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Exploring the Limits of Emulsion Polymerization of Styrene for the Synthesis of Polymer Nanoparticles

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Summary. Suspensions of polymer nanoparticles in water (latices) with average particle diameters between 20 and 80 nm were synthesized by batch emulsion polymerization of styrene using sodium dodecyl sulphate (*SDS*) as surfactant and potassium persulphate (*KPS*) as initiator. The influence of surfactant concentration, initiator concentration, monomer concentration, and reaction temperature on the final average particle diameters and size distributions of the latices were studied. The number of particles generated was proportional to the 0.56 power of the emulsifier concentration and to the 0.37 power of the initiator concentration in the whole concentration range which was observed. Furthermore, the final number of particles was dependant on the reaction temperature to the 2.06 power. With these correlations the average particle number as well as the average particle size could be estimated, and the results were in good agreement (±6%) with the experimental values. A reduction of the monomer/water ratio from 1:5 to 1:20 yielded smaller particle diameters, while leaving the particle number unaffected. The lower particle size limits for monomer ratios of 1:10 and 1:15 were estimated with diameters of about 18 and 16 nm.

Keywords. Colloids; Latex; Nanoparticles; Polymerizations; Surfactants.

Introduction

Emulsion polymerization is an important method for the production of colloidal polymer suspensions (latex) with a large diversity of industrial applications such as paints, coatings, adhesives, and polishes [1] or medical and biochemical applications, like drug delivery systems and immunoassays [2]. In these common products the average particle diameters are usually found in the size range of 80–500 nm, but emulsion polymerization has also proved to be a method to produce nanoparticles with smaller particle diameters [3–6].

For the emulsion polymerization the locations of the different components were first described in detail by *Harkins* [7, 8] and its kinetics by *Smith* and *Ewart* [9, 10], who proposed a three phase model for the polymerization reaction. These authors suggested that in the first phase the polymerization reaction is started in a particular number of micelles filled with monomer, which will serve as further reaction sites once they contain an initiated polymer chain. In the latter two phases the number of particles N remains constant (while the reaction rate changes), because all the micellar surfactant is adsorbed by the growing particles during the first phase. Since the final particle diameter d is inversely proportional to N ($d \propto \mathrm{N}^{-1/3}$) for a given amount of monomer, the number of particles which are generated in the first stage of the reaction should be therefore high to obtain small particles. This can be achieved *e.g.* by increasing the initial number of micelles and the influence of the initial surfactant concentration on the final particle diameters and particle size distributions has been investigated in numerous studies [11–14]. Furthermore the influences of initiator [9, 15, 16], reaction temperature [10, 11, 16], and monomer concentration [16–18] on the final particle number N have been

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discussed and quantified for styrene, but it should be pointed out that most of experimental verification was done with low or moderate concentrations of emulsifier and initiator and the final latices in these studies had average particle diameters above 50 nm.

In the current work a comprehensive study on the synthesis of polymer nanoparticles by emulsion polymerization of styrene with well known components such as sodium docecyl sulphate (*SDS*, surfactant) and potassium persulphate (*KPS*, water soluble initiator) is reported. The emulsifier and the initiator concentrations as well as the reaction temperature were varied over a wide range and the lower particle size limits of the method were investigated.

Results and Discussion

Influence of Surfactant Concentration

The recipes for the reactions, in which the initial amount of surfactant (m_{SDS}) was varied in order to investigate the dependence on the final average particle diameters (d_{w}, $d_{\mathrm{n,Phot}}$) on the surfactant concentration (c_{SDS}) can be found in Table 1 and the results are illustrated in Fig. 1a.

The final number of particles increased to the 0.56 power of the surfactant concentration for concentrations between 4.2 and 100 g/dm^3, which is in good agreement with the value of 0.6 proposed by *Smith* and *Ewart* [9]. It is generally accepted that a higher amount of surfactant generates a higher number of micelles with a higher overall surface area for radical entry and therefore a higher number of particles with smaller particle diameters can be expected. The observed broadening of the size distribution (higher values for $d_{\mathrm{w}}/d_{\mathrm{n}}$) at higher surfactant concentrations can be explained by the fact that at high surfactant concentrations not all of the surfactant is adsorbed by the generated particles during the initiation phase. The presence of micelles after this period leads to a certain extent to the formation of new particles throughout the polymerization reaction, and thus to a broadening of the final particle size distribution.

