EFFECT OF INITIAL POLYMERIZATION CONDITIONS ON THE STRUCTURE OF ETHYL ACRYLATE–METHACRYLIC ACID COPOLYMER LATEX PARTICLES

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Non-seeded semi-continuous emulsion copolymerizations of ethyl acrylate–methacrylic acid (85/15 wt. ratio) were carried out using various emulsifier and initiator concentrations and phase partitioning. The effect of the polymerization conditions on the particle size and morphology was investigated by means of scanning electron microscopy, light scattering and viscometry. Disintegration into smaller particles on alkali addition confirmed coagulative mechanism of the particle growth. This is distinct mainly if the colloidal stability of the polymerizing system is reduced due to lower concentration of the emulsifier and higher concentration of peroxydisulfate initiator which suppress double layer thickness of forming particles.

Emulsion polymerization is a complex process in which the radical addition polymerization proceeds in a heterogeneous system and its course is very closely connected with its colloidal properties. A number of mechanisms have been proposed for latex particle formation including primary particle formation by entry of a free radical into a micelle[1] and by homogeneous nucleation of oligomeric free radicals in the aqueous phase[2] or within microdroplets of monomer emulsion[3]. The theory of the homogeneous nucleation proposed by Fitch and Tsai[4] and extended by Hansen and Ugelstad[5] (HUFT) describes very well the emulsion polymerization of polar monomers and their copolymerization with water-soluble monomers such as acrylic and methacrylic acids and their derivatives. Fitch's theory implies that primary particles are formed in the aqueous phase by precipitation of oligomer radicals above a critical chain lenght. The basic principle of this theory is that the formation of primary particles takes place up to the point where the rate of formation of radicals in the aqueous phase is equal to the

rate of their disappearing by capture of radicals by particles already formed. The rate of new particles formation is

$$dN/dt = R_i - R_c - R_f \quad,$$

where R_i, R_c and R_f are rates of oligomer radical generation, oligomer radical capture and particle flocculation, respectively. Gilbert et al.[6] suppose that the primary particles are unstable and the precursor particles must undergo coagulation to form stable particles. It should be mentioned that coagulation of particles may be an important mechanism of subsequent particle growth[7]. Oligomeric radicals behave much like classical emulsifiers and their deposition on a particle or micelle is very probable. The criterion of cessation and commencement of particle formation is whether or not the rate of entry of newly-formed aqueous phase radicals into pre-existing particles exceeds the rate at which the primary radicals are formed. The process depends very strongly on the surfactant concentration and the mechanism may differ above and below its critical micellar concentration[8,9].

Polymer latices can be prepared by batch, semicontinuous and continuous emulsion polymerization. The semicontinuous process makes it possible to achieve relatively homogeneous chemical composition and it is preferred for rigorous process control[10]. Although it is used to prepare various copolymers and many industrial latices, our understanding of its fundamentals is still insufficient. Non-seeded semicontinuous emulsion polymerization with a monomer emulsion feed is a complex process in which particle nucleation and subsequent growth are very closely connected with the emulsifier concentration and batch volume changes during the process. The polymerization starts as a non-seeded process but the presence of arising polymer particles transforms the polymerization system to a seeded one. The reactor charge volume, surfactant concentration and the polymer content change continuously during the monomer emulsion addition. A typical feature of the process is a high immediate conversion of monomers exceeding 90%. Thus, the free radical polymerization proceeds under so-called monomer-starving conditions. It was shown in a previous work[11] that the process is affected very strongly by initial polymerization conditions. Under suitable conditions, the coagulative particle growth may proceed causing raspberry-like particle morphology. Alkali-soluble or alkali-swellable latex particles of ethyl acrylate–methacrylic acid copolymers that disintegrate during alkali addition indicate this type of particle morphology[12]. In this paper the effect of initial polymerization conditions on the particle structure was investigated in more detail.

