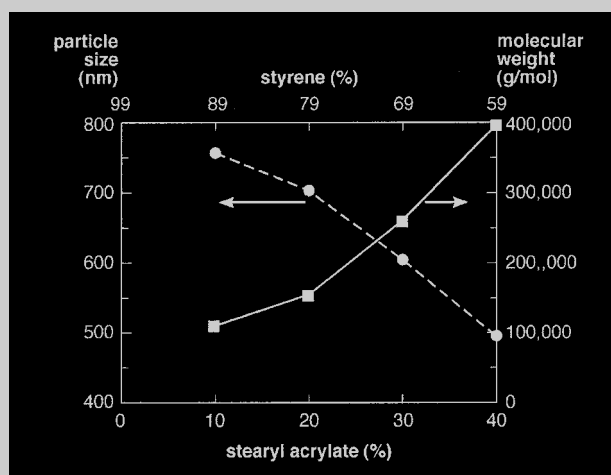


Full Paper: In emulsion polymerization also water insoluble hydrophobic monomers like stearyl acrylate can be used if cyclodextrin is added as a phase transfer agent. The characterization of the corresponding emulsion polymers by thermal analysis with DSC, by molecular weight determination with SEC and by measuring particle size distribution, particle density distribution (i.e. chemical composition and heterogeneity) and free cyclodextrin molecules in the aqueous phase with the analytical ultracentrifuge provides first indications for the following mechanism: An especially high transfer resistance exists for longer alkyl chains containing molecules at the interface between the monomer droplet and the water phase resulting in a concentration decrease in the polymerizing particle. Therefore, it is assumed that cyclodextrin and its ability to form a water soluble complex with hydrophobic molecules reduce the kinetic barrier and makes it easier for the stearyl acrylate to leave the monomer droplet. After arriving at the surface of the growing particle, the stearyl acrylate is released from the complex and able to enter it. Now the free cyclodextrin can start its transport function again. Only 5 wt.-% of cyclodextrin is necessary to polymerize almost 100% of stearyl acrylate.



Influence of stearyl acrylate on particle size and molecular weight of the dispersion polymerized in the presence of surfactant and methyl- β -cyclodextrin W7 M1,8 according to the experiments 1 to 4 in Tab. 1

Emulsion polymerization of hydrophobic monomers like stearyl acrylate with cyclodextrin as a phase transfer agent

Dedicated to Prof. Dr. Gerhard Wegner, Max-Planck-Institut für Polymerforschung in Mainz, on the occasion of his 60th birthday

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Introduction

During the emulsion polymerization the monomers diffuse from the monomer emulsion droplet through the water phase to the polymerizing dispersion particle. Styrene (S) and butyl acrylate (BA) are soluble enough for such a diffusion process and have a low enough transfer barrier at the interface between the monomer droplet and the water phase. However, monomers with long alkyl chains, like stearyl acrylate (SA) with his hydrophobic C₁₈ alkyl chain, can not be polymerized in emulsion as the water solubility is too low and the interfacial resistance at the monomer droplet surface too high. Therefore only small amounts of stearyl acrylate can be polymer-

ized in emulsion under special conditions^{1,2}. The solubility of stearyl acrylate is enhanced if water-soluble solvents like acetone or methanol are added to the water phase³. With the miniemulsion technique it is possible to polymerize stearyl acrylate in the monomer droplet without any diffusion of the monomer through the water phase^{4,5}.

On the other hand it is known in supramolecular chemistry that cyclodextrin is able to form a water soluble complex with a hydrophobic insoluble molecule⁶. Far more than ten thousand papers, patents, and patent applications are available on cyclodextrins and on their various applications^{7–11}. If this complex is used in emulsion

polymerization also water insoluble monomers can be polymerized. The corresponding technique was simultaneously developed in the laboratories of Rohm & Haas¹²⁾, where the monomer lauryl methacrylate was used, and in BASF Aktiengesellschaft¹³⁾, where the monomer stearyl acrylate was preferred. In both companies only a small amount of cyclodextrin was added to the reaction vessel and larger quantities of the very hydrophobic monomers could be polymerized. In the following section some experiments will be reported contributing to the characterization of that new type of emulsion polymerization and the corresponding polymer dispersion, which became of interest also in other laboratories¹⁴⁾.

Experimental part

Emulsion polymerization

The emulsion polymerization experiments were carried out in a four-necked glass reactor equipped with a mechanical stirrer (120 rpm), condenser, temperature control, monomer, and separate initiator feed and a nitrogen inlet. 360 g deionized water and methyl- β -cyclodextrin W7 M 1,8 from Wacker-Chemie GmbH, D-81737 München, were introduced into the reactor, and the mixture was stirred under nitrogen and heated to 80 °C. Separately the monomer emulsion was

prepared in a round bottom glass vessel mixing 210 g of deionized water with 600 g of the monomers according to the ratio given in Tab. 1 and 2 together with 20 g surfactant dodecyl benzene sulfonic acid sodium salt solution in deionized water with a solid content of 15%. 3 g of the total monomer emulsion were introduced into the reactor at 80 °C together with 20% of the initiator solution (3 g sodium persulphate in 120 g deionized water). After 15 min the remainder of the monomer emulsion was fed into the reactor over a period of 4 h together with the remainder of the initiator solution, followed by the addition of 1.9 g hydroxymethyl sulphonic acid and 2.4 g *t*-butyl hydroperoxide. After an additional 90 min, the resulting polymer dispersion was cooled down to room temperature. The solid content of the dispersion was 43% at pH 2 with a viscosity of 25 mPa · s.

