Exploring the limits of emulsion polymerization for the synthesis of polymer nanoparticles

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Summary. Suspensions of polymer nanoparticles in water (latex) with average particle diameters between 20 and 80 nm were synthesized by batch emulsion polymerization of styrene using s*odium 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 2.26 power. With these correlations the average particle number as well as the average particle size can be calculated and the results were in good agreement (± 6%) with the experimental values. A reduction of the monomer concentration lead to smaller particle diameters but also induced a smaller final number of particles under a certain monomer concentration, which has also been taken into account for estimation of the particle size. The lower particle size limit for the given system polymerized by emulsion polymerization was calculated with a diameter of about 17 nm.

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Introduction

Emulsion polymerization is an important method for the production of polymer dispersions (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 useful method to produce nanoparticles with smaller particle diameters [3-6].

For the emulsion polymerization system the locations of the different components and the kinetics of the polymerization reaction were first investigated and described in detail by *Harkins, Smith* and *Ewart* in the middle of last century [7-10]. These authors also proposed a three phase model for the polymerization reaction which still represents the basis for discussions in this field. In the first phase the reaction is started in a certain number of monomer filled micelles 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, because all the micellar surfactant is consumed by the growing particles. Since the final particle diameter d is inversely proportional to N ($d \propto N^{-1/3}$) the amount of particles which are generated in the first stage of the reaction should be high to obtain small particles for a given volume of monomer. This can be achieved for instance by increasing the initial number of micelles by using more surfactant or to provide more radicals for initiation by using a higher amount of initiator. A higher reaction temperature also leads to a higher number of particles for thermal initiators. The significant role of surfactant and initiator on the final number of particles generated has been investigated and discussed in detail in numerous studies.

Derived from emulsion polymerization also other polymerization techniques such as miniemulsion polymerization [11,12], microemulsion polymerization [13,14] or diffusion controlled emulsion polymerization [15] were developed and investigated for the synthesis of nanoparticles in the last two decades. In this context especially micro emulsion polymerization has proved to be a very powerful method to prepare ultrafine latices with particle diameters below 30 nm.

In the current work we report a comprehensive study on the preparation of polymer nanoparticles by emulsion polymerization. An often discussed model system (*Styrene/SDS/KPS/water*) was chosen for better comparison of the results with previous works using this system and the basic theoretical works in this field.

Results and Discussions

Influence of surfactant concentration

The recipes for the reactions which were carried out in order to investigate the dependence of the surfactant concentration on the final particle diameters can be found in Table 1 and the results are illustrated in Fig. 1a.

< Table 1 >

The final number of particles increased to the 0.56 power of the surfactant concentration, which is in good agreement with the value of 0.6 proposed by *Smith* and *Ewart* [13,14]. A higher amount of surfactant generates a higher number of micelles with a higher surface area for radical entry and therefore a higher possibility of initiation for the production of particles can be expected. A broadening of the size distribution (higher values for d_w/d_n) was observed when the surfactant concentration was increased. This can be explained by the fact that at high surfactant concentrations not all of the surfactant is consumed by the particles produced during 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. A similar behaviour is also observed in microemulsion polymerization which usually involves very high contents of emulsifiers [9,10].

Influence of initiator concentration and temperature

The number of particles increased with the initiator concentration [Table 2, Fig. 1b] with $N \propto [I]^{0.37}$ which is in good agreement with *Smith* and *Ewart* [13,14], who proposed that the generated number of particles N will be proportional to the 0.4 power of the initiator concentration.

< Table 2 >

Similar correlations for *KPS* were also found in microemulsion polymerization [13,14] and mini emulsion polymerization reactions using *styrene/SDS/KPS* [11,12] so it can be assumed that the exponent 0.4 resembles an unchanged value in emulsion poly-merization reactions with this system over a wide range of conditions.

An increase in the reaction temperature also yielded a higher number of particles due to the higher composition rate of the thermal initiator in the system

(Table 3, Fig. 1c) and therefore induced higher values of N with smaller particle diameters.

< Table 3 >

The particle size distributions of the final latices initiated with different amounts of *KPS* or at different reaction temperatures were in both cases found to be very similar within their reaction series. In contrast *Gerrens* reported [16] that higher initiator concentrations lead to narrower size distributions in the polymerization of styrene with *KPS* due to a shortening of the initiation phase. A similar behavior could also be expected for using higher reaction temperatures, due to the same reason. This effect was expected to be negligible in the reactions I1-I5 and T1-T4, due to the already short initiation times which were induced by the elevated temperatures and surfactant contents used.

