Synthesis and characterization of core-shell colloids with fluorocarbon cores

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SUMMARY:The synthesis of core-shell particles with polycrystalline fluorocarbon (MFA) cores (derived from preformed seeds) and highly crosslinked polystyrene (PS) shells via essentially surfactant-free emulsion polymerization is reported. The composite latexes in aqueous dispersion and in THF solution were characterized by light scattering, asymmetric field flow fractionation and TEM. The results indicate that while in aqueous dispersion one obtains core-shell particles with a narrow size distribution and a sharp fluorocarbon/ polystyrene interface, the dissolution of the latexes in THF leads to hollow sphere structures of crosslinked polystyrene.

Introduction

Core-shell latex particles are widely used in industrial applications, e.g. in paint and coating technology, as they allow to combine physical properties of two incompatible polymers on small length scales, a task usually difficult to achieve by polymer blending[1)]. The core-shell principle has recently been used to study the behavior of concentrated colloidal dispersions as well. By synthesizing highly crosslinked core-shell microgel colloids with a polystyrene (PS) core and a poly(t-butylacrylate) (PTBA) shell, a host-tracer system was designed[2,3)]. Adding a few core-shell particles into a host dispersion of PTBA microgel colloids, made invisible by use of a refractive index matching organic solvent, allowed to measure the tracer motion in a highly concentrated dispersion via dynamic light scattering and optical microscopy by virtue of the strongly scattering PS core[2,4)]. As the tracers are of the same size as the host particles and the shell guarantees that the interaction potential of the tracers is identical to that of the host particles, the measured mean square displacements (MSD) reflect the self diffusion of the host particles, i.e the short- and longtime self diffusion coefficients. If the tracer differs from the host (e.g. small tracers in a binary colloid mixture or in a polymer solution) it probes the mechanical properties of the host as demonstrated by converting MSDs into shear moduli $G'(\omega)$ and $G''(\omega)$ and comparing with measured mechanical data[5)]. After demonstrating that the inverse core-shell structure, i.e. PS shells on PTBA cores, can be realized with microgels as well[3)] we attempt to further extend the core-shell principle by polymerizing highly crosslinked PS shells around preformed poly(tetrafluoroethylene-co-perfluoromethyl-vinylether) (MFA) seed particles. The advantage of such tracer particles is threefold: (i) as narrowly distributed fluorocarbon latexes are available[6)], smaller core-shell tracers (for binary mixtures) become accessible. (ii) the larger refractive index difference with respect to PS increases detectability in tracer experiments. (iii) the optical anisotropy due the polycrystalline

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nature of the MFA seeds which was already widely used to study rotational colloidal motion in charge stabilized dispersions[7], allows to study the influence of shell properties (surface roughness, friction, lubrication) on rotational motion in highly concentrated colloidal dispersions. In the following we give a brief first account on success and current limitations of the synthesis and characterization of such core-shell particles.

Experimental

Materials

Styrene (S, Aldrich) and 1,3-Diisopropenylbenzene (DIPB, Aldrich) were distilled under reduced pressure in a nitrogen atmosphere. The monomers were stored at -18 °C until used. Potassium persulfate ($K_2S_2O_8$, Aldrich) was used as received. Deionized water obtained from a Millipore® system was purified with a low-pressure ultrafiltration unit (Berghof) with a membrane filter (pore size 0.1 μm). The seed emulsion MFA 620 [poly(tetrafluoroethylene-co-perfluoromethylvinylether), stabilized with Triton X 100 < 0.2% w/w and an unquantified amount of perfluorooctanoate; crystallinity is about 30%; n_D=1.362; from Ausimont S.p.A., Italy] was filtered through a Nylon filter (mesh size 40 μm) to remove the coagulate. The solid content of this emulsion was 29% w/w and the colloids had an average radius of 84 nm and a polydispersity of 6% (σ_D=0.06; see below) as determined by dynamic light scattering.

