Colloid Polym Sci 278:1205–1210 (2000)

SHORT COMMUNICATION

J. Šňupárek
L. Mrkvičková
O. Quadrat
Z. Walterová
P. Bradna

Effect of water-soluble cross-linker on the growth and properties of ethyl acrylate–methacrylic acid emulsion copolymer particles

Received: 2 February 1999
Accepted: 28 June 2000

J. Šňupárek
Institute of Polymeric Materials
University of Pardubice
532 10 Pardubice, Czech Republic

L. Mrkvičková · O. Quadrat (✉)
Z. Walterová
Institute of Macromolecular Chemistry
Academy of Science of the Czech Republic
162 06 Prague, Czech Republic
e-mail: quadrat@imc.cas.cz

P. Bradna
Spofa – Dental Co., Černokostelecká 84
110 00 Prague 10, Czech Republic

Abstract Model ethyl acrylate–methacrylic acid copolymer latices and latices of particles cross-linked by copolymerizing small amounts of water-soluble *N*,*N*′-methylenebisacrylamide were prepared by nonseeded semicontinuous emulsion copolymerization. Dynamic and static light scattering measurements indicated a slightly higher degree of polydispersity in the case of cross-linked particles, especially in the initial stages of polymerization. The hydrodynamic volume of the alkalinized particles controlling the viscosity properties of the dispersions decreased with the time of polymerization and in the case of cross-linked copolymer almost reached a constant value at about 1 h. The different character of the particle structure was confirmed by differences in particle disintegration after alkali addition or in the presence of methanol.

Key words Polymer colloids · Emulsion polymerization · Particle growth · Particle properties

Introduction

Particle formation in emulsion polymerization comprises two stages – particle nucleation and particle growth to the final size, which is accomplished by consumption of remaining free monomer within the particle. As the emulsion polymerization is usually initiated by a water-soluble initiator and proceeds in micelles of a surfactant, two basic mechanisms are operative in the particle nucleation stage – the micellar nucleation (primary and/or oligomeric radicals initiate the polymerization in micelles swollen by monomer) and the homogeneous nucleation (oligomeric radicals precipitate from the homogeneous aqueous phase after reaching a critical degree of polymerization and form primary particles) [1]. Both mechanisms are usually operative in a practical emulsion polymerization, the extent of the former and/or the latter being primarily affected by the monomer polarity (water solubility) and by the actual concentration of surfactant. The subsequent particle growth proceeds by polymerization in swollen polymer/monomer particles, by the capture of oligomeric radicals by existing particles and by coagulation of particles in all stages of their growth [2, 3].

In the nonseeded semicontinuous emulsion polymerization with a monomer emulsion feed that was used for the preparation of model particles [4], both nucleation and particle growth proceed simultaneously. A typical feature of such a semicontinuous process is a high immediate conversion of monomers and the polymerization under monomer-starving conditions, which is strongly affected by the initial polymerization conditions. Under suitable experimental conditions, the coagulative particle growth may yield particles with a raspberry-like morphology. The coagulative mechanism of particle growth was found in our previous work [4, 5], in which emulsion copolymers of ethyl acrylate and methacrylic acid were investigated. Such copolymers containing relatively high concentrations of carboxylic groups are alkali-swellable or alkali-soluble and are potentially usable as binders and thickeners in low or zero volatile organic compound emulsion paints. Copolymerization in emulsion under monomer-starving conditions gives copolymers with a relatively homogeneous composition of polymer chains and makes it possible to copolymerize monomers with different polarity, even water-soluble and water-insoluble ones [6, 7].

It should be mentioned that the solid contents of common emulsion commercial copolymers for practical use are 40–60 wt% and for special alkali-soluble and alkali-swellable copolymers they are around 25–30 wt%. To achieve high solid contents and a relatively homogeneous copolymer composition, a feeding period of several hours is necessary. Our previous experiments [8] showed that particles of copolymers of ethyl acrylate and methacrylic acid (85/15) prepared by this procedure arising at the beginning of polymerization process comprised completely alkali-soluble copolymer, while some colloid particles formed at long reaction times were only alkali-swellable. On the other hand, we found that particles of the copolymers with a small amount of copolymerized water-soluble cross-linker *N*,*N*′-methylenebisacrylamide did not disintegrate but were only alkali-swellable [9]. In this work, the effect of the polymerization period, i.e., the monomer emulsion feeding time, on the growth of colloid particles with and without cross-linker as well as some properties of emulsion copolymers were systematically investigated.

