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Hydrophilic Regions inside Colloidal Polymer Particles in Water

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Hydrophobic polymer particles in aqueous dispersions can be stabilized by either adsorbed surfactants or hydrophilic groups covalently attached to the polymers during the preparation. In either case the size and the morphology of the particles develop during the heterophase polymerization as a result of kinetic and thermodynamic competition or constraints. Thermodynamics tries to minimize the free energy under the given conditions, which in turn requires a certain mobility of the polymer chains in order to find the optimum arrangement. However, this can be hindered if the chains grow too rapidly to high molecular weights. The main contribution to the free energy of a colloidal dispersion is the surface free energy ($\Delta G_{\text{surf}} = \gamma A_{\text{P}}$) of the hydrophobic polymer chains in contact with water, governed by the interfacial tension (γ) and the overall surface area of the particles (A_{P}). Surfactants are mobile enough to ensure minimum surface free energy and solid sphere morphology of the particles throughout the entire polymerization. The situation might be completely different if hydrophilic groups attached to the polymer molecules exclusively can contribute to lower the interfacial tension between polymer and water. In such a case the mobility of the stabilizing, hydrophilic groups is governed by the longer and possibly still growing hydrophobic tails. Thus, one might expect for surfactant-free heterophase polymerizations under particular conditions deviations from the solid sphere morphology of the particles.

Indeed, such particles have been observed almost 30 years ago in transmission electron microscopy (TEM) images of samples collected during emulsifier-free emulsion polymerization of styrene.[1−4] A brief review of the formation of anomalous particles by "classical" emulsifier-free emulsion polymerization with peroxodisulfate as initiator can be found in ref 5. In addition, a detailed analysis of the experimental data was presented as well as an experimentally verified method to control the occurrence of this phenomenon by the addition of hydrophilic chain transfer agents such as thiomalic acid. Also for hydrophilic initiators other than peroxodisulfate such as poly(ethylene glycol)-azoinitiators, the formation of particles with less electron dense regions, which appear as voids on the TEM pictures, has been observed.[6,7] The application of poly(ethylene glycol) macromonomers during surfactant-free styrene emulsion polymerization as described in ref 8 also caused the generation of particles with voids in the course of the polymerization.

Anomalous particle morphologies were also observed in oligostyrene dispersions as described in refs 5 and 7. These oligomers were prepared by anionic polymerization, have a well-defined chemical structure, and contain one hydrophilic sulfonate end group per molecule. They can be dispersed in water and subsequently swollen with organic water-miscible solvents such as acetone, THF, and dioxane. Upon swelling, the morphology of the dispersed particles changes drastically and, depending on the chain length of the oligomers, either vesicles or porous particles are formed.[7] With X-ray absorption microscopy it has been proven that the anomalous morphologies are not drying artifacts during TEM sample preparation but do really exist in the dispersed state.[7] Some examples of the morphologies obtained with polystyrene latex particles and oligostyrene particles are combined in Figure 1.

There is another class of polymers that could also be considered in this context. Block copolymers prepared by controlled polymerization techniques under homogeneous polymerization conditions self-assemble in selective solvents and can form a huge variety of morphologies depending on the nature of the blocks, the ratio of the block lengths, the overall molecular weight, and the solvent properties.[11−21] In the context of polymer colloid chemistry these systems belong to the class of secondary polymer dispersions[22] as spherical block copolymer

