

Preparation of Narrowly Size Distributed Metal-Containing Polymer Latexes by Miniemulsion and Other Emulsion Techniques: Applications for Nanolithography

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Received October 14, 2008. Revised Manuscript Received February 26, 2009

It is demonstrated that the miniemulsion polymerization technique allows the preparation of highly uniform and practically monodisperse latex particles containing a hydrophobic metal complex like platinum(II)acetylacetonate, indium(III)acetylacetonate, zinc(II)tetramethylheptadionate, zincphthalocyanine, and chromium(III)benzoylacetonate, respectively, with different loading capacities. For some platinum and iron complexes, the homogeneity of the latexes can be improved even further by adapted emulsion techniques. By choosing different amounts of surfactant, we can adjust the particle size between 100 and 260 nm. To obtain larger particles up to 370 nm for a given metal complex, we performed an additional feeding of monomer. In this way, the particles can be easily modified by changing the polymer or the copolymer composition. Using a pure polymer core and semicontinuously adding a complex/monomer mixture leads to an increased size of the particles, which can contain additional metal complexes. The methodology was also applied for the preparation of alloyed Fe/Pt particles. The concentration relations were analyzed by inductively coupled plasma spectroscopy (ICP) and, mostly, energy-dispersive X-ray spectroscopy (EDX). When particles are deposited onto a substrate, the high homogeneity of the particle size results in hexagonally well-ordered monolayers of the metal-containing polymer particles. Such an encapsulation of metal complexes into particles of defined size makes them suitable for a wide variety of applications, especially in the context of nanolithography.

Introduction

Latex particles consisting of polystyrene or polyacrylates prepared by emulsion techniques were developed many years ago and are used for several applications like coatings and adhesives.¹ During reaction, the diffusion of the monomer through the water phase is the key step limiting this type of heterophase polymerization for many applications where encapsulation of water-insoluble materials is required, because a homogeneous diffusion of the monomer to the component to be encapsulated can not be guaranteed. For the encapsulation of insoluble materials into polymer latex particles, the technique of miniemulsion polymerization can be advantageously applied.^{2,3} A direct miniemulsion consists of a dispersed phase containing the monomer(s) and a hydrophobic component as costabilizing agent (osmotic pressure agent) and the continuous phase. The continuous phase is composed of a polar phase, usually water, and a surfactant. The initiator for radical polymerization can be located either in the dispersed or in the continuous phase. Especially in the case of either very hydrophobic or of more

hydrophilic monomers the polymerization is preferably started in the dispersed phase because of the low concentration of the hydrophobic monomer in the aqueous phase and to avoid secondary nucleation with the hydrophilic monomer, respectively. The two phases are mixed and ultrasonicated to achieve a miniemulsion with homogeneously distributed small and stable droplets which can be polymerized in a subsequent step. In contrast to other emulsion polymerization techniques, critically stabilized droplets are formed before polymerization and do ideally not change in number through diffusion processes before and during the polymerization. This leads to particles with unchanged concentration of any ingredients compared to the monomer phase before homogenization. Therefore, the technique of miniemulsion polymerization is suitable for the preparation of hybrid particles, consisting of polymers and incorporated substances. Many different compounds have been encapsulated by this process,^{2,3} e.g., to protect the incorporated substances or to improve the particle characteristics.

The encapsulated material can be either molecularly distributed in the particles as it is the case for a fluorescent dye containing particles which have been prepared as marker particles for biomedical applications,⁴ or the material can be encapsulated as aggregate, crystal, etc., as is the case for

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(1) Hauser, E. A.; Perry, E. *J. Phys. Chem.* **1948**, 52, 1175–1186.

(2) Landfester, K. *Annu. Rev. Mater. Res.* **2006**, 36, 231–279.

(3) Landfester, K. *Macromol. Rapid Commun.* **2001**, 22, 896–936.

(4) Weiss, C. K.; Lorenz, M. R.; Landfester, K.; Mailänder, V. *Macromol. Biosci.* **2007**, 7, 883–896.

the encapsulation of pigments^{5,6} and, as recently shown, for thermally labile azo-components,⁷ photoinitiators,⁸ and highly fluorescent quantum dots.⁹ A variety of metal oxide containing polymer latex particles are known. Several results were published on the incorporation of metal oxides into polymer latexes to improve the latex properties. Silica particles were functionalized and incorporated into poly- ϵ -caprolactone¹⁰ or polystyrene,^{11,12} and magnetite could be encapsulated by polystyrene.^{13,14} Besides the encapsulation of metal oxide hybrid particles by a polymer shell, metal oxide coated polymer particles, e.g., titania-coated polystyrene particles, were also produced applying the miniemulsion technique.¹⁵ In most cases, the metal or metal oxide and the polymer form two distinct phases. However, a homogeneous distribution of the metal throughout the polymer particle requires the application of metal compounds that are soluble at least in the monomer or even better in the polymer.

