

Some Factors Affecting the Particle Growth in Semicontinuous Emulsion Polymerization of Acrylic Monomers*

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Synopsis

Semicontinuous emulsion polymerization of ethyl acrylate/ethyleneglycol dimethacrylate (90/10) and butyl acrylate/ethyleneglycol dimethacrylate (90/10) was studied. In the process a monomer emulsion feed was used, and the particle growth and the particle flocculation were found to be a competitive process. This was affected by distribution of water phase as well as by the distribution of emulsifier between the initial reactor charge and the emulsion of monomers. Several periods of particle generation were found during the process. The extent of particle flocculation was strongly affected by electrolyte concentration in the system and by copolymerization of acid groups containing comonomers.

INTRODUCTION

Emulsion polymerization is a relatively complicated process in which the addition of polymerization kinetics is very closely connected with colloid properties of the polymerizing system. There are three intervals, which may be distinguished in a batch process: in interval I new particles are formed, in interval II the particle growth proceeds up to interval III in which the polymerization is completed. According to classical Harkins-Smith-Ewart¹ micellar theory based on styrene emulsion polymerization data, the nucleation of particles takes place solely in monomer swollen micelles which are transformed into polymer particles by absorption of radicals from the aqueous phase. This theory, however, does not satisfactorily describe the particle nucleation in cases of polar, i.e., more water-soluble monomers. The theory of homogeneous nucleation proposed by Fitch and Tsai² is now widely accepted.^{3,4} The primary initiator radical would be unlikely to move into an emulsifier micelle or an existing particle, because it is hydrophilic (prefers the aqueous phase, and it is repelled by micelles and particles if anionic emulsifiers are employed in the recipe. Fitch and Tsai have proposed a mechanism, which implies that primary particles are formed in an aqueous phase by precipitation of oligomeric radicals above a critical chain length. Oligomeric radicals should behave much like classical emulsifiers, and hence deposition on a particle or micelle is very probable. The rate of new particles formation there is $dN/dt = R_i - R_c - R_f$, where R_i , R_c , and R_f are rates of oligoradical generation, oligoradical capture, and limited flocculation of particles, respectively.

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The tendency of acrylic monomers to polymerize in water phase in absence of emulsifier is enhanced with increasing monomer polarity, as was shown in our previous work.⁵ The initial polymerization rate increases rapidly with the increasing emulsifier concentration; this indicates the possibility of a competitive action of both nucleation mechanisms (homogeneous and micellar). It was shown also by Peppard,⁶ from the results obtained with styrene, that nucleation took place both by homogeneous and micellar mechanisms. Sütterlin et al.⁷ investigated particle formation in relation to emulsifier concentration with a series of acrylates in batch polymerizations. The relationship of the number of particles vs. emulsifier concentration differed for different monomers. On the other hand, also the size of emulsifier micelles may influence the number of particles formed.⁸ This indicates that the micelles play an important role in the nucleation of particles at emulsifier concentrations above the critical micelle concentration (CMC).

Semibatch or semicontinuous emulsion polymerization is a widely used technique in the synthetic latex industry today. In this process a single reactor is used, but the monomer and some other ingredients are added continuously over a period of a few hours. Semicontinuous emulsion polymerization differs from the batch operations in several significant features: (1) the total volume of the reactor charge changes during the polymerization; (2) if monomers are added in an emulsion form, the surfactant concentration changes during the polymerization and the particle nucleation may proceed during all the reaction time. In this work, the particle growth and the changes in particle size distribution during the semicontinuous emulsion polymerization of some acrylic monomers were studied.

EXPERIMENTAL

Polymerizations were carried out in a 2000-mL stainless reactor at 80°C, under nitrogen atmosphere using persulfate/metabisulfite initiation system. Characteristic reaction conditions were as follows: (1) no seed latex, only a part of total amount of water, a part of total amount of emulsifier and all Na metabisulfite were charged into the reactor; (2) monomers were fed in an emulsion form; ammonium persulfate was dissolved in the emulsion; (3) monomer emulsion was continuously added into the reactor at a constant feeding rate (feeding time $\tau = 3$ h), polymerization proceeded at instantaneous conversions over 90% (starved polymerization); (4) solids content raised during the polymerization over 50 wt %.