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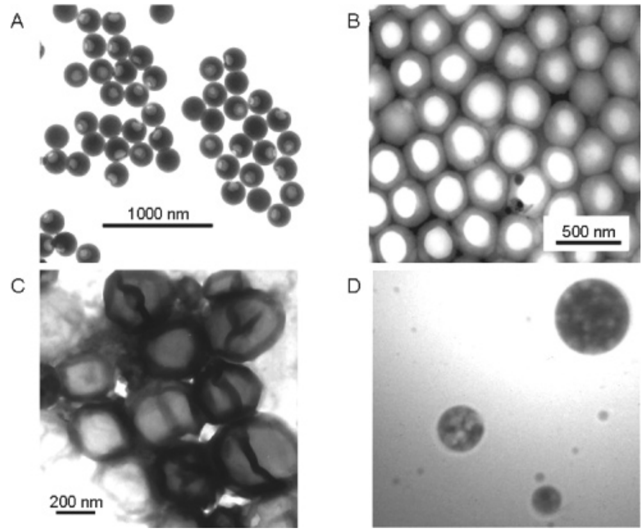

Figure 1. TEM images (A−C) and X-ray absorption microscopy image (D) of polystyrene particles showing various morphological features: (A) polystyrene particles prepared by surfactant-free emulsion polymerization with potassium peroxodisulfate as initiator;[5,9] (B) polystyrene particles prepared by surfactant-free emulsion polymerization with poly(ethylene glycol)-azoinitiator;[6,10] (C) oligostyrene particles dispersed in water and swollen with THF (one sulfonate end group, average number of styrene units 5);[5,7] (D) oligostyrene particles dispersed in water and swollen with THF (one sulfonate end group, average number of styrene units 12);[5,7] the largest particle has a diameter of about 1.2 μm.

micelles are analogous to latex particles. More specifically, they are self-stabilizing or surfactant-free polymer dispersions, as the soluble blocks are in fact covalently attached steric or electrosteric stabilizers. Interestingly, the aqueous heterophase copolymerization of styrene and acrylic acid is one of the oldest attempts to prepare block copolymers.[23] Eisenberg and coworkers studied the morphology of amphiphilic block copolymers after transferring them from solution in an organic solvent into an aqueous continuous phase.[13−15] Very recently, they also found bowl-shaped particles made of random amphiphilic copolymers of poly(styrene-*co*-methacrylic acid)[24] when a solution in dioxane was quenched with water. The TEM images of these particles resemble those of the polystyrene particles shown in Figure 1A.

Jiang et al.[25] reported recently that also small molecular weight polyimide (molecular weight of about 3600 g/mol) with two carboxylate end groups form particles with multiple morphologies when their THF solutions were precipitated by water with basic pH. Besides vesicles and porous spheres, these authors also observed dimpled beads or bowl-shaped aggregates.

These examples suggest that there might be a general rule or universal mechanism determining the formation of particles with such structures that deviate from the solid sphere morphology, by both the direct and the indirect preparation via emulsion polymerization or precipitation from solution, respectively. Clearly, both routes allow the fabrication of similar morphologies. The key for understanding this behavior is that throughout the preparation the system tries to minimize the interfacial free energy. For surfactant-free systems γ depends solely on the fraction of the hydrophilic groups per unit mass of polymer in contact with the continuous phase (at a given composition of the continuous phase), and A_P depends mainly on the number of particles at given mass of polymer. Consequently, ΔG_{surf} depends on characteristic properties of both the polymer molecules and the colloidal particles, i.e., the number-average molecular weight (M_n) and the average particle diameter (D), respectively.

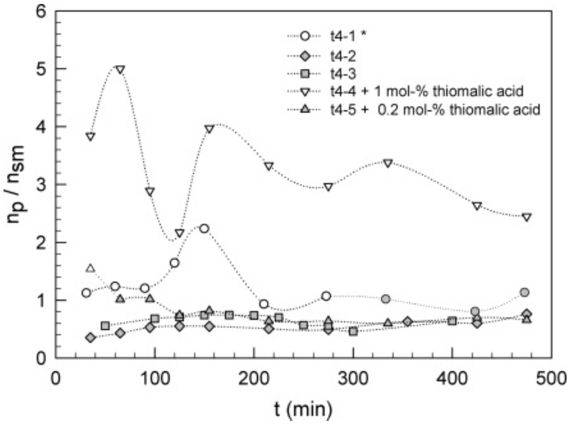

Figure 2. Change of n_P/n_{SM} during surfactant-free emulsion polymerization of styrene (for conditions and detailed prescription see refs 5 and 9); for a_S a value of 0.56 nm^2 was used corresponding to alkyl sulfates according to ref 26; the open symbols represent samples where bowl-shaped particles have been observed on TEM images as shown in Figure 1A for the sample after 120 min of run t4-1*; regarding the peculiarity with run t4-1* compared with runs t4−2 and t4−3 see ref 27.

