Coating of Colloidal Particles by Controlled Precipitation of Polymers

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ABSTRACT: A method is suggested for the coating of micron-sized particles by polymeric films based on surface-controlled precipitation. Polymer particles were coated by dextran and DNA in a water/ethanol mixture containing multivalent cations. A theoretical model for depositing polymers on colloidal particles is presented using the Smoluchowski solution for diffusion-controlled irreversible coagulation. Theoretical estimations appear to provide the proper particle and polymer concentration ranges in order to achieve smooth coverage. The optimal concentration range also was determined experimentally and agrees with the theoretical calculations. The controlled precipitation method of assembling thin films on colloids is compared with the layer-by-layer adsorption approach. Advantages and drawbacks of both approaches are discussed.

Introduction

The design of functional colloid particles is the focus of research in diverse areas, such as catalysis, biotechnology, medicine, ecology, and others. In general, the research on particulation implies the formation of a colloidal core of defined content and size, the preparation of a shell providing the required stability, release of core material, and catalytic or affinity properties. Tailoring of the different components of one particle becomes important in order to develop these functionalized colloids, i.e., to combine several properties in one core−shell structure.

As shown in previous papers,[1−3] one possible way to assemble various compounds on colloidal particles is the layer-by-layer (LbL) adsorption of oppositely charged macromolecules.[4,5] This method of multilayer film assembly provides a defined shell composition on a colloidal core. The shell thickness is a function of the number of assembled layers, and it can be tuned in the nanometer range. Up to now a variety of materials, such as synthetic polyelectrolytes, proteins, DNA, inorganic particles, and lipids, have been utilized as building blocks for shells on colloids. The LbL assembly method can be applied to coat various charged particles, such as organic and inorganic colloids, biological cells, or nanocrystals of pharmaceuticals. The size of particles explored for this method can be varied from 0.1 to 10 μm.

Noncharged macromolecules can also adsorb at the interface under certain conditions. This may happen, for example, due to hydrophilic−hydrophobic interactions between the macromolecules and the particles in the solution. By exploiting this, many different substances may be precipitated on the colloids, and the functional properties of the shells can be significantly extended. The coating of colloidal particles has already been achieved by the precipitation of inorganic salts on the surface of polystyrene latex particles.[6,7]

The problem in controlling polymer precipitation on colloids is as follows: one wants to precipitate the polymers before aggregation takes place. One also wants to use sufficiently high concentration of polymers and colloidal particles to perform the process in a reasonable time. This suggests modeling of the experimental situation to derive a range of optimal experimental parameters. In the present method, the particles are exposed to a solution of coagulated macromolecules. This process is similar to heterocoagulation of colloids. Coagulation kinetics are usually described on the basis of Smoluchowski theory,[8] which has been developed for a variety of practical cases.[9−11] The profile of the interaction energy of particles is included in the theory and may be estimated via several different physical models. The well-known DLVO theory takes into consideration electrostatic and molecular forces.[12−14] DLVO theory has now been extended to include hydrophobic and hydrophilic interactions.[13,15,16] Thus, the current experimental system may be analyzed and interpreted on the basis of the above-mentioned theories. An attempt is made here to simplify the theoretical models for description of this system, as well as to discover the main parameters controlling the coagulation process.

Theoretical Model of the Dropwise Technique

The polymer shell formation process is based on the coagulation of molecules onto the surface of colloidal particles. Brownian motion, hydrodynamic forces, electrostatic forces, etc., are all responsible for bringing the particles and macromolecules together. The contribution of each of these forces to the overall coagulation process should be estimated in order to develop a useful model of the process.

The problem of the diffusion of one particle toward another followed by their irreversible coagulation was first solved by Smoluchowski.[8] Here we introduce only the main points of the theory and adapt it to describe polymer macromolecules deposition on the colloidal particles in our system.

