Assembly of Latex Particles by Using Emulsion Droplets as Templates. 2. Ball-like and Composite Aggregates

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We report data on using the emulsion-based method for the assembly of ball-like aggregates of a positively charged (amidine) latex. The latex particles are strongly hydrophobized with the use of sodium dodecyl sulfate, which induces their adsorption into the bulk of the emulsion droplets. The droplets are then sterically protected against coalescence, and the particles gathered inside them are fixed. After the emulsion droplets are dissolved, a suspension of ball-like latex aggregates is obtained. The aggregates do not appear to be ordered, but their overall shape is precisely spherical. The process of fabricating ball-like aggregates was then combined with the assembly scheme for hollow supraparticles (presented in the first paper of this series). As a result, we have been able to obtain composite particles, whose cores are ball-like aggregates of amidine latex, surrounded by a shell of negatively charged sulfate latex. The core−shell structure was visualized by fluorescent microscopy. We also report data on the fabrication of composite particles by amidine heterocoagulation over hollow spherical shells from the sulfate latex. The described methods seem applicable to the assembly of ball-like and composite aggregates from colloid species other than latex beads.

1. Introduction

Core−shell and composite type colloid particles have been widely investigated recently, as these could find important applications in practical fields like catalysis, cosmetics, paper coating, and ceramics.[1−2] Interest is also shown in the fabrication and characterization of porous particles and aggregates.[3]

Presently, the composite particles are usually obtained by attaching a coat of smaller particles onto the surface of a bigger one. Such composites could be obtained by heterocoagulation when the core and the shell particles are of opposite surface charge.[4−6] Other techniques for formation of composites include dry mixing[7] or embedding.[8] The composites usually incorporate a combination of metallic/organic,[2] oxide/organic,[5−8] or two types of organic particles.[2] In some publications, successful combination of heterocoagulation, polymerization, and encapsulation is reported.[6]

We are not aware of any publications on composite particles whose core is not a single particle but an aggregate of particles instead. Methods for the production of hollow composite particles are still not available.

In the first paper of this series (ref 9; addressed hereafter only as "first paper"), we present the technique and the data on the assembly of ordered, empty spherical aggregates from latex particles. This technique is based on using emulsion droplets as templates, onto whose surfaces the particles are gathered, assembled into ordered structures, and fixed. The particles are then extracted from the emulsion droplets by dissolving the droplets in the surrounding environment. The different possibilities of the emulsion-based assembly scheme are summarized in Figure 1 of the first paper. In this study we describe the data on using the emulsion-based technique for the formation of ball-like latex aggregates in the bulk of the emulsion droplets. These aggregates are used further as a core for the fabrication of composite particles.

The Results and Discussion part of this paper is organized as follows: In section 3.1 we present the experimental data on the fabrication of ball-like aggregates from the amidine latex. Two different types of composite assemblies—with a full amidine core and with a hollow sulfate core—are presented in section 3.2. A discussion on the colloid interactions that emerge as driving factors in the formation of the ball-like and the composite particles is provided in section 4.

2. Experimental Section

2.1. Materials. The suspensions of latex microspheres were supplied by IDC Corporation. The sulfate fluorescent latex has a Texas Red dye incorporated inside the particles. A summary of the surface properties of these microspheres is given in the Supporting Information of the first paper of this series.[9] Prior to being used, the contents of the bottles were redispersed and sonicated for a few minutes.

The used chemical reagents were the same quality and from the same sources as the ones listed in the first paper.

2.2. Methods. As in the previous paper, the emulsions of 1-octanol in water are obtained with the use of a Janke and Kunkel Ultra-Turrax T25 rotor-stator type homogenizer, equipped with a S-25N 10G dispersing tool and control of the speed of rotation. The emulsions and latex supraparticle dispersions were prepared in volumes of 5−10 mL, handled, and stored in tightly capped disposable test tubes. The final dissolution of the emulsion drops and extraction of the latex aggregates and composites is carried out by quick injection of ethyl alcohol inside the tubes.