This dependence can be expressed by the ratio n_P/n_{SM} between the number of polymer chains per particle ($n_P = m_p N_A/M_n$) and the maximum number of chains if the particle surface is completely saturated with hydrophilic end groups ($n_{SM} = \pi D^2/a_S$). Here m_p is the mass of an average particle, N_A is Avogadro's number, and a_S is the surface area covered per hydrophilic end group at saturation of the particle surface. Values for M_n and D are easily accessible by standard experimental techniques. For a_S good estimates can be obtained from micellization data of surfactants with the corresponding hydrophilic group. If $n_P > n_{SM}$, then the number of polymer chains per particle is too high for a solid spherical particle, and hence, a larger interfacial area can be stabilized than given by the sphere with the average particular diameter. As $n_P/n_{SM} > 1$ means also that hydrophilic chain ends are buried inside the particles, they may gather in a particular spot and form the indentations or voids which for energetic reasons try to have contact with water instead with the hydrophobic polymer. The contrast in the X-ray absorption microscopy image (cf. Figure 1D) proves that the less dense regions are really filled with water, and hence, the continuous phase penetrates the particles. One might consider these particles as more or less draining because the chains are stiff and water is a good solvent for the ionic groups in the hydrophilic regions. The data in Figure 2 confirm that the ratio n_P/n_{SM} is a good indicator of whether the occurrence of non-solid-sphere morphologies can be expected as in all samples with $n_P \leq n_{SM}$ only solid-sphere-like particles have been observed. In this case the number of chains per particle is low enough that all hydrophilic end groups can occupy sites at the particle−water interface.

Finally, both routes to prepare colloidal particles with non-solid-sphere morphologies − either the direct by heterophase polymerization or the indirect by dissolution and precipitation − possess essential common features. In either case the particles are highly swollen after formation, and hence, the chains are mobile enough to take up the morphology corresponding to the minimum free energy. The anomalous morphologies are determined on the molecular scale by the fraction of hydrophobic and hydrophilic groups and on the particle scale by the geometric size. With increasing conversion and water content during the direct and indirect route, respectively, the chain mobility decreases until at a certain point the morphology freezes.

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References and Notes

(1) Cox, R. A.; Creasey, J. M.; Wilkinson, M. C. *Nature (London)* **1974**, *252*, 467−469.

(2) Cox, R. A.; Wilkinson, M. C.; Creasey, J. M.; Goodall, A. R.; Hearn, J. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 2311−2319.

(3) Goodall, A. R.; Wilkinson, M. C.; Hearn, J. *J. Colloid Interface Sci.* **1975**, *53*, 327−331.

(4) Goodall, A. R.; Wilkinson, M. C.; Hearn, J. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 2193−2218.

(5) Tauer, K.; Deckwer, R.; Kühn, I.; Schellenberg, C. *Colloid Polym. Sci.* **1999**, *277*, 607−626.

(6) Tauer, K.; Müller, H.; Rosengarten, L.; Riedelsberger, K. *Colloids Surf., A* **1999**, *153*, 75−88.

(7) Tauer, K.; Riedelsberger, K.; Deckwer, R.; Zimmermann, A.; Dautzenberg, H.; Thieme, J. *Macomol. Symp.* **2000**, *155*, 95−104.

(8) Kawaguchi, S.; Tano, K.; Maniruzzaman, M.; Ito, K. *Macromol. Symp.* **2000**, *150*, 101−108.