Influence of the monomer concentration

In the classical view of *Smith* and *Ewart* 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 suspended 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-M7 (listed in Table 4 and illustrated in Fig. 1d) as long as the monomer concentration was above a concentration of about 50 g/L. Then a drop in the number of particles was observed and a similar tendency was found in the reactions M8-M11 (not shown graphically) using higher amounts of *SDS* and *KPS* (Table 4). As reported [17], the decomposition rate of *KPS* is decreased at lower styrene concentrations and this leads to a smaller number of monomer particles under a certain concentration limit.

< Table 4 >

< Fig. 1 >

Estimation of the final number of particles and lower particle size limit

From the correlations above the theoretical number of particles derived the following relationship for the estimation of N,

$$N = k \, [KPS]^{0.37} \, [SDS]^{0.56} \, [T]^{2.26}$$

and this formula may be used for concentrations of styrene above 50 g/L as mentioned before. The constant k was obtained as the average value from the reactions listed in Tables 1-3 and the results for N were in good agreement (± 20%) with the experimental values obtained. The reproducibility of the final number of particles of a typical polymerization experiment, was found approximately in the same range as tested with the latices E1-E4. 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 *p.e.* for a latex with an average diameter of 50 nm the average final latex diameter can be predicted with an accuracy of ± 2.5 nm. This underlines the power of the model for this system above a certain concentration. The lower size limit for an emulsion containing 100 g/L of monomer can be estimated, when we insert a value of 250 g/L (solubility limit) of SDS, 10 g/L *KPS* and a temperature of 100 °C (reflux) into the equation derived, and a value of about 17 nm was obtained.

Experimental

Styrene was distilled under reduced pressure before and use. Sodium docecyl sulphate (ROTH) and *potassium persulphate* (Fluka) were of analytical grade and used as received. The water which was used in the experiments was deionized by ion exchange and filtered through a microfiltration membrane and had a final conductivity between 1.0 and 1.5   S/cm.

All reactions (Tables 1-4) were carried out in a 750 ml four necked flask equipped with a tangential stirrer, a nitrogen inlet and a reflux condenser connected to a bubble counter. In the beginning *SDS* was dissolved in 550 ml of water (500 ml were used for KPS-amounts > 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 reaction temperature under stirring and dissolved oxygen was removed by flushing with a gentle stream of nitrogen. A solution of the initiator in 50 ml water (100 ml for KPS amounts > 2.5 g) was added within a few seconds to start the reaction, then the mixture was stirred at reaction

temperature for four hours under nitrogen atmosphere. After this period the conversions of styrene were analyzed gravimetrically.

The final average particle number and weight diameters 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 seconds) were performed. From the average weight and number diameters the ratio d_w/d_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. From the values of the absorbance and the polymer content of the final latex the average particle diameter $d_{n,Phot}$ was calculated using tables for the scattering cross sections from the Mie-theory [18]. 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.

Acknowledgments

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Tables

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

Latex	SDS / g	$N *10^{18}$ / dm^{-3}	$d_{w,DLS}$ / nm	$d_{n,Phot}$ / nm	$d_w/d_{n,DLS}$ / -
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	49.2	48.4	1.034
E5	30	1.93	46.4	43.4	1.065
E6	60	2.08	42.4	42.3	1.129

In all reactions: Styrene: 60g, Water: 600g, KPS: 0.5g , T: 60°C

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

Latex	KPS / g	$N *10^{18}$ / 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: Styrene: 60g , Water: 600g , SDS: 20g , T: 80°C

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

Latex	T / °C	$N *10^{18}$ / dm^{-3}	$d_{w,DLS}$ / nm	$d_{n,Phot}$ / nm	$d_w/d_{n,DLS}$ / -
T1	60	1.20	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	1.077