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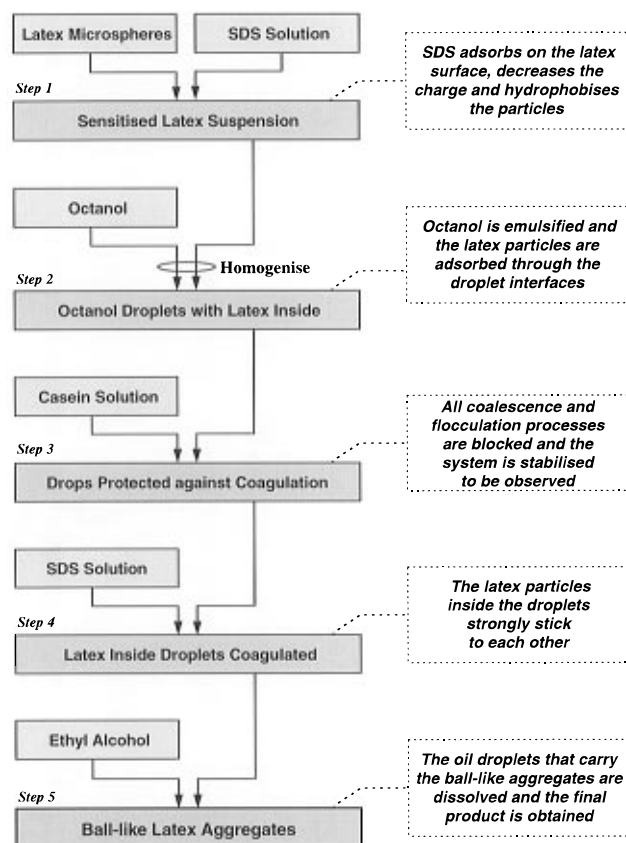
Figure 1. Flowchart of the multistage assembly of ball-like aggregates from the amidine latex. The boxes on the right briefly describe the physical processes that take place along at step.

The samples were observed by optical microscopy in transmitted or fluorescence (reflected) illumination. The pictures were obtained on an Olympus Vanox microscope using a Plan 40/0.65 objective. The fluorescence latex was excited by using a 100 W high-pressure mercury lamp and an interference filter at 550 nm. The way of preparing the samples for the microscopy is the same as the one in the first paper of the series.[9] The digital camera image capture and processing are also described there. The same applies for the electrophoretic mobility measurements.

3. Results

3.1. Ball-like Aggregates from the Amidine Latex.
These experiments were carried out with latex microspheres of positive surface potential. The only functional group present on the particle surfaces is the amidine group $(C(NH_2)=NH_2^+)$.[10,11]

The overall scheme for obtaining ball-like aggregates is presented in Figure 1. The first step of the process is to modify the surface properties of the latex particles, so that they adsorb and penetrate inside the octanol droplets. As described in the first paper, the addition of monobasic glutamic acid as a sensitizing agent could cause the slow penetration of the latex particles from the water phase into the bulk of the droplets. The monobasic glutamic acid however acts slowly (more than 20 min) and does not seem to affect all of the latex particles to the same extent, as some particles remain adsorbed on the interface or dispersed in the water. For this reason we resorted to the anionic surfactant SDS, which proved to be a very quick
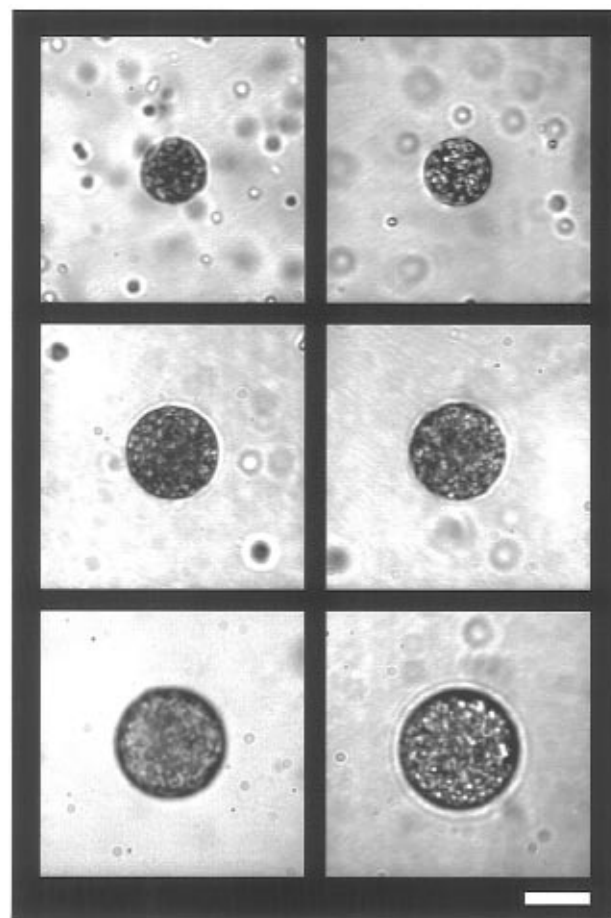
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Figure 2. Digitized panel of emulsion droplets filled with amidine latex beads. SDS is used to induce the particle adsorption and penetration (step 2 in Figure 1). To outline the polydispersity of the samples, droplets of various sizes are presented. Bar = 10 μm.

and efficient hydrophobizing agent for the amidine microspheres.