Materials: Butyl acrylate, ethyl acrylate, acrylic acid (BASF), technical grade, ethyleneglycol dimethacrylate (Röhm), technical grade, sulfoethyl methacrylate (gift sample Dow), Fenopon EP 120 (ammonium salt of nonyl-phenol polyethylene-glycoether sulfate—34% active matter) (GAF), ammonium persulfate and sodium metabisulfite (Lachema), p.a. grade, distilled water.

Total Polymerization Charge: Monomers 800 g, water 700 g, Fenopon EP 120 52 g, ammonium persulfate 12 g, sodium metabisulfite 6 g (in experiments with variable initiator concentrations the weight ratios persulfate/metabisulfite = 2/1 were kept constant).

Particle size distributions were estimated by electron microscopy, 10 wt %,

of ethyleneglycol dimethacrylate was used in monomer mixtures to crosslink the soft polymer particles.

RESULTS AND DISCUSSION

The studied system was complicated from several points of view. The polymerization started as unseeded system in the initial period, but in later stages the presence of polymer particles changed the system to a seeded one. The polymerization was initiated by persulfate/metabisulfite redox system supposing the radical production by reaction⁹



Ammonium persulfate was fed continuously with the monomer emulsion into the reactor containing the reducing part of the initiation system. The reaction is very fast at 80°C; thus, a formation of ca. 5×10^{18} free radicals/s was supposed in the standard recipe. Under such a relatively high rate of radical formation, the polymerization proceeded at instantaneous conversions $c_p \sim 0.9$. So the reaction charge volume V_t (relating to the time of the emulsion feeding t) could be calculated

$$V_t = V_{0w} + \int_0^t \frac{dV_w}{dt} + \frac{\rho_m}{\rho_p} \int_0^t \frac{dV_m}{dt}$$

where V_m and V_w are volumes of monomer and water in the emulsion feed, ρ_m and ρ_p are densities of monomer and polymer, respectively, and V_{0w} represents the initial volume of water in the reactor charge.

The rate of particle formation according to Fitch depends on the generation rate of oligomeric radicals R_i , and it is decreased by the oligomeric radicals capture by existing particles and by flocculation of existing particles. Thus, the particle formation during the studied semicontinuous process should be affected by the instantaneous concentration of free emulsifier in the system and also by the polymer/water phase ratio at a given time $(V_p/V_w)_t$. If a constant amount of emulsifier, water, and monomer is used, the emulsifier concentration development depends on the initial distribution ratio of water and emulsifier between the reactor charge and the monomer emulsion. These are named $(R/E)_W$ and $(R/E)_E$, respectively. Also the ratio V_p/V_w changes during the polymerization and its course depends on $(R/E)_W$ ratio as is shown in Figure 1.

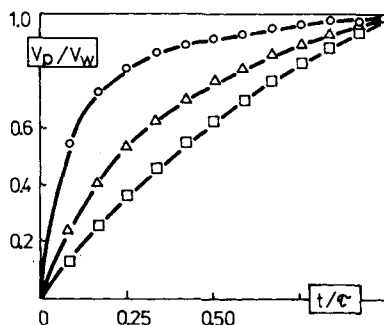


Fig. 1. Development of the V_p/V_w ratio for various $(R/E)_W$ ratios: (O) 0.077; (Δ) 0.400; (\square) 1.333.