Preparation of latexes

The shell was synthesized by an essentially surfactant-free seeded emulsion polymerization process (no surfactant was added in addition to that on the seeds). The polymerization was carried out in a 250 mL three-necked flask equipped with a reflux condensor, a nitrogen inlet and a mechanical stirrer. The flask was immersed in a silicon oil bath thermostated at the reaction temperature (70 °C). 20 g of the seed emulsion MFA 620 were diluted with 166 g of deionized water and added to the flask. The content was stirred at 350 rpm and flushed with nitrogen for about 30 minutes. 0.09 g of the initiator ($K_2S_2O_8$), dissolved in 20 g of preheated water (70 °C), were then added into the reactor. 5.38 g of a mixture of styrene (monomer) and diisopropenylbenzene (crosslinker) with a molar ratio of 5:1 were then continuously fed over 2-3h by use of an injection pumpe (Bioblock Scientific) in order to polymerize a crosslinked shell (crosslink density 1:10) around the MFA seeds. The polymerization was stopped after 24h.

Methods

For the dynamic and static light scattering (DLS, SLS) measurements a standard light scattering equipment (ALV DLS/SLS-5000F) from ALV, Langen, was used employing an argon ion laser (Innova 90-2; from COHERENT) at a wavelength of λ=488 nm. From cumulant analysis[8] of the intensity autocorrelation function measured by DLS the hydrodynamic radius R_H and the polydispersity index $\sigma_D=[(<D^2>-<D>^2)^{1/2}]/<D>$ are

determined, where $<D^n>$ denotes the n-th moment of the distribution of diffusion coefficients. It should be noted that in case of small polydispersities ($\sigma_D \leq 0.1$) this quantity is equal to the polydispersity index σ_R (R=radius), accessible by TEM and fractionation techniques (see below), irrespective of the specific form of the particle size distribution (PSD).

To analyze the SLS data the measured intensities I(q) were fitted with a core-shell model[9], treating the particles as Rayleigh-Debye-Gans scatterers, taking into account polydispersity for the cores and assuming shells of uniform thickness.

As light scattering does not yield access to the shape of the PSD and the cumulant analysis cannot resolve small polydispersities well enough to capture incipient secondary nucleation during core-shell synthesis, a field flow fractionation unit with an asymmetric channel (AFFF, CONSENXUS) was employed to determine the PSD in aqueous dispersion. Here, the separation according to particle size is achieved by the competition between a cross flow through a membrane and Brownian diffusion of the particles. For particle number counting a UV-detector (Knauer, Wellchrom Filterphotometer K-2000) was used.

The transmission electron microscopy (TEM) pictures were produced with a ZEISS EM 902 microscope using an acceleration voltage of 80 keV. Replica were prepared by shading the samples with platinum/carbon under an angle of 20°.

Results and Discussion

From DLS and AFFF first evidence for a succesful synthesis of core-shell particles can be derived. In aqueous dispersion one finds R_H=106 nm, σ_D=0.06 and R_H=103 nm, σ_R=0.08 from DLS and AFFF, respectively. The AFFF-curve shown in Figure 1a indicates a narrow, unimodal PSD. This rules out the possibility that in addition to core-shell particles pure PS-particles have been formed by secondary nucleation.