Experimental

Emulsion polymerization

Nonseeded semicontinuous emulsion polymerizations were carried out in a 2-l glass reactor at 80 °C, under a nitrogen atmosphere, using ammonium peroxysulfate (Merck) initiator. Technical grade ethyl acrylate (Chemical Works, Sokolov), methacrylic acid (Roehm, Darmstadt) and *N*,*N*′-methylenebisacrylamide (Cyanamid) in emulsion using demineralized water and Disponil AES 60 (Henkel, 34% active matter) as surfactant were fed at a constant rate into the reactor containing the initial reactor charge. The polymerizations were carried out at constant feeding rates but different feeding times of the monomer emulsion, i.e., with different final solid contents of the latex as shown in Table 1. The experiments with feeding times shorter than 10 min were carried out using the recipe for 10-min feeding time with the same feeding rate but the reaction was interrupted after an appropriate shorter time. The maximum latex solids were 24 wt% and the pH of the samples at the end of the polymerization was 2–3. Samples of the N series were prepared without cross-linker; samples of the C series were cross-linked by 1.25 wt% *N*,*N*′-methylenebisacrylamide.

Static light scattering

Samples

Original acid dispersions (pH ~ 3) diluted to a concentration (0.1–5.0) × 10^{-4} g cm^{-3} with distilled water acidified with HCl to pH 3 were measured. Strongly dilute acid dispersions were purified optically through a glass filter having a porosity of 400–1000 nm, by a mild overpressure of nitrogen.

To prepare alkalinized samples (pH ~ 9), a solution of sodium hydroxide was added to 1 wt% dispersions and these stock solutions were stabilized for 1 day. To suppress polyelectrolyte behavior of the systems, the stock solution was diluted with a 0.2 M aqueous NaCl solution alkalinized to the pH required.

To prepare samples in methanol, 1 wt% stock solution of original dispersion in methanol was further diluted with pure methanol to the concentration required. In such a way, the content of water in the solutions decreased in the case of low-solid and high-solid dispersions from about 7 to 0.7 wt% and from 1 to 0.1 wt%, respectively. After alkalinization or methanol addition, the dispersions were cleaned optically by ultracentrifugation [10] (Beckmann L-55, rotor SW-1, 10,000 rpm for 2 h).

Measurement

The static light scattering (SLS) was measured (Fica 40000 photogoniodiffusometer) in the range of scattering angles $\theta = 30$–150° with vertically polarized light of wavelength $\lambda_o = 546$ nm and $\lambda_o = 365$ nm.

Table 1 Polymerization recipe. Initial reactor charge in all experiments: water, 400 g; AES60, 1.3 g; ammonium peroxosulfate, 0.4 g

Monomer emulsion feed composition/feeding time/solids content						
Samples (non-cross-linked)	N/1	N/2	N/3	N/4	N/5	N/6
Feeding time (min)	10	20	30	60	120	180
Final polymer content (wt%)	4.32	8.18	11.57	15.72	21.25	24.11
Monomer emulsion feed composition (g)						
Water	40	80	120	240	480	720
Disponil AES 60	0.65	1.3	1.95	1.5	7.8	11.7
Ethyl acrylate	17	34	51	102	204	306
Methacrylic acid	3	6	9	18	36	52
Samples (cross-linked)	C/1	C/2	C/3	C/4	C/5	C/6
Feeding time (min)	10	20	30	60	120	180
Final polymer content (wt%)	4.32	8.18	11.57	15.72	21.25	24.11
Monomer emulsion feed composition (g)						
Water	40	80	120	240	480	720
Disponil AES 60	0.65	1.3	1.95	1.5	7.8	11.7
Ethyl acrylate	16.75	33.50	50.25	100.5	201.0	301.5
Methacrylic acid	3	6	9	18	36	54
N,*N*′-Methylenebisacrylamide	0.25	0.50	0.75	1.5	3.0	4.5

The dependence of excess the Rayleigh ratio $R(K)$ (normalized intensity of the scattered light) on the scattering vector $K = (2\pi/\lambda)\sin\theta/2$ was measured [11].