The monomer stearyl acrylate (SA) was crystalline, had an acid content of less than 0.1%, a density of $\rho = 0.856 \text{ g/cm}^3$ at 35 °C and showed DSC melting points at 13 °C, 20 °C, and 35 °C. It was stabilized with 200 ppm hydroquinone monomethyl ether. The comparative poly(stearyl acrylate) (PSA) was prepared in a batch process adding 2% butyl peroctoate to the monomer stearyl acrylate at 80 °C. The PSA showed a DSC melting point at 48 °C. Bigger amounts of PSA can be produced as a dispersion in the following way: 791 g deionized water, 20 g methyl- β -cyclodextrin W7 M 1,8, 33 g surfactant dodecyl benzene sulphonic acid sodium salt solution in deionized water with a solid content of 15%, 2 g acrylic acid and 198 g stearyl acrylate were introduced into the reac-

Tab. 1. Polymerization of styrene (S), acrylic acid (AS) and stearyl acrylate (SA) by means of methyl- β -cyclodextrin W7 M1,8 (CD)

Experiment	Composition monomers			cyclo-dextrin CD/%	glass transition temperature/°C	Analytical data		Particle density theory		AUC values/(g/cm ³)
	S/%	AS/%	SA/%			particle size/nm	molecular weight \bar{M}_w /(g/mol)	with CD/(g/cm ³)	without CD/(g/cm ³)	
Comparative 1	99.0	1.0			107	416	196,000		1.055	1.052
Comparative 2	99.0	1.0		5.0	106	574	840/100,000	1.071	1.055	1.050
1	89.0	1.0	10.0	5.0	78	766	840/110,000	1.061	1.045	1.047
2	79.0	1.0	20.0	5.0	78	766	840/155,000	1.049	1.033	1.040
3	69.0	1.0	30.0	6.0	36	616	840/261,000	1.040	1.021	1.028
4	59.0	1.0	40.0	8.0	19	494	840/397,000	1.038	1.012	1.012

Tab. 2. Polymerization of *n*-butyl acrylate (BA), styrene (S), acrylic acid (AS) and acrylate (SA) by means of methyl- β -cyclodextrin W7 M1,8 (CD)

Experiment	BA/%	Composition monomers			cyclo-dextrin CD/%	glass transition temperature/°C	Analytical data		Particle density theory		AUC values/(g/cm ³)
		S/%	AS/%	SA/%			particle size/nm	molecular weight \bar{M}_w /(g/mol)	with CD/(g/cm ³)	without CD/(g/cm ³)	
Comparative 3	49.5	49.5	1.0			22	428	185,000	1.068	1.068	1.067
Comparative 4	44.5	44.5	1.0	10.0		22	413	249,000	1.054	1.054	1.067
Comparative 5	39.5	39.5	1.0	20.0		22	351	206,000	1.040	1.040	1.067
5	44.5	44.5	1.0	10.0	5.0	14	560	260,000	1.070	1.054	1.054
6	39.5	39.5	1.0	20.0	5.0	6	542	470,000	1.056	1.040	1.034
7	34.5	34.5	1.0	30.0	5.0	-9	219	598,000	1.043	1.027	1.031

tor, stirred at 250 rpm under nitrogen and heated up to a temperature of 80 °C. 1 g initiator sodium persulphate in 39 g deionized water were added to the reactor within 1 min. After 15 min the same amount of initiator in water was added over a period of 8 h. After an additional 90 min the resulting polymer dispersion was cooled down to room temperature. The solid content of the dispersion was 20%. A film of this dispersion had a melting point, as measured by DSC, of 48 °C.

Thermal analysis

The DSC traces were recorded on a DSC 820, serial number TA8000, from Mettler-Toledo. The dried polymer dispersions were packed in an aluminum pan, cooled down from room temperature to -110 °C at a rate of 20 °C/min and after 7 min heated up to 150 °C at a rate of 20 °C/min. The glass transition temperature, T_g , and the crystallization temperature were determined from the first scan.

Measurement of particle size

The z-average particle diameter was obtained by photon correlation spectroscopy according to ISO 13321 in the diluted dispersions with a solid content of about 0.005%. The Autosizer IIC of Malvern was used with a He-Ne laser at a wavelength of 633 nm, with a single scattering angle of 90° and a temperature of 23 °C. The values of the average particle size (Tab. 1 and 2) were obtained by the so-called cumulants analysis¹⁵⁾ with the approximate refractive index values 1.333 for the water phase and 1.60 for the polymer particle.

Molecular weight determination

Average molecular weights were measured by size exclusion chromatography (SEC) using an apparatus with a HPLC pump (Kontron), an autosampler (Gilson 231), a set of four Tosohaas TSK columns (HXL 3000, 4000, 6000, 7000, each 300 × 7.8 mm i.D.) and a DRI detector (ERC 7515). Tetrahydrofuran (THF) was used as the eluent and the calibration was carried out with narrowly distributed polystyrene standards of known molecular weight. The samples were dissolved in THF ($c = 1.25 \text{ mg} \cdot \text{cm}^{-3}$) and an injection volume of 200 μm^3 was used. For the eluent volume flow rate through the columns 0.8 $\text{cm}^3 \cdot \text{min}^{-1}$ was selected, all experiments were carried out at a temperature of 21 °C.

