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On the Preparation of Organosilicon μ-Spheres: A Polycondensation in μ-Emulsion?

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ABSTRACT: Polycondensation of methyltrimethoxysilane in the presence of the surfactant benzethonium chloride yields strictly spherical organosilicon micronetworks of controlled size in the range of 3 nm $\leq R \leq$ 15 nm with R the particle radius. After a short induction period the size of the particle increases linearly with the cube root of added monomer volume which proves the number of growing nuclei to be constant with time or conversion, whereas the mechanism controlling the number of growing nuclei remains unclear. In many respects the polycondensation resembles a condensation in μ-emulsion although the surface are per surfactant molecule (headgroup area) is shown to decrease with decreasing particle size, a fact which is not yet understood. The particle density in solution is only about one-third of the dry particle density which means that the μ-network is considerably swollen in solution.

Introduction

Polymerization in microemulsion has developed into a powerful technique for the preparation of strictly spherical micronetworks.[1,2] The final size of the polymerized particles is solely governed by the ratio of surfactant to monomer concentration, although a detailed understanding of changes in particle size during the course of reaction is still lacking.[3,4] Two simple models have been proposed to predict the final particle size at full conversion which differ in some minor details, only.

In the first model[2] the hydrophobic alkyl chains of the surfactant are not solubilized by the encapsulated polymer but rather remain "phase-separated" on the surface of the microsphere, thus increasing the sphere radius by a surfactant layer thickness b. Simple geometric calculations lead to the following relation between the fleet ratio S and the spherical radius R at full conversion

$$S \equiv \frac{m_{\mathrm{surf}}}{m_{\mathrm{p}}} = \left(\frac{R^3}{(R-b)^3} - 1\right)\frac{\rho_{\mathrm{p}}}{\rho_{\mathrm{surf}}} \tag{1}$$

with m_{surf} and m_{p} the masses and ρ_{p} and ρ_{surf} the densities in solution (not the bulk densities) of polymer and surfactant, respectively. Eventually the spherical radius R (which we identify as the Stokes radius R_{h} derived from the diffusion coefficient) emerges from eq 1 as

$$R = b\left[1 - \left(1 + \frac{\rho_{\mathrm{surf}}}{\rho_{\mathrm{p}}}S\right)^{-1/3}\right]^{-1} \tag{2}$$

For a model system of styrene/diisopropenylbenzene, cetyltrimethylammonium bromide (CTAB), and the oil-soluble initiator azobis(isobutyronitile) (AIBN), eq 2 was shown to nicely fit the experimental data within the stable regime $0.2 \leq S \leq 4$. More recently,[5] eq 2 was scrutinized because the fitted surfactant layer thickness b = 3.4 nm is apparently unreasonably high as the fully stretched surfactant chain is, at the most, 2.8 nm long. Also, the calculated headgroup area per surfactant a_0 = 0.14 nm^2 is somewhat smaller than the commonly adopted value for CTAB of a_0 = 0.19 nm^2. Recently, a more realistic model was evaluated[5] which makes the surfactant chain partly penetrate into the polymer matrix. This calculation finally arrives at

$$S^{-1} = \frac{N_{\mathrm{A}}\bar{\rho}}{3M_{\mathrm{surf}}}a_0R - C \tag{3}$$

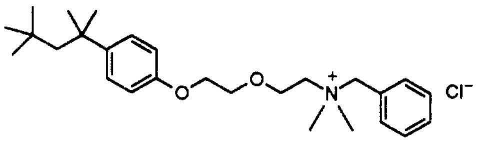
with N_{A} Avogadro's number, M_{surf} the molar mass of the surfactant, $\bar{\rho}$ the particle density in solution, and the other quantities defined in the text above. The constant C depends on the contribution of the headgroup of the surfactant of the hydrodynamic radius and adopts values very close to 1.