The required SDS concentration for the hydrophobization is very low. Concentrations of SDS on the order of 4×10^{-6} M were already enough to induce latex penetration inside the droplets. Increasing the concentration further increased the speed and efficiency of the particle collection by the droplets until at a concentration about 8×10^{-6} M a "catastrophic" event occurred: the particles quickly and irreversibly coagulated outside the droplets. For the experiments we settled at a concentration of 7.5×10^{-6} M, at which SDS induced particle adsorption and penetration inside the oil droplets within a few tens of seconds. The octanol droplets were introduced at a concentration of 1 vol %, the same as in the supraparticle experiment. The volume concentration of the latex was 0.5−0.6 vol %, so the droplet bulk was loosely filled with particles. The latex/octanol/SDS system was homogenized in 5−7 cycles, each including 60 s of processing at 8000 min^{-1}, followed by 30 s at rest. This resulted in the engulfment of the latex microspheres inside the octanol droplets (Figure 2). The latex microspheres gathered in this way inside the droplets did not seem to be ordered in a 3D or 2D manner (even if there was some ordering, the conditions of microscopic observation did not permit its visualization). The overall shape of these aggregates however was precisely spherical, determined by the shape of the droplets (Figure 2).

Before extracting from the octanol droplets the spherical latex clusters, it was necessary to introduce some steric
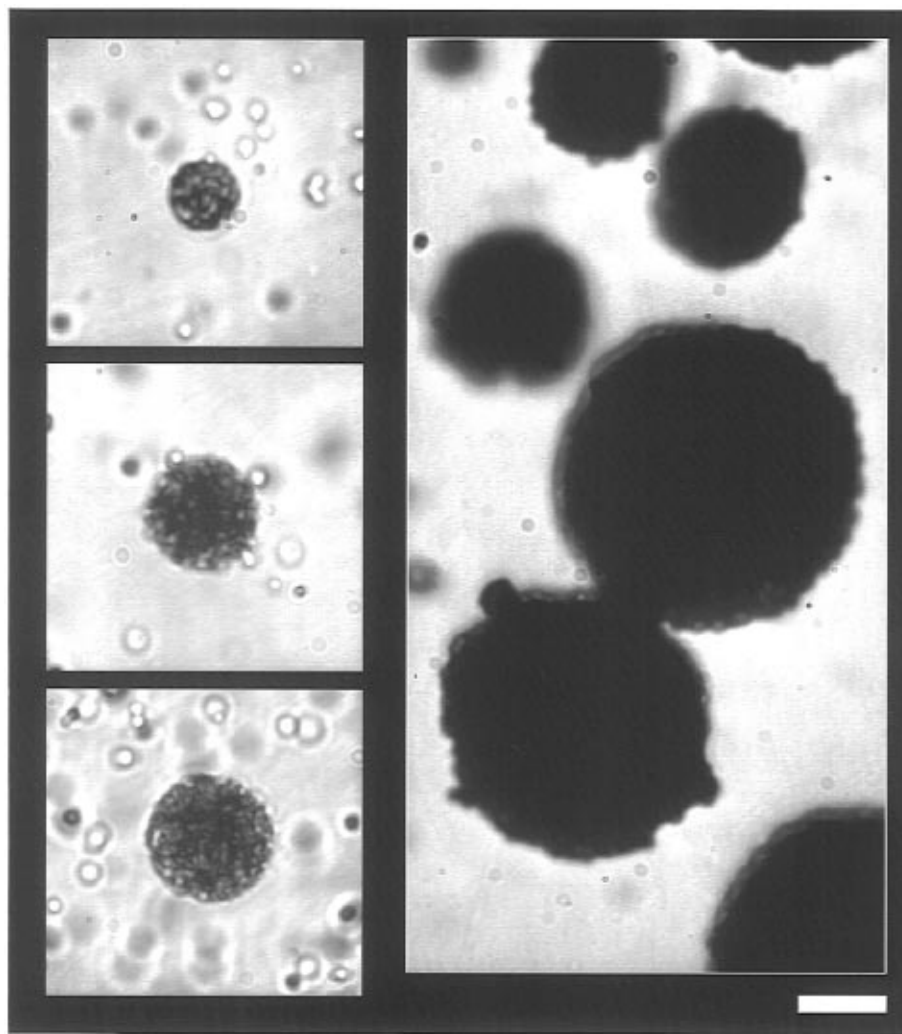
Figure 3. Ball-like aggregates of different size obtained by the scheme in Figure 1: left column, suspended aggregates; right column, aggregates dried over a glass surface. Bar = 10 μm.

