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Adsorption and Polymer Film Formation on Metal Nanoclusters

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ABSTRACT: We examine experimentally and theoretically the effect of polymer adsorption layers on the stability of metal nanoclusters. We find that, somewhat contrary to expectation in this low volume fraction limit, the thickness of the adsorbed layer does not increase linearly with the number of repeating units in the chain (i.e., molecular weight), N. Rather, in the range we examine experimentally it decreases with molecular weight, in agreement with our model predictions. The number of contacts between the polymer chain and the cluster surface, i.e., polymer anchoring points, increases significantly with N, as does the polymer volume fraction in the adsorbed layer. As a result, although a large fraction of active surface sites remains available, particles stabilized by long chains resist flocculation, while particles stabilized by short chains do not.

1. Introduction

Metallic fragments created by the energy-induced decomposition of metal complexes exhibit a high degree of reactivity, which constitutes the main driving force for the nucleation and growth of metallic particles with sizes ranging from several nanometers to several microns.[1−5] The ability to control metal particle size, size distribution, morphology, geometry, and dispersion as part of the synthetic process directly translates to an ability to design the material properties so that the final product is specifically tailored to its designated function,[6−8] such as optical devices.[9−12] The control of particle size is commonly achieved by the use of capping agents such as polymers, which are present in the solution during the metal cluster formation reactions. These polymer molecules typically interact with the growing metal particles, ultimately inhibiting the aggregation process.[13−17] In most cases, the nature of the polymer-induced cluster stabilization process is not well understood,[18] and knowledge of the interactions between the metal and the polymer is limited. However, it is generally accepted that the polymer chains adsorb onto the metal particles, thereby saturating the reactive metal surface and creating a steric barrier to cluster growth.

Polymer adsorption onto surfaces is dominated by a balance between the chain conformational entropy (which favors thick layers) and the polymer−substrate interactions (which favor adsorption in a flat configuration with many contact points). As a result (if the polymer concentration in solution is relatively dilute), short chains that have a small number of adsorption sites tend to form dilute layers whose thickness is of the order of the chain radius of gyration, while longer chains adsorb more strongly, forming relatively thin layers (see, for example, refs 19−22). Similar trends apply to polymer adsorption on small particles whose dimensions are equivalent to the chain radius of gyration (see, for example, refs 23−25).

Polymer adsorption onto metal nanoclusters differs from adsorption onto other substrates because the cluster interface is “unstable”, namely, incompatible with the surrounding medium. Polymer adsorption arrests cluster−cluster aggregation by saturating the surface reactive sites as well as by creating a steric layer. Indeed, previous studies on the effect of adsorbing polymer on metal clusters have shown an inverse correlation between the nanocluster size and the polymer concentration in the surrounding media (see, for example, refs 26 and 27), accompanied by a considerable narrowing in the particle size distribution. This may be attributed to the fact that the adsorbed layer density increases with increasing solution concentration.[28] However, to date, little is known regarding the structure and properties of the adsorbed polymer layer.

In this paper we investigate the effect of polymer molecular weight on the formation of adsorption layers on cobalt nanoclusters, synthesized via the thermal decomposition of cobalt−carbonyl complexes.[29−31] Specifically, we examine the layer thickness, number of contact points, and density, as those can provide insight into the bonding mechanisms between the cobalt clusters and the capping polymer and shed light on the relationship between polymer adsorption and the cluster size and size distribution.

High-resolution transmission electron microscopy (TEM) is the technique of choice for nanoparticle size analysis, but this technique provides only information regarding the size of the metal cores[32,33] and not of the polymer layer adsorbed on the surface of the particle. The thickness of the polymer layer adsorbed on the metal nanoclusters may be determined directly or indirectly by coupling the TEM experiments with additional analytical methods. Previous studies by Reetz et al.[33] have combined the use of TEM imaging with scanning tunneling microscopy techniques (STM) to elucidate the thickness of the layer formed by the adsorption of low molecular weight stabilizing molecules on metallic clusters. STM images allowed the determination of the average diameter of the whole particle (metallic core + capping shell), while TEM images provided the average diameter of the metallic core. By subtracting the latter from the first, it was possible to

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evaluate the thickness of the capping layer. In systems in which the particles are stabilized by polymer molecules, this type of analysis is not as effective due to the signal attenuation caused by the thickness of the polymer layer. Hence, this paper describes a novel method for the measurement and analysis of the thickness of the stabilizing polymer layer using a combination of TEM and thermogravimetric analysis (TGA). Coupled to the experimental procedure, we also developed a theoretical approach to aid in the semiquantitative interpretation of the experimental results.