$$R(K) = K'cMP(K)Q(K), \qquad (1)$$

where K' is the scattering optical constant of the system and c and M are the concentration and particle weight, respectively. Dimensions of scattering particles larger than $\lambda/20$ (where λ is the wavelength in the medium) bring about internal (intramolecular) interference of scattered light, which is characterized by the particle scattering factor $P(K)$. For monodisperse spherical particles at infinite dilution, $P(K)$ is defined by the equation [12]

$$P(K) = [(3/K^3D^3)(\sin KD - KD\cos KD)]^2. \qquad (2)$$

To estimate the diameter of the colloid particle, D, the $P(K)$ functions were calculated for a definite D value and were then compared with experimental plots of $R(K)$ versus K^2 [13] in the range of high values of $K(\theta > 90°)$, where the structural function $Q(K)$ describing an external (intermolecular) interference of scattered light was not operative at the particle concentrations used (Fig. 1). Regarding the polydispersity of the colloid particles, the z-average $\langle D\rangle_z$ of the particle diameter was probably obtained.

Owing to the decreasing sensitivity to the polydispersity with increasing wavelength of incident light in the solvent used [14] the values of the average diameter obtained for polydisperse dispersions rise. Hence, the ratio of colloid particle sizes obtained at two different values of λ, $[\langle D\rangle_z]_{546}/[\langle D\rangle_z]_{365}$, was used as a qualitative criterion of polydispersity.

To characterize macromolecules of samples of the N series in solutions after alkali or methanol treatment, the SLS data analysis was performed according to the equation

$$c/R(\theta) = (K')^{-1}\left\{[\langle M\rangle \mathrm{w} P(\theta)Q(\theta)]^{-1} + 2BC\right\}, \qquad (3)$$

where $R(\theta)$ is the Rayleigh ratio representing the intensity of scattered light and $K' = 2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2(\lambda_0^4 N_\mathrm{A})^{-1}$ is the scattering optical constant in which n is the refractive index of the solvent used and N_A is Avogadro's number. $\langle M\rangle_\mathrm{w}$ is the weight-average molecular weight and B is the second virial coefficient. For a quantitative evaluation of a SLS measurement performed with a multicomponent system a value of the refractive index increment ($\mathrm{d}n/\mathrm{d}c$), measured after the establishment of the dialysis equilibrium between the polymer solution and the polymer-free mixed solvent, must be used. Since no such data were available for the aqueous multicomponent system under study, values of $[c/R(0)]_{c=0}$ obtained by double extrapolation of $c/R(\theta)$ to zero c and θ, were used as a qualitative measure of solubility. Since, in contrast to aqueous media, a constituent copolymer is soluble in methanol [8], the values of $[c/R(0)]_{c=0}$ derived from SLS data obtained with methanol solutions were also used for a comparison. In an excess of methanol, on the other hand, we assume to obtain $\langle M\rangle_\mathrm{w}$ from the angular and concentration limit, $[c/R(0)]_{c=0} = (K'\langle M\rangle_\mathrm{w})^{-1}$, using SLS data of the concentration series prepared by diluting gradually with pure methanol and values of $\mathrm{d}n/\mathrm{d}c$ calculated as $\Sigma w_\mathrm{i}(\mathrm{d}n/\mathrm{d}c)_\mathrm{i}$, i.e., linear combination of products of weight fractions w_i and $(\mathrm{d}n/\mathrm{d}c)_\mathrm{i}$ values for homopolymers of individual copolymer components. $P(\theta)$ is a single-particle scattering factor and $Q(\theta)$ is a structural function (see earlier). The method of the evaluation of the experimental data is described in detail elsewhere [8].

Dynamic light scattering

The dynamic light scattering (DLS) was measured with an Autosizer Lo-C (Malvern, UK), which provided inverse z-average values of the particle diameter, $\langle 1/D\rangle_z^{-1}$. The mean particle diameter and the particle number in Table 2 were determined using laser submicron particle analyzers (Coulter N4 Plus, Coulter, Miami, USA and Coulter Nano-Sizer, Coulter Electronics, UK).

Viscometry

The hydrodynamic volume of the dispersion particles alkalinized with ammonium hydroxide at infinite dilution (intrinsic viscosity) was measured with a capillary dilution viscometer of the Ubbelohde type at a shear stress of about 0.6 Pa.