$(R/E)_E$ Factor and the Monomer Polarity

The total number of particles in the reactor, N_R , formed during the polymerization of EA/EGDMA (90/10) and BA/EGDMA (90/10) in relation to $(R/E)_E$ is shown in Figure 2. In these experiments a constant ratio $(R/E)_W = 0.4$ and a constant total amount of emulsifier were used. The total number of particles in the early stages of polymerization was much greater at $(R/E)_E = 1.0$; in the following course, however, a limited flocculation of particles proceeded. In the case of $(R/E)_E = 0.02$ the number of particles appearing in the initial polymerization period was smaller by about 1–2 logarithmic orders, and their number did not change much during the following polymerization. The tendency of growing particles to flocculate depends predominantly on the ratio between the total surface area of particles and an instantaneous concentration of emulsifier. Both these values changed during the polymerization and the extent of the limited flocculation was governed mainly by the saturation of the particle surface by emulsifier. In the case of $(R/E)_E = 1.0$, the specific particle surface area was about $100 \text{ m}^2/\text{cm}^3$; this decreased rapidly in the following polymerization course, as is shown in Figure 3. The total particle numbers and, consequently, also the specific surface areas exhibited oscillations during the polymerization. This indicates that a generation of new particles proceeded even in the case in that the system tended to particle flocculation. Such oscillations have been usually observed in polymerization in continuous stirred tank reactors,^{10,11} and they are associated with particle formation and growth factors. High rates of particle formation occur when the free emulsifier concentration is large. The particles then can grow rapidly, generating enough surface area to cause emulsifier starved system with very small rate of particle formation, even with particle flocculation. Since emulsifier is continuously added, it is possible for the system to return to an emulsifier excess condition.

Figure 2 shows that the system with ethyl acrylate produces smaller particles in comparison with butyl acrylate polymerization. In polymerization of ethyl acrylate more oligomeric radicals should appear due to its greater water solubility. In later stages of polymerization, however, polyethyl acrylate particles should undergo flocculation to a greater extent than polybutyl acrylate particles ac-

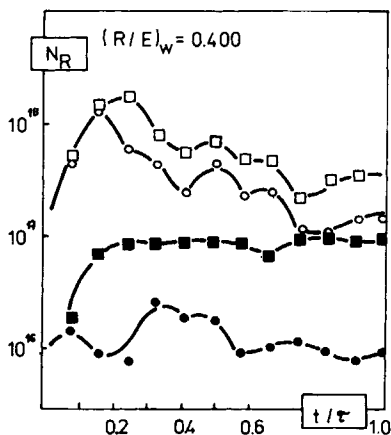


Fig. 2. Development of total particle number N_R in systems EA/EGDMA (90/10) and BA/EGDMA (90/10) at different $(R/E)_E$ ratios 1.00 [(O) BA; (□) EA] and 0.02 [(●) BA; (■) EA].

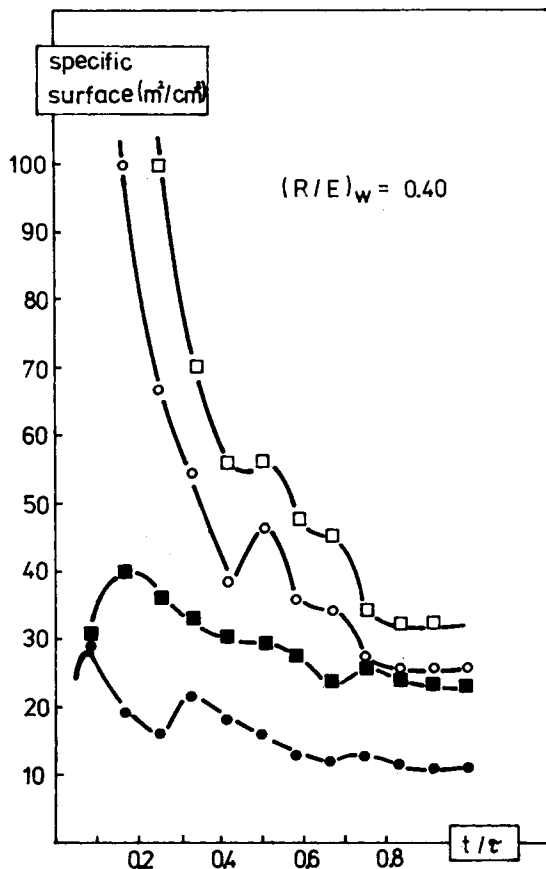


Fig. 3. Development of specific surface areas in systems EA/EGDMA (90/10) and BA/EGDMA (90/10) at different $(R/E)_E$ ratios 1.00 [(O) BA; (□) EA] and 0.02 [(●) BA; (■) EA].