2. Experimental Procedure

In these experiments, 45 mL of a 2% (w/v) solution of polystyrene (Alfa Aesar) of either $\bar{M}_n = 13\,000$ g/mol, $\bar{M}_n = 25\,000$ g/mol, or $\bar{M}_n = 120\,000$ g/mol (all three with PDI = 1.06) in toluene (Fischer Scientific) was added to a three-neck, jacketed reaction flask, after an aliquot was removed for FTIR analysis. 45 mL of a 1×10^{-2} M solution of $Co_2(CO)_8$ in toluene was prepared and was added to the reaction flask, after removing an aliquot for FTIR analysis as well. The combined solution had final PS and $Co_2(CO)_8$ concentrations of 1 wt % and 5×10^{-3} M, respectively. The reaction flask was pressurized with dry N_2, and an aliquot was again removed for FTIR analysis. The decomposition was carried out at 90 °C with constant stirring for approximately 8 h. The reaction was deemed complete when all infrared carbonyl absorption bands of $Co_2(CO)_8$ have disappeared, in both the terminal carbonyl region at 2000−2100 cm^{-1} and the bridging carbonyl region at 1858 and 1867 cm^{-1}. All FTIR measurements were performed on a Nicolet Magna 870 spectrophotometer, with a resolution of 1 cm^{-1} and 3000 scans.

TGA samples were prepared by centrifuging an aliquot of a previously reacted solution containing cobalt nanoclusters capped with polystyrene of $\bar{M}_n = 13\,000$ g/mol, $\bar{M}_n = 25\,000$ g/mol, or $\bar{M}_n = 120\,000$ g/mol using an Eppendorf Concentrator 5301 centrifuge at 17 000 rpm. This separated excess solvent from the polymer-coated nanoclusters. The supernatant toluene solution was removed, and the remaining particles were washed with both toluene and hexane to remove any excess unbound polymer or partially reacted cobalt carbonyl fragments. The suspension was centrifuged again, and the process was repeated three times. Upon completion, the particles were placed onto a TGA pan, and the data were collected using a TA Instruments TGA model 2050.

TEM samples were obtained by placing a small droplet of the reacted solution containing the polymer-coated cobalt particles onto a Formvar-coated copper TEM grid from Ted Pella. The grid rested on a thin piece of tissue paper so that the liquid will drain into the paper leaving a very thin film on the grid itself. The TEM analysis was performed on a JEOL 4000EX high-resolution electron microscope with an operating voltage of 200 keV.

Dynamic light scattering (DLS) particle size determination was performed on 10 mL samples removed from the reaction solutions. The samples were placed in standard scintillation vials (∼27.4 mm diameter) as the sample cells. Measurements were conducted on a Brookhaven DLS system equipped with a 35 mW, 632.8 nm wavelength HeNe laser and a stepping motor, allowing data collection at angle increments of 0.01°. The results were analyzed by using CONTIN, NNLS (nonnegative least squares), and Williams−Watts size distribution programs.

3. Calculations of Polymer Layer Characteristics

3.1. Experimental Data Analysis. The thickness of the polymer capping layer can be calculated using a combination of transmission electron microscopy (TEM) and thermal gravimetric analysis (TGA) experimental methods.[33,34] The first step in the determination of polymer layer thickness using the TGA experimental results is to calculate the average number of cobalt clusters present in the sample, N_C. This can be done as follows:

$$N_C = \frac{\text{total number of Co atoms}}{\text{number of Co atoms per cluster}} = \frac{\left(\dfrac{m_{\text{sample}} w_{\text{Co}} N_A}{\text{MW}_{\text{Co}}}\right)}{\epsilon\left(\dfrac{D_{\text{cluster}}}{d_{\text{Co}}}\right)^3} \qquad (1)$$

where ϵ is the volume fraction of the cobalt atoms in the cluster, m_{sample} is the mass of the sample placed in the TGA pan, and w_{Co} is the mass fraction of the cobalt moiety after the decomposition of the polymer. The volume of a cobalt cluster is given as $V_C = (4\pi/3)(D/2)^3$, and the volume of the polystyrene-coated cobalt cluster is given by $V_{\text{Tot}} = (4\pi/3)[(D + 2L_{\text{eff}})/2]^3$, where D is the average cluster diameter as determined from TEM images and L_{eff} is the effective average polymer layer thickness adsorbed on the cobalt cluster and determined from TGA measurements. The volume of the polystyrene layer alone on each cluster is given by $V_{PS} = m_{\text{sample}} w_{PS}/N_C\rho$, where w_{PS} is the mass fraction of the polymer moiety in the sample as determined from TGA measurements. Therefore, since $V_{\text{Tot}} = V_C + V_{PS}$, it is possible to calculate L_{eff}, the effective thickness of the polymer layer, as follows:

$$L_{\text{eff}} = \frac{1}{2}\left[\frac{6 w_{PS} \text{MW}_{\text{Co}} \epsilon}{\pi \rho w_{\text{Co}} N_A}\left(\frac{D}{d_{\text{Co}}}\right)^3 + D^3\right]^{1/3} - \frac{D}{2} \qquad (2)$$

where ρ is the density of a thin film of polystyrene, evaluated at 1.045 g/cm^3.[35]

From the value of L_{eff}, shown schematically in Figure 1a, it is also possible to calculate the average number of repeating units, n_{eff}, that would correspond to that particular average chain length, according to the expression:

$$n_{\text{eff}} = \frac{1 + \cos\theta}{2(1 - \cos\theta)}\left(\frac{L_{\text{eff}}}{\sigma l}\right)^2 \qquad (3)$$

where θ for polystyrene is 109.5°, σ is the steric hindrance factor, which is 2.3 for polystyrene at room temperature,[36] and l is the C−C bond length of 1.54 Å. However, the actual number of free repeating units that exist between two anchoring points, n_{loop}, and that are part of the chain that extends out and forms the thickness of the polymer layer is given by

$$n_{\text{loop}} = 2n_{\text{eff}} - 1 \qquad (4)$$

where it is assumed that the polymer chains form a loop and that the minimum of one repeating unit acts as the pivot point, as shown in Figure 1b.

3.2. Theoretical Model. The adsorption of polymers onto flat substrates has been widely examined (see, for example, refs as above). More recently, a few studies focused on polymer adsorption onto small particles whose dimensions are similar to, or smaller than, that of the chain radius of gyration.[23−25] However, because of the complexity of the problem, these studies do not provide simple scaling rules that can be used to understand the overall system behavior. In a previous study,[28] we used a simple mean-field model to examine polymer

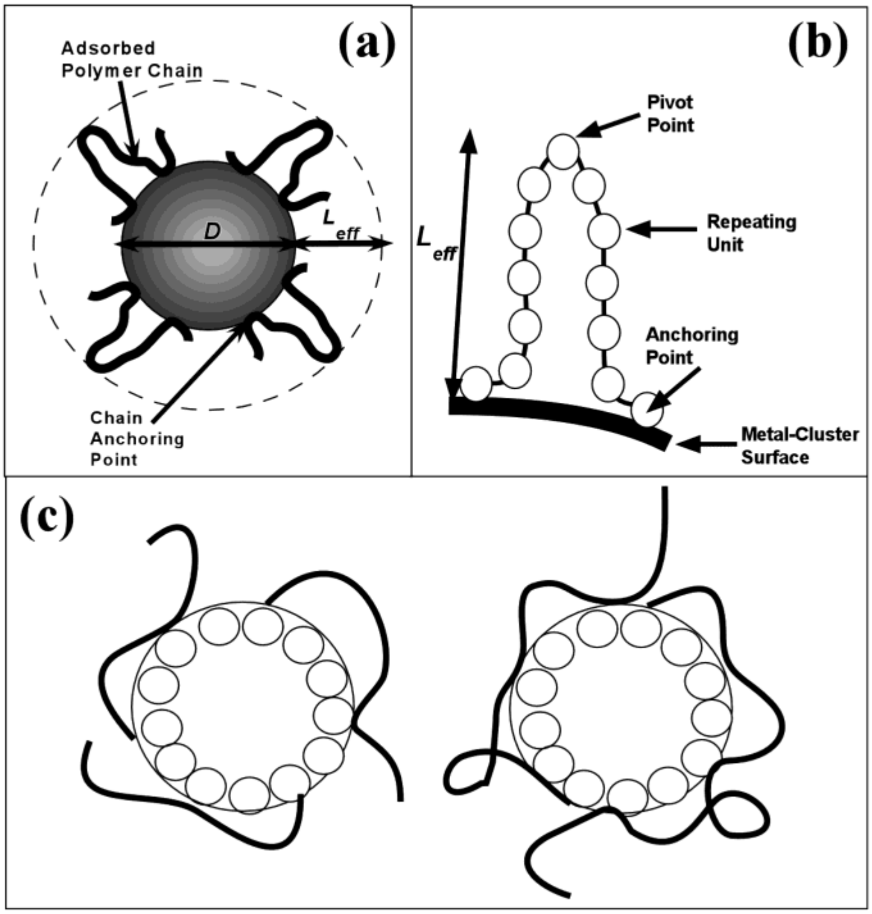

Figure 1. (a) Schematic description of the effective average polymer layer adsorbed on the cobalt cluster, L_{eff}. (b) Schematic description of the actual number of free repeating units that exist in a polymer loop formed between two anchoring points, n_{loop}, and that are part of the chain that extends out and forms the thickness of the polymer layer. (c) Schematic description of the number of monomers bound to the surface that are determined mainly by the chain geometry.