Analytical ultracentrifugation (AUC)

All measurements were performed in an eight-cell AUC setup (a modified Spinco-Beckman AUC, Model E, Palo Alto, CA^{16,17)}) and in a homemade AUC-particle sizer¹⁸⁾. Sedimentation runs for fractionation according to size were performed in aqueous dispersions as well as in organic solvents (mostly THF), thus yielding information about particle size distribution as well as molecular weight distribution. Density gradient runs for fractionation according to particle density (i.e. according to chemical composition) were performed both in aqueous and in organic media. Not only long lasting classical static density gradients¹⁶⁾ were performed

but also fast dynamical density gradients with a special overlay technique of solvent (water) over solution (dispersion) within the AUC-measuring cell during the run¹⁹⁾. The same overlay technique was used to detect quantitatively small amounts of low molecular weight compounds like cyclodextrin in the water phase (serum) of the dispersion.

Results and discussion

Thermal properties

The polymer produced by drying a polystyrene dispersion stabilized with 1% acrylic acid has a T_g of 107 °C as measured via DSC (see comparative experiment 1 in Tab. 1). This temperature is not essentially changed by the addition of 1% to 5% cyclodextrin to the emulsion polymerization process (see comparative experiment 2 in Tab. 1). If in addition to cyclodextrin also stearyl acrylate in an amount of 10%, 20%, 30% or 40% is added, the T_g of the corresponding polymer film continuously decreases down to 19 °C (experiment 1 to 4 in Tab. 1). Representatives of these four experiments are the corresponding DSC traces of the dried polystyrene dispersion (comparative experiment 1) and of the dried dispersion with 40% stearyl acrylate (experiment 4) as given in Fig. 1. The glass transition temperature, T_g , is much lower on using stearyl acrylate but an endothermal peak arising from the melting of pure poly(stearyl acrylate) at a temperature of about 48 °C is not detected. This is the first indication of a complete copolymerization of stearyl acrylate and styrene in the presence of the phase transfer agent cyclodextrin.

The experiments were repeated in a similar way by replacing half the amount of styrene with *n*-butyl acrylate. Without stearyl acrylate and cyclodextrin the T_g of the dried dispersion is 22 °C as expected for the copolymer of styrene and *n*-butyl acrylate (comparative experi-

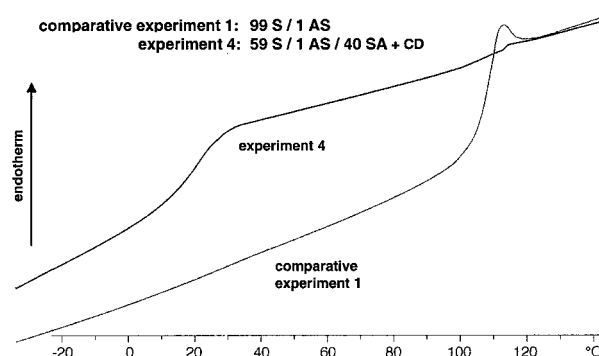


Fig. 1. DSC-analysis of polymers produced by drying a polystyrene dispersion stabilized with 1% copolymerized acrylic acid (see comparative experiment 1) and by drying a polystyrene dispersion, which was received by emulsion polymerization of 59% styrene (S), 1% acrylic acid (AS), and 40% stearyl acrylate (SA) in the presence of methyl- β -cyclodextrin W7 M1,8 (CD) as a phase transfer agent (see experiment 4)

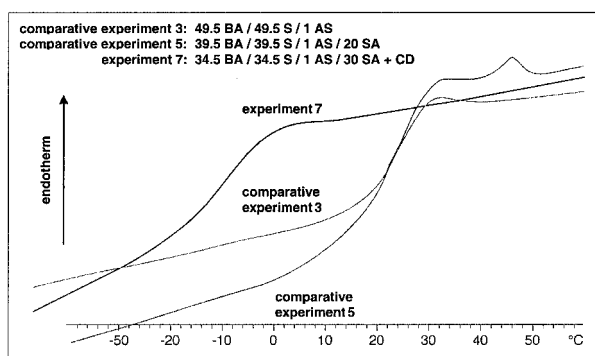


Fig. 2. DSC-analysis of polymers produced by drying a polymer dispersion based on 49.5% *n*-butyl acrylate (BA), 49.5% styrene (S), and 1% acrylic acid (AS) (see comparative experiment 3), by drying a polystyrene dispersion, which was received by emulsion polymerization of 39.5% BA, 39.5% S, 1% AS and 20% stearyl acrylate (SA) (see comparative experiment 5) and by drying a polystyrene dispersion, which was received by emulsion polymerization of 34.5% BA, 34.5% S, 1% AS, and 30% SA in the presence of methyl- β -cyclodextrin W7 M1,8 (CD) as a phase transfer agent (see experiment 7)

ment 3 in Tab. 2 and Fig. 2). If 10% and 20% stearylacrylate is added to the emulsion and polymerized without the presence of cyclodextrin, the T_g of the copolymer remains unchanged (comparative experiment 4 and 5 in Tab. 2) but the melting point of pure poly(stearyl acrylate) is detected at 48 °C (comparative experiment 5 in Fig. 2) and a larger amount of that polymer is floating at the surface of the polymer dispersion. As expected, styrene and *n*-butyl acrylate do not copolymerize with stearyl acrylate without the presence of the phase transfer agent. But after the addition of cyclodextrin (experiment 5, 6 and 7 in Tab. 2) copolymerization takes place, the T_g of the corresponding film is continuously reduced with an increasing amount of stearyl acrylate and no melting peak is detected (experiment 7 in Fig. 2). Based on these experiments, the T_g of a completely amorphous poly(-stearyl acrylate) can be extrapolated to the value of -57 °C with the Fox-equation.