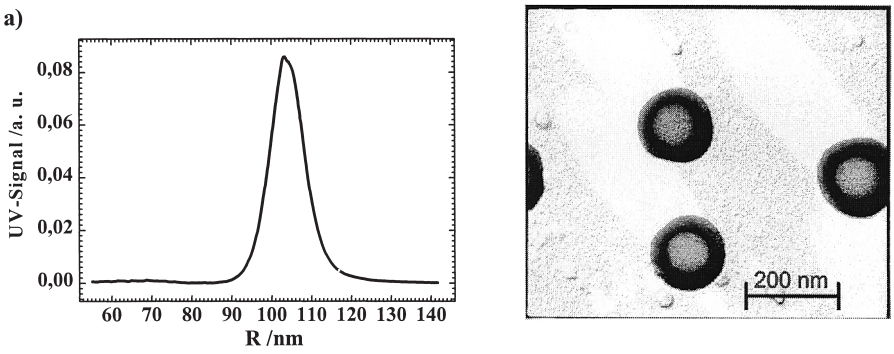

Figure 1: a) Particle size distribution of MFA/PS core-shell particles as measured by asymmetric field flow fractionation. The average radius is 103.4 nm and the polydispersity is 8.4%. b) TEM picture of the MFA/PS colloids prepared from emulsion. Replica was prepared by shading the sample with platinum/carbon under an angle of 20°.

As the MFA particles have no UV contrast, they are invisible in AFFF. To exlude the (unlikely) possibility that PS forms only homolatexes, leading to a binary mixture of pure PS and pure MFA particles, we determined the PSD with aerosol spectroscopy[10] as well, since this method yields sufficient contrast for MFA particles. No evidence for secondary nucleation was found.

The final verification of a core-shell morphology is given by the TEM picture depicted in Figure 1b, showing a bright core and a dark, spherically shaped shell, separated by a sharp interface. As the fluoropolymer is degraded by the electron beam, the fluorinated core appears brighter. However, no inclusions of PS into the MFA phase are discernible. Thus, the chosen number density of seed particles was sufficiently high and the monomer feed was slow enough to preclude secondary nucleation and PS shells of about 20 nm thickness were formed around the MFA cores.

For use of the MFA/PS core-microgel shell latexes as tracer particles in organic solvents, their solubility properties are crucial. From the analysis of aqueous dispersion alone one cannot be sure if the shell is completely closed and if the thickness of the shell is sufficient to overcompensate the oleophobic nature of the fluorinated core. For a first test we tried to redisperse the purified and freeze-dried core-shell particles in THF. Redispersion was slow and ultrasonification was applied to speed up the process. Phase separation occurred into a solid coagulate and a supernatant, the turbidity of the latter implying the existence of particulate structures. After removal of the coagulate by filtration, the supernatant was diluted and studied by SLS and DLS. The normalized intensity, depicted in Figure 2a, shows a form factor minimum which clearly indicates the existence of colloidal entities in the supernatant. As a first estimation of particle size and polydispersity a fit with the form factor of polydisperse homogeneous spheres[11] was applied, yielding $\langle R \rangle$=211 nm and σ_R=0.1. While the polydispersity compares well with the value of σ_D=0.1 derived from DLS, the radius is significantly higher than the DLS value R_H=160 nm (σ_D=0.1 implies $R_H=\langle R^6 \rangle / \langle R^5 \rangle \approx \langle R \rangle$ [11]). While homogeneous sphere curve (Figure 2a, dashed line) fits the data only around the P(q) minimum, a significant improvement can be achieved by employing core-shell model with a polydisperse core and a uniform shell thickness[9] (solid line).

The main deviations from the experimental data occur at high scattering angles and can be attributed to a large extent to instrumental artifacts (back reflection from the outlet window of the index match vat). The fit yields a particle radius of R_{C+S}=186 nm, a core radius R_C=111 nm and a core polydispersity $\sigma_R^C = 0.26$. From analogous analysis of PTBA/PS core-shell microgels[12] it is known that the fit always leads to unreasonably high values for the polydispersity of the cores, most likely due to the artifical assumption of constant shell thickness. However, reasonable values for R_{C+S} and R_C are obtained from this model. Using these values to calculate the volume swelling ratio S of the PS shell (using the thickness of the unswollen shell determined in aqueous dispersion allows to determine volume swelling ratio S of the shell[3]) lead in case of PTBA/PS latexes to S=2.1 which is the volume swelling ratio

for homogeneous 1:10 crosslinked PS microgels. For the MFA/PS particles the core radius obtained from the model would imply a volume swelling of 1.74 for the MFA core. Considering the oleophobic nature of MFA such an uptake of THF seems rather unlikely. In addition, the swelling ratios of the PS shell calculated from the determined particle radii are far too high as compared to homogeneous PS microgels.

