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Comment on the Development of Particle Surface Charge Density during Surfactant-Free Emulsion Polymerization with Ionic Initiators

Klaus Tauer

Max-Planck-Institut für Kolloid und Grenzflächenforschung,
Kantstrasse 55, D-14513 Teltow-Seehof, Germany

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In a recent note[1] Sarah Peach reports on the relation between particle surface charge density (σ) and particle stability in a surfactant-free emulsion polymerization. She comes to the conclusion that σ scales with the particle size (D) and that consequently small (precursor) particles are unstable against coagulation because of their low surface charge density. Unfortunately, no experimental evidence is given for these conclusions.

In this comment experimental results of a surfactant-free styrene emulsion polymerization with potassium peroxodisulfate (KPS) are presented[2] with respect to the development of surface charge density in the course of the polymerization in order to check its scaling behavior with particle and polymer properties, respectively.

In a surfactant-free emulsion polymerization with ionic initiators stabilization as well as destabilization are purely electrostatic. The particle size develops in such a way that a minimal interfacial energy between the particles and water is reached and hence a stable polymer dispersion is formed. After nucleation the growth of the particles may occur not only by monomer consumption but in some cases also by particle coalescence as it was experimentally shown for emulsifier-free polymerizations of vinyl chloride[3] and styrene,[4,5,8] respectively. Consequently, the resulting particle size in a surfactant-free emulsion polymerization with ionic initiators is the result of well-balanced nucleation, growth, and coalescence processes. Under these circumstances the question of how the particle surface charge density develops in the course of the polymerization is of fundamental interest.

The only source of charges in that particular polymerization is the initiator. The charges on the particles are bound to the polymer molecules only by the initiation step if termination of a growing chain with primary radicals is neglected. Hence, the number of charges per particles (n_L) is governed by two parameters (cf. eq 1): the particle size as also mentioned in ref 1 and additionally by the average molecular mass of the polymer (M) which was not considered in ref 1. In eq 1 d_p is the polymer density, N_A is Avogadro's constant, f_T is a factor that considers whether the termination is by combination ($f_T = 2$) or by disproportionation ($f_T = 1$), and f_{CEG} is a factor taking into account that also uncharged radicals can start the chain growth even in the case of ionic initiators[6] ($f_{CEG} \leq 1$). The charged oligomers which are adsorbed onto the particle water interface and are also distributed into the aqueous phase are not separately considered.[7] Equation 1 also does not consider if there are charged groups buried inside the particles.

$$n_L = f_T f_{CEG} d_p N_A \frac{\pi D^3}{6M} \qquad (1)$$

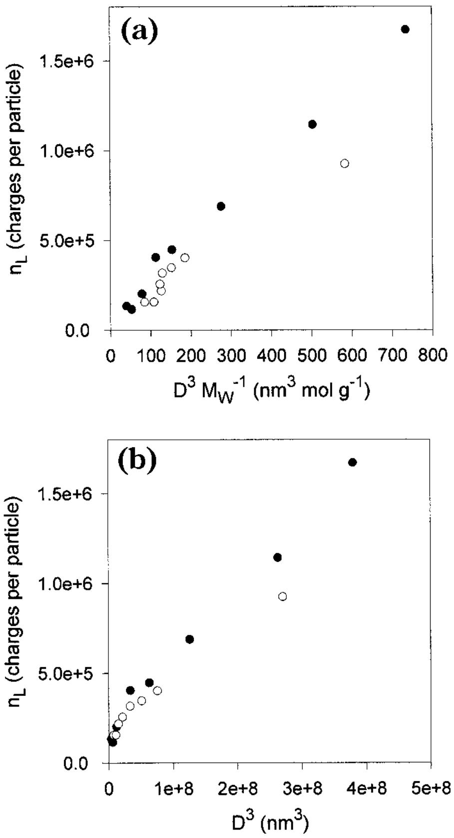

Figure 1. (a) Plot of the number of charges per particle (n_L) as a function of the number of polymer chains per particle (D^3M^{-1}); the open and filled circles represent samples obtained by repeating the polymerization but with different sampling times. (b) Plot of the number of charges per particle (n_L) as a function of the particle volume (D^3); the open and filled circles represent samples obtained by repeating the polymerization but with different sampling times.

From eq 1 results eq 2 for the surface charge density of the particles where F is the Faraday equivalent.

$$\sigma = \frac{F}{N_A} \frac{n_L}{\pi D^2} = f_T f_{CEG} d_p \frac{F}{6} \frac{D}{M} \qquad (2)$$

According to eqs 1 and 2 n_L scales with the number of chains per particle or D^3M^{-1} and σ scales with DM^{-1}, respectively. These results fundamentally deviate from that presented in ref 1 which suggests $n_L \propto D^3$ and $\sigma \propto D$ and do not consider a change in the molecular mass with the polymerization time. However, the experimentally observed decrease in the number of particles just after nucleation lasts up to 50 min.[5,8] During this period of time changes of the molecular mass take place which have to be considered in the scaling relations.