Polymer particles have been produced with hydrophobic lanthanoide complexes that are soluble in the monomer phase; such particles can be used for biomedical applications.¹⁶ The polymerization of the monomers in the presence of some complexes within the miniemulsion droplets leads to the spontaneous formation of highly organized layered nanocomposite particles.¹⁷ By the use of the new colloidal approach the size, interparticle distance and the metal content can be chosen more flexible related to the micellar technique.^{18–20} Additionally, the new strategy offers a higher hexagonal order of the particles on the substrate. Up to now, the homogeneous encapsulation of hydrophobic metal complexes in nanoparticles is hardly known in the literature.²¹

Here, we show that the homogeneous incorporation of a large variety of different metals as hydrophobic metal complexes into (hydrophobic) polymer particles is possible by using the miniemulsion process where Ostwald ripening

is efficiently suppressed.²² Therefore, the concentration of every compound in the droplets remains constant during the polymerization. Complexes of main group elements like indium and aluminum were incorporated as well as complexes of transition group metals like zinc or platinum. Because of the high homogeneity in particle size, the polymer particles can be regularly arranged on the surface of a substrate. By plasma etching, the polymer can be removed, leaving behind a metal particle with a size defined by the complex concentration within the polymer. The distance between these metal particles is governed by the starting diameter of the polymer particles and can thus be controlled experimentally. The finally obtained metal particles immediately offer catalytic applications²³ or may open a novel route toward ordered arrays of quantum dots. Finally, such a hexagonal particle array may be used as etching mask to transfer a nanopattern into an underlying substrate.²¹

Experimental Section

Materials. Styrene and MMA (Merck, 99%) were distilled before use. The initiator 2,2'-azobis(2-methylbutyronitrile) (V59, Wako), sodium dodecylsulfate (SDS (Lancaster, 99%)), Lutensol AT50 (BASF), and hexadecane (Merck, 99%) were used without further purification. Ammoniumlaurate was synthesized by lauric acid (Merck, 99%) and 25% ammonia (1.5 times in excess). Deionized water was used as continuous phase.

Platinum(II)acetylacetonate (Pt(AcAc)₂, 98%), indium(III)acetylacetonate (In(AcAc)₃, 98%), iron(III)tetramethylheptadionate (Fe(TMHD)₃, 99%), zinc(II)tetramethylheptadionate (Zn(TMHD)₂, 99%), vinylferrocene (Strem, 99%), Fe(III)tetramethylheptadionate (Strem, 99%), and zinc(II) phthalocyanine (ZnPc, 98%) were received from Strem; chromium(III)benzoylacetone (>95% Cr) from Acros; and iron(III)diphenylpropanedionate and iron(III)benzoylacetone from ABCR. The complexes were used without further purification. Dibenzoylmethane (98%), 1-phenyl-1,3-butadiene (99%), and tetramethylheptadione (TMHD, 98%) were received from Aldrich and used without further purification.

Preparation of Metal-Containing Latexes by the Miniemulsion Approach. In the standard miniemulsion approach, the dispersed phase contains 2 g of monomer, 40 mg of V59, and 60 mg of hexadecane as a hydrophobe. Depending on the application, different amounts of a metal complex were dissolved in the dispersed phase. The dispersed phase was then added to the continuous phase typically consisting of 23 mg of SDS dissolved in 8 g of water. The emulsion was stirred for 1 h and then ultrasonicated for 3 min at 90% amplitude (Branson sonifier, 450 W, 1/2 in. tip) under ice cooling. The polymerization was carried out in a 50 mL flask at 72 °C for 12 h.

Preparation of Metal-Containing Latexes by the Emulsion Approach. For the dispersed phase, 2 g of monomer, 40 mg of V59, and various metal compounds were mixed. The continuous phase consisted of 25 g of 20 wt % ethanol/water solution and 10–80 mg of SDS. The combined phases were stirred vigorously for 1 h at room temperature. After heating to 72 °C, the polymerization was carried out under powerful stirring for 12 h.