According to data of various authors.^{7,12,13} In their recent work Sütterlin and Markert¹⁴ also found that ethyl acrylate forms smaller particles in polymerization by semicontinuous process. We suppose that this phenomenon may be explained by the presence of carboxylic groups chemically bound onto the polyacrylate particle surface. These carboxylic groups result from the autocatalyzed acid hydrolysis of ester groups, which proceeds in polymerization of ethyl acrylate to greater extent, as it was shown in our previous work^{15,16} and also by Fitch et al.¹⁷ The growth of mean particle diameters d_n , d_s , d_v , and d_r for EA/EGDMA (90/10) and BA/EGDMA (90/10) is shown in Figure 4. Several maximas and minimas in these relationships again indicate periodic generation of new particles in both systems. The differences between d_n , d_s , d_v , and d_r are caused by the polydispersity of the systems.

The shape of particle size distribution changed with EA/BA ratio, as is shown in Figure 5. The cumulative volume distribution curves in the middle and at the end of polymerization ($t/\tau = 0.5$ and 1.0) indicate the differences in particle growth of monomers with different polarity and different tendency to acid hydrolysis. The distribution curves of all these systems were very similar at the beginning of the polymerization,¹⁸ but differentiated during the following polymerization course. Especially in the case of butyl acrylate polymerization,

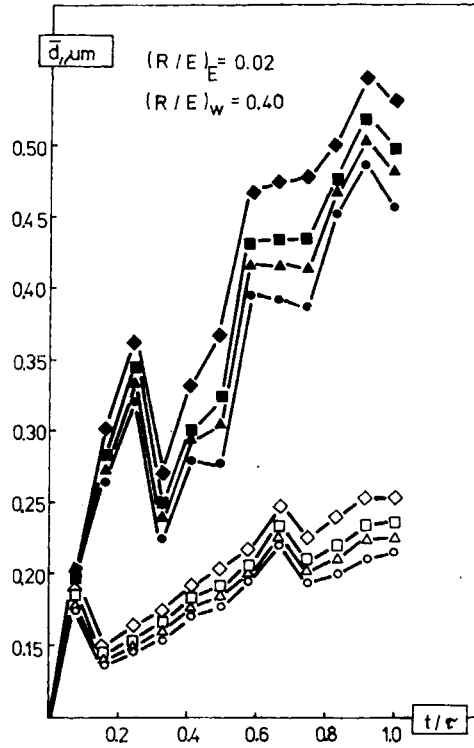


Fig. 4. Particle diameter growth for systems EA/EGDMA (90/10) and BA/EGDMA (90/10) under the same conditions: $\bar{d}_n = \sum n_i d_i / \sum n_i$; [(O) EA; (●) BA]; $\bar{d}_s = (\sum n_i d_i^2 / \sum n_i)^{1/2}$ [(Δ) EA; (▲) BA]; $\bar{d}_v = (\sum n_i d_i^3 / \sum n_i)^{1/3}$ [(□) EA; (■) BA]; $\bar{d}_r = \sum n_i d_i^3 / \sum n_i d_i^2$ [(◇) EA; (◆) BA].