A plot of the experimental data of the model system styrene/CTAB according to eq 3, S^{-1} vs R_{h}, gives a perfectly straight line, the slope of which yields a_0 = 0.19 nm^2 which is in agreement with the literature.

We report here on the polycondensation of methyltrimethoxysilane[6-9] in μ-emulsion, the course of reaction of which is even much less transparent than the "simple" polymerization in the μ-emulsion described above. The use of the term "polycondensation in μ-emulsion" will certainly invoke controversial discussions. However, in a limited range the final size of the condensated particles is well described by eq 2 or 3 as will be shown below.

Experimental Section

Synthesis of the Silicon Particles/Silicon Microemulsion. A total of 25 g (0.184 mol) of methyltrimethoxysilane (Wacker Chemie) was slowly added to a stirred (300 rpm) solution of 0.03 g (7.5 mmol) of sodium hydroxide and various amounts of benzethonium chloride (Aldrich; 1) in 125 g of water at 20 °C.



benzethonium chloride

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After addition of the final amount of methyltrimethoxysilane, the reaction mixture was stirred for another 5 h. The alkoxysilane and the surfactant were used as supplied without further purification.

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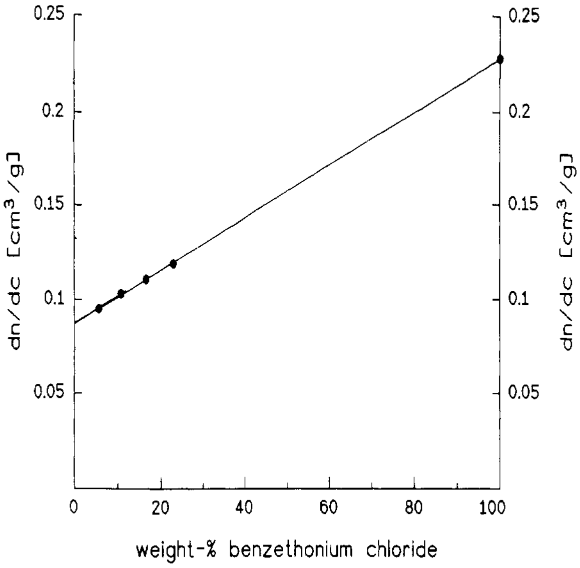

Figure 1. Refractive index increment of the μ-emulsion vs the weight fraction of the surfactant benzethonium chloride in the organosilicon μ-gel.

Table 1. Characterization of the Samples

S	$1/S$	R_h (nm)	R_g (nm)	ρ	$M_w \times 10^6$ [a]	ρ_p (g/cm^3)
0.06	16.67	19.5	14.5	0.75	4.20	0.23
0.07	14.44	16.7	13.3	0.80	3.64	0.31
0.075	13.33	14.7	11.3	0.77	2.34	0.29
0.09	11.11	13.4	<10	<0.75	1.87	0.31
0.12	8.33	12.7	10.5	0.82	1.65	0.33
0.15	6.67	11.3	<10	<0.88	1.32	0.35
0.20	5	11.0	<10	<0.9	1.28	0.37
0.25	4	10.6	<10	<0.94	1.03	0.35
0.3	3.33	10.5	<10	<0.95	0.82	0.29
0.4	2.5	13.6	16.8	1.24	1.55	

[a] Particle molar mass including surfactant.

The surface tension was measured with a MWG Lauda tensiometer at 25 °C, at a total particle concentration of approximately 82 g/L. Static and dynamic light scattering measurements were performed with a commercially available instrument consisting of a Stabilite 2060-11s krypton ion laser (Spectra Physics), operating at 500-mW output power and 647.1-nm wavelength, a goniometer Sp-86 (ALV), and an ALV-3000 digital correlator/structurator as described elsewhere.[10,11] All measurements were carried out at 20 °C.