Table 1. ζ-Potentials of the Colloid Species Involved in the Assembly of Ball-like Amidine Latex Aggregates[a]

system	ζ-potential, mV	pH	notes
amidine latex	114.7 ± 10.1	6.2	cf. with Table 2 of first paper—same latex but after 2 months of storage
amidine latex + 4.3×10^{-6} M SDS	4.62 ± 3.3	5.8	the particles penetrate inside the oil droplets
amidine latex + 8.3×10^{-6} M SDS	-27.5 ± 7.2	6.2	the particles coagulate outside the oil droplets
amidine latex + casein + 1.7×10^{-4} M SDS	-66.3 ± 5.1	$\approx$7	stable sample, low polydispersity
octanol emulsion droplets + 4.3×10^{-6} M SDS	-65.60 ± 17.3	6.2	unstable samples, high scattering of data

[a] 5×10^{-4} M NaCl is added to all the samples. The concentrations of the other substances are similar to those in the assembly scheme.

stabilizer, protecting the oil droplets against coalescence and the latex balls from coagulation with each other. Similarly to the first paper, we used a casein solution at a concentration of 0.5 g/L. The droplet/particle complexes stabilized by casein could be stored for a prolonged period of time in a suspended state but could not survive the ethanol extraction step. As in the supraparticle experiments (first paper) the gathered particles required some further binding or coagulation in order to gain the necessary structural stability. This was achieved by adding a more concentrated SDS solution to raise the SDS concentration up to 1×10^{-4} M (step 4 in Figure 1). When ethyl alcohol was injected in a 1:1 ratio to the system after 10 min (step 5 in Figure 1), the octanol droplets were dissolved and the ball-like aggregates remained intact and dispersed (Figure 3). As there is no cavity inside the spherical aggregates, their mechanical stability is higher than that of the shell-like supraparticles. After the octanol

was removed from the surrounding environment (by centrifuging, washing, and resuspending the aggregates in a casein/SDS solution), the latex balls could easily be deposited on the solid surface by drying. Pictures of such deposited and dried balls are also presented in Figure 3. The amidine spheres are a basic component of the composite particles described in the following section.

We measured the electrophoretic mobility of the amidine latex after sensitization with two SDS concentrations. The results, recalculated as ζ-potentials, are presented in Table 1. It is seen that while the amidine latex in its native state possessed a very high positive potential, the treatment with SDS led to almost complete discharging of the latex surfaces. At SDS concentrations above the "catastrophic" point of 8×10^{-6} M the latex potential became negative. The octanol droplets and the stabilized and bound latex balls also possessed a significant negative potential.
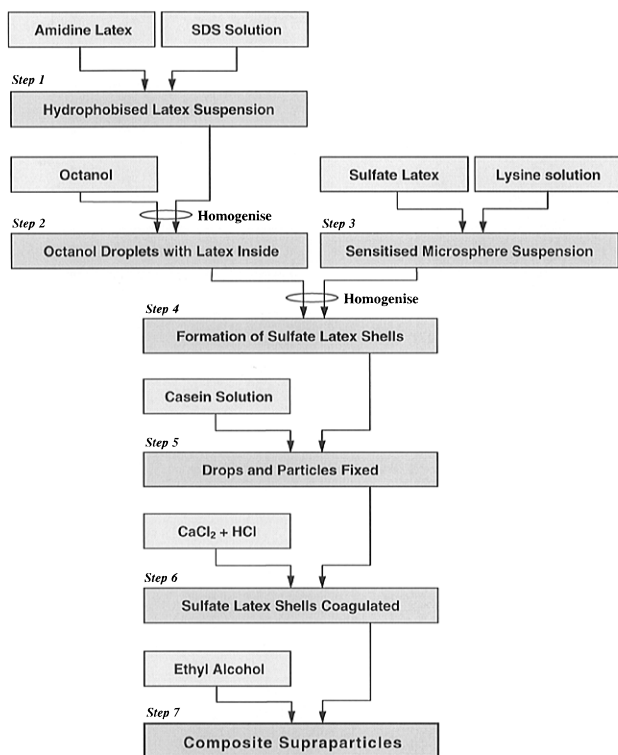
Figure 4. Flowchart for the assembly of composite supraparticles. The final product has a spherical core from aggregated amidine latexes, over which a shell of sulfate latexes is deposited.

3.2. Composite Assemblies. One interesting possibility, provided by the method, is the fabrication of supraparticles including more than one colloid component. We have assembled composite particles by using both the sulfate and amidine latexes and by combining their assembly schemes.

Amidine Latex Core/Sulfate Latex Shell Assemblies. These composite particles consist of a core of aggregated amidine microspheres surrounded by a shell of sulfate latexes. The flowchart of their assembly is presented in Figure 4. The process first included the formation of ball-like aggregates from the amidine latex inside the octanol droplets. We then used the method for formation of sulfate latex shells on the droplet surfaces, reported in the first paper, to surround the amidine latex with a sulfate shell.