adsorption from semidilute solution on aggregating colloidal particles; we found that the adsorbing polymer reduces the effective surface tension between the particles and the solvent, thereby reducing the driving force for flocculation. In this section we derive a similar, *simple* mean-field model to examine the effect of chain molecular weight on the properties of a polymer layer adsorbed on a spherical particle, modifying it to account for dilute polymer solutions and neglecting the effect of the particle−suspension surface tension. Our goal is to derive scaling laws relating the chain length to the adsorbed layer characteristics.

The system considered consists of a fixed number of metal clusters, N_c, of a fixed diameter D immersed in a solvent. The solution also contains a *dilute* solution of polymer chains of molecular weight $\bar{M}_n$ and number of persistence units N, at a fixed monomer volume fraction Φ. For simplicity, we assume that the solvent is a Θ solvent for the polymer so that χ, the Flory parameter,[36] is $^1/_2$ and the chain radius of gyration R_g scales as $N^{1/2}$.

In solution, the free energy of the polymer chains is dominated by their translational entropy, which scales as the number of chains in solution (proportional to Φ/N) times ln Φ. Thus, for a fixed polymer volume fraction increasing the chain molecular weight decreases the translational entropy. On the other hand, decreasing Φ may increase *or* decrease the entropy, since the function $\Phi \ln \Phi$ varies nonmonotonically.

Polymer adsorption onto the metal clusters is set by a balance between the adsorption energy per monomer at contact with the metal cluster, the polymer−solvent mixing energy, and the loss of configurational entropy due to chain confinement on the surface. Thus, the free energy of the polymer adsorbed onto a cluster is given by (in the limit where the polymer volume fraction in the adsorbed layer is high)

$$F_c = nN\phi^2 + n\frac{R_g^{\,2}}{L^2} - \left(\frac{D}{a}\right)^2 \phi\delta \tag{5}$$

where n is the number of adsorbed chains, ϕ the volume fraction of polymer in the layer, L the adsorbed layer thickness, a the monomer surface projection, and δ the adsorption energy per unit. All energies are given in units of kT, where k is the Boltzmann coefficient and T the temperature, and we neglect numerical constants of order unity (e.g., $4\pi/3$). It should be noted that the volume fraction in the layer, ϕ, is coupled to the layer thickness and the number of adsorbed chains through the following relationship $\phi = 3nNa^3/(4\pi(R + L)^3 - R^3)$, where R is the particle radius and a is the polymer segment size. Thus, eq 5 can be written as a function of n and L only, and minimization of F_c with respect to L will yield its equilibrium value.

Since the system is a closed one, polymer adsorption reduces the number of chains in solution and thus the volume fraction. As a result, the sum of all adsorbed chains (equal to the number of clusters times n) and

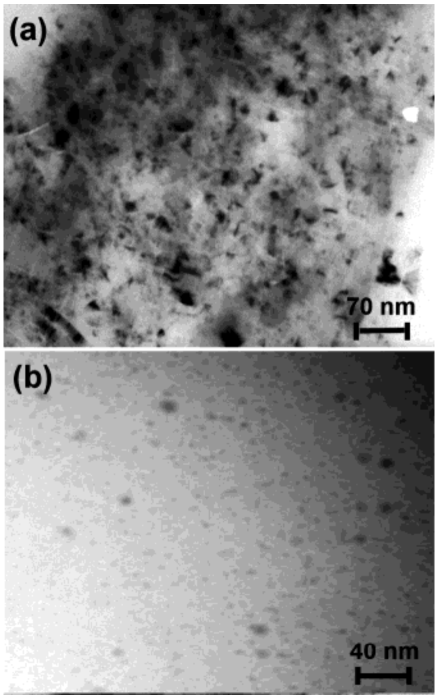

Figure 2. (a) TEM micrograph of cobalt nanoclusters formed in the presence of polystyrene with $\bar{M}_n = 25\,000$ g/mol as the stabilizing agent. Particle size is calculated to an average of 135 ± 17 Å. (b) TEM micrograph of cobalt nanoclusters formed in the presence of polystyrene with $\bar{M}_n = 120\,000$ g/mol as the stabilizing agent. Particle size is calculated to an average of 167 ± 21 Å.

the free chains in solution (which scales as the solution volume fraction divided by N) must be a constant.