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The stationary diffusion flux of polymer molecules to the mobile collector (the colloidal particle in our case) is

$$J = 4\pi(R_p + R_c)(D_p + D_c)n_p \quad (1)$$

where R_p, D_p, R_c, and D_c are the radius and the diffusion coefficient for the polymer molecules and for collectors, respectively; n_p is the number of polymer units, referring not only to single polymer molecules but also to aggregates of polymer molecules. Using the Einstein equation for the diffusion coefficient $D = k_B T/6\pi\eta R$ (where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity), eq 1 may be rewritten as

$$J = \frac{2}{3}\frac{k_B T}{\eta}\left(\sqrt{\frac{R_c}{R_p}} + \sqrt{\frac{R_p}{R_c}}\right)^2 n_p = a_{pc} n_p \quad (2)$$

Here a_{pc} is the frequency of collision between the polymer units and the collector:

$$a_{pc} = \frac{2}{3}\frac{k_B T}{\eta}\left(\sqrt{\frac{R_c}{R_p}} + \sqrt{\frac{R_p}{R_c}}\right)^2 \quad (3)$$

The number of the polymer units n_p in the system decreases as polymer units stick to the collectors. The rate of change of polymer units is equal to the flux to the collector multiplied by the number of collectors, N_c:

$$\frac{dn_p}{dt} = -JN_c = -a_{pc} n_p N_c \quad (4)$$

Initially, the system contains only one type of particle. Coagulation leads to the formation of n_k aggregates that consist of k primary particles. The number of aggregates, n_k, containing k molecules, increases due to aggregation of other aggregates containing i and $k - i$ molecules and decreases due to aggregation of n_k aggregates with any another aggregate. This leads to the equation

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1} a_{i,k-i} n_i n_{k-i} - \sum_{i=1}^{\infty} a_{i,k} n_i n_k, \quad k \geq 1 \quad (5)$$

where a_{ij} is the collision frequency for aggregates containing i and j primary particles. The $^1/_2$ coefficient eliminates double counting in the first sum. The a_{ij} coefficients depend on the radius according to eq 3. The radius of the aggregate increases slowly with respect to the number of initial particles in the aggregate as $R_k \sim k^{1/3}$. For this reason we may suggest $a_{ij} \approx a$. Introducing the new variable $n_p = \sum_{k=1}^{\infty} n_k$, equal to the total number of particles in the system after summing over all k in eq 5, leads to

$$\frac{dn_p}{dt} = -\frac{a}{2} n_p^2 \quad (6)$$

The solution is the well-known Smoluchowski formula for so-called fast coagulation (each collision leads to aggregation) kinetics,

$$\frac{n_p(t)}{n_0} = \frac{1}{1 + t/T_{Sm}} \quad (7)$$

where n_0 is the initial concentration of the monomers and T_{Sm} is the so-called half coagulation time (i.e., the time in which the number of aggregates is reduced to half the initial number). In an aqueous solution under normal conditions ($T = 295$ K)

$$T_{Sm} = \frac{2}{a n_0} = \frac{3\eta}{4 k_B T n_0} = \frac{2 \times 10^{11}}{n_0\ [\mathrm{cm}^{-3}]}\ [\mathrm{s}] \quad (8)$$

Later, Fuchs extended the diffusion problem to include the radial interaction potential barrier $U(h)$, where h is the shortest distance between surfaces.[9] The so-called retardation factor is defined as

$$W = \int_0^{\infty} \frac{\beta(h)}{(h+2)^2} \exp\left(\frac{U(h)}{kT}\right) dh \quad (9)$$

where the function $\beta(h)$ describes the additional force due to the viscous flow when the surfaces draw together.[13] In this case, the Smoluchowski−Fuchs model may describe the behavior of the system, with Brownian transport and the retardation factor providing the probability of coagulation upon collision. Using this factor, J is replaced by J/W in eq 1, and correspondingly, $T_{Sm} \rightarrow T_{Sm}W$ in eq 8.

In our system the electrolyte concentration in the solution is typically greater than 10^{-2} M; hence, the Debye shielding radius is less than 3 nm. Electrostatic interaction may therefore be neglected for the particle transport process.

In a continuously stirred suspension the velocity gradient in the fluid $\Gamma = \partial v_\theta/\partial z$ may intensify the transport of particles. We use the Levich approach[10] for estimation of the hydrodynamic flux of the particles,

$$J_h = \frac{4}{3}\Gamma(R_p + R_c)^3 n_p \quad (10)$$

The ratio of the hydrodynamic (eq 10) and Brownian (eq 2) flux of the polymer individual macromolecules or aggregates (R_p) to the large colloidal particles (R_c) is

$$\delta = \frac{J_h}{J} \approx \frac{2\eta}{k_B T}\Gamma R_c^2 R_p \quad (11)$$