Results and discussion

The effect of the feeding period length on the particle size of samples prepared with and without cross-linking agent and of cross-linked samples is shown in Fig. 2. In these experiments all measured values represent mean particle sizes at the end of individual experiments according to the polymerization recipes summarized in

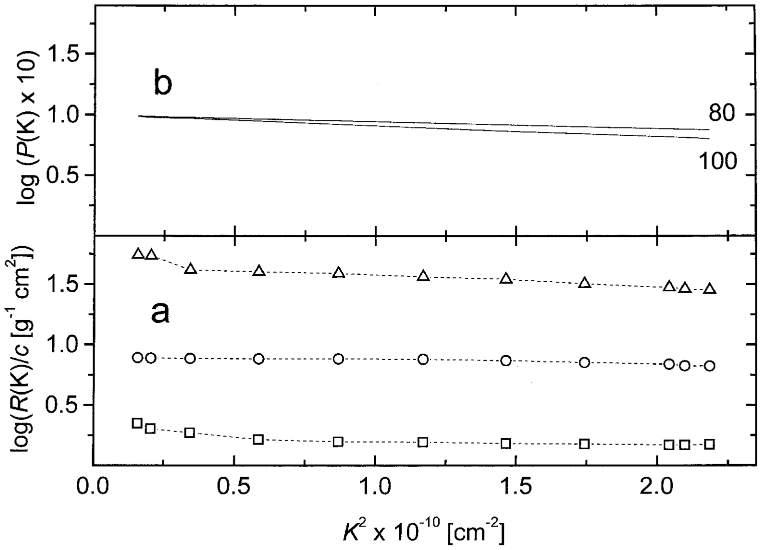

Fig. 1 The modified Guinier plot of **a** the scattering curves of dispersions prepared during different monomer feeding time (min) 4 (□), 20 (○), 120 (△). **b** Particle scattering factors, $P(K)$, calculated according to Eq. (2) are parameterized by the particle diameter in nanometers

Table 2 Final mean particle size measured by dynamic light scattering and particle number in relation to the feeding time in C series polymerizations. Coulter N4 Plus unimodal particle size analysis was used for the particle number calculation

Feeding time (min)	Mean particle diameter (nm)	Total particle number, *N*	Particle number in 1 cm^3
0.5	2298	1.43×10^{11}	3.56×10^{8}
1	45.1	3.79×10^{16}	9.37×10^{13}
1.5	27.1	2.62×10^{17}	6.45×10^{14}
2	23.5	3.49×10^{17}	8.56×10^{14}
3	34.1	2.63×10^{17}	6.38×10^{14}
4	32.5	4.05×10^{17}	9.73×10^{14}
5	32.3	5.15×10^{17}	1.23×10^{15}
10	54.5	2.15×10^{17}	4.88×10^{14}
20	66.6	2.35×10^{17}	4.90×10^{14}
30	67.0	3.47×10^{17}	6.66×10^{14}
60	80.8	3.95×10^{17}	6.17×10^{14}
120	89.3	5.85×10^{17}	6.65×10^{14}
180	97.0	6.85×10^{17}	6.12×10^{14}

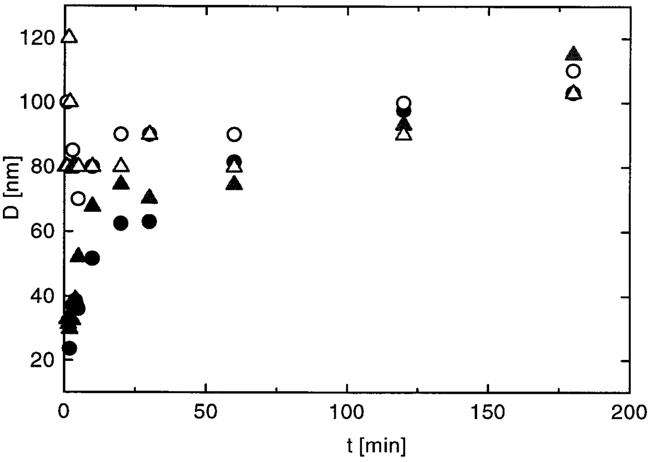

Fig. 2 The dependence of particle diameter, *D*, on the monomer feeding time. Static light scattering: *open symbols*; dynamic light scattering: *filled symbols*; sample N: *triangles*; sample C: *circles*