4. Results and Discussion

In this work we have studied the effect of polymer molecular weight on the formation of cobalt nanoclusters via the thermal decomposition of cobalt–carbonyl complexes.[29–31] We focus on the characteristics of the adsorbed polymer layer, since it provides insights regarding the interactions between the metal particle and the polymer which may then be used to control the metal cluster size and properties.

On the basis of previous analysis of polymer adsorption in the dilute volume fraction limit,[19–21,23–25,28,37,38] we expect that longer polymer chains will adsorb more readily and strongly than shorter chains and that the layer thickness will increase with the polymer chain molecular weight (see, for example, refs 39–42 and 22). The range of repulsive interactions, which scales as the layer thickness, is therefore expected to increase with N as well. Translated to the polymer–metal nanoparticle system, these results indicate that longer polymer chains will form thicker layers and stabilize the particles against flocculation more effectively than shorter chains.

In Figure 2 we compare TEM micrographs of cobalt clusters capped by a relatively short polystyrene chain ($\bar{M}_n = 25\,000$ g/mol) and a relatively long one ($\bar{M}_n = 120\,000$ g/mol). The average particle size calculated for the first sample is 135 Å (measured directly from the TEM image). Particles obtained with polystyrene with a $\bar{M}_n = 13\,000$ g/mol show similar morphology but a higher average size of 202 Å. Clearly, the particles in the case of the lower molecular weight polymer are neither spherical nor uniform in size, and several flocculates may be observed. In contrast, the cobalt particles formed in the presence of high molecular weight chains exhibit spherical symmetry and uniformity of size, with an average of 167 Å. We conclude that, as preliminary data suggest, the average cluster size is reduced and flocculation inhibited as a function of chain length, but the dependence of cluster size on polymer molecular weight is highly nonlinear.[43] Moreover, as shown below, we can relate the stabilization mechanism directly to the formation of dense polymer adsorption layers.

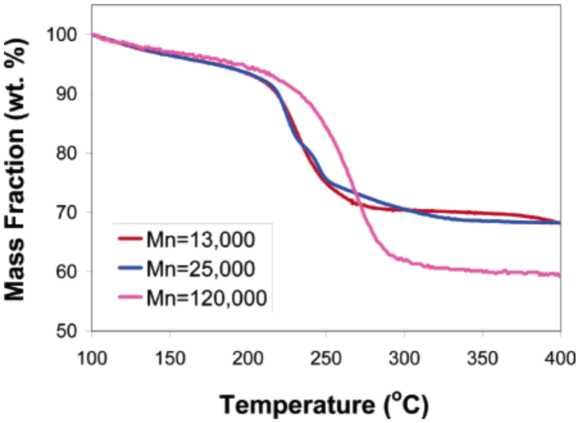

Figure 3. Experimental TGA results of cobalt nanoclusters capped by polystyrene with $\bar{M}_n = 13\,000$ g/mol, $\bar{M}_n = 25\,000$ g/mol, and $\bar{M}_n = 120\,000$ g/mol.

Figure 3 shows the TGA results of mass loss as a function of temperature for three samples with masses of 2.171, 2.789, and 2.687 mg for three different polymer molecular weights. These are used (as described in section 3) to calculate the parameters of the adsorbed polystyrene layers, as summarized in Table 1. It is important to note that the overall monomer volume fraction of the polystyrene, Φ, was kept constant in all three cases, and only the molecular weight of the polymer was varied. Thus, polymer concentration does not play a role in determining the characteristics of the adsorbed layer.[28] Also, the particle size is of the same order of magnitude in all three cases.

We see that, contrary to expectation, the polymer layer thickness tends to decrease with increasing chain length. Our model calculation predicts that the layer thickness (for fixed polymer volume fraction in solution and a given particle size) scales as[45]

$$L_{\mathrm{eff}} \sim \frac{a\delta N}{\ln N}\left(1 - \sqrt{1 - \frac{\ln N}{\delta^2 N}}\right) \qquad (6)$$

Indeed, the layer thickness roughly scales as N, in agreement with previous analysis.[21,22,39–42] However, that applies *only in the limit of short chains*. Above a critical molecular weight the layer thickness decreases with N, with a relatively mild slope. Thus, for chains shorter than the critical N value the layer thickness increases rapidly with N, while above this value it decreases slowly, in agreement with the experimental results obtained in Table 1.