The Γ term may be estimated by $\Gamma \approx \omega\rho/L$, where $\omega \sim 1\ \mathrm{s}^{-1}$ is the rotation speed of the liquid in the vessel, $\rho \sim 0.3$ cm is the radius of the cell, and $L \sim 3$ cm is its depth, giving $\Gamma \sim 0.1\ \mathrm{s}^{-1}$. Substituting this value of Γ, as well as the other known constants, into eq 11, we have $\delta \approx 0.05 R_c^2 R_p$ [μm]. Hydrodynamic transport of the macromolecules to the particles becomes significant when $\delta > 1$. In our system, $R_c > 100 R_p$, which means hydrodynamic transport would only be significant for particles with diameter $2R_p > 25$ μm. Thus, only Brownian movement is important for the transport processes in the present system.

Now, consider a system containing n_0 small polyelectrolyte molecules (radius R_p) and N_0 large colloidal particles (R_c) at the initial moment of time. Since $R_c \gg R_p$, coagulation of the polyelectrolyte molecules does not considerably change the radius of colloidal particles. Hence, equations for both aggregation processes can be written as

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1} a_{i,k-i} n_i n_{k-i} - \sum_{i=1}^{\infty} a_{i,k} n_i n_k - \sum_{i=1}^{\infty} b_{i,k} N_i n_k \quad (12)$$

$$\frac{dN_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1} c_{i,k-i} N_i N_{k-i} - \sum_{i=1}^{\infty} c_{i,k} N_i N_k \quad (13)$$

The third item in eq 12 reflects additional decrease of the concentration of the polymer units containing k polyelectrolyte molecules due to the aggregation on the colloidal particles. If $a_{ik} = a$, $b_{ik} = b$, $c_{ik} = c$, and we introduce $n_p = \sum_{k=1}^{\infty} n_k$, $N_c = \sum_{k=1}^{\infty} N_k$, and the dimensionless parameters $n = n_p/n_0$, $N = N_c/N_0$, eqs 12 and 13 may be simplified in a similar manner to that outlined above. This simplification yelds

$$\frac{dn}{dt} = -\frac{n^2}{T_p W_p} - \frac{Nn}{T_{pc} W_{pc}} \quad (14)$$

$$\frac{dN}{dt} = -\frac{N^2}{T_c W_c} \quad (15)$$

where, in accordance with eq 8 and eq 3,

$$T_p = \frac{2 \times 10^{11}}{n_0\,[\mathrm{cm}^{-3}]}\,[\mathrm{s}], \quad T_c = \frac{2 \times 10^{11}}{N_0\,[\mathrm{cm}^{-3}]}\,[\mathrm{s}], \quad \frac{T_{pc}}{T_c} = 4\frac{R_p}{R_c} \quad (16)$$

Here T_p and W_p are the Brownian diffusion times and coagulation retardation factors for the coagulation of particles with particles; T_c and W_c, for colloids with colloids; and T_{pc} and W_{pc}, for particles with colloids, respectively. The solutions of eqs 14 and 15 are

$$N = \frac{1}{1 + \dfrac{t}{T_{pc} W_{pc}}} \quad (17)$$

$$n = 1 - \frac{T_{pc} W_{pc}}{T_c W_c}\Big/\left(1 - \frac{T_{pc} W_{pc}}{T_c W_c} + \frac{T_{pc} W_{pc}}{T_p W_p}\right) \times \left(1 + \frac{t}{T_c W_c}\right)^{T_c W_c / T_{pc} W_{pc}} - \frac{T_{pc} W_{pc}}{T_p W_p}\left(1 + \frac{t}{T_c W_c}\right) \quad (18)$$

Heterocoagulation of the particles on the colloids should be maximized in our experiment. This requires minimal homocoagulation of the particles and colloids. In terms of coagulation times, $T_{pc}W_{pc} < T_pW_p < T_cW_c$.

Using the above conditions and arguments, we now describe the layer-by-layer deposition technique. When one polyelectrolyte layer is deposited on a colloidal surface, the polyelectrolyte molecules and colloidal particles initially have different charges. During the deposition process, the polyelectrolyte molecules eventually overcharge the colloid surface. Hence, at some time, the charge on the colloidal particles is zero, and the particles can coagulate. To prevent this situation, the condition $T_{pc} \ll T_c$ should be satisfied. This can be achieved by using a large excess of polyelectrolyte with respect to the colloidal particle concentration.