(9) The polymerizations were carried out as follows: 1930 mL of water, 91.1 g of styrene monomer, 0.021 g of sodium hydrogen carbonate buffer, and, if necessary, the thiomalic acid chain-transfer agent (either 1 or 0.2 mol % relative to styrene monomer) were charged in the reactor under stirring and purged with nitrogen gas. After at least 30 min the temperature was equilibrated (70 °C), and the reaction was started by injecting 1.872 g of KPS dissolved in 70 mL of degassed water. The reheating up to 70 °C after injecting the initiator solution occurred within less than 2 min. Samples of almost 100 mL volume were taken from the bottom valve of the reactor at different polymerization times.

(10) The poly(ethylene glycol)−polystyrene−poly(ethylene glycol) triblock copolymer particles were prepared by batch ab initio aqueous heterophase polymerization with the following recipe: 60 g of water, 7.8 g of styrene, 9.14 g of PEGA200, which is a symmetrical poly(ethylene glycol)-azoinitiator with poly(ethylene glycol) chains with an average molecular weight of 200 g/mol, 82 °C.

(11) Ruzette, A.-V.; Leibler, L. *Nat. Mater.* **2005**, *4*, 19−31.

(12) Yang, Z.-g.; Yuan, J.-j.; Cheng, S.-y. *Gong. Gaof. Xuebao* **2003**, *16*, 287−292.

(13) Choucair, A.; Eisenberg, A. *Eur. Phys. J. E* **2003**, *10*, 37−44.

(14) Burke, S.; Eisenberg, A. *High Perform. Polym.* **2000**, *12*, 535−542.

(15) Zhang, L.; Eisenberg, A. *Polym. Adv. Technol.* **1998**, *9*, 677−699.

(16) Kugaz, K.; Zhang, L.; Moffit, M.; Eisenberg, A. *Vysokomol. Soedin., Ser. A Ser. B* **1996**, *38*, 582−593,.

(17) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31−71.

(18) Winnik, M. A. *Chemtracts: Macromol. Chem.* **1990**, *1*, 346−348.

(19) Antonietti, M.; Forster, S. *Adv. Mater.* **2003**, *15*, 1323−1333.

(20) Liu, T.; Liu, L. Z.; Chu, B. Formation of amphiphilic block copolymer micelles in nonaqueous solution. In *Amphiphilic Block Copolymers*; Alexandridis, P., Lindmann, B., Eds.; Elsevier: Amsterdam, 2000; pp 115−149.

(21) Cogan, K. A.; Gast, A. P. *Macromolecules* **1990**, *23*, 745−53.

(22) Tauer, K. *Colloids Colloid Assemblies* **2004**, 1−51.

(23) Dunn, A. S.; Melville, H. W. *Nature (London)* **1952**, *169*, 699−700.

(24) Liu, X.; Kim, J.-S.; Wu, J.; Eisenberg, A. *Macromolecules* **2005**, *38*, 6749−6751.

(25) Wang, J.; Kuang, M.; Duan, H. W.; Chen, D. Y.; Jiang, M. *Eur. Phys. J. E* **2004**, *15*, 211−215.

(26) Evans, D. F.; Wennerström, H. *The Colloidal Domain*; VCH Publishers: New York, 1994; p 163.

(27) During a 2 week period two students jointly carried out their first emulsion polymerization (sample t4-1). They took 10 samples over the whole duration. On the TEM pictures of sample 1-7 taken between 30 and 273 min after the start anomalous particles appeared. Two attempts (samples t4-2 and t4-3) to reproduce these results failed. In comparison to the students' results, the repeated runs resulted in polymers with an up to a factor of 3 higher average molecular weight. The conclusion was that in the students' run some chain transfer agent (perhaps some lubricant from the stirrer dropped from the shaft into the reactions mixture) was accidentally present. Indeed, polymerizations in the presence of thiomalic acid as chain transfer agent resulted in anomalous particles.

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