The layer thickness also decreases with the strength of the adsorption energy δ, in agreement with our expectation that the stronger the adsorption energy, the stronger the bonding between any chain and the surface. The strength of the adsorption energy is not only a function of the type of chemical interactions possible between the metal surface and the polymer segments

Table 1. Polymer Chain Calculations[a]

mol weight of polystyrene (g/mol)	polystyrene concn (wt %)	average particle size (±10 Å)[b]	L_{eff}	n_{eff}	n_{loop}	no. of anchoring points/chain (±0.8)
13 000	1.0	202	50.8	51.4	101.8	1.3
25 000	1.0	135	38.4	29.4	57.8	4.2
120 000	1.0	167	37.9	28.7	56.5	20.4

[a] Calculations of polystyrene chain dimensions and number of anchoring points onto cobalt clusters, for three average molecular weights of polystyrene [b] As obtained from dynamic light scattering (DLS) measurements.

Table 2. Surface Cobalt−Polymer Interaction Calculations[a]

mol wt of polystyrene (g/mol)	av particle size (±10 Å)	no. of chains/no. of surf. Co atoms	no. of anchoring points/no. of surf. Co atoms	% unbound surf. Co atoms
13 000	202	2.64×10^{-2}	0.034	~97
25 000	135	1.02×10^{-2}	0.048	~95
120 000	167	5.58×10^{-3}	0.094	~90

[a] Calculations of extent of adhesion of polystyrene chains onto cobalt clusters, and the relative number of unreacted surface metal sites.

(as indicated by χ) but also a function of the conformational changes required to accommodate the polymer on the surface of the cluster. Hence, shorter chains will be “stiffer” than longer chains and will form less loops on the surface, i.e., will have a lower anchoring frequency, as shown schematically in Figure 1c.

The number of anchor points, per chain, is given by

$$n_{\mathrm{anchors}} \sim \frac{\ln N}{\delta\left(1 - \sqrt{1 - \dfrac{\ln N}{\delta^2 N}}\right)} \qquad (7)$$

which increases with the chain length, in agreement with the measurements shown in Table 1. Indeed, for a fixed adsorption energy ($\delta \approx 3.3$), eq 7 yields for the ratio of N, 120:25:13, a ratio of contacts of 20:4:1.9, very similar to the experimental measurements.

Another important and related factor is the distance between available reactive sites on the surface of the cluster. If we assume that each surface atom can act as a reactive site for polymer binding, then the number of “free” surface atoms will give an indication as to the effectiveness of the capping process and the potential stability of the resulting metal particles. The number of surface cobalt atoms associated with a polystyrene chain (in the three samples examined) can be calculated from the following expression:

$$\frac{\text{no. of surface Co}}{\text{no. of chains}} = \frac{w_{\mathrm{Co}}\bar{M}_{\mathrm{n}}[D^3 - (D - 2d)^3]}{w_{\mathrm{PS}}\mathrm{MW}_{\mathrm{Co}}D^3} \qquad (8)$$

where the number of polystyrene chains is given by $(m_{\mathrm{sample}}w_{\mathrm{PS}}/\bar{M}_{\mathrm{n}})N_{\mathrm{A}}$, and the number of surface cobalt atoms is given by $\epsilon N_{\mathrm{C}}[D^3 - (D - 2d)^3)]/d^3$. Table 2 shows the results for the three molecular weights of polystyrene used in this study. The higher molecular weight polystyrene is a somewhat more efficient capping agent than its lower molecular weight counterparts. However, in all three cases a relatively large fraction (over 90%) of reactive sites remain available. It is important to note that the interaction expected between the surface cobalt atoms and polystyrene chains involves the weak coordination of the π-orbitals of the pendant arene groups of polystyrene to the d-orbitals of the growing cobalt nanoclusters.[44] This weak bonding affinity is clearly evidenced by the overall poor capping efficiency of polystyrene.