EXPERIMENTAL

Dispersions

Five latex dispersions of ethyl acrylate–methacrylic acid (15 wt.%) copolymers (EM) were prepared by semicontinuous emulsion polymerization under various conditions. In their preparation, the amounts of emulsifier and initiator and partition of water between reactor charge and monomer emulsion feed were changed (Table I). The polymerizations were carried out in a 3-l stainless reactor at 80 °C, under nitrogen atmosphere, using ammonium peroxydisulfate as initiator. Technical grade ethyl acrylate (Chemical Works, Sokolov, Czech Republic) and methacrylic acid (Roehm, Darmstadt, Germany) were emulsified in water using Disponil AES 60 (sodium alkylaryl-poly(ethylene glycol) sulfate, Henkel, Dusseldorf, Germany). The emulsion (Table I) was fed at a constant rate during 3 h into the reactor containing the initial charge heated to the polymerization temperature. The latices contained 25 wt.% solids, pH was 1–2.

Sample Preparation

Standard samples were prepared by purification of EM dispersions by dialysis (Dialysierschlauch Kalle AG, Wiesbaden, Germany) against twice distilled water until constant conductivity was attained. Neutralized samples were prepared by addition of an excess NH_4OH to adjust pH of dispersions to 9.4–9.6 (PHM64 digital pH-meter, combined G 2321 electrode, Radiometer, Copenhagen).

Light Scattering Measurements

The diameters of particles were determined by light scattering methods. Static light scattering (SLS) was measured by means of a Fica 40000 photodiffusometer 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.

TABLE I
Polymerization recipes (in g) for ethyl acrylate (EA)–methacrylic acid (MMA) copolymer dispersions

Dispersion	Water		Emulsifier		Initiator	
	R	E	R	E	R	E
EM 1	800	400	13	39	2	2
EM 2	400	800	13	26	2	2
EM 3	400	800	2.6	26	2	2
EM 4	200	1 000	0	13	3	6
EM 5	200	1 000	0	13	6	6

R initial reactor charge, *E* emulsion monomer feed. Content of EA and MMA in a monomer feed 340 and 60 g, respectively.

The dependence of excess Rayleigh ratio $R(K)$ (normalized intensity of scattered light) on scattering vector $K = (2\pi/\lambda) \sin \theta/2$, where λ is the wavelength of scattered light, was measured. For colloid dispersions, $R(K)$ is given by the superposition of internal and external interference of the scattered light[13,14]. When the dimensions of scattering particles are larger than $\lambda/20$, the internal interference is given, in principle, by the scattering factor $P(K)$. For monodisperse spherical particles at infinite dilution, $P(K)$ is defined by the equation[15]:

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

where d is particle diameter. In the dilute latices studied, maxima on the experimental dependences $R(K)$ vs K at low K values were observed. This phenomenon was caused by the effect of external interference as a consequence of nonrandom arrangement of uniform particles in space. Thus, to estimate the particle diameter d, the $P(K)$ functions were compared with the experimental plots $R(K)$ vs K in the range of high values of K ($0 > 90°$). Regarding high polydispersity of dispersions the z-average $\langle d \rangle_z$ of particle diameter was obtained.

The hydrodynamic size of particles was measured by dynamic light scattering (DLS) using a Coulter Nano-Sizer (Coulter Electronic Ltd, England) apparatus which provides inverse z-average values $\langle 1/d \rangle_z^{-1}$.

Viscometry

The effective hydrodynamic volume of swollen (neutralized) dispersion particles was characterized by the intrinsic viscosity, $[\eta]$, obtained by extrapolation of η_{sp}/c values measured in a Ubbelohde dilution viscometer to zero concentration of dispersion particles ($c = 0$). The specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η is the viscosity of a dispersion system and η_0 of continuous medium. Aqueous NH_4OH (pH 9.5) was employed for dilution. The influence of electrostatic interactions between ionized carboxylic groups on the expansion of the particles was reduced by NaCl addition. Under these conditions, the plots of reduced viscosity η_{sp}/c vs c were not curved by the polyelectrolyte effect, enabling thus the determination of $[\eta]$.

Scanning Electron Microscopy

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 their aggregation. The samples were sputter-coated with a thin gold layer (10 nm). To improve the contrast, the observation was carried out with the mica tilted surface 60° to the electron beam.