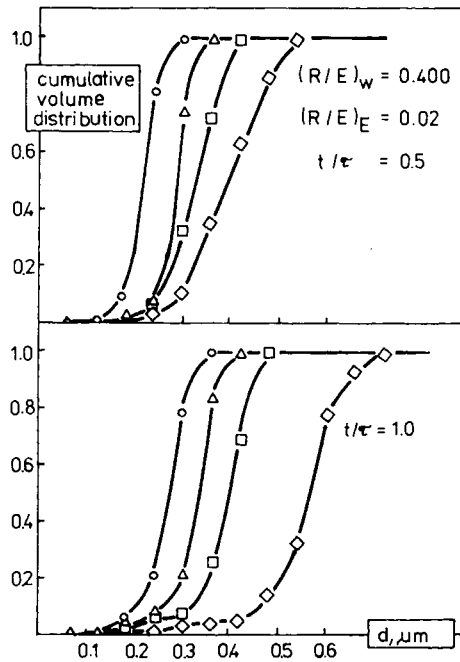


Fig. 5. Cumulative volume distributions at $t/\tau = 0.5$ and 1.0 in relation to copolymer composition, BA/EA/EGDMA (wt %): (O) 0/90/10; (Δ) 45/45/10; (□) 70/20/10; (◇) 90/0/10.

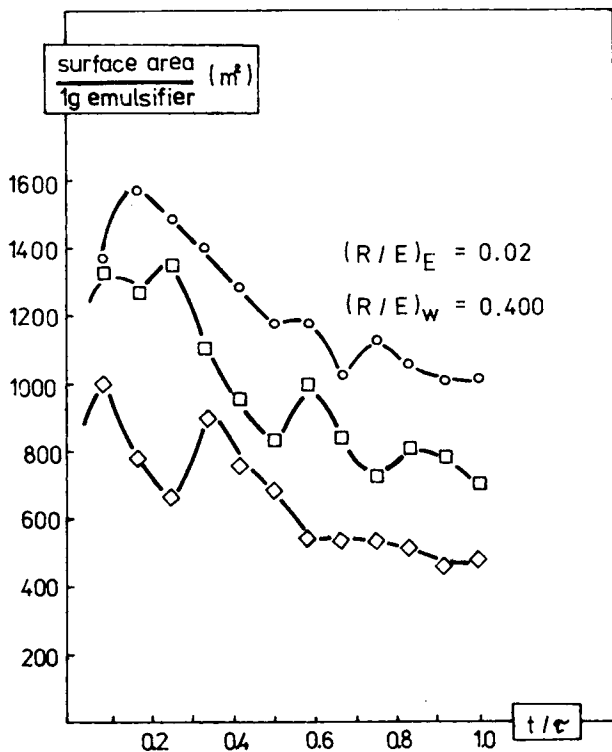


Fig. 6. Development of particle surface/1.0 g emulsifier monomer feeds, BA/EA/EGDMA (wt %): (○) 0/90/10; (□) 70/20/10; (◇) 90/0/10.

the particle size distribution curves became broader at the end of polymerization. This was probably caused by secondary flocculation and by the fact that the rate of particle growth increased with particle size. Since larger particles contain, on average, a higher concentration of free radicals and thus exhibit a more rapid growth rate, the observed particle size distribution is skewed toward the large end. This behavior was already predicted by Stockmayer.¹⁹ In Figure 6 it is shown that the particle surface belonging to 1.0 g of emulsifier gradually decreased during the polymerization. The surface area at a given time t/τ increased with the increasing content of EA in the system. That means that the greater is the content of EA in the monomer mixture, the less emulsifier is necessary for stabilizing the system. The suggestion that a great role here play carboxylic groups chemically bound onto particle surface is borne out also by particle size distribution curves of copolymers BA with acrylic acid and sulfoethyl methacrylate, respectively (Fig. 7). Copolymerization of these two monomers with butyl acrylate pushed the BA/EGDMA distribution curve toward the EA/EGDMA one. It was shown in our previous work that BA/AA (99/1) copolymer contained similar concentration of carboxylic groups on the particle surface as polyEA homopolymer. The two systems also exhibited similar mechanical stability.^{14,15}