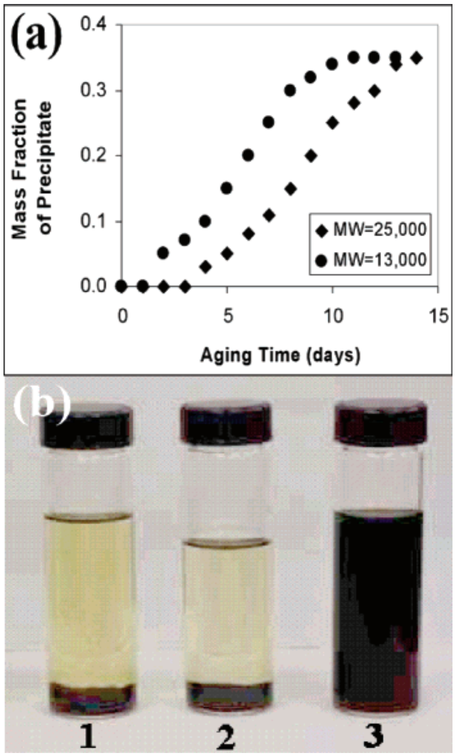

Figure 4. (a) Plots of the aggregation and settling of the cobalt nanoparticles after the adsorption of polystyrene as a function of time for polystyrene molecular weight of 13 000 and 25 000 g/mol. (b) Photographs of the suspensions of cobalt nanoparticles formed by the adsorption of the three polystyrene systems, with molecular weights of 13 000 (1), 25 000 (2), and 120 000 g/mol (3).

How does this affect the stability of the metal nanoparticles? As shown in Figure 4a,b, cobalt nanoparticles capped by polystyrene with molecular weight of 13 000 g/mol flocculate and settle relatively quickly (Figure 4a). Particles capped by adsorption of polystyrene with molecular weight of 25 000 g/mol (Figure 4a) settle somewhat more slowly, while, during the same time frame, no further aggregation and settling in observed for the 120 000 g/mol chains (Figure 4b). This seems counterintuitive, since the layer thickness (and thus the range of steric interactions stabilizing against flocculation) decreases with chain length (Table 1). Moreover, this trend cannot be explained through saturation of the surface active sites, since in all cases a large fraction of surface atoms remains available. Thus, the increase in stability must be attributed to an increase in the *strength*, rather than range, of the steric interactions between the polymer-coated particles.

The repulsive interactions between adsorbed polymer layers scale with the polymer density in the layer.[39−42] Calculating the volume fraction of polymer in the adsorbed layer, we find

$$\phi \sim \sqrt{\frac{\ln N}{N\left(1-\sqrt{1-\frac{\ln N}{\delta^2 N}}\right)}} \qquad (9)$$

Therefore, ϕ and the repulsive interactions increase with the chain length N. Flocculation should therefore be more easily suppressed in suspensions stabilized by high molecular weight polymers than short ones, despite the fact that the layer thickness is lower and that a large fraction (~90%) of reactive sites remain available.

In conclusion, we examine here, experimentally and theoretically, the effect of polymer adsorption layers on the stability of metal nanoclusters. We find that (somewhat contrary to expectation in this low volume fraction limit[21]) the thickness of the adsorbed layer does not increase linearly with N; rather, in the range we examine experimentally, it decreases with molecular weight, in agreement with our model predictions. The number of contacts per chain does increase significantly with N, as does the polymer volume fraction in the adsorbed layer. As a result, although a large fraction of active surface sites remain available, particles stabilized by long chains resist flocculation, while particles stabilized by short chains do not.