RESULTS

Due to different polymerization conditions used in the preparation of the dispersions, the size of their particles differed in a broad range $d_{DLS} = 44$–$2\,650$ nm (Table II). More detailed information on the shape and morphology of the particles was obtained by their direct observation using SEM. In the micrographs, Figs 1*a*–3*a*, flat and eliptical plate-like objects were found because soft particles were deformed during their deposi-

tion on the solid mica surface and because the flat objects were not imaged perpendicularly. Every plate in the micrographs corresponded to an individual particle as the size of equivalent spheres calculated from the diameter and height of the plates was in accordance with the light scattering results. Closer inspection of particles of EM 4 and EM 5 dispersions revealed the presence of large wrinkled particles of irregular shape originating probably from interpenetration of several smaller particles (Figs 2*a*, 3*a* and 3*b*). As shown in the figures, a small number of particles of a diameter lower by an order of magnitude was also found along with large particles.

TABLE II
Ethyl acrylate–methacrylic acid copolymer dispersions: particle diameters and intrinsic viscosities at pH 9.5

Dispersion	d_{SLS}, nm		d_{SLS}, nm		$[\eta]$, dl g^{-1}	
	A	*B*	*A*	*B*	0.01 M NaCl	0.04 MNaCl
EM 1	50	50	44	44	1.50	0.92
EM 2	100	80	91	72	2.05	1.20
EM 3	110	80	103	75	1.60	1.03
EM 4	200[a]	80	430	53	0.95	0.47
EM 5	–[b]	80	2 650	83	0.43	0.29

A original dispersion; *B* recovered dispersion (after alkalization and acification); [a] large particles removed during filtration of the dispersion; [b] out of the scope of SLS measurement.
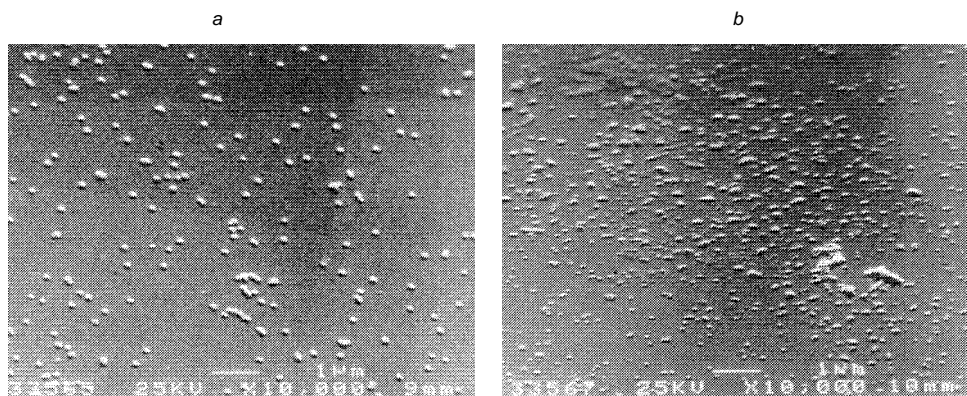