$(R/E)_W$ Factor and Electrolyte Concentration

Another factor affecting the capture of oligomeric radicals and flocculation of particles was the distribution of water phase between reactor and monomer

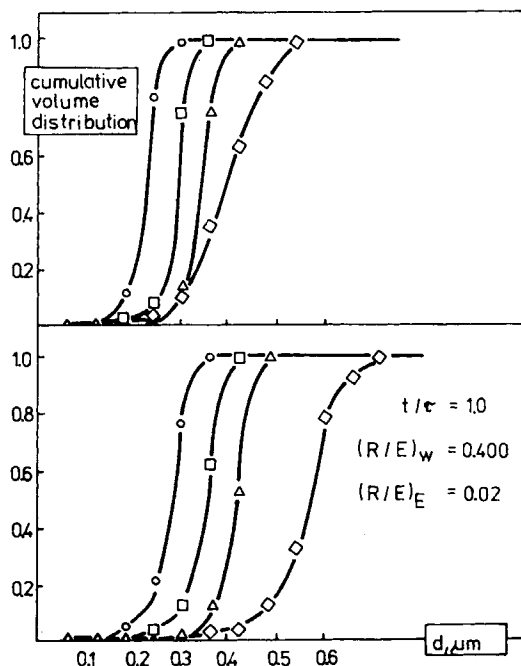


Fig. 7. Cumulative distributions at $t/\tau = 0.5$ and 1.0 for various monomer feeds, BA/EA/EGDMA/KA/SEMA (wt %): (○) 0/90/10/0/0; (□) 85/0/10/5/0; (Δ) 85/0/10/0/5; (◇) 90/0/10/0/0.

emulsion $(R/E)_w$. As is shown in Figure 1, high values of the ratio $(R/E)_w$ impede the development V_p/V_w during the polymerization. The higher V_p/V_w is, the greater the probability of collision of oligomeric radicals with existing particles. Total numbers of particles appearing in polymerization of EA/EGDMA (90/10) at various initial $(R/E)_w$ ratios are shown in Figure 8. The extent of particle flocculation at low values $(R/E)_w$ was impeded also by greater electrolyte concentration in the initial reactor charge. In the polymerization recipe, all the amount of reducing agent was added into the initial reactor charge. Consequently, decreasing of $(R/E)_w$ ratio from 1.333 to 0.077 led to increasing

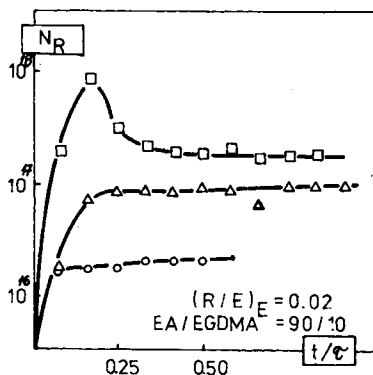


Fig. 8. Development of total number of particles, N_R , in the system EA/EGDMA (90/10) at different $(R/E)_w$ ratios: (○) 0.077; (Δ) 0.400; (□) 1.333.