For light scattering the concentrations of the samples were adjusted from 0.1 to 0.25 g/L by adding 10^{-4} M aqueous KBr solution. The samples were filtered several times through a 0.22-μm filter (Millex GS filter) into dust-free cylindrical quartz cuvettes. The diffusion coefficient was determined from the intensity time correlation function by the methods of cumulants. Except for low added volumes of monomers (see discussion) the correlation functions showed only a little deviation from a single-exponential decay; i.e., the normalized second cumulant $\mu_2 \leq 0.05$. The refraction index increments were measured at different surfactant to monomer ratios with a special, home-built interferometer[12] utilizing a laser diode (Toshiba; wavelength $\lambda = 650$ nm). As shown in Figure 1 the experimental data show a linear dependence on the weight fraction of surfactant.

Results and Discussion

The results are summarized in Table 1 where the particle dimensions in terms of the radius of gyration, R_g, and the hydrodynamic radius, R_h, and the particle molar masses M_w are given for different fleet ratios S. The molar mass and the radius of gyration are determined by static light scattering according to standard procedures and the hydrodynamic radius is evaluated from the diffusion coefficient measured by dynamic light scattering by formal application of the Stokes law

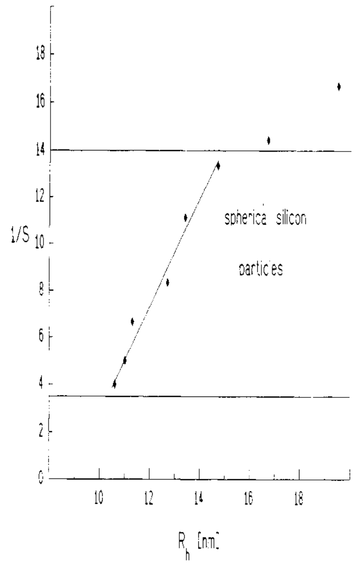

Figure 2. Particle radius R_h plotted as a function of the inverse fleet ratio S^{-1} according to eq 3. The solid line represents the fit to the data in the linear regime marked by the horizontal lines.

$$R_h = \frac{kT}{6\pi\eta_0 D} \tag{4}$$

with kT the thermal energy and η_0 the solvent viscosity.

An upper limit of the particle density ρ_p is derived from the molar mass and the hydrodynamic radius as

$$\rho_p = \frac{3M}{4\pi N_A R_h^{\,3}} \tag{5}$$

which neglects the effect of polydispersity on M and on R_h. Even for quite narrow size distributions identification of M and M_w and of R_h with $\langle 1/R_h \rangle_z^{-1}$ leads to a significant overestimation of the density.[13] Also, application of eq 5 requires a spherical particle shape which is documented by the values of the ratio $\rho \equiv R_g/R_h \approx 0.775$. For the small particles R_g can no longer be measured as the values drop below 10 nm.

In Figure 2 the inverse ratio S^{-1} is plotted versus the hydrodynamic radius of the microspheres. A linear dependence for $0.07 \leq S \leq 0.3$ is observed in agreement with eq 3. Thus, the described polycondensation of methyltrimethoxysilane is phenomenologically similar to a polymerization in μ-emulsion. The determination of the area per surfactant molecule from the slope of the linear part in Figure 2 requires the particle density ρ_p to be known. From the molar mass M_w and the hydrodynamic radius R_h an average density of $\rho_p \approx 0.33$ g/cm^3 is derived (see Table 1) which eventually leads to an area per surfactant molecule of $a_0 = 15.5$ nm^2, a value much higher than $a_0 = 0.18$ nm^2 found for CTAB.

A critical examination of the results immediately raises some important questions:

(1) Is the number of growing particles constant with increasing conversion?

(2) Does the polycondensation start in a micelle or in the water phase?

(3) What determines the number of growing nuclei?

(4) Why is the headgroup area of benzethonium chloride more than 10 times as large as for CTAB?

(5) How does the surfactant stabilize the growing particles and prevent interparticle condensation?