a   b

FIG. 1
Scanning electron micrographs of dispersion EM 3; *a* original dispersion, *b* recovered dispersion (after alkalization and acidification)
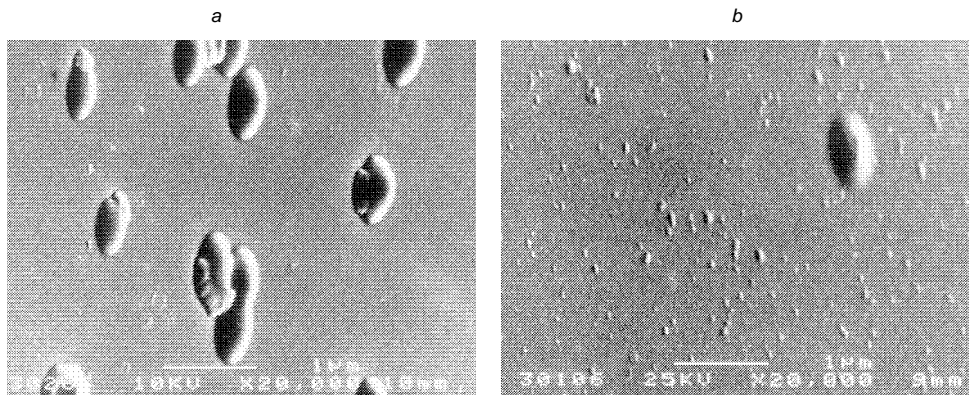
FIG. 2
Scanning electron micrographs of dispersion EM 4; *a* original dispersion, *b* recovered dispersion
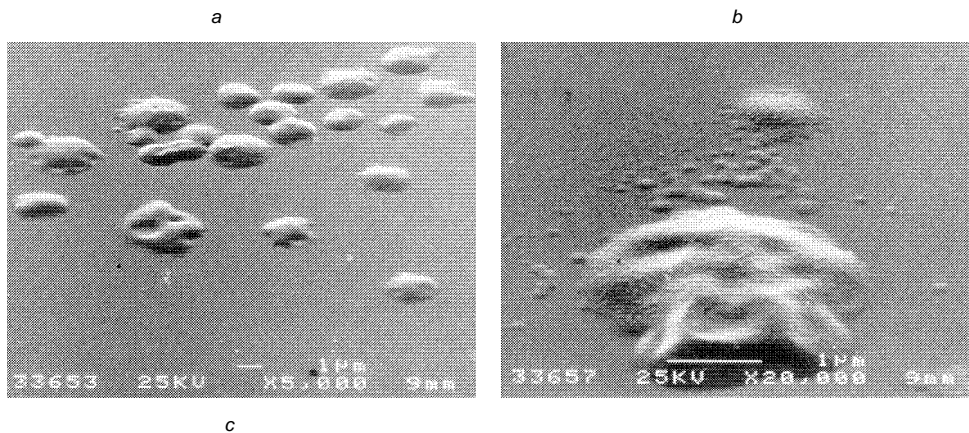(after alkalization and acidification)

FIG. 3
Scanning electron micrographs of dispersion EM 5;
a, *b* original dispersion, *c* recovered dispersion
(after alkalization and acidification)

Although the majority of particles in the micrographs seemed compact and homogeneous, their microstructure might be strongly heterogeneous due to the coagulative mechanism of particle growth[7]. This assumption could be checked by treating the dispersions with alkali and recovery of the material by acidification[12]. As a result of strong electrostatic repulsion between polymer segments bearing ionized carboxylic groups, the particles swell and may disintegrate into smaller crosslinked fragments[12,16]. The degree of their crosslinking is reflected in the effective hydrodynamic volume, proportional to $[\eta]$; the extent of particle disintegration can be estimated from the decrease in particle size after recovery of the neutralized dispersion system by acidification (acetic acid, pH 3.4–3.6).

The same sizes of the original and recovered particles of EM 1 dispersion found by light scattering (Table II) show that the particles prepared with a high content of emulsifier and high amount of water in the reactor charge, which ensured formation of very small ($d_{DLS} = 44$ nm) particles, did not disintegrate on swelling, i.e., the particles seem to be homogeneous with respect to the test method used.

On the other hand, dispersions EM 2 and EM 3 prepared recipes providing intermediate ($d_{DLS} \approx 100$ nm) particles displayed a decrease of about 30% in particle size on
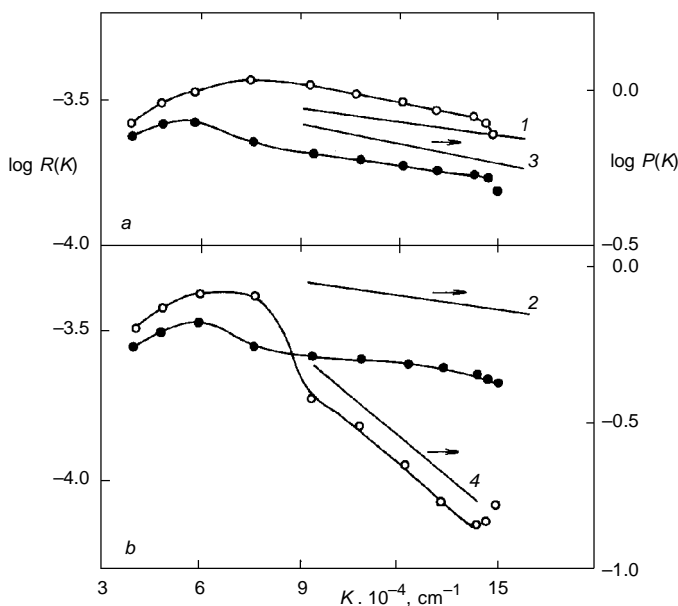