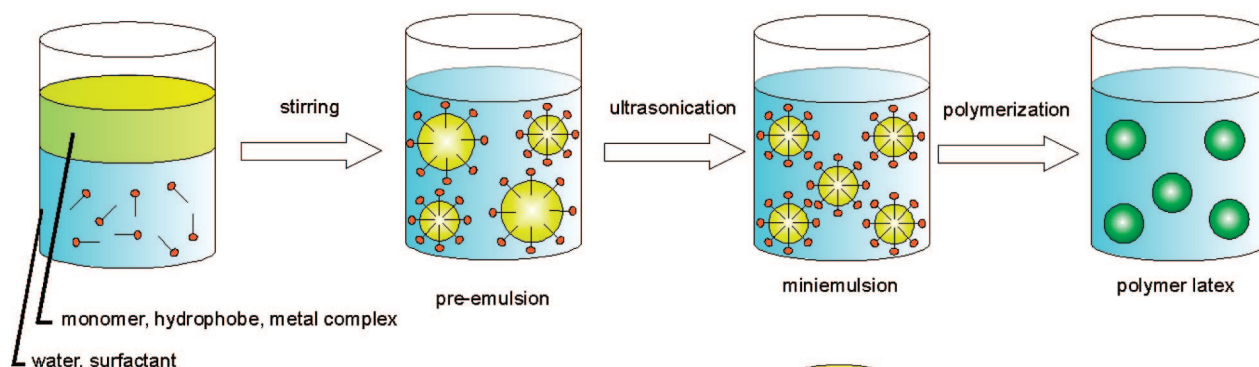
Seed Polymerization (Preparation of Particles Increased in Size with Additional Styrene). To 0.2–0.5 g of a 20 wt % seed latex prepared as described above was added 100 mL of an ethanol/water (0–20 wt %) mixture. The mixture was heated up to 85 °C

- (5) Tiarks, F.; Landfester, K.; Anonietti, M. *Macromol. Chem. Phys.* **2001**, *202*, 51–60.
- (6) Steiert, N.; Landfester, K. *Macromol. Mater. Eng.* **2007**, *292*, 1111–1125.
- (7) Volz, M.; Walther, P.; Ziener, U.; Landfester, K. *Macromol. Mater. Eng.* **2007**, *292*, 1237–1244.
- (8) Volz, M.; Ziener, U.; Salz, U.; Zimmermann, J.; Landfester, K. *Colloid Polym. Sci.* **2007**, *285*, 687–692.
- (9) Fleischhaker, F.; Zentel, R. *Chem. Mater.* **2005**, *17*, 1346–1351.
- (10) Joubert, M.; Delaite, C.; Bourgeat-Lami, E.; Dumas, P. *New J. Chem.* **2005**, *29*, 1601–1609.
- (11) Zhang, S. W.; Zhou, S. X.; Weng, Y. M.; Wu, L. M. *Langmuir* **2005**, *21*, 2124–2128.
- (12) Tiarks, F.; Landfester, K.; Antonietti, M. *Langmuir* **2001**, *17*, 5775–5780.
- (13) Holzapfel, V.; Lorenz, M.; Weiss, C. K.; Schrezenmeier, H.; Landfester, K.; Mailander, V. *J. Phys.: Condens. Matter* **2006**, *18*, 2581–2594.
- (14) Ramirez, L. P.; Landfester, K. *Macromol. Chem. Phys.* **2003**, *204*, 22–31.
- (15) Zhang, M.; Gao, G.; Li, C. Q.; Liu, F. Q. *Langmuir* **2004**, *20*, 1420–1424.
- (16) Vancaeyzeele, C.; Ornatsky, O.; Baranov, V.; Shen, L.; Abdelrahman, A.; Winnik, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 13653–13660.
- (17) Ramirez, L. P.; Antonietti, M.; Landfester, K. *Macromol. Chem. Phys.* **2006**, *207*, 160–165.
- (18) Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000–1005.
- (19) Spatz, J. P.; Roescher, A.; Möller, M. *Adv. Mater.* **1996**, *8*, 337–340.
- (20) Spatz, J. P.; Chan, V.; Mößner, S.; Kamm, F.; Plettl, A.; Ziemann, P.; Möller, M. *Adv. Mater.* **2002**, *14*, 1827–1832.
- (21) Manzke, A.; Pfahler, C.; Dubbers, O.; Plettl, A.; Ziemann, P.; Crespy, D.; Schreiber, E.; Ziener, U.; Landfester, K. *Adv. Mater.* **2007**, *19*, 1337–1341.

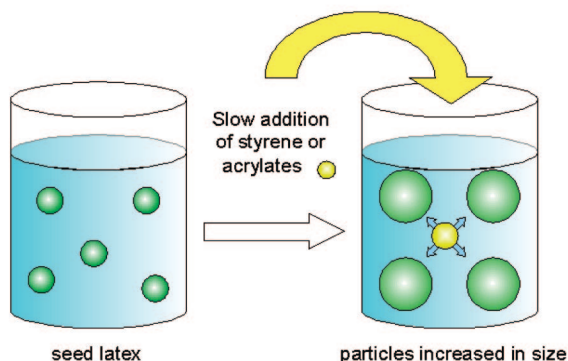
(22) Finsy, R. *Langmuir* **2004**, *20*, 2975–2976.

(23) Yang, M. X.; Somorjai, G. A. *Langmuir* **1998**, *14*, 1458–1464.