The controlled precipitation method can also be used for materials other than charged macromolecules. Under these conditions, the electrostatic barrier preventing homocoagulation is absent ($W_{pc} = W_p = W_c = 1$), and more care should be taken in selecting the concentrations N_0 and n. The following two conditions must be satisfied and contradict one another: (1) The macromolecule concentration should be high enough to cover the colloidal particles faster than monocoagulation take place. (2) The concentration cannot be too high; otherwise, large aggregates of macromolecules will form before heterocoagulation can occur on the colloidal particles. Unfortunately, these conditions are mutually exclusive: hence, a dropwise technique was used. During the entire processing time the macromolecule concentration is never high enough to allow macromolecule coagulation to large aggregates. However, by continuously adding material dropwise, the concentration remains consistently high enough to cover the colloidal particles before they can aggregate.

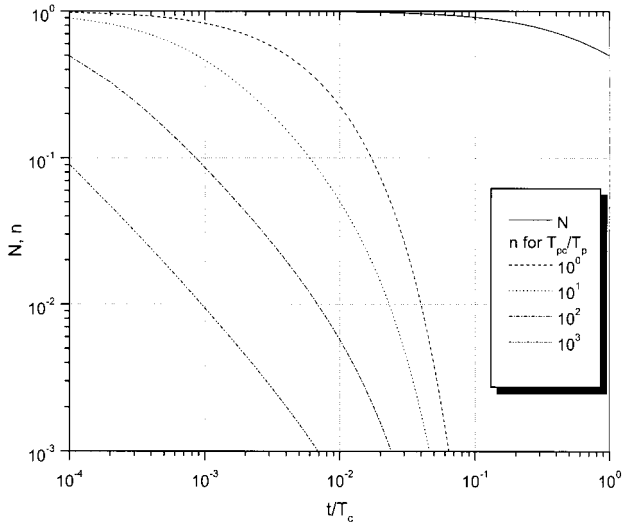

Figure 1. Coagulation kinetics of particles (N, solid line) and macromolecules (n) for different ratios of the precipitation times: $T_{pc}/T_p = 1$ (dash), $T_{pc}/T_p = 10$ (dot), $T_{pc}/T_p = 100$ (dash−dot), and $T_{pc}/T_p = 1000$ (dash−dot−dot).

Theoretical estimates of the coagulation kinetics of colloidal particles (N, eq 17) and macromolecules (n, eq 18) are presented in Figure 1. The number of colloidal particles, N, should not decrease significantly; therefore, the deposition time should be less than T_c ($t < T_c$). In accordance with condition 1, a majority of the macromolecules must coagulate on the interface during the deposition step; however, the size of the aggregates of macromolecules should be much less than the diameter of colloidal particles. The optimal value for the decrease in concentration is in the range $10^{-3} < n < 10^{-2}$. Furthermore, enough steps have to be carried out so that the particles will be covered by macromolecules in the time $t < T_c$. With the above arguments, the optimal time ratio is $T_{pc}/T_p \sim 10^3$.

As an example, we present estimates of the relevant parameters for our experiment. The colloidal particle diameter is $2R_c \sim 4 \times 10^3$ nm, while the diameter of the macromolecule as estimated by AFM or by light scattering is $2R_p \sim 4$ nm. Hence, from eqs 16 $T_{pc}/T_c \sim 4 \times 10^{-3}$ and $T_{pc}/T_p \sim 4 \times 10^{-3} n_0/N_0$. To satisfy condition 1, the concentration of macromolecules n_f giving complete coverage of the colloidal particles may be estimated as $n_f/N_0 \approx (R_c/R_p)^2 \approx 10^6$. The number of drops is given by $K_s = n_f/n_0$. Satisfying condition 2 implies that $T_{pc}/T_p \sim 4 \times 10^3/K_s$ should not be very high. However, since $T_{pc}K_s \leq T_c$, the homocoagulation of colloidal particles is expected to be small during the deposition process; thus, $K_s \leq 100$ and $n_0/N_0 \approx n_f/N_0\, K_s \approx 10^4$. Figure 1 shows the time dependence of the number of the particles for

different T_{pc}/T_p values. The flux is proportional to the number of aggregates, and we should add new portions of macromolecule when n decreases significantly (i.e., more than 100 times). This corresponds to coagulation of most of the macromolecules upon the particle surface. The time between drops should be smaller than T_p in K_s time. So, as shown in Figure 1, the drop time for $K_s = 100$ corresponds to 0.01 on the time axis. Enough macromolecules have coagulated by the time $T_{pc}/T_p \geq 100$. In this way, we can calculate concentrations N_0 and n_0 and calculate the time between drop additions.