Fig. 4

Light scattering function $R(K)$ of the original (○) and recovered dispersion (●). Dispersions: *a* EM 1, $c = 0.025$ wt.%; *b* EM 2, for original dispersion $c = 0.0025$ wt.%, for recovered dispersion $c = 0.05$ wt.%. (Particle scattering factors $P(K)$ calculated from Eq. (*1*) for particle diameters: *1, 2* 80 nm, *3* 110 nm, *4* 200 nm.)

alkali and acid treatment. This result suggesting disintegration of dispersion particles was manifested by a decrease in both the slopes of $R(K)$ functions at high values of K (Fig. 4) and particle diameters measured by dynamic light scattering (Table II), and also confirmed by electron microscopy (Fig. 1*b*).

Different behaviour has been observed with EM 4 and EM 5 dispersions, where a low content of emulsifier, a small volume of the initial reactor charge, and higher concentrations of the initiator were used to obtain large particles (Table II). On alkali addition, a pronounced particle disintegration was found (Figs 2*b* and 3*b*): with EM 4 dispersion, the diameter of original particles, $d_{DLS} = 430$ nm, decreased to 53 nm after recovery of the system by acidification and with EM 5 dispersion, even more dramatic decrease in particle size from $d_{DLS} = 2\ 650$ to 83 nm occurred. In this case a significant decrease in hydrodynamic volume of the subparticles (Table II) suggests much higher degree of their crosslinking in comparison with EM 1–EM 3 dispersions.

It is surprising that subparticles with a higher degree of crosslinking are released from original large dispersion particles which, at the same time, disintegrate to a greater extent. One could expect that higher probability of crosslinking reactions occurring under these conditions would lead to dispersion particles crosslinked within the whole volume resulting in a small extent of disintegration. The opposite results found in the study suggest that crosslinking reactions proceed mainly before the coagulative stage of particle growth, i.e., large particles are produced by coagulation of already existing crosslinked particles at later stages of polymerization as proposed earlier[12].

DISCUSSION

The results have confirmed the coagulative mechanism of particle growth in the non-seeded semicontinuous emulsion polymerization the extent of coagulation being very strongly dependent on the initial polymerization conditions. In this process several periods of nucleation of new particle crops are followed by particle flocculation. As was shown in our previous paper[8], the particle number and, consequently, also the specific surface area and surface tension may exhibit some oscillations during the feeding of the monomer emulsion. It was suggested that particles grow rapidly, generating sufficient surface area resulting in an emulsifier-starved system with very small rate of particle formation, even with particle flocculation. Since the emulsifier is continuously added, it is possible for the system to return to the emulsifier excess condition.

The extent of flocculation is primarily governed by (i) the total amount of emulsifier, (ii) the water phase distribution between the initial reactor charge and the monomer emulsion feed, and (iii) the concentration of initiator.

The role of the first factor is evidenced by the EM 1 dispersion where the highest emulsifier concentration ensured high colloidal stability of the originating particles and, hence, formation of very small particles. The second factor is well documented by EM 2 and EM 3 dispersions where a lower water content in the initial reactor charge and a

lower total amount of emulsifier led to formation of larger particles. In this case, the particle disintegration on alkali treatment confirmed significant influence of the coagulative stage during the period of particle growth (Table II).

The effect of the third factor is shown by EM 4 and EM 5 dispersions. Ammonium peroxydisulfate acts as an initiator but, on the other hand, it is also an electrolyte. In an electrostatically stabilized system, the electrolyte lowers the double layer thickness and, as a consequence, it decreases the colloidal stability of particles. Thus, increased concentration of the initiator enhances the flocculation of primary particles at the initial stages of the process as well as that of mature particles in the later stages. In addition, the initiator SO_4^{2-} groups can have a significant impact upon the particle morphology due to their influence on the particle interfacial tension[17]. With these dispersions, the presence of higher concentrations of the initiator, mainly in the initial reactor charge, increases the probability of chain transfer reactions leading to a higher extent of cross-linking of particles in the initial stages of polymerization. Under these conditions, large particles composed of strongly crosslinked subparticles can be formed as indicated by the methods used.

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