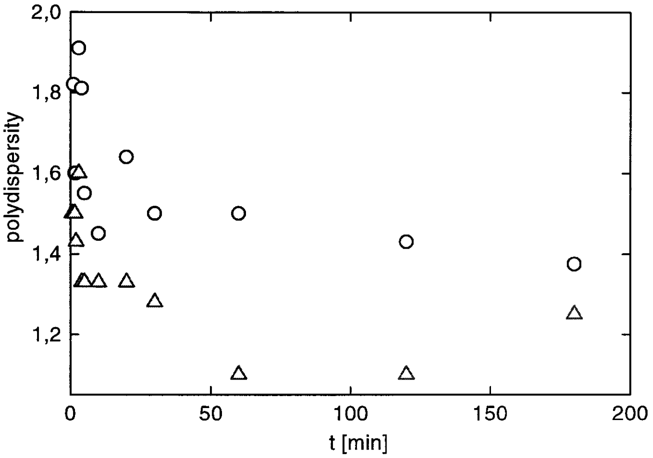

Fig. 3 The dependence of the polydispersity of colloid particles, D_{546}/D_{365}, on the monomer feeding time, *t*. For the data notation, see Fig. 2

Table 1. These results suggest no significant influence of a small amount of the *N*,*N*′-methylenebisacrylamide cross-linker on the particle formation and growth. The mean particle size of N and C dispersions measured by both DLS and SLS exhibited a similar relationship with respect to the feeding time (Fig. 2).

The polydispersity estimated as the ratio of the emulsion polymer particle size measured at two different wavelengths (365 and 546 nm) was found to be a little lower in the case of non-cross-linked particles (Fig. 3). In both series of experiments, the polydispersity decreased with the increasing content of solids. A similar trend in the size nonuniformity should be suggested by the value of the structure parameter $\rho = D_G/D_H$[15], the ratio of the particle sizes determined by SLS and DLS. The value of this for the monodisperse hard sphere in θ conditions is $\rho \sim 0.77$ and it increases with increasing size nonuniformity because of different statistical averages of size resulting from the measurement methods mentioned [16]. According to the fact just described one can deduce from Fig. 2 that the uniformity of the disperse system increased with feeding time.

The course of the particle size versus time dependence results from the competition between the formation of new particles (slow increase and small changes in mean diameter with respect to the increased solid content) and their coagulation (rapid increase in the mean diameter within a period with a small increase in polymer solids) and is in agreement with our previous results [17].

In the system, the methacrylic acid investigated is fully miscible with water, whereas ethyl acrylate is only partially miscible. In the chosen concentration range, *N*,*N*′-methylenebisacrylamide is also water-soluble. The semicontinuous process under monomer-starving conditions, i.e., continuous feeding of monomers at a slow rate during the polymerization, is a necessary procedure to obtain relatively homogeneous copolymer and to avoid homopolymerization of methacrylic acid in the aqueous phase. Semicontinuous emulsion polymerization performed without charging any seed particles into the reactor at the start of polymerization and feeding of monomers in the form of an emulsion is a relatively complicated system. From the very initial stages of the reaction, both particle nucleation and particle growth occur simultaneously. The mechanism of nucleation at the start of the reaction is very probably a complex process comprising initiation of polymerization in the aqueous phase. It is very strongly affected by surfactant if its concentration is above the critical micelle concentration. An oligomeric radical behaves much like a surfactant molecule and its incorporation into the micelle structure is obvious. Under such conditions,

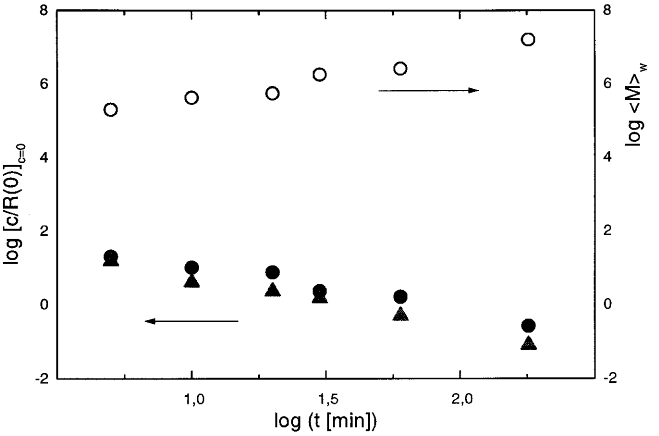

Fig. 4 The values of $\log[c/R(0)]_{c=0}$ or $\log \langle M\rangle_w$ with respect to the monomer feeding time, t, after alkalinization (*circles*) or methanol treatment (*triangles*)

