EFFECT OF COAGULATIVE MECHANISM OF PARTICLE GROWTH ON THE STRUCTURAL HETEROGENEITY OF ETHYL ACRYLATE–METHACRYLIC ACID COPOLYMER LATEX PARTICLES

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Latex particles of ethyl acrylate–methacrylic acid copolymers prepared by semicontinuous emulsion polymerization with a monomer emulsion feed were found to disintegrate into smaller subparticles on alkalization. This phenomenon observed by light scattering and scanning electron microscopy is explained in terms of heterogeneous structure of latex particles which are agglomerates of small particles formed by coagulation during polymerization. The influence of particle size and polymerization route on particle heterogeneity is discussed.

In emulsion polymerization the radical-initiated vinyl monomer addition proceeds in a heterogeneous colloidal latex system. The mechanism of polymerization comprises a stage in which particles nucleate and another stage in which the nuclei grow to a larger size by polymerization. In fact, the particle nucleation and growth stages overlap or occur concurrently. The nucleation is not always fully reproducible and successive polymerizations using the same recipe may give different numbers of particles. Generally, the number of nucleated particles depends on many factors such as the type and concentration of emulsifier, polarity of monomers, type and concentration of electrolyte, the rate of radical generation as well as on the polymerization process.

The basic mechanism which is operative in particle nucleation comprises: entry into micelles[1,2] (radicals from the aqueous phase initiate the polymerization in micelles and in monomer particles directly), homogeneous nucleation[3 – 6] (polymerization degree of oligomeric radicals in aqueous phase increases until it reaches a critical value, the radicals precipitate and form primary particles), and coagulative nucleation[7,8] (precursor particles formed by either of the two steps undergo coagulation to form stable particles).

This discussion deals with latices prepared by non-seeded and seeded emulsion copolymerization of ethyl acrylate and methacrylic acid. Non-seeded semicontinuous emulsion polymerization with a monomer emulsion feed is a complex process in which particle nucleation and subsequent growth are very closely associated with changes in colloid stability and composition of the polymerizing system during the process. The reaction charge volume, emulsifier concentration and polymer fraction change continuously during the monomer emulsion addition. Radical polymerization proceeds as a rule under monomer-starved conditions with an instantaneous conversion[9] over 90%. Final particle stability depends strongly on the distribution of emulsifier between the initial reactor charge and monomer emulsion feed, on the distribution of water between the reactor and monomer emulsion, on the type of emulsifier and on electrolyte concentration[10]. It was shown that the system oscillates during the polymerization between colloidally more or less stable states as a result of generation of new particles followed by their capture by older ones and their coagulation[11].

Semicontinuous process makes it possible to prepare copolymers of a relatively narrow chemical distribution. Generally, the slower is the rate of monomer addition, the slower polymerization rate and narrower distribution of copolymer composition results. A starved semicontinuous copolymerization can be used for preparation of a narrow distribution of copolymer composition in systems with disparate reactivity ratios and even with very different water solubility. It is apparent, however, that the mechanism of particle growth in such polymerization is very complicated. That is why a polymerization using the same monomer ratio but a slightly different polymerization recipe may give particles with different macrostructure.

In the previous studies of ethyl acrylate–methacrylic acid latex copolymers alkalized in the presence of methanol, anomalous results were obtained[12]. They indicated disintegration of original latex particles into small crosslinked subparticles during alkalization and suggested the heterogeneity of latex particles probably caused by agglomeration during polymerization. In this paper the structure of latex particles prepared in a different way was investigated in more detail.

EXPERIMENTAL

Dispersions. Three latex dispersions of ethyl acrylate–methacrylic acid copolymers containing 15 wt.% of methacrylic acid were prepared (Table I). Semicontinuous polymerizations were carried out in a 3-l stainless steel reactor at 80 °C, under nitrogen atmosphere, using ammonium peroxodisulfate–sodium disulfite initiator system. Technical grade ethyl acrylate (Chemical Works, Sokolov, The Czech Republic) and methacrylic acid (Roehm, Darmstadt, Germany) in emulsion using Disponil AES 60 (Na alkylaryl polyglycol ether sulfate, 34% of active substance, Henkel) were fed at a constant rate during 3 h. After polymerization the latex contained 25 wt.% of solids and pH was 1 – 2.