Miniemulsion technique:



Core-shell-approach:



Emulsion technique:

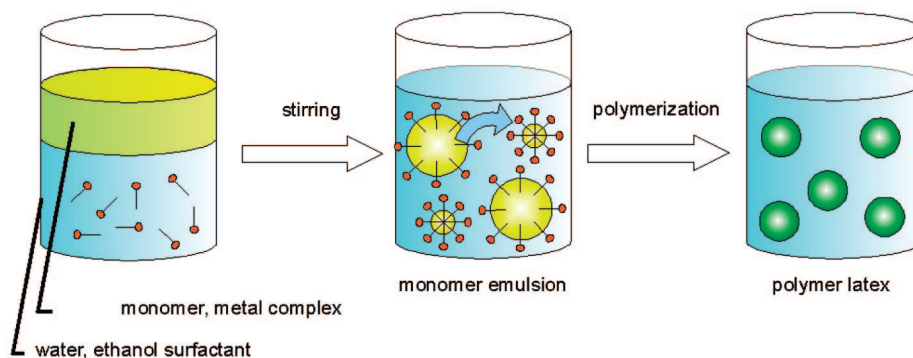


Figure 1. Preparation techniques for metal-containing latex particles.

under vigorous stirring. Different amounts of styrene and initiator (e.g., 2–4 g styrene with 7 wt % V59) were slowly (1 mL/h) added with a syringe.

Preparation of Metal Nanoparticles from Loaded Polymer Latexes. After dilution of the original latex with water to 0.5 wt % solid content, a 0.5 μ L drop is deposited onto a cleaned and plasma pretreated silicon substrate. By evaporating the solvent under a controlled atmosphere, a hexagonally ordered monolayer of the loaded polymer latexes is obtained. Subsequently, the latexes are exposed to an oxygen plasma provided by a commercially available etching device (Plasmalab 80 Plus ICP RIE, Oxford Instruments). Under almost perfect conservation of their original position, the resulting dots consist of independently nucleated metal particles in a residual polymer matrix. Finally, these hybrid particles are annealed at temperatures of up to 1000 $^{\circ}$ C (depending on the size of the particles after plasma exposure) in an oxygen atmosphere for a short period of time.²¹

Preparation of Substrates Used for EDX and X-ray Mapping. Arrays of metal complex containing polystyrene particles were prepared on carbon coated copper TEM grids by a dropping method. For the particles determined for plasma etching, an additional silicon

layer of 20 nm was evaporated on the carbon-coated TEM grid before the solution was dropped on the substrate.

Analytics. The particle size and size distribution (PDI) were measured by dynamic light scattering (Malvern Zetasizer nano series in the multi narrow mode or the Sympatec Nanophox). For the measurement, 1 mL of diluted latex (solid content <1 wt %) was used. From the DLS measurement, the size and width of particle size distribution (as PDI) are calculated from the following equation

$$\ln(G1) = a + bt + ct^2 + dt^3$$

where $G1$ is a correlation function.

The second order cumulant b is converted to a size using the dispersant viscosity and instrumental constants. The coefficient of the squared term c , when scaled as $2c/b^2$, is defined as the polydispersity index (PDI). The PDI is a measure of the particle size distribution and the PDI is a dimensionless number that describes the heterogeneity of the sample; it can range from 0 (monodisperse) to 1 (polydisperse).

Table 1. Hydrophobic Metal-Complex-Loaded Polystyrene Latexes

metal	sample	metal content (wt %, wrt monomer)	metal complex	SDS (wt %, wrt monomer)	hydrodynamic diameter (DLS) (nm)	Polydispersity index (PDI)
no metal	ES_M_00			1.15	102 ± 12	0.081
platinum	ES_M_01	0.50	Pt(AcAc) ₂	1.15	118 ± 12	0.038
platinum	ES_M_02	0.99	Pt(AcAc) ₂	1.15	105 ± 10	0.029
indium	ES_M_03	0.45	In(AcAc) ₃	1.15	133 ± 9	0.002
indium	ES_M_04	0.86	In(AcAc) ₃	1.7	123 ± 13	0.067
zinc	ES_M_05	0.37	ZnPc	1.7	156 ± 12	0.039
zinc	ES_M_06	0.30	Zn(TMHD) ₂	1.15	115 ± 13	0.027
chromium	ES_M_07	0.24	Cr(III)benzoylacetate	1.15	110 ± 16	0.085
chromium	ES_M_08	0.80	Cr(III)benzoylacetate	1.35	145 ± 17	0.043
iron	ES_M_09	0.26	Fe(III)benzoylacetate	1.15	160 ± 22	0.073
iron	ES_M_10	0.10	Fe(III)diphenylpropanedionate	1.15	120 ± 18	0.109
iron	ES_M_11	0.53	Vinylferrocene	1.15	154 ± 13	0.045
iron	ES_M_12	0.23	Fe(TMHD) ₃	1.15	107 ± 9	0.162

The particle morphology as well as the homogeneity was analyzed by transmission electron microscopy (Philips EM400). The sample was prepared on a 400 mesh TEM grid.