Table 1. Recipes and results for the reactions with different surfactant concentrations

Latex	m_{SDS} (g)	$\mathrm{N} \times 10^{18}$ (dm^{-3})	$d_{\mathrm{w,DLS}}$ (nm)	$d_{\mathrm{n,Phot}}$ (nm)	$d_{\mathrm{w}}/d_{\mathrm{n,DLS}}$
E1	2.5	0.39	76.4	75.7	1.039
E2	5	0.58	69.3	64.4	1.012
E3	10	1.01	56.1	53.8	1.032
E4	20	1.39	49.4	49.0	1.056
E5	30	1.93	46.4	43.4	1.065
E6	60	2.08	42.4	42.3	1.129

In all reactions E1–E6: Styrene: 60 g, Water: 0.6 dm^3, *KPS*: 0.5 g, *T*: 60°C

Influence of Initiator Concentration and Temperature

In order to investigate the dependence of the final average particle diameters on the initiator concentration, the initial amount of the *KPS* (m_{KPS}) was varied according to Table 2. The final number of particles increased with the initiator concentration (c_{KPS}) with $\mathrm{N} \propto c_{KPS}{}^{0.37}$ (Fig. 1) which is in good agreement with the value of *Smith* and *Ewart* [9], who proposed that the generated number of particles N is proportional to the 0.4 power of the initiator concentration. This relation was also verified experimentally by *Bartholomé et al.* [11] in a concentration range between and 0.8 and 60 g/dm^3. Similar correlations for *KPS* with $\mathrm{N} \propto c_{KPS}{}^{\sim 0.4}$ were also found in miniemulsion polymerization [19] and microemulsion polymerization [20] reactions using styrene/*SDS*/*KPS* indicating that the exponent 0.4 stays unchanged in emulsion polymerization reactions with *KPS* over a wide range of conditions. It was further observed that the size distributions of the final latices were very similar, which contrasts the results of *Gerrens* [16], who reported narrower size distributions with increasing initiator concentration and explained this by the shortening of the initiation phase. This effect seems to be less distinct in the reactions I1–I4, which seems reasonable to the higher reaction temperatures and emulsifier contents used compared to those by *Gerrens*.

An increase of the reaction temperature yielded a higher number of particles (Table 3, Fig. 1c) due to the higher decomposition rate of the thermal initiator in the system and therefore a higher number of radicals which are available for initiation. The particle size distributions of the final latices T1–T4 conducted at different reaction temperatures were found to be very similar within this reaction series. In general a narrower size distribution is expected, due to a shortening of the initial phase, but this effect was not observed in the reactions T1–T4 and latices with similar size distributions were obtained.