Latex EM 1 was prepared by polymerization in the presence of emulsifier in the initial reactor charge. In the preparation of latex EM 2, a low amount of water, no emulsifier in the initial reactor charge and a higher concentration of ammonium peroxodisulfate were used to obtain particles of larger size. Latex EM 3 was prepared by a seeded semicontinuous emulsion polymerization with initial reactor charge containing small amount of EM 1 latex particles and a small concentration of emulsifier.

Light scattering measurements. The diameters of particles were determined by light scattering methods. Static light scattering (SLS) was measured by means of photodiffusometer Fica 40000 in the angular range $\theta = 30 - 150°$ with vertically polarized light of wavelength $\lambda_0 = 546$ nm. The samples were optically purified using sintered glass filter Jena Glass F 4. All measurements were carried out at 25 °C with samples stabilized one day after their preparation.

The dependence of excess Rayleigh ratio $R(K)$ (reduced intensity of scattered light) on scattering vector $K = (2\pi/\lambda) \sin(\theta/2)$, where λ is the wavelength of light scattered, was measured. To estimate particle diameter d, the $P(K)$ functions were calculated according to the equation[13]

$$P(K) = [(3/K^3d^3)\,(\sin Kd - Kd\,\cos Kd)]^2 \qquad (1)$$

and compared with the experimental plots $R(K)$ vs K in the range of high values of K ($\theta > 90°$). The size of particles was also measured by dynamic light scattering (DLS) using a Coulter Nano-Sizer (Coulter Electronic Ltd, England) apparatus.

Scanning electron microscopy (SEM) was performed using a JSM 6400 JEOL electron microscope. Samples were prepared by spraying highly dilute dispersions with a microspraying device on freshly split surfaces of mica. This procedure ensured uniform distribution of dispersion particles on a mica surface without marked aggregation. The samples were sputter-coated with a thin gold layer (10 nm). To improve the contrast, the observation was carried out in the electron beam tilt angle to the mica surface 60°.

TABLE I
Polymerization recipes (in g) for latices EM 1, EM 2 and EM 3

Recipe	EM 1	EM 2	EM 3
Reactor charge			
Water	400	200	400
Seed latex EM 1	0	0	40
Disponil AES 60	2.6	0	0
Ammonium peroxodisulfate	2.0	0	0
Monomer emulsion feed			
Water	800	1 000	800
Disponil AES 60	26	13	26
Ammonium peroxodisulfate	2	6	4
Ethyl acrylate	340	340	340
Methacrylic acid	60	60	60

RESULTS

Particle diameters of the latex samples determined by light scattering methods differed (Table II). On alkalization with NH_4OH to pH 9.4 – 9.6 the latex copolymers did not dissolve but only swelled[14] as the polymer material was crosslinked[15]. After acidification with acetic acid to pH 3.6 – 3.8 the latex character of such recovered systems was restored again. However, the dimensions of particles were smaller as indicated by the decrease in the slopes of $R(K)$ functions at higher values of K (Fig. 1) as well as in

TABLE II

Latex particle diameters determined by static (d_{SLS}, nm) and dynamic light scattering (d_{DLS}, nm). A original latex, B recovered latex (after alkalization and acidification)

Latex	d_{SLS}		d_{DLS}	
	A	B	A	B
EM 1	100	80	103	75
EM 2	400	80	430	53
EM 3	230	170	226	175