Particle size and molecular weight

Cyclodextrin is not only forming a complex with the hydrophobic monomer but also with the surfactant thus enhancing the critical micelle concentration²⁰. Therefore an influence on the particle size and consequently also to the molecular weight¹⁴ is expected. If 5% cyclodextrin is added to the polymerizing styrene/stearyl acrylate-system the micelle concentration is reduced and the particle size of the resulting dispersion is increased from 416 nm to 574 nm (compare the particle size of comparative experiment 1 with that of comparative experiment 2 in Tab. 1). Also in the *n*-butyl acrylate containing system the particle

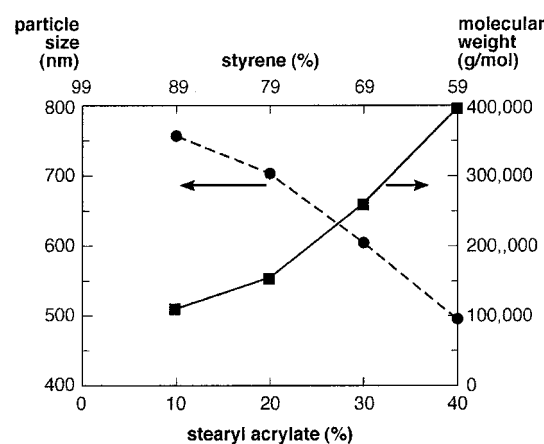


Fig. 3. Influence of stearyl acrylate on particle size and molecular weight of the dispersion polymerized in the presence of surfactant and methyl- β -cyclodextrin W7 M1,8 according to the experiments 1 to 4 in Tab. 1

size is increased by the addition of cyclodextrin (compare comparative experiment 4 with experiment 5 and comparative experiment 5 with experiment 6 in Tab. 2).

On the other hand, with an increasing amount of stearyl acrylate smaller particles are produced containing polymers with higher molecular weight. By changing in the styrene/stearyl acrylate-system, e. g. the amount of stearyl acrylate from 10% to 40%, the particle size is reduced from 766 nm to 494 nm and the molecular weight enhanced from 110,000 to 397,000 g/mol (see experiment 1 to 4 in Tab. 1 and Fig. 3). Again similar results are obtained in the *n*-butyl acrylate containing system (see experiment 5 to 7 in Tab. 2).

An additional SEC peak for the molecular weight $M_w = 840$ g/mol could be assigned to methyl- β -cyclodextrin W7 M 1,8 (see Tab. 1). The detected molecular weight is smaller than the calculated $M_w \approx 1300$ g/mol for methyl- β -cyclodextrin W7 M 1,8 as the hydrodynamic volume of this ring molecule corresponds to the hydrodynamic volume of the polystyrene tangle with a molecular weight of $M_w = 840$ g/mol.

Particle size

The increased average particle size after addition of cyclodextrin can be explained with the assumption that a part of the surfactant is complexed by cyclodextrin. As a result, the number of surfactant micelles is reduced during the particle formation phase and less but bigger particles are formed during the polymerization process.

For the decreasing particle size with increasing amount of stearyl acrylate two explanations are possible:

1. By stearyl acrylate the surfactant is pushed out from the complex with cyclodextrin and more surfactant micelles are formed. Therefore the number of particles is increased and the particle size becomes smaller. Now

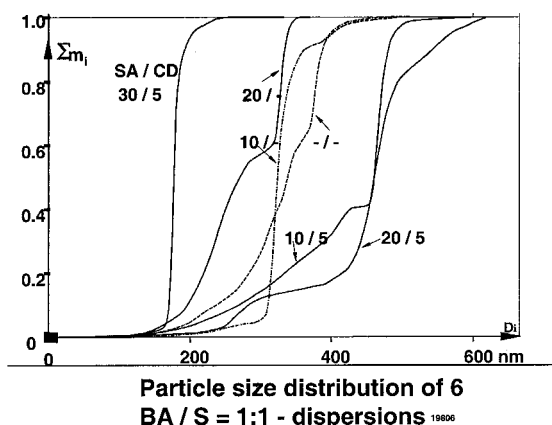


Fig. 4. AUC particle size distribution diagrams of 6 different dispersions based on *n*-butyl acrylate (BA)/styrene (S), 1% acrylic acid (AS) and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD), as described in Tab. 2

also the total particle surface covered by surfactants is increased and less micelles are available for secondary nucleation resulting in a narrower particle size distribution as measured in the analytical ultracentrifuge (see experiment 7 with SA/CD = 30/5 in Fig. 4). But also the opposite was observed depending on the composition of the initial charge and the continuous feed.