In Figure 3 the particle radius is plotted versus the cube root of the volume of added monomer. A straight line is

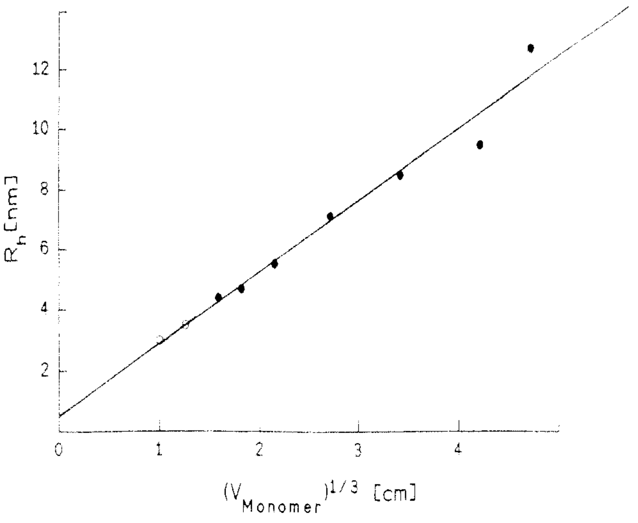

Figure 3. Particle radius R_h as a function of the cube root of added methyltrimethoxysilane volume. Fleet ratio after all monomer has been added: $S = 0.12$.

observed which extrapolates to $R_h = 0.5$ nm for no added monomer. This plot impressingly demonstrates that after a certain "induction" period the growth of the particles is homogeneous; i.e., the number of growing "nuclei" remains constant until all monomer is added. Also, Figure 3 gives a vague hint that the nucleation takes place in the water phase; i.e., at the early stage of polycondensation the surfactant does not form a micellarlike structure around the growing nuclei, because the curve in Figure 3 almost hits the origin. If the empty micelles present would be filled with the growing nuclei, the curve should bend upward at small added volumes and yield the micellar radius of benzethonium chloride at zero added volume of monomer. The micellar radius of benzethonium chloride is, however, not easily determined as the correlation function of benzethonium chloride in water shows two diffusion processes with $R_h = 0.8$ nm and $R_h \approx 40$ nm, respectively. The large hydrodynamic radius might originate from a vesicular structure which is currently under investigation, whereas the small radius might belong to a single surfactant molecule or, less probable, to a small spherical micelle. For this complication the data analysis of the correlation function is quite ambiguous at low added methyltrimethoxysilane volumes, which are shown as open symbols in Figure 3, accordingly.

Our conclusion, that the nuclei do not start to grow within normal micelles, is also supported by the surface tension measurements shown in Figures 4 and 5. In Figure 4 the surface tension is plotted against the volume of added monomer. Below 12.5 mL of added monomer (total added amount: 105 mL) the surface tension remains approximately constant, whereas it increases at larger added monomer volume. Obviously, above 12.5 mL of added monomer volume empty micelles are no longer present in the solution as the growing particles now need more and more surfactant molecules for stabilization and eventually draw the surfactant molecules from the air/water interface, thus increasing the surface tension as displayed in Figure 4. The surface tension measured after complete addition of the monomer is plotted versus the fleet ratio S in Figure 5. At very large S-values, i.e., $S \geq 0.3$, the surface tension is seen not to increase even if all monomers are added which indicates that free (i.e., empty) micelles still exist in solution. Such an excess of surfactant is not accounted for in the model calculation discussed above and therefore the linear relationship between S^{-1} and R_h must break down. This point is marked by the lower horizontal line in Figure 2. It is interesting to note that the hydrodynamic radius for $S > 0.3$ starts to increase again in contradiction to theoretical expectation. This indicates either the end of a stable regime of the μ-emulsion or that the free, excess surfactant starts to form the vesicular structures, again, as mentioned above. In the latter case the autocorrelation function should exhibit two well-defined, almost single exponentially decaying relaxation modes in contradiction to the experimentally observed correlation functions showing one broad relaxation mode. Thus, for $S > 0.3$ the growing particles become instable and tend to aggregate, which is also indicated by the increased value of ρ (see Table 1).

