantly. In accordance with results of Yeliseeva and co-workers,⁷ a different degree of adsorption saturation in an equilibrium state at the end of polymerization was found: the highest at poly(ethyl acrylate) and the lowest at poly(2-ethylhexyl acrylate) particles. From this fact different surface areas occupied by an emulsifier molecule in the saturated adsorption layers also result. The table also shows relative values of the areas found by titration of deionized dispersions by sodium lauryl sulfate (Texapon K 12) in comparison with the data

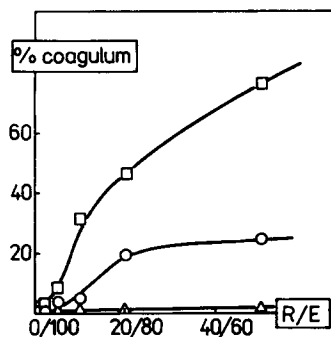


Fig. 4. Coagulum formation during polymerization of different alkyl acrylates in relation to R/E distribution of Fenopon EP 120: (\square) 2-EHA; (\circ) BA; (\triangle) EA.

TABLE I
Characteristic Properties of Poly(alkyl Acrylate) Dispersions Prepared with Fenopon EP 120 at $R/E = 50/50$

Monomer	EA	BA	2-EHA
Surface tension (20% solids), mN/m	42.6	47.1	47.1
\bar{d}_r ($\Sigma n_i d_i^3 / \Sigma n_i d_i^2$), μm	0.24	0.23	(0.23) ^a
Specific particle surface, m^2/cm^3	25.00	26.09	(26.09)
Degree of adsorption saturation at equilibrium at end of polymerization, %	66.3	49.6	46.5
Relative surface per molecule of emulsifier:			
Fenopon EP 120 at equilibrium	1.00	1.04	(1.04)
Fenopon EP 120 at saturation	1.00	0.78	(0.73)
Sodium lauryl sulfate (Texapon K 12) at saturation (by titration of ion-exchanged samples)	1.00	0.63	—
Sodium lauryl sulfate (Yeliseeva ⁷)	1.00	0.71	—

^a Approximate value due to difficulties in microscopic estimation.

found with this emulsifier by Yeliseeva. It may be concluded that the minor differences in the adsorption of emulsifier at the polymer particle surfaces with different polarity at equilibrium, i.e., at the end of the monomer emulsion addition, do not explain the differences in the amount of appearing coagulum. The results of Yeliseeva even indicate that the poly(butyl acrylate) particles should have been better stabilized by emulsifier than the poly(ethyl acrylate) particles, due to a higher affinity of the lipophilic part of the emulsifier molecule to the surface of lower polarity. It seems reasonable to take into account also the effect of the groups that are chemically bound on the particle surface. This is borne out also by the fact that a great amount of coagulum appeared during the polymerization of butyl acrylate at $R/E = 50/50$ also when some other emulsifiers were used. For example, with Fenopon EP 110, 42 wt.%; with Etoxan AF 5, 50%; with Gafac LO 529, 86%; and with Gafac RA 600, even 100% of the total polymer was coagulated. On the other hand, the coagulum formation was essentially decreased by incorporation of sulfo or carboxyl groups on the particle surface, as the data in Figure 5 show. These groups were incorporated by copolymerization of butyl acrylate with acrylic acid and sulfoethyl methacrylate, respectively. Part II of this study deals with the characterization of the particle surfaces in relation to coagulum formation, i.e., in relation to particle stability.⁹

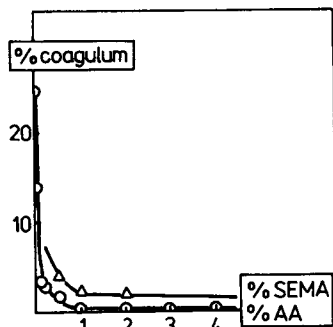


Fig. 5. Coagulum formation during copolymerization of butyl acrylate with acrylic acid and sulfoethyl methacrylate in relation to the amount of copolymerized functional monomer. Distribution ratio R/E of Fenopon EP 120 = 50/50: (O) BA/SEMA; (Δ) BA/AA.

CONCLUSIONS

In semicontinuous emulsion polymerization with addition of monomers in the form of an emulsion, the tendency of the polymerization system to form coagulum was greatly impeded by the emulsifier distribution between the initial reactor charge and the emulsion of monomer. The tendency to coagulum formation increased with increasing alkyl length of alkyl acrylate. There were no significant differences in emulsifier adsorption at the particle surfaces at the end of polymerization, i.e., at equilibrium state. A significant factor, however, seems to be the concentration of chemically bound functional groups situated on the particle surface, which are able to strongly minimize particle coagulation in the case of insufficient covering of particle surface by emulsifier.

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