2. With increasing amount of stearyl acrylate more hydrophobic oligomers are formed and the homogeneous nucleation is favored during the particle nucleation phase resulting in more and smaller particles.

Molecular weight

With a greater amount of stearyl acrylate, the smaller particles lead to a higher molecular weight of the polymers in the particle. This can be explained by the enhanced compartmentation of the radicals during the emulsion polymerization process. That means the radical concentration per particle is reduced, termination of the growing chain becomes less probable, and the molecular weight of the resulting polymer is enhanced.

Characterization by analytical ultracentrifugation (AUC)

The analytical ultracentrifuge can fractionate both dispersion particles with a size from 5 nm to 3 μ m and dissolved macromolecules with a molecular weight from 300 g/mol to 10^{14} g/mol by two completely different methods, the sedimentation run and the density gradient run.

a) In the sedimentation run the big particles or the big molecules are settling out faster than the smaller ones. The particles are detected by a turbidity optics (light scat-

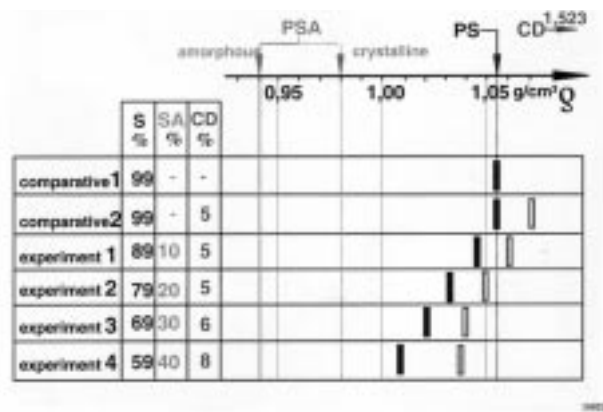


Fig. 5. Calculated density diagram for dispersion particles based on styrene (S), 1% acrylic acid (AS) and an increasing amount of stearyl acrylate (SA) as described in Tab. 1 with (dark bands on the left) and without (bright bands on the right) the built-in component methyl- β -cyclodextrin W7 M1,8 (CD)

tering) and the molecules by a Schlieren optics (refractive index differences).

b) In the sedimentation run with turbidity optics at a small measuring slit in the middle of the AUC-cell, simultaneous characterization of the particles by light scattering is possible to determine the particle size distribution¹⁶. In the so-called H₂O/D₂O sedimentation analysis not only the particle size distribution but also the particle density distribution is measured¹⁸.

c) In the overlay sedimentation run¹⁹ with Schlieren optics the dispersion is overlaid with pure water inside a synthetic boundary or valve type AUC cell during the run at 5,000 rpm. Thus, also low molecular weight components like cyclodextrin are quantitatively detected within the clear serum after additional running at 40,000 rpm for 10 to 60 min.

d) In the density gradient run with Schlieren optics the particles are separated according to their density, that means according to their chemical composition. For the density gradient there are two possibilities¹⁹:

- By overlaying H₂O over D₂O within a synthetic boundary in the measuring cell, a dynamic radial density gradient between $\rho = 1.0$ g/cm³ (H₂O) and $\rho = 1.1$ g/cm³ (D₂O) is established within 10 min.

- With heavy iodized sugar such as metrizamide ($\rho = 2.1$ g/cm³), a static radial density gradient between $\rho = 1.1$ g/cm³ and $\rho = 1.25$ g/cm³ is established inside the measuring cell within 18 h. The lower density limit can be decreased to $\rho = 1.0$ g/cm³ by the addition of methanol. This is necessary for detecting poly(stearyl acrylate) with a density of $\rho = 0.94$ g/cm³ in the amorphous and $\rho = 0.98$ g/cm³ in the crystalline state.

The principle of separation according to the particle density is shown in Fig. 5. The more amorphous poly(-stearyl acrylate) with a low density of $\rho = 0.940$ g/cm³ is

copolymerized in the polystyrene particle including 1% acrylic acid of high density $\rho = 1.055 \text{ g/cm}^3$ the lower is the density of the resulting styrene / stearyl acrylate copolymer particle and the more to the left is appearing the particle turbidity band in the measuring cell where the density also is becoming lower towards the left side. Cyclodextrin has a density $\rho = 1.523 \text{ g/cm}^3$ and is on the outer right of the experimental density region. If 5% cyclodextrin would be included in the dispersion particle its density would be increased by 0.016 g/cm^3 , as indicated by the bright bands on the right-hand side in Fig. 5.

Polymer dispersion based on styrene / stearyl acrylate

For the polymer dispersions based on styrene with an increasing amount of stearyl acrylate, the theoretical particle densities were calculated, as given in Tab. 1, both with the assumption that cyclodextrin was included in the particle and that cyclodextrin was still in the water phase (serum). In the dynamic $\text{H}_2\text{O}/\text{D}_2\text{O}$ density gradient run (see Fig. 6) and in the static density gradient run (see Fig. 7), where the measuring bands are arranged comparable to Fig. 5, the real particle densities were determined. These measured AUC particle density values, as summarized in Tab. 1, indicate that stearyl acrylate is incorporated into the polystyrene particles and cyclodextrin is not found inside the particle. Poly(stearyl acrylate) particles do not exist separately (see Fig. 7) as no turbidity