The amidine latex was destabilized with the use of SDS, as described in the previous section. The system was homogenized in six cycles, each including 60 s of treatment and 30 s of rest between the cycles. In this process, the amidine beads penetrated and aggregated inside the octanol droplets (step 2 in Figure 4). Meanwhile, the sulfate beads were sensitized by a lysine hydrochloride solution. The dispersions of the octanol/amidine latex and the sensitized sulfate latex suspension were mixed in a ratio of 1:1. The final concentration of the amidine and the sulfate latexes after mixing was 0.13 vol %, and the oil amounted to 0.75 vol %. The mixture was briefly homogenized in three cycles of 30 s of processing followed by 30 s of rest (step 4 in Figure 4). This allowed the formation of sulfate latex shells on the droplet surfaces (similar to the ones described in the first paper). The adsorption of the sulfate latex microspheres is possibly enhanced by the electrostatic attraction to the positively charged core. Some loss of latexes and decrease of the final yield occurred during this step due to the buildup of heterocoagulate deposits on the walls of the test tubes.

After the core−shell structures were formed, the process followed the sulfate latex fixation and extraction scheme described in the first paper. The composite particles were sterically stabilized by adsorption of casein (concentration = 1 g/L). The overlying sulfate shell was strongly coagulated in the next step by a mixture of 10^{-2} M HCl and 5×10^{-3} M $CaCl_2$ (step 6 in Figure 4). The octanol droplets inside the already fixed composite particles were dissolved by addition of ethanol. We provide pictures of the finally obtained composites in Figure 5. The overall shape of the composite assemblies was usually close to spherical but not very smooth and regular. In the transmitted mode of illumination, one cannot distinguish which particles belong to the amidine type and which to the sulfate type, as their optical properties are identical. Still, a certain distinction between the core and the shell is noticed, possibly due to the difference in the densities of packing inside the aggregated latex phases. The yield of the process was below 10% due to losses by deposition and heterocoagulation. Once the composites are obtained, they can be concentrated and purified by centrifugation and stored in a suspended state or dried over a solid surface.

To prove and visualize the existence of core−shell structures, we carried out experiments in which the sulfate latex was substituted with a sulfate fluorescent latex. The results of the electrophoretic measurements of the original and the sensitized fluorescence latex are given in Table 2. This latex has a lower charge and surface potential, but its response to sensitization with lysine is not very pronounced and it behaved sluggishly when processed according to the flowchart in Figure 4. The fluorescent shell/amidine core supraparticles were observed both in transmitted and fluorescent illumination. Comparative pictures of both modes of observation are presented in Figure 6. Two of the features of the particles in fluorescence illumination reveal their core−shell structure: (i) at appropriate focusing of the objective, one can sharply recognize the fluorescent beads around the composite and (ii) the intensity of the fluorescent response from the composites appears uniform or concentrated at the surroundings of the supraparticles (if the fluorescent beads were uniformly mixed with the amidine ones, the biggest intensity would be recorded at the central region). The fluorescence illumination also allows us to visualize the discrete particles of the sulfate latex shell that cannot be observed in transmitted light (no figure is shown, as this is poorly captured by the digital camera). We observed that the sulfate latex shell lacks the 2D ordering of the empty sulfate supraparticles, though some small ordered patches are distinguished. The particle ordering in the shell is possibly disrupted due to the strong electrostatic attraction to the underlying aggregated amidine core. On the other hand, this attraction gives the composites compactness and mechanical stability.