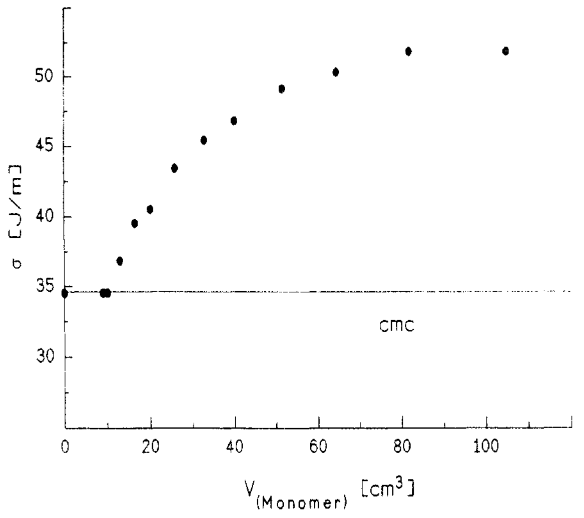

Figure 4. Surface tension σ versus added methyltrimethoxysilane volume V. Fleet ratio after all monomer has been added: $S = 0.09$. As a reference the surface tension of benzethonium chloride in pure water above the cmc is given as the horizontal line.

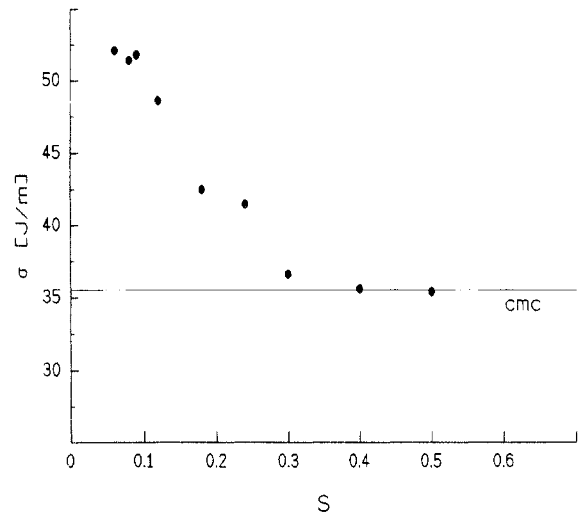

Figure 5. Final surface tension σ after all monomer has been added as a function of the fleet ratio S. The line marked cmc represents the surface tension of benzethonium chloride in a mixture of 8 wt % methanol and water above the cmc. The fraction of methanol corresponds to the amount being formed during the condensation reaction.

Conversely, at a fleet ratio lower than $S = 0.06$ the μ-emulsion becomes unstable; i.e., during the addition of methyltrimethoxysilane partial precipitation occurs. This point approximately coincides with the upper bound of the linear dependence of S^{-1} as a function of R_h as is indicated by the upper horizontal line at $S = 0.07$ in Figure 2.

Table 2. Number of Particles N_p in Solution at c = 82 g/L, Number of Surfactant Molecules per Particle N_s, and Surface Area per Surfactant Molecule a_s for Different Fleet Ratios S

S	$N_p \times 10^{18}$	$N_s \times 10$	a_s (nm^2)
0.06	1.9	530	9.0
0.07	2.2	531	6.6
0.075	3.4	364	7.46
0.09	4.4	344	6.56
0.12	5.6	358	5.66
0.15	6.6	384	4.2
0.20	7.1	476	3.2
0.25	9.1	460	3.1
0.3	11.9	423	3.3

The discussion so far supports the picture of a polycondensation in μ-emulsion in formal analogy to the polymerization discussed in the Introduction. Whereas the particle growth of the polymerization in μ-emulsion is still a matter of controversy, the present polycondensation is shown to proceed at a constant number of growing particles after a short induction period, during which the number of eventually growing particles is determined. Due to the above mentioned complex surfactant structures which disturb data analysis at low conversion, the formation of the growing nuclei could not be traced in the present work and is still under investigation.