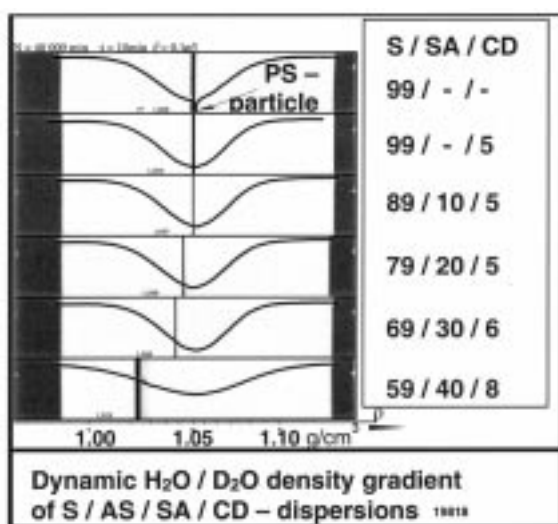


Fig. 6. Schlieren photos of dynamic $\text{H}_2\text{O}/\text{D}_2\text{O}$ density gradient runs of 6 dispersions based on styrene (S), 1% acrylic acid (AS) and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD) as described in Tab. 1. The Schlieren line with the broad minimum is composed of both the differentiated refractive index corresponding to the radial $\text{H}_2\text{O}/\text{D}_2\text{O}$ density gradient within the AUC cell and the narrow or broad turbidity bands corresponding to the accumulation of the particles at one radial position for homogeneous copolymer particles or at different radial positions for chemically heterogeneous copolymer particles

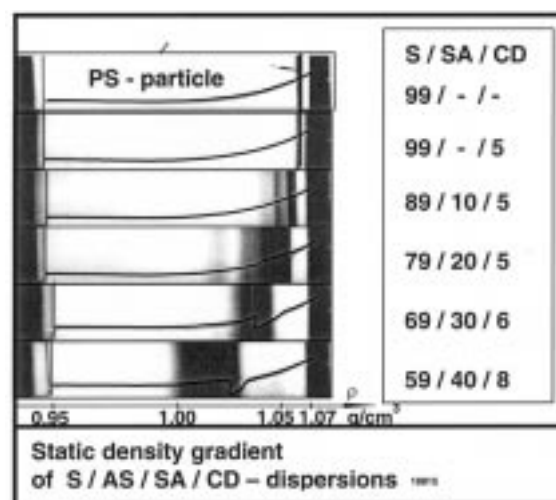


Fig. 7. Schlieren photos of static density gradient runs of 6 dispersions based on styrene (S), 1% acrylic acid (AS), and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD), as described in Tab. 1. The climbing exponential Schlieren base line represents the differentiated refractive index corresponding to the radial methanol/ H_2O /metrizamide density gradient and the narrow or broad turbidity bands corresponding to the accumulation of the particles at one or at different radial positions

bands are found at a density of $\rho = 0.98 \text{ g/cm}^3$ for the pure poly(stearyl acrylate) which mostly is crystalline. The broader the bands with increasing amount of stearyl acrylate (see Fig. 7) the higher the chemical non-uniformity of the different dispersion particles. For the dispersion with 40% stearyl acrylate, the stearyl acrylate and the corresponding styrene content can vary from one particle to the other between $\pm 8\%$.

The measured particle densities compared with the calculated values in Tab. 1 indicate that the cyclodextrin is not inside the particle. Therefore it must be in the serum as shown in the overlay sedimentation run (see Fig. 8). Without cyclodextrin only about 1.5% of oligomers are detected within the clear aqueous serum in the form of a gaussian Schlieren peak. This oligomer peak grows with increasing amount of cyclodextrin, which indicates that the cyclodextrin is in the serum of the dispersion outside the particle. From the Schlieren peak area the weight percentage of the free cyclodextrin and the oligomers in the serum were calculated (see Fig. 8).

Till now it was shown that stearyl acrylate is almost quantitatively inside and cyclodextrin outside the particle (see Fig. 6 to Fig. 8) but the copolymerization is verified only by thermal analysis and not yet by the AUC. To do so the non-crosslinked dispersion particles are dissolved by diluting the dispersion 1:100 in THF which is completely miscible with water. In the static 80% THF/20 diiodomethane density gradient run with Schlieren optics the dissolved polymer molecules can be detected by the

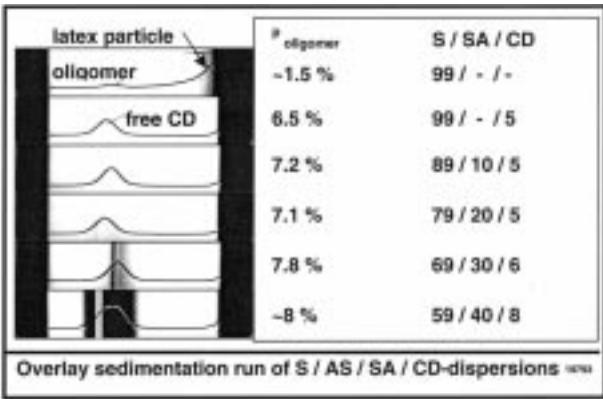


Fig. 8. Schlieren photos of overlay sedimentation runs of 6 dispersions based on styrene (S), 1% acrylic acid (AS), and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD) as described in Tab. 1. During the run at 5,000 rpm the dispersion is overlaid with pure water within the AUC measuring cell. Thus, also dissolved low molecular weight components in the serum, such as cyclodextrin, are quantitatively detected in the form of a gaussian Schlieren peak after additional running at 40,000 rpm for 10 min