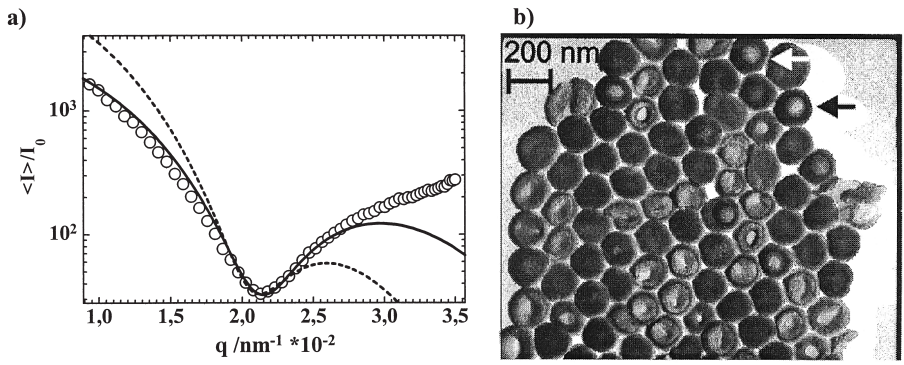

Figure 2: a) Normalized scattering intensity <I> of the MFA/PS colloids in THF plotted versus scattering vector q. Solid line: calculated core-shell formfactor with R_1=111 nm; R_2=186 nm; σ_{R1}=26%; n_D(MFA)=1.362; n_D(PS)=1.599; n_D(THF)=1.407. Dashed line: calculated homogeneous sphere formfactor with R=211 nm and σ_R=10%. b) TEM picture of the MFA/PS colloids after dispersion in THF. Replica was prepared by shading the sample with platinum/carbon under an angle of 20°.

A hint to the origin to these discrepancies comes from the TEM pictures prepared from THF dispersion of the core-shell particles depicted in Figure 2b. Here, one sees that the majority of the particles are hollow spheres flattened to doughnut shaped structures by the sample preparation as indicated by the length of the shadows. However, some particles which still contain the MFA cores are visible as well (arrows). This could explain the failure of the SLS data analysis with a core-shell model. Tentative fits with a hollow sphere model were inconclusive as well, most likely due to an unquantified, but significant amount of intact core-shell latexes. In order to properly analyze SLS data one would have to separate out the core-shell particles, e.g. by preferential sedimentation.

The mechanism that leads to the hollow sphere structures is not clear at present. It seems unlikely that this is due to dissolution of the uncrosslinked "MFA" chains in THF. Rather the appearance of hollow spheres could be caused by breakage of the core due to ultrasonification in the redispersing process. Alternatively, a nonuniform distribution of crosslinks could on swelling yield large holes in the PS shells allowing the MFA cores to escape. If the former is the case, the synthesis of MFA core- PS-microgel shell particles and destruction of the cores by ultrasonification in organic solvent could be considered as a new, albeit somewhat bizarre route to obtain microgel hollow sphere structures.

Conclusion

We have demonstrated that it is possible to polymerize highly crosslinked polystyrene shells around preformed fluorocarbon seeds made out of polycrystalline poly(tetrafluoroethylene-co-perfluoromethylvinylether) while essentially preserving the narrow size distribution of the seeds. When dissolving the core-shell particles in tetrahydrofuran static light scattering and TEM results show that the fluorocarbon cores vanish, leaving hollow polystyrene shells. If this is due to the destruction of the cores during sample preparation or due to an escape of the whole cores via holes in the shell formed by inhomogeneous swelling is not clear at present. Further clarification requires experiments where the shell thickness as well as the sample preparation procedures are varied. Work along these lines is in progress.

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