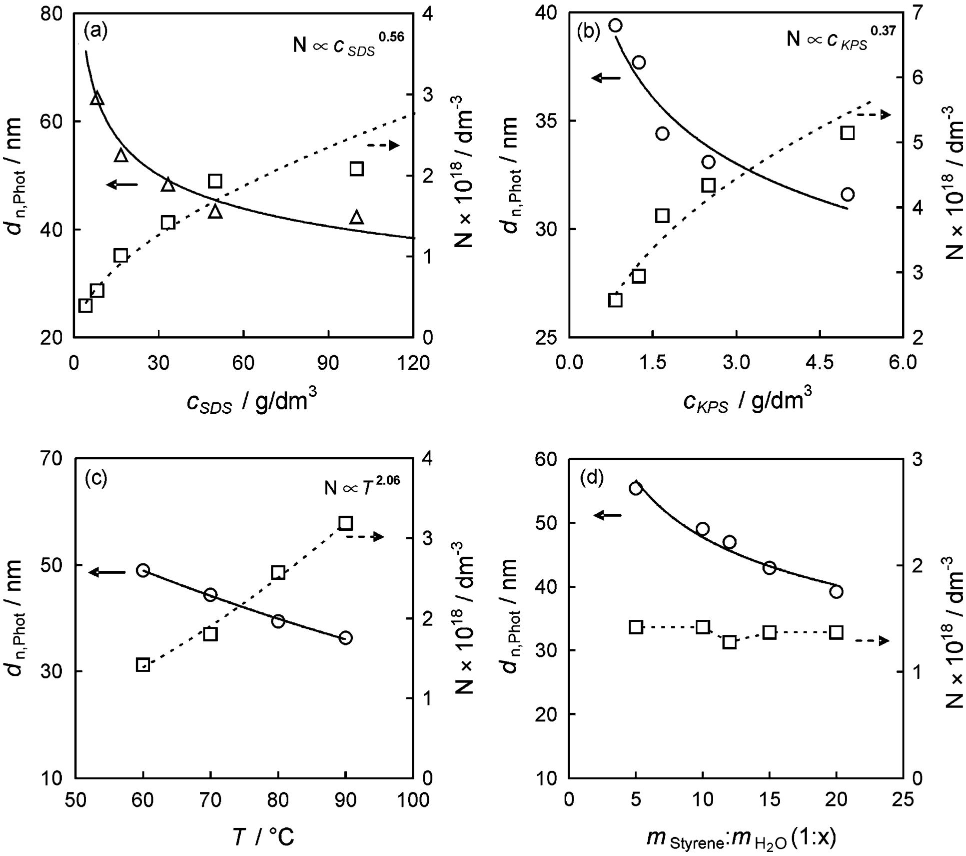

Fig. 1. Variations of *d* and N with (a) the surfactant concentration, (b) the initiator concentration, (c) the reaction temperature, (d) the monomer content in the system

Table 2. Recipes and results for the reactions with different initiator concentrations

Latex	m_{KPS} (g)	$N \times 10^{18}$ (dm^{-3})	$d_{w,DLS}$ (nm)	$d_{n,Phot}$ (nm)	$d_w/d_{n,DLS}$
I1	0.5	2.57	38.2	39.4	1.057
I2	0.75	2.94	40.3	37.7	1.054
I3	1	3.87	39.4	34.4	1.057
I4	1.5	4.34	37.8	33.1	1.058
I5	3	5.15	32.8	31.6	1.078

In all reactions I1–I5: Styrene: 60 g, Water: 0.6 dm^3, *SDS*: 20 g, *T*: 80°C

Table 3. Recipes and results for the reactions at different reaction temperatures

Latex	T (°C)	$N \times 10^{18}$ (dm^{-3})	$d_{w,DLS}$ (nm)	$d_{n,Phot}$ (nm)	$d_w/d_{n,DLS}$
T1	60	1.39	49.4	49.0	1.056
T2	70	1.80	43.8	44.4	1.057
T3	80	2.57	38.2	39.4	1.057
T4	90	3.19	36.7	36.3	1.067

In all reactions T1–T4: Styrene: 60 g, Water: 0.6 dm^3, *SDS*: 20 g, *KPS*: 0.5 g

Influence of the Monomer Concentration

In the classical view of *Smith* and *Ewart* [9] at a constant temperature the number of particles should be mainly determined by the emulsifier and the initiator concentration. Once the final number of particles has been initiated in the micelles, the particles will grow from the monomer, which is supplied by the droplets dispersed in the aqueous phase. In this sense the final particle size will decrease when the initial amount of monomer in droplets is decreased, while the number of particles remains constant. This behavior was observed in the reactions M1–M5 (listed in Table 4 and illustrated in Fig. 1d) for styrene:water ratios (m_{Styrene}:$m_{\mathrm{H_2O}}$) between 1:5 and 1:20. A similar tendency was also found in the reactions M6–M8 (not shown graphically) using much higher amounts of *SDS* and *KPS* (Table 4). For M1–M5 the breadth of the size distribution increased when the ratio of styrene:water was decreased. This indicates

Table 4. Recipes and results for the reactions with different monomer concentrations

Latex	m_{Styrene} (g)	$\mathrm{N} \times 10^{18}$ (dm^{-3})	$d_{\mathrm{w,DLS}}$ (nm)	$d_{\mathrm{n,Phot}}$ (nm)	$d_{\mathrm{w}}/d_{\mathrm{n,DLS}}$
M1	100	1.42	55.4	55.4	1.030
M2	60	1.39	49.4	49.0	1.056
M3	50	1.20	52.5	47.0	1.050
M4	40	1.37	43.9	42.9	1.062
M5	30	1.37	39.8	39.2	1.071
M6	100	11.8	–	27.0	–
M7	60	11.0	–	25.1	–
M8	40	10.7	–	21.0	–