Heterocoagulation over Shell-Like Assemblies. In the first paper we describe how the emulsion assembly method could be used for obtaining ordered empty shells of latex particles. One easy though somewhat trivial possibility for fabrication of composites is to introduce these shell-like assemblies into suspensions of latex of opposite charge that will deposit on the shells by heterocoagulation. This is not a real emulsion-based assembly, as it is closer to the common heterocoagulation-based composite particles obtained by attaching a coating of smaller beads on a big particle of opposite charge.[4−6] First we prepared a dispersion of octanol droplets covered with an ordered shell of the sulfate latex, according to the procedure described in the first paper (up to step 2, Figure 2 in the first paper). The concentrations of the latex, lysine, and oil were the same as those in the first paper. The sulfate-covered octanol droplets were then introduced into a 0.15
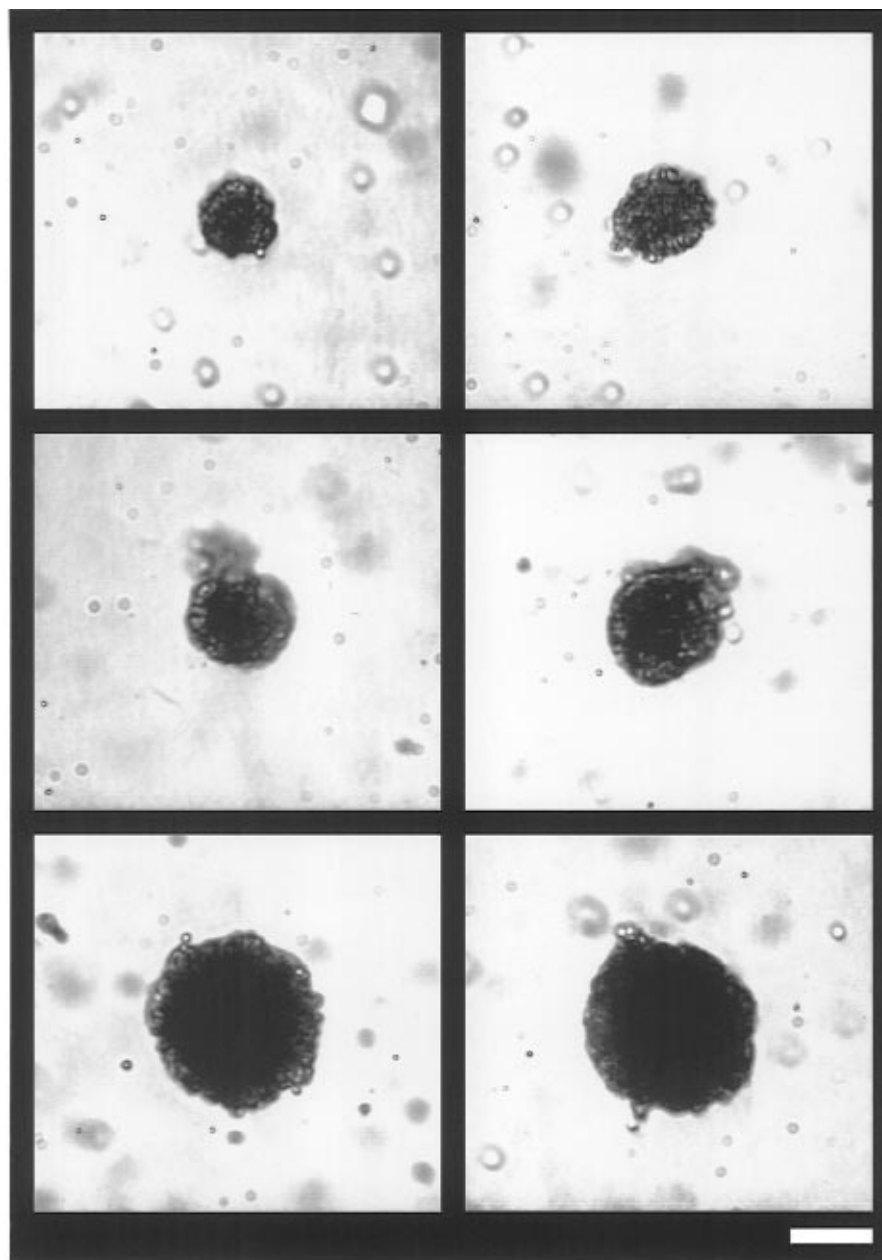
Figure 5. Amidine latex core/sulfate latex shell composite assemblies of various sizes in transmitted illumination. The core−shell structure is suggested by the different densities of the aggregated latexes. Bar = 10 μm.

Table 2. ζ-Potential Data for the Fluorescent Latexes Involved in the Composite Assembly Scheme[a]

system	ζ-potential, mV	pH	notes
fluorescent latex	-64.2 ± 5.5	5.7	sample slightly aggregated
fluorescent latex + lysine	-57.6 ± 4.3	6.7	responds slowly to sensitisation

[a] 5×10^{-4} M NaCl is added to the samples. Compare also with Table 1 from the first paper.

vol % suspension of (nonsensitized) amidine beads. The positively charged amidine microspheres are attracted to the shells from the negatively charged sulfate latex and deposit on their surfaces. After 2 min of shaking, the system was stabilized by 0.5 g/L of casein.

The obtained composites were stable enough to survive droplet extraction without further fixation. This stability could be attributed to the strong electrostatic attraction between the sulfate latex core and the heterocoagulated shell. Pictures of these types of aggregates are presented in Figure 7. In the figure, one can distinguish the underlying spherical core of the sulfate latex, but the overlying heterocoagulated shell is not ordered and is of unequal thickness, so the shape of the particles is uneven.

This is a common problem in the fabrication of hetero-coagulated composites.[12] In our case, the situation is complicated by the lack of intensive stirring and by the presence of single unadsorbed sulfate microspheres that are also incorporated in the heterocoagulated core. Although these problems could be avoided, we have not elaborated further the heterocoagulation method. Its further development can bring about the production of multilayer composite particles with a hollow spherical space in the center.