The particles were also analyzed by a Hitachi S-5200 high-resolution scanning electron microscope (HRSEM) in combination with EDX (from EDAX Ametek). For the X-ray mapping, a special TEM holder out of Beryllium was used to minimize scattering events and to increase the signal-to-noise ratio. SEM images were evaluated applying the program ImageJ.

The inductively coupled plasma (ICP) measurements (TU Munich) were analyzed in the optical emission spectroscopy mode with a resolution of <1 ppm. For this purpose, 300 μ L of the latex was injected in a 5000–10 000 °C argon plasma and analyzed with a VARIAN-VISTA simultaneous spectrometer.

Results and Discussion

The hybrid nanoparticles with incorporated hydrophobic metal complexes were prepared by three different techniques, which are summarized in Figure 1. They will be discussed in the following sections.

Preparation of Metal-Complex-Containing Polymer Latexes by Miniemulsion Technique. In the first approach, metal-containing latexes were prepared by the miniemulsion technique. Here, the metal compound, the oil-soluble initiator V59, and hexadecane as osmotic pressure agent were dissolved in styrene. After mixing, the dispersed phase was added to the continuous phase, consisting of water and the surfactant SDS. Subsequently, the two phases were emulsified by stirring and ultrasonication, followed by polymerization. Thereby, it is assumed that the metal complex builds a homogeneous glassy solution in the polystyrene. There is no evidence for phase separation within the particles.

For the incorporation of metals, different acetylacetonate derivatives were synthesized to obtain high solubility in the monomer phase and low water solubility. With the miniemulsion approach, it could be shown that many different metal complexes can be easily incorporated into a polymeric matrix (Table 1).

In the miniemulsion approach, the chosen metal complex has a major influence on the emulsion stability and particle size distribution. The particle size, its deviation (given as $\pm\sigma/2$), and the polydispersity index (PDI) were measured by dynamic light scattering. It has to be mentioned that although the PDI is defined exactly (see Experimental Section), it gives a range rather than a precise measure of homogeneity because of the indirect method of size deter-

mination. To obtain a high degree of incorporation, it is necessary that the metal complexes are highly hydrophobic and soluble in the monomer. Therefore, different metal complexes were tested. Generally, we used acetylacetonate (AcAc) as well as substituted acetylacetonate complexes because of their high stability and good accessibility. Substituted acetylacetonate complexes deliver a higher lipophilicity. In general, any lipophilic and stable metal complexes, as for example ZnPc or ferrocene complexes are suitable for incorporation. Without the incorporated metal complex, the size of the particles and the stability of the emulsion are mainly determined by the amount of surfactant used and the sonication time applied. In the case of metal-containing latexes, there is evidence that the metal complex also affects these parameters.

A metal complex with no noticeable influence on the resulting polymer particles is Pt(AcAc)₂. The addition of the complex to the styrene miniemulsion leads to very homogeneous, narrowly distributed particles (see Figure 2). Generally, the size of the droplets in a styrene miniemulsion can be tuned between 70 and 200 nm, depending on the surfactant concentration.³ The maximum platinum content experimentally verified was about 1 wt %, but the upper limit is probably reached at the solubility of Pt(AcAc)₂ in styrene with 1.5 wt %.

Compared to platinum(II)acetylacetonate, indium(III)acetylacetonate seems to have a significant influence on the interface and interface stability, respectively. The formed particles are exceptionally uniform in size, but the emulsions are stable only until a certain concentration of indium(III)-acetylacetonate (about 200 wt %) with respect to SDS is reached. We assume that the indium ion is coordinated to the sulfate group of the surfactant, which could explain the irregular surface morphologies in Figure 2. Further small "objects" sometimes noticeable between the particles can not be attributed unambiguously to a certain chemical species. The interface activity (interfacial tension: ~ 35 mN/m for the water/styrene and ~ 14 mN/m for the water/(styrene + 1 wt % In(AcAc)₃) interface) could additionally explain the high homogeneity as well. In contrast to indium(III)acetylacetonate, the maximum platinum(II)acetylacetonate content is just limited by its solubility in styrene, and no interface activity was observed.