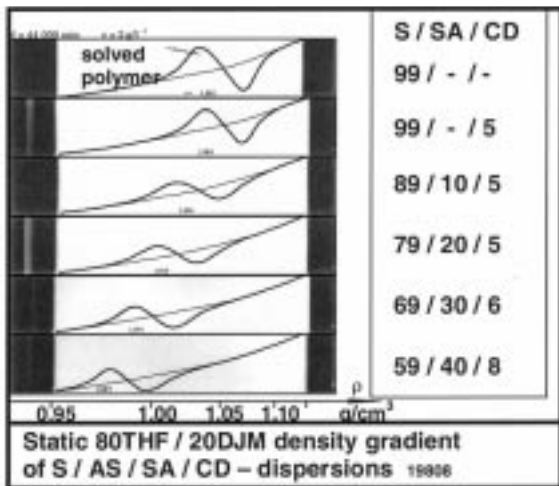


Fig. 9. Schlieren photos of static 80% THF / 20 diiodomethane density gradient runs of dissolved macromolecules received by diluting in the ratio of 1:100 with THF 6 different aqueous dispersions based on styrene (S), 1% acrylic acid (AS), and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD), as described in Tab. 1. The density of the macromolecules corresponding to the midpoints of the double Schlieren peak decreases with increasing amount of stearyl acrylate

diffusion broadened double Schlieren peak (see Fig. 9). The average density of the polymer (the middle of the double Schlieren peak) is decreasing with increasing amount of stearyl acrylate. The double Schlieren peak is symmetric also at higher stearyl acrylate content, that means the stearyl acrylate is copolymerized homogeneously in all polymer chains and no homopoly(stearyl acrylate) is formed.

Polymer dispersion based on *n*-butyl acrylate/styrene/stearyl acrylate

Comparable AUC experiments with polymer dispersions based on *n*-butyl acrylate/styrene with an increasing amount of stearyl acrylate give similar results. The theoretical particle densities is calculated again assuming that both cyclodextrin is incorporated into the particle and cyclodextrin is still in the serum (see Tab. 2). In the dynamic H₂O/D₂O density gradient run (see Fig. 10) and in the static density gradient run (see Fig. 11) the real particle densities can be determined. These measured AUC particle density values, as summarized in Tab. 2, indicate again that stearyl acrylate is incorporated in all *n*-butyl acrylate/styrene copolymer particles if cyclodextrin is present and cyclodextrin is not found inside the particle.

For both samples without cyclodextrin, pure poly-(stearyl acrylate) (PSA) particles are detected at a density of $\rho = 0.98 \text{ g/cm}^3$ and the density of the butyl acrylate/styrene copolymer (P(BA/S)) particles is not decreased (see comparative experiment 4 and 5 in Fig. 11 with SA/CD = 10/- and SA/CD = 20/-). These dispersions have the same particle density of $\rho = 1.067 \text{ g/cm}^3$ both for the

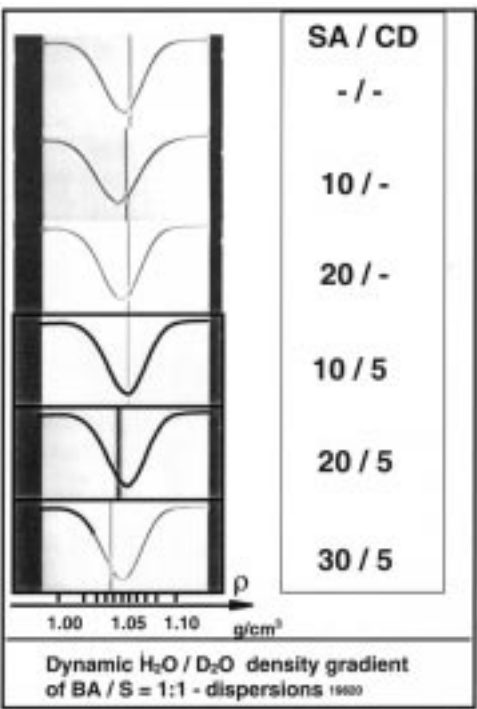


Fig. 10. Schlieren photos of dynamic H₂O/D₂O density gradient runs of 6 dispersions based on *n*-butyl acrylate (BA)/styrene (S), 1% acrylic acid (AS), and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD), as described in Tab. 2. The Schlieren line with the broad minimum is composed of both the differentiated refractive index corresponding to the radial H₂O/D₂O density gradient within the AUC cell and the narrow or broad turbidity bands corresponding to the accumulation of the particles at one or different radial positions comparable to Fig. 5