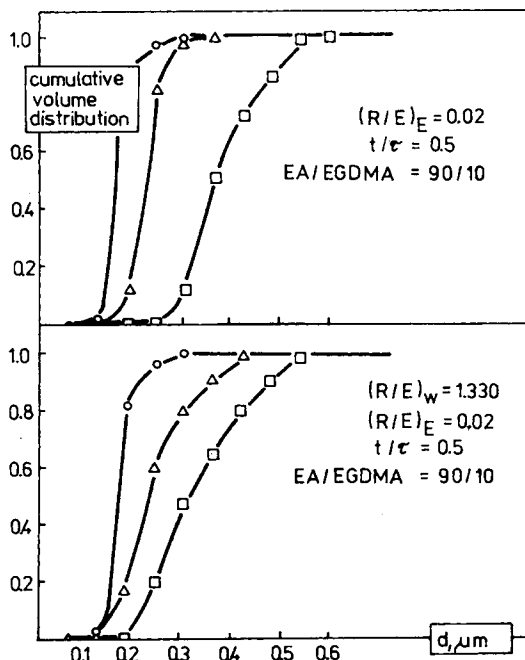


Fig. 9. Cumulative volume distributions in the system EA/EGDMA (90/10) at $t/\tau = 0.5$ for various $(R/E)_W$ ratios and various concentrations of electrolyte in the initial reactor charge. Top: $(R/E)_W$, C_{I_R} (mol/L): (O) 1.333, 0.08; C_{NaClR} (mol/L): (O) 0.08, 0; (Δ) 0.08, 0.13; (\square) 0.08, 0.26.

of initial sodium metabisulfite concentration from 0.08 to 0.64 mol/L. In anionically stabilized systems electrolyte lower the electric double layer thickness and as a consequence decrease the particle stability. This results in particle flocculation to a greater extent. A similar action also is exercised by the addition of NaCl to the initial reactor charge. This is shown in Figure 9, where particle volume distributions at $t/\tau = 0.5$ are compared. The effect of NaCl addition on the specific particle surface during the polymerization is evident from Figure 10. Rapid decreasing of the particle surface indicates a greater extent of particle flocculation in presence of electrolyte.

Acid groups from primary radicals $\text{OSO}_4\cdot$ and $\text{SO}_3\cdot$ remain chemically bound at the particle surface where they increase the electric charge and improve the particle stability. On the other hand, increased initiator concentration in water phase negatively affects the particle stability. E.g., in polymerization of BA/EGDMA (90/10) system with constant $(R/E)_W$ and $(R/E)_E$ ratios, the increasing initiator concentration led to rapid particle flocculation even in very early stages of polymerization. Particle volume distributions at $t/\tau = 0.16$ are shown in Figure 11. A further increase of the initiator concentration resulted in spontaneous coagulation of the system. Similar results concerning continuous polymerization of vinyl acetate were published also by Kiparissides et al.¹¹

CONCLUSIONS

In semicontinuous emulsion polymerization with a monomer emulsion feed the particle nucleation and particle growth proceeds as a competitive process.

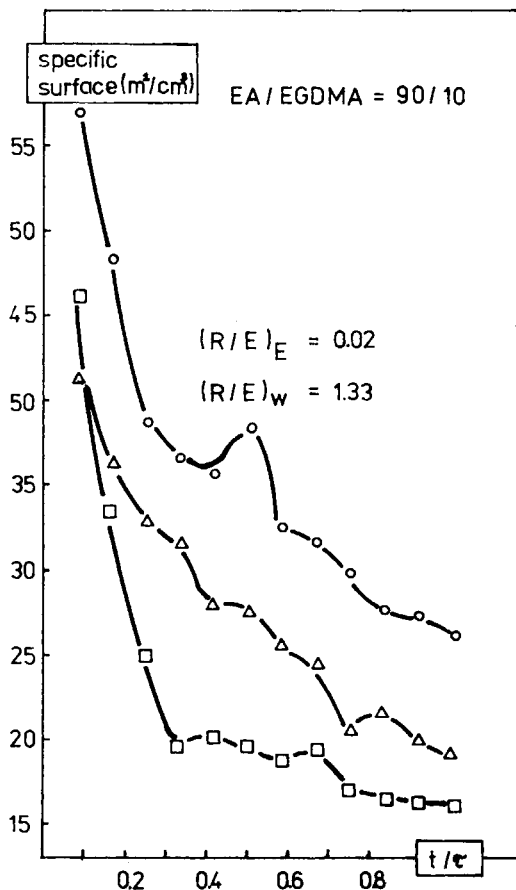


Fig. 10. Development of specific particle surface in the system EA/EGDMA (90/10) for various electrolyte concentrations in the initial reactor charge: C_{IR} , C_{NaClR} (mol/L): (○) 0.08, 0; (Δ) 0.08, 0.13; (□) 0.08, 0.26.