M1–M5: Water: 0.6 dm^3, *SDS*: 20 g, *KPS*: 0.5 g, *T*: 60°C
M6–M8: Water: 0.6 dm^3, *SDS*: 60 g, *KPS*: 1.5 g, *T*: 80°C

that two factors will mainly influence the size distribution. On the one hand, as explained before, the initial phase should be kept short to obtain a narrow distributed latex after initiation. On the other hand, if the particles obtained after initiation will have more time to grow, due to a higher amount of initial monomer, then the final size distribution will be narrower. This has also been suggested by *Vanderhoff* and *Bradford* [17] and experimentally shown by *Gerrens* [16].

Estimation of the Final Number of Particles and Lower Particle Size Limits

From the correlations between the concentrations of the different components and N given above, the final number of particles can be estimated with the following relationship for styrene:water ratios between 1:5 and 1:20.

$$\mathrm{N} = \mathrm{k} \cdot c_{KPS}{}^{0.37} \cdot c_{SDS}{}^{0.56} \cdot T^{2.06}$$

Formula 1

The constant k was calculated as the mean average value obtained from the reactions listed in Tables 1–4. The calculated results for N were in good agreement (±20%) with all the experimental values obtained. The reproducibility of the final number of particles in the polymerization experiments, was found approximately in the same range (±20%) as tested with the latices E1–E4, which were synthesized four times each. An error of 20% in the estimated value for the number of particles induces an error in the final particle diameter of approximately 6%, which means *e.g.* for a latex with an estimated average diameter of 50 nm the average final latex diameter can be predicted within a range of ±3 nm. The lower size limits for emulsion polymerization of styrene using *SDS*/*KPS* can be estimated by inserting the values of 200 g/dm^3 (solubility of *SDS* in water), 10 g/dm^3 *KPS*, and a temperature of 100°C (reflux) into the equation derived. This results particle numbers of $\sim 2.7 \times 10^{19}\,\mathrm{dm}^{-3}$ and average particle diameters of about 18 and 16 nm can be estimated for styrene:water ratios of 1:10 and 1:15.

Experimental

Styrene was distilled under reduced pressure before use. *SDS* (99%, Roth) and *KPS* (99%, Fluka) were used as received. The water which was used in the experiments was deionized by ion exchange and filtered through a microfiltration membrane. It had a final conductivity between 1.0 and 1.5 μS/cm.

All reactions (Tables 1–4) were carried out in a 750 cm^3 four necked flask equipped with a tangential stirrer, a N_2 inlet, and a reflux condenser connected to a bubble counter. In the beginning *SDS* was dissolved in 550 cm^3 of water (500 cm^3 were used for $m_{KPS} > 2.5$ g), and styrene was added under stirring at a rate of 400 rpm to form emulsions with fine droplets. The emulsions were heated to the reaction temperature under stirring and dissolved O_2 was removed by flushing with a gentle stream of N_2. A solution of the initiator in 50 cm^3 H_2O (100 cm^3 for $m_{KPS} > 2.5$ g) was added within a few seconds to start the reaction, then the mixture was stirred at reaction temperature for 4 h under N_2. After this period the conversions of styrene were analyzed gravimetrically and values of higher than 98% were found in all reactions.

The final average particle number and weight diameters (d_{n}, d_{w}) were obtained by DLS measurements on an ALV CGS-3 Goniometer. To determine the average particle diameters five runs for the correlation function (each 30 s) were performed. From the average weight and number diameters the ratio $d_{\mathrm{w}}/d_{\mathrm{n}}$ was calculated as a measure for the size distribution. Furthermore, the absorbance/turbidity of the dispersions was measured on a Beckman DU-64 spectrophotometer at a wavelength of 546 nm. The average particle diameter $d_{\mathrm{n,Phot}}$ was calculated using tables for the scattering cross sections from the *Mie*-theory [21] with the values of the absorbance and the polymer content of the final latex. The average particle diameters obtained by turbidity measurements and DLS measurements were in good agreement and the particle diameter derived from turbidity measurements was used for further calculation of the average number of particles in the latices.

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