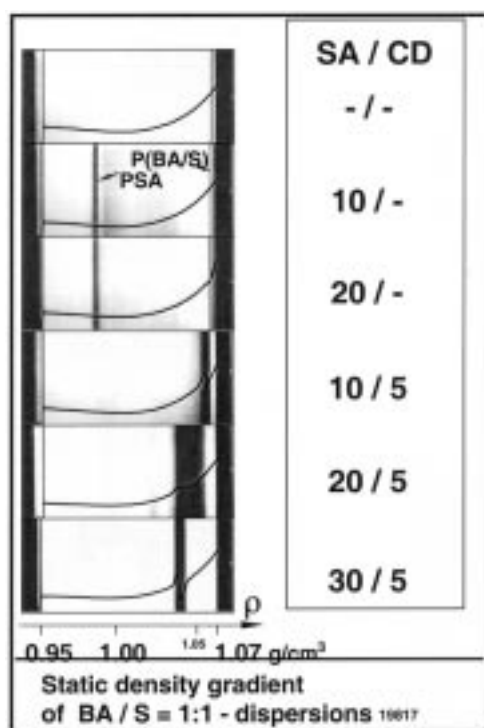


Fig. 11. Schlieren photos of static density gradient runs of 6 dispersions based on *n*-butyl acrylate (BA)/styrene (S), 1% acrylic acid (AS), and an increasing amount of stearyl acrylate (SA) with different amounts of methyl- β -cyclodextrin W7 M1,8 (CD), as described in Tab. 2. The climbing exponential Schlieren base line represents the differentiated refractive index corresponding to the radial methanol/H₂O/metrizamide density gradient and the narrow or broad turbidity bands correspond to the accumulation of the particles at one or different radial positions comparable to Fig. 7

smaller and for the bigger particles in the particle size distribution, as indicated by the evaluation of the H₂O/D₂O sedimentation analysis. But the dispersions with copolymerized stearyl acrylate in the presence of cyclodextrin have a slightly decreased particle density for the smaller particles in the size distribution, which means that the smaller particles have a little more stearyl acrylate incorporated than the bigger ones.

Beside the particle density distribution also the particle size distribution is given by the evaluation of the H₂O/D₂O sedimentation analysis (see Fig. 4). The samples with no or low stearyl acrylate content have a broad more or less bimodal particle size distribution. The samples with higher stearyl acrylate content have smaller particles and a narrower size distribution. With increasing amount of cyclodextrin the particle sizes are increasing, as already discussed above (see Tab. 2).

Reaction mechanism

Based on the described experiments the following reaction mechanism for the copolymerization of stearyl acryl-

ate in the presence of cyclodextrin can be proposed both on a thermodynamic and on a kinetic base:

1. The less probable thermodynamic model using the classical two-film theory²¹⁾ would suggest that the different phases are in thermodynamic equilibrium at the interface. From the emulsified monomer droplet a few stearyl acrylate molecules are dissolved in the water phase according to the specific solubility. However, this concentration is too low to enable the stearyl acrylate to participate in the emulsion polymerization process. But the stearyl acrylate is complexed by cyclodextrin in the water phase. Therefore, additional stearyl acrylate monomers can leave the monomer droplet and are complexed again in the water phase. Thus, the concentration of the cyclodextrin stearyl acrylate complex is increased until it can successfully compete with the other monomers in the polymerization process. In the case of the homogeneous nucleation, the growing oligomer is becoming more and more hydrophobic until the hydrophilic cyclodextrin is pushed out of the complex with the copolymerized stearyl acrylate. Also at the surface of a growing hydrophobic particle the cyclodextrin is pushed out of the complex and the released stearyl acrylate is able to enter the particle. Now the free cyclodextrin is ready to accept a new stearyl acrylate monomer starting the transport cycle for stearyl acrylate from the monomer droplet to the polymerizing center again like a phase transfer agent does.

2. More likely is the kinetically based explanation which assumes that in the presence of stearyl acrylate mass transfer resistances between the monomer droplet and the polymerizing center are of importance. That means the rate of polymerization exceeds the rate at which the monomer is supplied to the polymerizing center. Furthermore it is assumed that the diffusion rate through the aqueous phase does not determine the emulsion polymerization rate²²⁾. However the interfacial resistance to monomer transfer can be dominant both at the water-polymer particle interface and at the monomer droplet-water interface²³⁾. M. Nomura²⁴⁾ demonstrated quantitatively that for a longer alkyl chain containing molecule, the concentration decrease in the polymer particle is due mainly to the resistance to mass transfer at the interface between the monomer droplet and the water phase. Therefore, it is concluded that cyclodextrin and its ability to form a water soluble complex²⁵⁾ reduce the kinetic barrier for the stearyl acrylate migration through the interface from the monomer droplet to the water phase. After the complex arrived at the polymerizing center, the stearyl acrylate is released as discussed before and the free cyclodextrin can start its transport function again.

As already shown for the radical copolymerization of the dissolved equimolar cyclodextrin/monomer complexes in water²⁵⁾, it is expected in the emulsion polymerization, too, that the copolymerization parameters will

differ if cyclodextrin is used knowing that not only stearyl acrylate but also the monomers like styrene and butyl acrylate are complexed²⁶⁾.

Conclusion

The copolymerization of very hydrophobic monomers like stearyl acrylate in emulsion polymerization with methyl- β -cyclodextrin W7 M 1,8 as a phase transfer agent enables the production of new polymer dispersions. The scientific aspects of this new type of emulsion polymerization are fascinating. Only the fundamental topics are discussed until now and many questions are left unanswered. Further discussion is needed concerning for example the influence of the copolymerization parameters²⁵⁾ of the complexed monomers, the influence of different surfactants²⁰⁾ forming a complex with methyl- β -cyclodextrin W7 M 1,8 and last but not least the reaction mechanism itself.

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