In contrast to many other acetylacetonate complexes, Fe(AcAc)₃ has a comparably high solubility in water (1.7

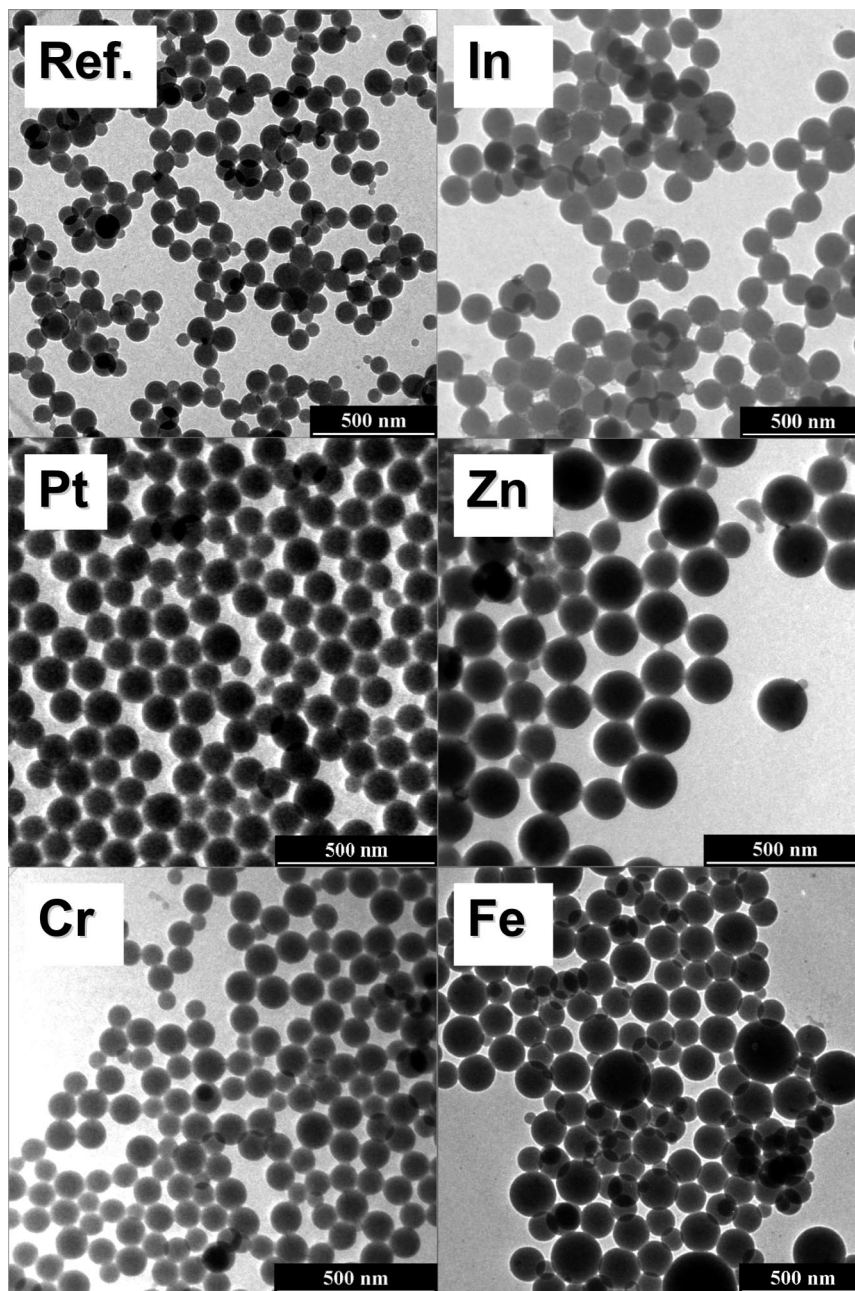


Figure 2. TEM images of metal-free polystyrene particles (Ref.) and different metal-containing latexes. The used complexes are platinum(II)acetylacetonate (ES_M_01), indium(III)acetylacetonate (ES_M_03), chromium(III)benzoylacetonate (ES_M_07), zinc(II) phthalocyanine (ES_M_05), and iron(III)benzoylacetonate (ES_M_09).

g/L at 20 °C, Merck), and the encapsulation of this complex in polymer particles can not be easily performed. Therefore the more hydrophobic and thus poorly water-soluble compounds iron(III)phenylacetylacetonate, -dibenzoylmethane, and -tetramethylheptadione (TMHD) were used. Besides the acetylacetonate complexes, ferrocene can be employed similarly with a strikingly high solubility in styrene, which allows a significantly increased loading of the particles with metal complex (up to ~20 wt %). Such ferrocene-containing particles show a broad size distribution and the comparably high vapor pressure of ferrocene leads to loss of material from the particles. To avoid sublimation, vinylferrocene was employed as comonomer with styrene but the size distribution of the resulting hybrid particles is not significantly changed (polydispersity index (PDI) 0.045). In summary, iron

compounds show a more destabilizing influence on the miniemulsion. This could be caused by the high ion strength of iron ions, which results in a destabilizing effect on the anionically stabilized droplets. Only with sterically demanding ligands as tetramethylheptadione or phenylacetylacetonate can good results be achieved through shielding the metal center.

Contrary to Figure 2, where a relative broadening of the particle size distribution can be observed upon the addition of Cr(III)benzoylacetonate to the monomer mixture, the PDI (0.085, 0.043) rather points to no significant influence of the metal salt on the size distribution.