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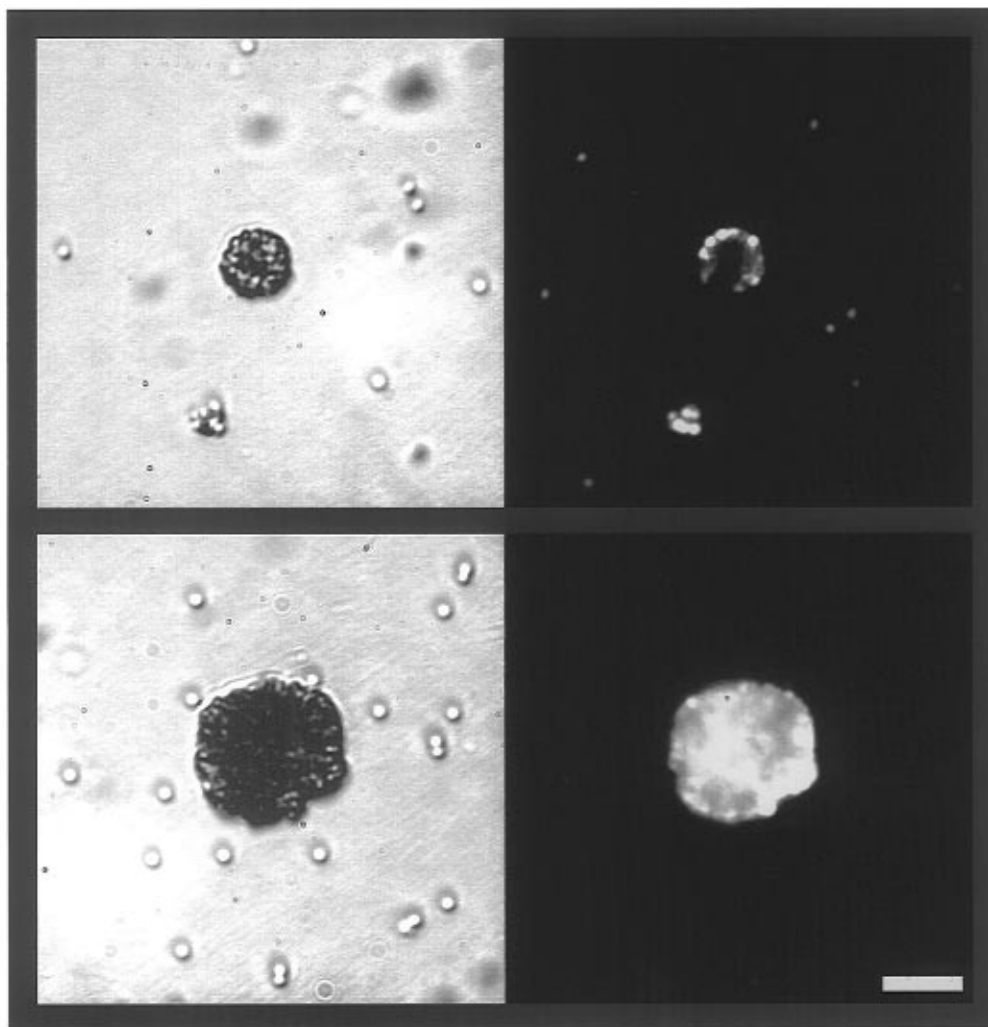
Figure 6. Comparative pictures of composite particles with a core of (nonfluorescent) amidine latex and a shell of fluorescent sulfate latex: left, transmitted bright-field illumination; right, reflected fluorescence illumination. Bar = 10 μm.

4. Discussion

The highly charged amidine latex in its original state is unable to adsorb and penetrate inside the octanol droplets. This may result from electrostatic or hydration interactions (see the Discussion in the first paper of this series). The sodium dodecyl sulfate molecules are highly interfacially active, and they carry one negative charge each. These molecules could attach to the latex surface by two types of interactions: (i) electrostatic attraction between the negatively charged SDS molecule and the amidine groups on the latex surface and (ii) hydrophobic attraction between the hydrocarbon SDS chain and the polystyrene surface. We expect that both of these are operative in the neutralization of the positive charges on the amidine microspheres, the hydrophobic attraction being the leading one. Because of the very strong attachment of the SDS molecules to the latex surface, the amount of SDS required for latex hydrophobization is very low. An increase of the SDS concentration results in recharging (Table 1). Recharging does not occur when amino acids are used as sensitizing agents—compare with the previous paper. Therefore, SDS adsorbs on the latex microspheres much more strongly than the amino acids. This difference possibly arises from the lack of hydrophobic attraction between the amino acid molecules and the latex surface.