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References and Notes

(1) Mason, M. G. *Phys. Rev. B* **1983**, *27*, 748.
(2) Lee, S.-T.; Apai, G.; Mason, M. G.; Benbow, R.; Hurych, Z. *Phys. Rev. B* **1981**, *23*, 505.
(3) Apai, G.; Lee, S.-T.; Mason, M. G. *Solid State Commun.* **1981**, *37*, 213.
(4) Tomanek, D.; Schluter, M. *Phys. Rev. Lett.* **1986**, *56*, 1055.
(5) Chelikowsky, J. R.; Redwing, R. *Solid State Commun.* **1987**, *64*, 843.
(6) Alivisatos, A. P.; Harris, A. L.; Levinos, N. J.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1988**, *89*, 4001.
(7) Kernizan, C. F.; Klabunde, K. J.; Sorensen, C. M.; Hadjipanayis, G. C. *J. Appl. Phys.* **1990**, *67*, 5897.
(8) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555.
(9) Lin, S.-Y.; Chow, E.; Hietala, V.; Villeneuve, P. R.; Joannopoulos, J. D. *Science* **1998**, *282*, 274−276.
(10) Cregan, R. F.; Mangan, B. J.; Knight, J. C.; Birks, T. A.; Russell, P. St.; Roberts, P. J.; Allan, D. C. *Science* **1999**, *285*, 1537.
(11) Zhou, J.; Zhou, Y.; Ng, S. L.; Zhang, H. X.; Que, W. X.; Lam, Y. L.; Chan, Y. C.; Kam, C. H. *Appl. Phys. Lett.* **2000**, *76*, 3337.
(12) Weber, M. F.; Stover, C. A.; Gilbert, L. R.; Nevitt, T. J.; Ouderkirk, A. J. *Science* **2000**, *287*, 2451.
(13) Caruso, F.; Möhwald, H. *Langmuir* **1999**, *15*, 8276.
(14) Sinha, A.; Das, S. K.; Kumar, B. R.; Chakroborty, S.; Rao, V.; Ramachandrarao, P. *J. Mater. Synth. Process.* **2000**, *8*, 109.
(15) Sidorov, S. N.; Bronstein, L. M.; Valetsky, P. M.; Hartmann, J.; Colfen, H.; Schnablegger, H.; Antonietti, M. *J. Colloid Interface Sci.* **1999**, *212*, 197.
(16) Tannenbaum, R.; Flenniken, C. L.; Goldberg, E. P. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 2421.
(17) Bradley, J. S.; Milnar, J. M.; Hill, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 4016.
(18) Wiesner, J.; Wokaun, A.; Hoffmann, H. *Prog. Colloid Polym. Sci.* **1988**, *76*, 271.
(19) Diamant, H.; Andelman, D. *Macromolecules* **2000**, *33*, 8050.
(20) Netz, R. R.; Andelman, D. Submitted to *Phys. Rep.*, in press.
(21) Aubouy, M. *Phys. Rev. E* **1997**, *56*, 3370.
(22) Aubouy, M.; Guiselin, O.; Raphael, E. *Macromolecules* **1996**, *29*, 7261.
(23) Aubouy, M.; Dimeglio, J. M.; Raphael, E. *Europhys. Lett.* **1993**, *24*, 87.
(24) Nowicki, W. *Macromolecules* **2002**, *35*, 1424.
(25) Zherenkova, L. V.; Mologin, D. A.; Khalatur, P. G.; Khokhlov, A. R. *Colloid Polym. Sci.* **1998**, *276*, 753.
(26) Rotstein, H.; Novick-Cohen, A.; Tannenbaum, R. *J. Stat. Phys.* **1998**, *90*, 119.
(27) Rotstein, H.; Tannenbaum, R. *J. Phys. Chem. B* **2002**, *106*, 146.
(28) Dan, N. *Langmuir* **2000**, *16*, 4045.
(29) Tannenbaum, R. *Inorg. Chim. Acta* **1994**, *227*, 233.
(30) Tannenbaum, R. *Langmuir* **1997**, *13*, 5056 and pertinent references therein.
(31) Tadd, E.; Bradley, J.; Tannenbaum, R. *Langmuir* **2002**, *18*, 2378.
(32) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.
(33) Reetz, M. T.; Helbig, W.; Quaiser, S. A.; Stimming, U.; Breuer, N.; Vogel, R. *Science* **1995**, *267*, 367.
(34) Hariharan, R.; Russell, W. B. *Langmuir* **1998**, *14*, 7104.
(35) Wallace, W. E.; Wu, W. L.; Beck Tan, N. C.; Satija, S. *Proc. Am. Phys. Soc.* **1998**, APS March Meeting, Session A13; Thin Films, Abs A13−11.
(36) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(37) Linse, P.; Piculell, L.; Hansson, P. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998.
(38) Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Stanley Thornes Pub. Ltd.: London, UK, 1991.
(39) deGennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(40) de Gennes, P. G. *J. Phys. (Paris)* **1976**, *37*, 1445.
(41) de Gennes, P. G. *Macromolecules* **1982**, *15*, 492.
(42) de Gennes, P. G. *Macromolecules* **1981**, *14*, 1637.
(43) Tikku, S.; Zubris, M.; Tannenbaum, R.; Dan, N. Unpublished results, 2002.
(44) Rotstein, H.; Tannenbaum, R. Functionalization and Surface Treatment of Nanoparticles. In *Advances in Nanoscale Materials and Nanotechnology; Book Series;* Baraton, M.-I., Ed.; American Scientific Publishers: Stevenson Ranch, CA, 2003; pp 103−126.
(45) The procedure for obtaining this result is detailed in ref 28: First, the free energy of the layer (eq 5) is minimized with respect to the layer thickness, L. This value is calculated for the optimal configuration as a function of the number of adsorbed chains, n. The optimal value of n is calculated by equating the chemical potential of the chains in solution and that of the chains on the surface.

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