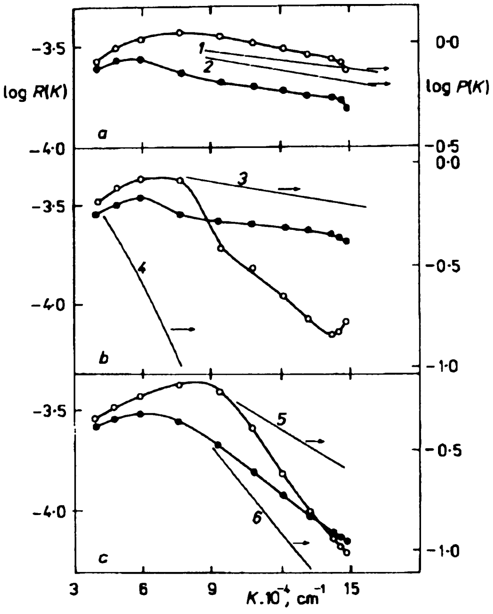


FIG. 1

Light scattering function $R(K)$ of the original (○) and recovered latex (●). Latices: *a* EM 1, c = 0.025 wt.%; *b* EM 2, c = 0.0025 wt.% (○), c = 0.05 wt.% (●); *c* EM 3, c = 0.006 wt.%. Particle scattering factors $P(K)$ were calculated according to Eq. (*1*) for particle diameters: *1* 80 nm, *2*, *3* 100 nm, *4* 400 nm, *5* 170 nm, *6* 250 nm diameters obtained from dynamic light scattering (Table II). The larger the particles were, the deeper decrease in their diameter occurred.

A deeper insight into these changes was obtained by SEM, where the dimensions of particles could be directly compared on micrographs (Figs 2 – 4). In spite of the fact that the latex spheres were displayed as flat and eliptical particles, the SEM size of latex particles was in accord with the results obtained from the other methods. The micrographs show that the changes in particle size after their recovery by acidification specifically depend on the original particle dimensions. While latex EM 1 particles (*d* ~ 100 nm) were practically unchanged, a pronounced decrease in the particle diameter of latex EM 2 (*d* ~ 430 nm) was found. However, from the light scattering measurements it is obvious that even for latex EM 1 a small decrease in *d* values (103 ⇒ 75 nm) appeared. These results confirm our assumption[12] that the structure of

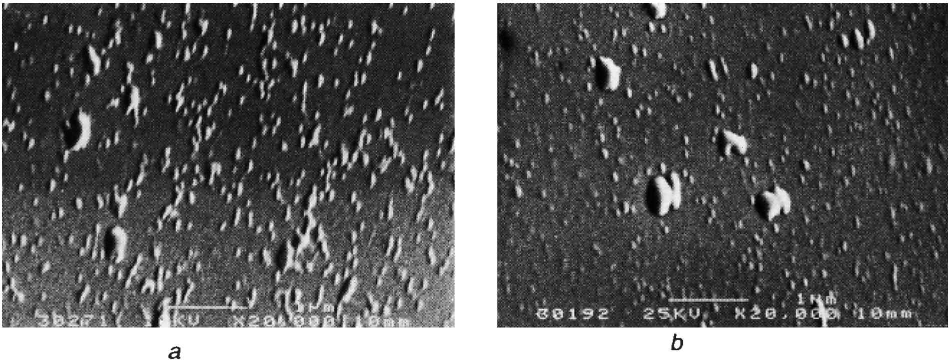


FIG. 2
Scanning electron micrographs of latex EM 1. *a* original latex, *b* recovered latex (after alkalization and acidification)