Polymer particles containing 1.4 wt % zinc complex Zn(TMHD)_2 (equal to 0.30 wt% pure zinc) exhibit almost the same polydispersity (PDI 0.027) as, for example, latexes

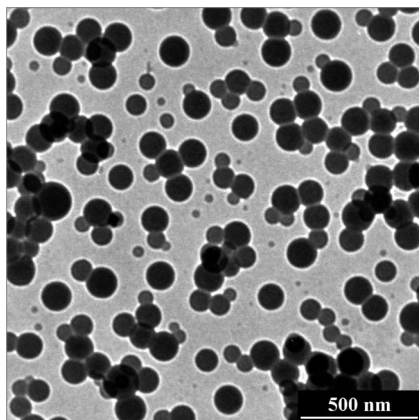


Figure 3. General example for a sample (in this case containing 1 wt % $\text{In}(\text{TMHD})_3$ related to monomer) prepared with CTAB (1 wt % related to monomer).

with $\text{Pt}(\text{II})$ acetylacetonate (PDI 0.029), but $\text{Zn}(\text{TMHD})_2$ shows a destabilizing effect comparable to indium(III)acetylacetonate. To avoid the interaction between $\text{Zn}(\text{TMHD})_2$ and SDS, another zinc complex, namely zinc phthalocyanine (ZnPc), with a more shielded metal center was used. Because of the low solubility of ZnPc in styrene, this metal compound can be dispersed only in styrene and not dissolved in reasonable quantities. Nevertheless, it is possible to prepare ZnPc -containing particles, but with a relatively broader size distribution compared to $\text{Zn}(\text{TMHD})_2$ as precursor (PDI 0.039).

To minimize interactions between the surfactant and the positively charged metal compound, we decided to substitute the anionic surfactant SDS by cationic surfactants. However, less homogeneous particles are formed with cetyltrimethylammoniumbromide as surfactant (see Figure 3).

In further studies, cationic or nonionic cosurfactants shall be employed to optimize the particle size distribution.

As shown in the above examples, the miniemulsion approach is a very efficient way to incorporate a wide variety of metal complexes in polystyrene nanoparticles by a careful choice of complexes with suitable ligands. On the one hand, distracting interactions can occur between the metal ion and the surfactant; on the other hand, the incorporation is limited to the solubility of the corresponding complex in the dispersed phase. In the present report, the complex content could be varied between 0.5 and 3 wt % with respect to monomer.

Preparation of Particles Increased in Size with Additional Styrene. For some applications like nanolithography, it is desirable to control the diameters in a wider range especially toward larger particles. After plasma etching of a dense monolayer, for example, the particle diameter determines the interparticle distance of the resulting metal dots.²¹ To increase the particle size of already existing polymer particles, we chose a core-shell approach. As seed latex the platinum containing polystyrene latex ES_M_02 and styrene as additional monomer were used (see Table 1).

The size of the entire polymer particle can be easily adjusted by the amount of added monomer. So the particle size was increased from 105 nm step by step up to 370 nm (Figure 5, Table 2). By dissolving platinum(II)acetylacetonate in the added shell-forming styrene, even particles with the

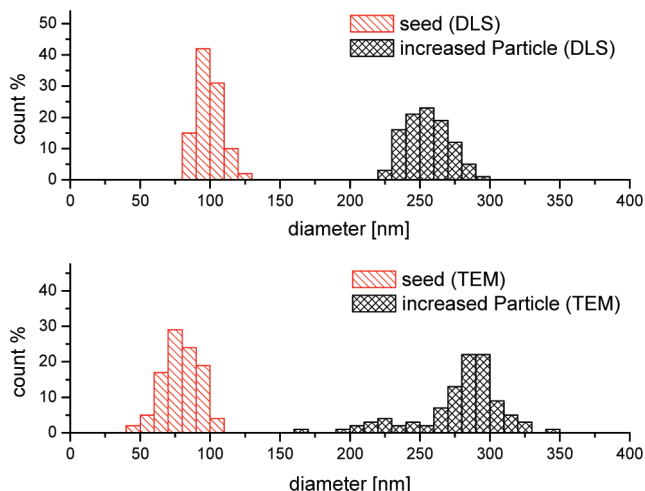


Figure 4. Size distribution before and after growth determined by DLS (top) and TEM (middle); example for seed particles (ES_M_02, Figure 5a) increased in size with additional styrene (ES_M_02_Upt_3, Figure 5d).

platinum complex in the shell could be prepared. As diffusion processes take place during the size enhancement, the quantity of platinum(II)acetylacetonate could vary in the shell. To reach higher homogeneities and to allow a good diffusion of the hydrophobic complex to the core particles, we added ethanol to the continuous phase of the seed latex. This leads to significantly higher homogeneities of the latexes' size. Another effect of short chain alcohols is the decrease in the critical micelle concentration (cmc) of SDS and the polymerization rate.²⁴ The best results were obtained with an ethanol content of 15–20 wt % (see Figure 5). The maximum resulting particle size was 370 nm. In cases with high amounts of monomer addition, it is reasonable to add small amounts of additional surfactant for stability purposes. Unfortunately, the appearance of secondary particles cannot be totally excluded. As can be seen in Figure 4, among the enlarged particles, there are also some small ones that might arise from secondary nucleation.