A convenient preparation time is $T_c \sim 10$ min $= 600$ s. Hence, from eqs 16, $N_0 \sim 4 \times 10^8$ cm^{-3}, or using the known value of the radius, we obtain $N_0 \sim 2$ wt %. In the dropwise technique, a drop of polymer solution has a volume $V_d \sim 10\ \mu$L, which is added to colloidal particle suspension of volume $V \sim 10$ mL, resulting in a dilution of 10^3 times. Therefore, $n_0 \sim 4 \times 10^{15}$ cm$^3 \sim 0.5$ mg/mL. Finally, the estimated time between drops should be $T_{step} \sim T_{pc} \sim 5$ s. If we wish to decrease the number of steps K_s, the concentration must be increased in an inversely proportional manner. So, for the case of $K_s \sim 10$, the concentration of the macromolecule solution would be $n_0 \sim 5$ mg/mL. However, this higher concentration will increase the macromolecular coagulation resulting in nonuniform layer structure.

With this simplest model of the precipitation processes, the order of magnitude for the concentrations to be used experimentally can be predicted. Our experience has shown that the N_0, n_0 range was predicted quite well and gives a nice starting point for the optimization of the process.

Experimental Section

Materials. Sodium poly(styrenesulfonate) (Na−PSS, MW ~ 70 000), poly(allylamine hydrochloride) (PAH, MW ~ 50 000), and acridine orange (AO) were obtained from Aldrich. For confocal fluorescence microscopy, the PSS were labeled with Rhodamine (PSS-Rd) according to ref 17. $TbCl_3$ was purchased from Merck. All commercial polyelectrolytes were used without further purification except for PSS, which was dialyzed against Milli-Q water (MW cutoff 14 000) and lyophilized.

DNA and dextran (MW ~ 76 000) labeled with rhodamine were purchased from Sigma. DNA was labeled by mixing with AO with molar ratio 7:1 between phosphate groups and AO, respectively.[18]

Dispersions of monodispersed weakly cross-linked melamine formaldehyde particles (MF particles) with a diameter 4 and 6.5 μm were purchased from Microparticles GmbH (Berlin, Germany).

Methods. Confocal micrographs were taken with Leica TCS SP, equipped with a 100× oil immersion objective. The excitation wavelength was chosen according to the particular label.

Experimental Results

Two different approaches were used to stimulate of the precipitation of various polymers on colloidal melamine formaldehyde particles. In the first approach, the suspension of MF particles was mixed with Me^{3+} ions, and then the polyanion PSS was added, leading to the formation of precipitates of Me^{3+}/PSS. The suspension (1 mL) was continuously stirred during the dropping (10 μL) of PSS-Rd solution (1 mg/mL) until the final PSS-Rd concentration reached a given value (Table 1). The PSS-Rd/Tb^{3+} complex is slowly formed. After 10−15 min the particles were centrifuged, and the amount of PSS-Rd not bound to the particles was determined by supernatant fluorescence. Table 1 presents the data on the final concentrations of MF particles and Tb^{3+} ions and concentration of PSS after addition to the suspension. Remarkably, the amount of PSS-Rd absorbed to MF particles is about 80−85% for all investigated PSS-Rd concentrations. It should be noted that we always have an excess of charges for Tb^{3+} in order to complex all PSS-Rd molecules with metal ions. The MF particles were observed by confocal microscopy. A typical image of MF particles covered with the PSS-Rd/Tb^{3+} complex is shown in Figure 2. The fluorescence coverage of MF particles is rather smooth. There were almost no fluorescent species found outside of the particles. Such a picture is characteristic for all three experiments with different PSS-Rd amounts added to the MF particle suspensions containing Tb^{3+} ions. Fluorescent PSS-Rd is homogeneously distributed on the surface of MF particles. Since the total amount of added PSS-Rd was varied by a factor of 10, and the percentage of PSS-Rd found in the supernatant does not change significantly, one could conclude that the amount of PSS-Rd adsorbed on colloidal particles linearly increases with increasing amount of PSS-Rd added to the suspension, at least for the MF particle concentration range examined here.