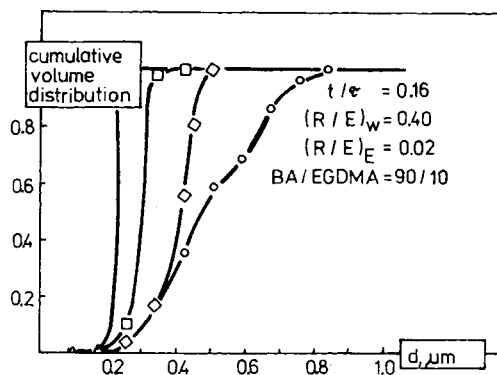


Fig. 11. Cumulative volume distributions in system EA/EGDMA (90/10) at $t/\tau = 0.16$ for various concentrations of initiator. C_{IR} = concentration (mol/L) of sodium metabisulfite in the initial reactor charge: (Δ) 0.03; (□) 0.08; (◇) 0.16; (○) 0.32.

Several periods of particle nucleation followed by particle flocculation appear. The process is affected by the water phase and emulsifier distribution between the initial reactor charge and monomer emulsion. The extent of particle flocculation is strongly affected by electrolyte concentration in the system. Excess of water-soluble initiator may lead even to spontaneous coagulation of the polymerization charge in spite of the stabilizing effect of higher concentration of chemically bound strong acid surface groups. The tendency of particles towards flocculation decreases if carboxylic groups are present at the particle surface. These are formed by acid hydrolysis or may be incorporated into polymer by copolymerization with, e.g., acrylic acid.

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References

1. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
2. R. M. Fitch and C. H. Tsai, *Polymer Colloids*, R. M. Fitch, Ed., Plenum, New York, 1971, p. 73.
3. F. K. Hansen and J. Ugelstad, *J. Polym. Sci.*, **16**, 1953 (1978).
4. F. K. Hansen and J. Ugelstad, *J. Polym. Sci.*, **17**, 3033, 3047, 3069 (1979).
5. J. Šňupárek, Jr., *Angew. Makromol. Chem.*, **88**, 61, 69 (1980).
6. B. Peppard, thesis, Iowa State University, 1974.
7. N. Sütterlin, H. J. Kurth, and G. Markert, *Makromol. Chem.*, **177**, 1594 (1976).
8. I. Piirma and P. C. Wang, *Emulsion Polymerization*, I. Piirma and J. L. Gardon, Eds., ACS Symposium Series. No. 24, American Chemical Society, Washington, D.C., 1976, p. 34.
9. K. L. Berry and J. H. Peterson, *J. Am. Chem. Soc.*, **73**, 5195 (1951).
10. H. Gerrens, *Kolloid Z.*, **227**, 93 (1968).
11. C. Kipparisides, J. F. MacGregor, and A. E. Hamielec, *Polymer Colloids II*, Fitch, Ed., Plenum, New York, 1979, p. 555.
12. V. I. Yeliseeva and A. V. Zuikov, *Polym. Prepr.*, **16**, 143 (1975).
13. B. R. Vijayendran, *Polymer Colloids II*, Fitch, Ed., Plenum, New York, 1979, p. 209.
14. N. Sütterlin and G. Markert, 27th IUPAC Int. Symp. Macromol., Strasbourg, 1981, p. 341.
15. J. Šňupárek, Jr., *J. Appl. Polym. Sci.*, **24**, 909 (1979).
16. J. Šňupárek, Jr. and A. Tuťálková, *J. Appl. Polym. Sci.*, **24**, 915 (1979).
17. R. M. Fitch, C. Gajria, and P. J. Tarcha, *J. Colloid Interface Sci.*, **71**, 107 (1979).
18. J. Šňupárek, Jr., Z. Klečková, and A. Tuťálková, 27th IUPAC Int. Symp. Macromol., Strasbourg, 1981, p. 345.
19. W. H. Stockmayer, *J. Polym. Sci.*, **24**, 314 (1957).

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