The experimental results[9] clearly support eqs 1 and 2. Figure 1a shows that the number of charges per particle scales over the whole range with D^3M^{-1}. The reproducibility of the investigations is surprisingly good as the molecular-weight distribution is pretty broad (M_W/M_N up to 10) and the question arises of what is the proper average. However, the correlation between n_L and D^3 is nearly linear only for larger particle sizes (longer polymerization times) (cf. Figure 1b) where D^3 dominates the relation and the change in the molecular

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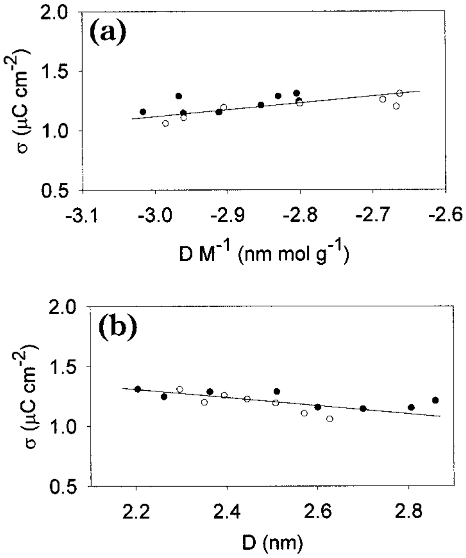

Figure 2. log−log plot of the particle surface charge density (σ) as a function of DM^{-1}; the open and filled circles represent samples obtained by repeating the polymerization but with different sampling times. (b) log−log plot of the particle surface charge density (σ) as a function of the particle size (D); the open and filled circles represent samples obtained by repeating the polymerization but with different sampling times.

mass is additionally less pronounced. Also, a thought line through the data points does not cross the origin contrary to the plot in Figure 1a.

The difference between both descriptions is, in the case of the surface charge density, much clearer. Figure 2a shows a good correlation between σ and DM^{-1} whereas the data depicted in Figure 2b do not support $\sigma \propto D$. The correlation between σ and D in the experimental data suggests a decreasing surface charge density with an increasing particle size.

These experimental results are not suited to support the idea that small particles have a lower surface charge density and hence are unstable to coagulate. The surface charge density of the particles just after nucleation should be higher as the molecular mass increases, especially in the very early stages of an emulsion polymerization.[10] In that particular polymerization considered here the molecular mass increases over the whole duration of the polymerization which can be explained as follows. The reaction starts in the aqueous solution with the formation of oligomers. After nucleation, the main locus of polymerization are the monomer-swollen particles. The monomer concentration in the particles is higher the larger the particles are and, hence, the molecular mass is higher as well.

In conclusion, experimental results of the development of particle charge density in the course of a surfactant-free emulsion polymerization of styrene with KPS proof that the number of charges per particle and the surface charge density scale with $n_L \propto D^3M^{-1}$ and $\sigma \propto DM^{-1}$, respectively. These results show that the particle surface charge density is higher the lower the molecular mass is and, consequently, the small particles just after nucleation consisting of oligomers possess higher surface charge densities than the larger particles later in the course of the polymerization.[11]

A full paper that reports different aspects of experimental investigations of the KPS-initiated stabilizer-free emulsion polymerization of styrene is in preparation.

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References and Notes

(1) Peach, S. *Macromolecules* **1998**, *31*, 3372.
(2) The polymerization was carried out in a 2 L all-glass reactor equipped with a heating jacket, a stirrer, a condenser, and a nitrogen inlet and outlet. To 1820 mL of water were added 91.1 g of styrene and 0, 021 g of sodium hydrogencarbonate as the buffer. Then the mixture was stirred under a nitrogen atmosphere until the reaction temperature of 70 °C was reached. The polymerization was started by adding 1, 872 g of KPS dissolved in 180 mL of water. Samples of approximately 100 mL of volume were taken during the duration of the polymerization (6 h). The samples were characterized with respect to particle size by dynamic light scattering (Nicomp particle sizer model 370, PSS Santa Barbara, CA), molecular mass (GPC in tetrahydrofuran calibration with polystyrene standards), surface tension (TD1, Lauda Königshofen, Germany), and surface charges per particle (PCD-02, Mütek, Herrsching, Germany). The polymerization was repeated with a sampling at different times to check reproducibility.
(3) Tauer, K.; Neelsen, J.; Hellmich, C. *Acta Polym.* **1985**, *36*, 665.
(4) Kühn, I.; Tauer, K. *Macromolecules* **1995**, *28*, 8122.
(5) Tauer, K.; Kühn, I. In *Polymeric Dispersions: Principles and Applications*; Asua, J. M.; Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; p 49.
(6) Tauer, K.; Deckwer, R. *Acta Polym.* **1998**, *49*, 411.
(7) There is experimental evidence to do so as the interfacial tension of the latexes increases during the polymerization from 45 to 71 mN m^{-1}, indicating that the concentration of surface-active oligomers in the aqueous phase is not that high.
(8) Goodall, A. R.; Wilkinson, M. C.; Hearn, J. In *Polymer Colloids II*; Fitch, R. M. , Ed.; Plenum Press: New York, 1980; p 629.
(9) The number of charges per particle and the surface charge density were determined with a particle charge detector indicating the streaming potential. The latex samples with a known solid content were titrated with a polyelectrolyte standard (0, 1 mM polydiallyldimethylammoniumchloride solution) to determine the point of zero charge. These titrations were carried out with at least four different latex concentrations. The amount of charges per gram of latex solid was calculated from the slope of the polyelectrolyte consumption versus the latex concentration plot. Then the charges per particle were calculated using the sizes determined by dynamic light scattering and the weight-average molecular mass from GPC was used for the calculations whenever an average molecular mass was needed. The latexes were not cleaned before the investigations as it turned out that after dialysis the latexes became unstable and were coagulated. However, dialysis would lead to unrealistic results as the stabilizing oligomers are also the result of the polymerization process and hence their consideration in the overall analysis is necessary. In this sense it might be useful to consider the measured number of charges per particle as apparent values.
(10) Tauer, K.; Jaeger, W.; Reinisch, G. *Acta Polym.* **1981**, *32*, 728.
(11) There is experimental evidence that the molecular mass increases over the whole duration of the polymerization.

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