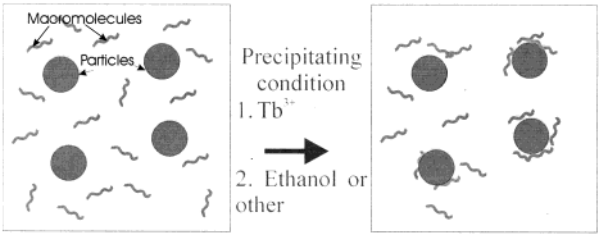

Figure 2. Confocal fluorescent microscopy image of MF particles covered with PSS-Rd/Tb complex.

Table 1

expt no.	MF particle concn (cm^{-3})	$TbCl_3$ (M)	PSS (mg/mL)	supernatant fluores (%)	est amount of PSS monolayers
1	10^8	10^{-3}	0.04	10	20
2	10^8	10^{-3}	0.2	15	80
3	10^8	3×10^{-3}	0.6	13	250

A second approach for the controlled precipitation of polymers onto the surface of colloidal particles consists of decreasing the polymer solubility by the dropwise addition of a miscible solvent. DNA and dextran have been chosen due to their low solubility in ethanol, the MF particle suspension (1.5 mL) having a particle concentration 5×10^8 cm^{-3}, contained DNA molecules in a concentration 3×10^{14} cm^{-3}. Ethanol was added dropwise to the suspension until the total volume reached 4.5 mL. During the addition of ethanol, the suspension was shaken. The ethanol/water mixture (ethanol 60%) causes the slow precipitation of DNA molecules. After 15 min the suspension was centrifuged. The supernatant fluorescence revealed that about 20% of DNA labeled with acridine orange was not bound to the particles. Analogously, the experiment was carried out using the precipitation of rhodamine-labeled dextran. The suspensions consisted of 1 mL of MF particles at a concentration of 5×10^8 cm^{-3} and dextran with a concentration of 3×10^{15} cm^{-3}. It was found that about 5% of the dextran remained in the supernatant after particle centrifugation. Typical confocal fluorescence microscopy images are presented in Figure 3. As found in the previous case of PSS-Rd, no fluorescence from molecular aggregates outside of the particles was found,

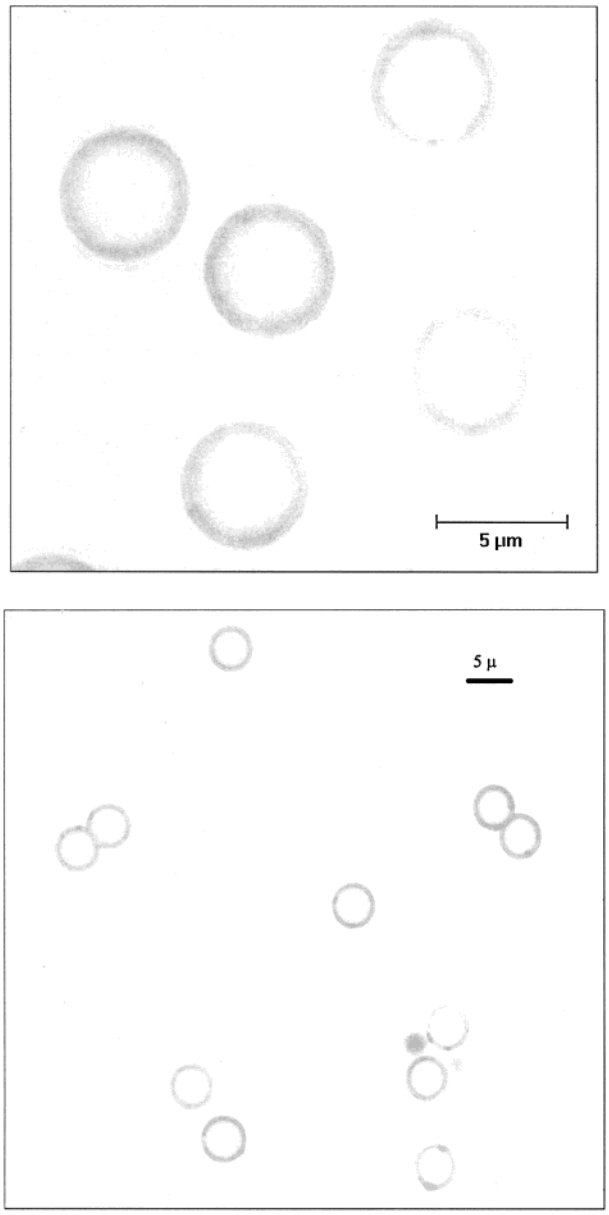

Figure 3. Confocal fluorescent microscopy image of MF-particles covered with dextran-Rd (a, top) and DNA labeled with AO (b, bottom) precipitated by dropping ethanol in aqueous solution. Some particles are out of focus in equatorial plane.