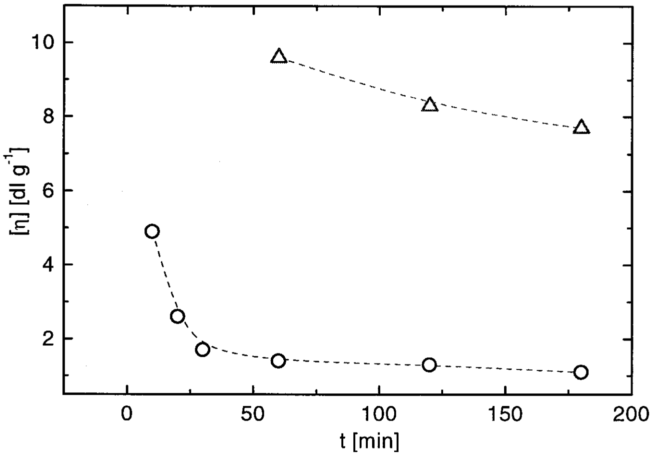

Fig. 5 Dependence of the hydrodynamic particle volume, $[\eta]$, on the feeding time, t. For the data notation, see Fig. 2

relatively large particles used to appear in first seconds after the start of monomer emulsion feeding as their concentration is very low and the surfactant prevents their fast coagulation [17]. The rate of the particle number change, dN/dt, during the emulsion polymerization depends on the rate of initiation in the aqueous phase, R_i, and on the rates of capture of oligomeric radicals, R_c, and particle flocculation, R_f [18].

$$dN/dt = R_i - R_c - R_f \tag{4}$$

It was also suggested that the primary particles are unstable and must undergo coagulation to form stable particles [3]. A stepwise increase in the mean particle diameter and an oscillation in particle number is a typical feature of the nonseeded semicontinuous emulsion polymerization in which the monomers are fed in the form of an emulsion [2, 17]. This indicates the coagulative mechanism of the particle growth and the competitive periodic nucleation of new particles. The experiments discussed here exhibited a similar course in particle size and particle number during the polymerization as shown in Table 2.

The extent of the disintegration of the particles after alkalinization or methanol addition was expressed as $\log[c/R(0)]_{c=0}$. This measure of disintegration is inversely proportional to the mass of residual particles. Ethyl acrylate/methacrylic acid copolymers, not cross-linked with *N*,*N'*-methylenebisacrylamide, exhibited a decrease in $\log[c/R(0)]_{c=0}$ values and an increase in molecular weight (obtained from measurement of dispersions after alkalinization) with increased feeding time. This indicates an increased extent of random cross-linking of polymer chains especially in the later stages of polymerization (Fig. 4). This type of cross-linking results from radical-transfer reactions and is typical of polymerization of acrylic monomers [19].

After alkalinization, the effective hydrodynamic volume, $[\eta]$, of the dispersion particles prepared without any cross-linking agent (the branching or even slight cross-linking of such particles is caused solely by radical-transfer reactions) is several times higher than that of particles cross-linked with 1.25 wt% *N*,*N'*-methylenebisacrylamide as shown in Fig. 5, and it decreases with the feeding time. In the case of particles cross-linked with a cross-linking agent the hydrodynamic volume drops strongly in the first stages of polymerization and remains constant after 30 min of polymerization. Clearly, besides decreasing the particle swelling, the cross-linker prevents the alkali treatment disintegration of particles so that the desired rheological properties of such products can be achieved reproducibly.

Conclusion

It was demonstrated that during the emulsion copolymerization the polydispersity of the lattices showed changes, the character of the change being similar, irrespective of the presence or absence of the cross-linking agent under study, while the polydispersity of intentionally cross-linked particles is a little higher mainly in the initial stages of polymerization. However, according to the viscosity measurements, the low hydrodynamic volume of cross-linked alkalinized particles attains, after a steep drop within 60 min of the feeding time, its limiting, virtually constant value. This behavior allows one to prepare alkali-swellable particles with defined and reproducible properties, which is a crucial precondition for manufacturing such materials.

Acknowledgement The Grant Agency of the Czech Republic is thankfully acknowledged for supporting this work by grant GACR no. 104/96/1373.

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