In all reactions: Styrene: 60g , Water: 600g , SDS: 20g , KPS: 0.5g

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

Latex	Styrene / g	$N *10^{18}$ / dm^{-3}	$d_{w,DLS}$ / nm	$d_{n,Phot}$ / nm	$d_w/d_{n,DLS}$ / -
M1	100	1.42	55.4	55.4	1.060
M2	60	1.42	49.4	49.0	1.047
M3	50	1.20	52.5	47.0	1.050
M4	40	1.37	43.9	42.9	1.048
M5	30	1.37	39.8	39.2	1.071
M6	20	0.95	39.2	38.9	1.118
M7	10	0.64	32.0	35.4	1.115
M8	100	11.8	-	27.0	-
M9	60	11.0	-	25.1	-
M10	40	10.7	-	21.0	-
M11	20	4.84	-	21.9	-

M1-M7:   Water: 600g , SDS: 20g , KPS: 0.5g , T: 60°C
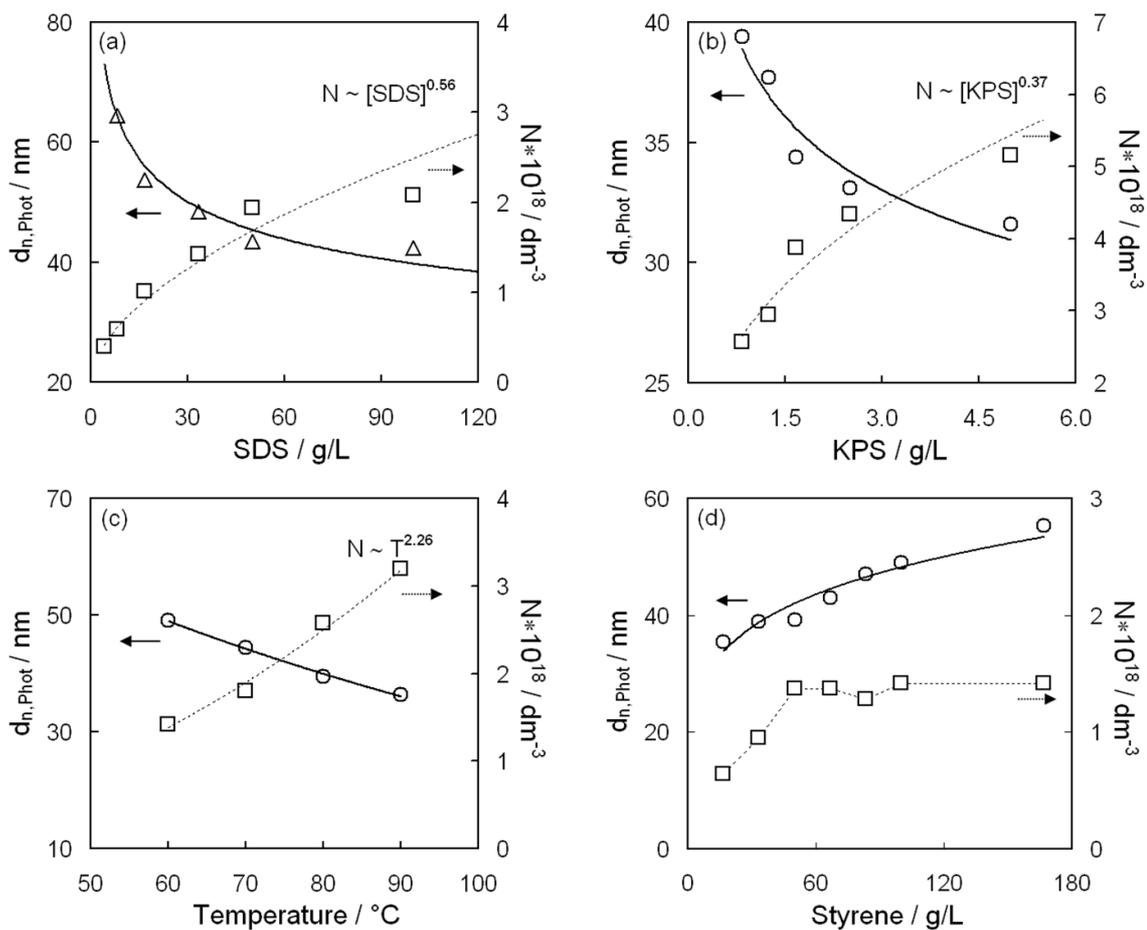M8-M11:   Water: 600g , SDS: 60g , KPS: 1.5g , T: 80°C

Figures

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