We now return to questions 4 and 5 concerning the large a_0 value of benzethonium chloride and to the mechanism of particle stabilization. In Table 2 some relevant quantities are listed as a function of the fleet ratio S such as the number of particles, N_p, at constant overall concentration c = 82 g/L, the number of surfactant molecules per particle, N_S, and the surface area per surfactant molecule a_s calculated from N_p and the surface of a single particle $4\pi R_h^2$. Here the symbol a_s is introduced as opposed to a_0 determined by eq 3.

Whereas ideally the value of a_0 derived from Figure 2 should be identical to the values of a_s given in Table 2, a large difference is experimentally found along with the surprising fact that a_s decreases with decreasing particle radius. In the derivation of eq 3 the surface area per surfactant molecule is assumed to be independent of S in contrast to the experimental results shown in Table 2. Thus, the evaluation of a_0 from Figure 2 yields a completely wrong result which could have already been anticipated by the extremely low ordinate of the fitted curve in Figure 2 of −20.4, which is usually expected to be close to −1. We are now left with some miraculous numbers for a_s as a function of S which are still much higher than those for CTAB, which requires further comments. As opposed to the polystyrene μ-spheres, the surface of the organosilicon particles is not completely hydrophobic, because of the ionic Si–O$^-$ groups at the surface. These anionic charges stabilize the surface, whereas the methylsilane group is hydrophobic and destabilizes the particle. Thus, in a naive view, the surfactant molecules are only required to stabilize the hydrophobic "patches" on the particle surface. As a consequence, the area per surfactant molecule reflects the fraction of hydrophobic patches on the particles rather than the headgroup area of a surfactant molecule in a closely packed layer.

It is quite obvious that the cationic surfactant headgroup does not form an ion pair with the Si–O$^-$ surface groups of the organosilicon particle, because this would increase the hydrophobicity of the surface as the hydrophobic tail of the surfactant is exposed to the water phase. It rather appears that the particles are stabilized by an amphoteric surface consisting of the Si–O$^-$ anions and the R_4N^+ cations, with their hydrophobic part being adsorbed onto the hydrophobic patches of the particle surface.

This picture does not even qualitatively account for the decrease of a_s with decreasing particle size. The extremely low particle density $\rho_p \approx 0.33$ g/cm^3 in solution as compared to the "dry" density of roughly 1 g/cm^3 supports the existence of an inner surface which might be stabilized by surfactant as well. In order to qualitatively explain the a_s values in Table 2, the ratio of the inner to outer surface should increase with decreasing particle radius which is highly improbable. A detailed investigation of the inner "fractal" structure of the particles will be performed in the near future.

Eventually, a quite keen explanation will be offered: With an excess of surfactant the hydrophobic Si–CH_3 groups are easily stabilized and a certain fraction of hydrophobic patches is being formed. A lack of surfactant at low fleet ratio would leave the hydrophobic patches at the surface unstabilized which could affect the conformation of a condensating monomer at the surface, i.e., the Si–CH_3 groups could preferentially point to the hydrophobic inner part of the particle. Unfortunately, the number of Si–O$^-$ groups on the surface is not easily accessible which prohibits a more quantitative discussion.

Conclusion

The polycondensation of methyltrimethoxysilane in the presence of the surfactant benzethonium chloride shows the phenomenology of a polycondensation in μ-emulsion. Whereas the constant number of growing particles supports this hypothesis, the decreasing surface area per surfactant molecule with increasing fleet ratio reveals the polymerization mechanism to be much more complicated. Further investigations are needed and are in progress.

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