The observed "catastrophic" coagulation of the particles outside the octanol droplets above 8×10^{-6} M SDS appears to be connected with passing through the point of zero surface charge. The hydrophobized latex particles of positive charge (below 8×10^{-6} M of SDS) will have the tendency to attract and penetrate into the negatively charged octanol droplets (Table 1). Once the hydrophobized amidine beads attain a negative charge due to the excess of SDS adsorbed on the surface (above 8×10^{-6} M SDS), they will be repelled from the droplet surfaces and will coagulate outside the droplets. This finding has an important practical application, as it demonstrates that the ball-like assembly scheme is apt to work only if the hydrophobized particles and the emulsion droplets have been modified to possess opposite surface charges. It also explains in a simple way why it is easier to obtain ball-like aggregates from amidine rather than from the sulfate latex. It might also be added at this point that the amidine latex is more susceptible to hydrophobization than sulfate latex because of the absence of OH groups on the surface, the latter groups being not responsive to electrostatic modification but keeping the latex surface hydrophilic.

The almost complete neutralization of the charges on the amidine latex surfaces makes the microspheres coagulated by van der Waals and hydrophobic interactions.[13] The coagulation strength increases after an additional quantity of SDS is added to the system before the oil droplets are dissolved in the surrounding environment. The origin of the gain of structural stability caused by adding additional SDS in still somewhat unclear. It

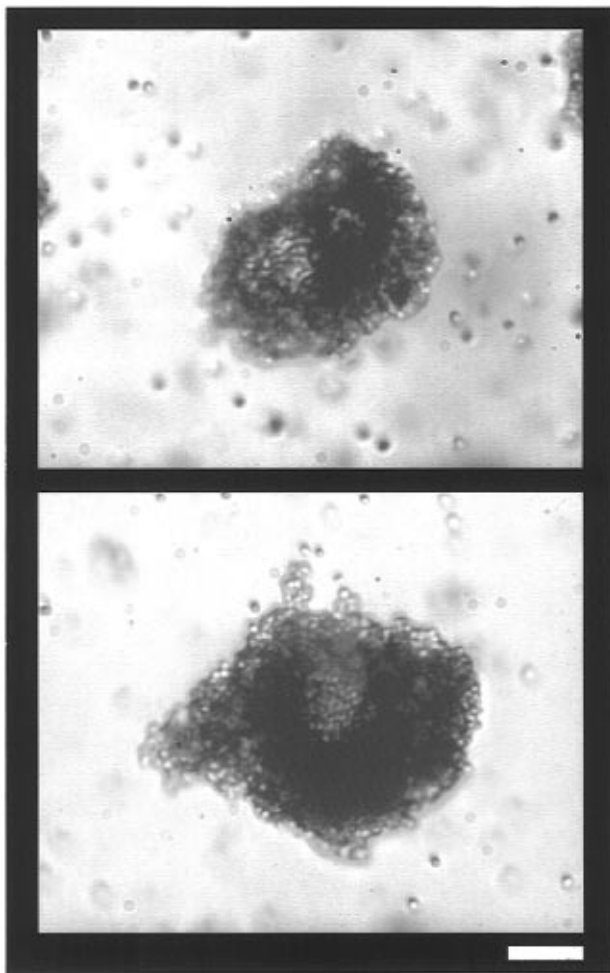(13) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1992.

Figure 7. Composite aggregates obtained by heterocoagulation of amidine latexes over spherical empty shells of sulfate latexes. Bar = 10 μm.

may be speculated that the strength of interparticle adhesion increases because of the strong irreversible coagulation during passing of the point of zero charge or because of cross-binding of the particles with SDS molecules hydrophobically adsorbed on one of the particles and electrostatically attracted to the positive surface groups on the other particle. The strong coagulation combined with the many contacts between the particles in the 3D aggregates gives the ball-like aggregates the mechanical strength that allows their drying over solid substrates.

The ball-like aggregates obtained by the emulsion method do not seem to possess the ordering that is characteristic of the supraparticles presented in the first paper of the series. The use of oil droplets as carriers however is a crucial factor for the overall regular spherical shape of the colloid clusters. The spherical shape, combined with the increased porosity and considerable mechanical strength of the aggregates, may make such kinds of suspensions practically usable, e.g. in the preparation of substrates for heterogeneous catalysis. The composite particles described in section 3.2 could find a similar application.

5. Concluding Remarks

This paper concludes the description of supraparticle, ball-like, and composite aggregates obtained by using emulsion drops as templates for the assembly of latex beads. The data reported in this as well as in the first paper of the series do not encompass all of the possibilities of the assembly and dissolution emulsion scheme. We believe that, by choosing appropriate modifiers of the colloid interactions, composites and supraparticles comprising other colloid species than latex particles could be assembled.

The method is also potentially applicable for the production of more functionalized composites than the core−shell structures presented above. This could be achieved by assembling together more than two types of colloid species or by introducing directionally specific particle−particle interactions.