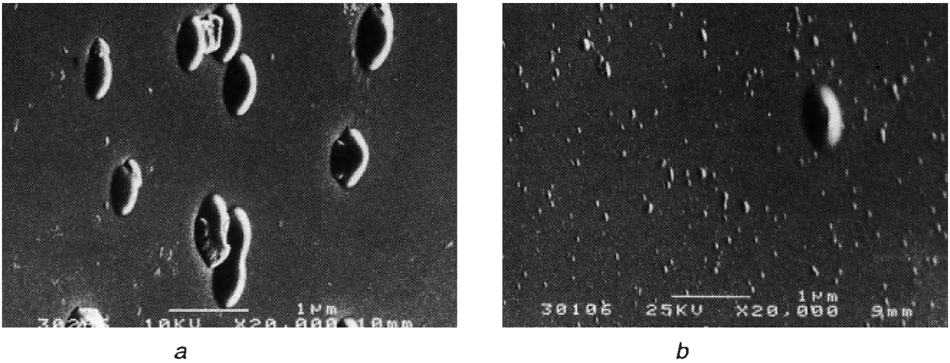


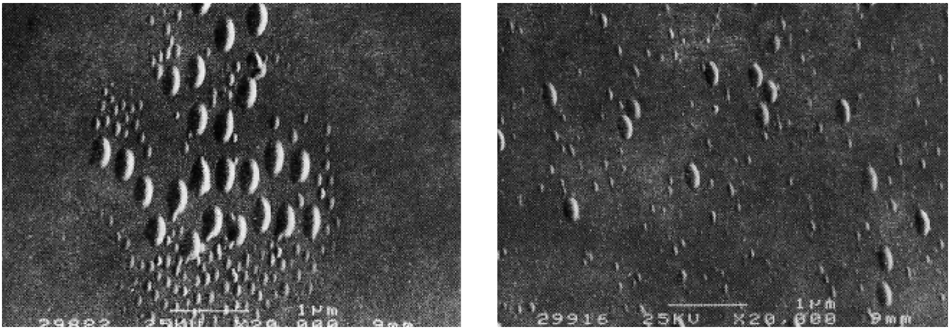
FIG. 3
Scanning electron micrographs of latex EM 2. *a* original latex, *b* recovered latex (after alkalization and acidification)

the latex particles prepared by semicontinuous emulsion polymerization need not always be homogeneous and the particle may disintegrate during the alkalization into smaller, insoluble and colloidally stable subparticles. It is also obvious that the structure of latex particles is closely related to their way of preparation.

On the other hand, the structural changes in latex EM 3 prepared by a seeded semicontinuous emulsion polymerization are rather different. The particle size distribution of the latex was bimodal; both small (ca 100 – 150 nm) and large particles (ca 350 – 400 nm) show a narrow distribution (Fig. 4*a*). After recovery of particles by acidification their size slightly decreased (Fig. 1*c*, Table II), but the bimodal distribution of particles was preserved (Fig. 4*b*).

DISCUSSION

The results of light scattering measurements and scanning electron microscopy have shown a considerable disintegration of the large latex particles (latex EM 2) during alkalization (Table II, Fig. 3). This suggests that the latex particles were formed by coagulation of smaller particles; their crosslinked structure caused them not to lose identity and not to disintegrate on alkalization. The finding indicates a very important role of coagulative mechanism of particle growth in semicontinuous emulsion polymerization with a monomer emulsion feed. In such polymerization particle nucleation and growth proceed simultaneously as competitive processes. Final particle size may be controlled by changing some polymerization variables. Under extreme conditions, as in the case of latex EM 2, the observed increase in particle diameter is caused by coagulation of already existing particles at later stages of polymerization. The extent of this coagulation is limited by colloid stability (or instability) of the system.



a

b

FIG. 4
Scanning electron micrographs of latex EM 3. *a* original latex, *b* recovered latex (after alkalization and acidification)

On the other hand, in the case of small particles (latex EM 1, Fig. 2) the coagulative process concerns mainly the coagulation of precursor particles leading to the formation of primary particles which subsequently retain water-soluble oligomers. Further polymerization proceeds within these particles which are swollen with monomers.

Although the polymerization recipe of latex EM 3 was very similar to that of latex EM 1, the presence of seed particles considerably affected the distribution of particle size of latex EM 3 as well as the structure of its particles. The polymerization in this case proceeds both in swollen and in primary seed particles as in non-seeded polymerization of latex EM 1. Thus, particles with bimodal distribution of size are obtained (Fig. 4*a*). Due to coagulative mechanism of particle growth, the size of particles increases but their pronounced heterogeneous structure caused by the presence of seed particles survives. This is reflected in their bimodal distribution even after alkalization (Fig. 4*b*).

It is apparent that the difference in structure of small and large particles need not be significant in many common latices of hydrophobic polymers prepared in a similar way. In alkali-swellable or alkali-soluble copolymers, however, this difference could be very important with respect to the possibility of disintegration of latex particles during alkalization.

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