for either DNA or dextran. This means that most of DNA or dextran molecules are harvested on the surface of the particles. The particle surface is again rather homogeneous that is shown in the fluorescent confocal microscopy images (Figure 3b). The estimation of average thickness of polymer film on colloid for these cases of DNA gives value about 50 monomolecular layers of DNA, i.e., thickness of about 100 nm.[19]

We believe that, as in the case of precipitation of polyelectrolytes by complexing with metal ions, the amount of DNA or dextran molecules collected on one particle is the total amount of precipitated polymer molecules divided by the number of particles. Hence, the amount of adsorbed macromolecules can be tuned in a certain range. Thus, the concept of controlled precipitation, i.e., assembling of polymer on the surface of colloid particles, is realized either by insoluble complex formation with small ions or by solvent-induced precipitation. These methods for assembling films onto colloids could be useful for a wide class of molecules.

Discussion

The results described above demonstrate that the slow heterocoagulation process of polymers in suspensions of colloidal particles can be qualitatively described in a simple model. This enables choice of suitable parameters for controlling the coating of particles with polymeric films. The proper choice of concentrations of polymer macromolecules and particles along with speed of coagulation provides coverage of a defined amount of precipitated polymer on each particle. Actually, the particles statistically harvest the coagulated polymers and their complexes with multivalent ions on the colloidal surface. As revealed by confocal microscopy images, the resulting coating on the particles is homogeneous for all systems investigated. The thickness of the polymeric film on colloids can be tuned in the range of a few monomolecular layers.

Naturally, the described method should be compared with the coating of colloidal particles by means of layer-by-layer adsorption of oppositely charged polyelelctrolytes, which also provides defined shell composition and thickness on colloidal particles. The controlled precipitation (CP) method can employ many compounds, of which many cannot be used by means of the LbL assembly. Here we illustrated only the possibilities of building shells composed of only one component (DNA), utilizing noncharged polymers (dextran), and complexes between ions and polyelectrolytes (Tb/PSS). Certainly, the conditions to induce precipitation, such as solvent change or adding of complex ions, might be found for a wide class of polymers. The controlling of precipitation on colloids implies the search for an adequate window in the possible range of polymer concentration, particles, and coagulation speed for each polymer one wishes to make the shells. The data presented in Table 1 show that theoretical estimations of the concentration parameters in the system on the basis of a simple coagulation model give good agreement with experimentally observed optimal values. One advantage of the CP method to cover colloidal particles that it is significantly less time-consuming in order to build the film consisting of tens of monomolecular layers than the LbL technique. By CP methods the assembly is actually carried out a single step.

Nevertheless, we do not oppose the LbL method. Both methods complement each other. Indeed, the assembling of two oppositely charged polyelectrolytes could not be done by controlled precipitation because of the fast coagulation of polyelectrolyte complexes. In this case the film can be assembled only by the LbL technique. Also, the ordering of monomolecular layer in the normal to the colloidal surface seems to be better achived by LbL adsorption than the CP method. While the LbL technique usually results in the formation of stable films, the CP assembled films may be easily decomposed by increasing the polymer solubility or by complex-ion extraction. The real benefit may be realized by a combination of both of these methods, introducing many opportunities to assemble multicomposite films. A wide variety of materials, despite their charge or molecular weight, can be incorporated in the film. The stepwise compilation of LbL- and CP-assembled building blocks promotes the solution of diverse tasks related to micro- and nanostructuring materials. For instance, inorganic

reactions between previously spatially located reagents in the shell or encapsulation of CP-assembled polymers, like DNA or dextran, within LbL-assembled polyelectrolyte capsules could be exploited.[3,20,21] Research toward such modifications of the shells is currently underway in our laboratory.

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