Preparation of Metal-Compound-Containing Polymer Latexes by Emulsion Technique. Though the miniemulsion technique provides very good results, for some applications, highly ordered monolayers are required, making even still narrower size distributions mandatory. To reach higher homogeneities for some metal complexes, emulsion polymerization techniques proved to be valuable. As a standard emulsion polymerization process in water would fail because of the limited solubility of the metal complex in water (see Introduction), a mixture of styrene containing V59 as initiator and a metal complex was emulsified in 20 wt % ethanol/water under addition of small amounts of SDS. The alcohol increases the solubility in the continuous phase of both the metal complex and the monomer and has a major influence on particle homogeneity.²⁵ The polymerization was performed overnight at 72 °C under vigorous stirring. Platinum-containing particles with a very narrow size distribution and a theoretical platinum content of 1 wt % could be success-

(24) Chern, C.-S.; Yu, T.-C.; Hu, L.-L. *J. Appl. Polym. Sci.* **2006**, *100*, 4406–4411.

(25) Zhang, J. H.; Chen, Z.; Wang, Z. L.; Zhang, W. Y.; Ming, N. B. *Mater. Lett.* **2003**, *57*, 4466–4470.

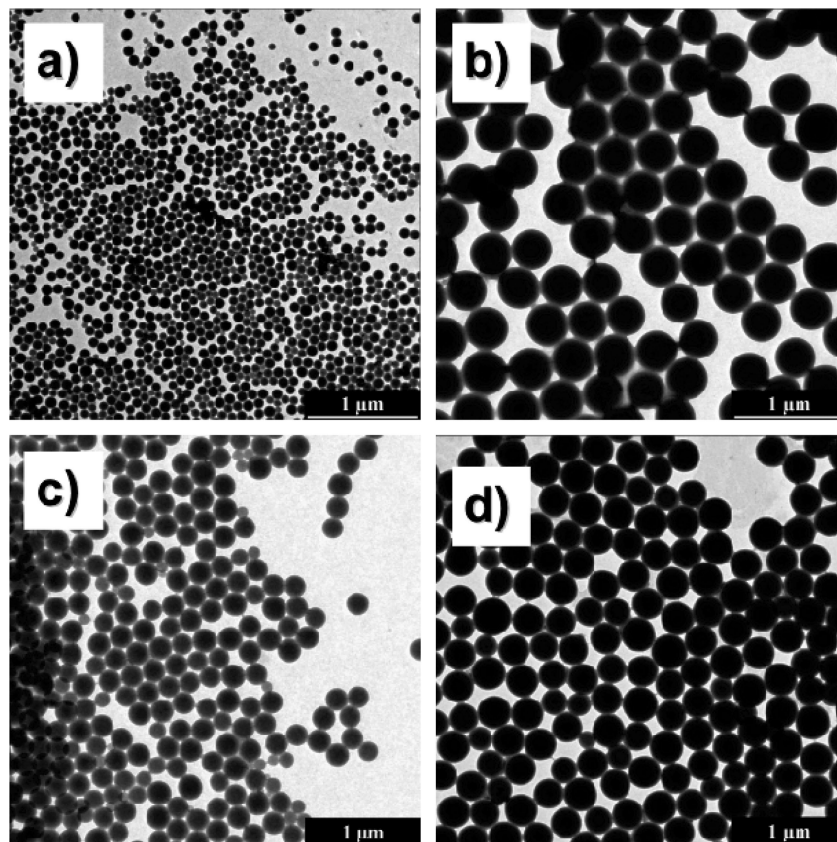


Figure 5. Different particles: (a) platinum-containing seed latex. (b–d) styrene with additional platinum(II)acetylacetonate, (d) 20 wt % ethanol (see Table 1).

Table 2. Platinum-Containing Seed Particles Increased in Size with Different Amounts of Styrene

sample	seed size (nm)	ratio added monomer/seed particle wt/wt	hydrodynamic diameter (DLS) (nm)	ethanol content (%)	platinum occurrence	TEM (see Figure 5)
ES_M_02	105		105 ± 10	0	seed	a
ES_M_02_UPt_1	105	50	374 ± 17	20	seed and shell	b
ES_M_02_UPt_2	105	33	194 ± 12	15	seed and shell	c
ES_M_02_UPt_3	105	50	253 ± 13	15	seed and shell	d

fully prepared (see Figure 6). Thereby, it is assumed that the $\text{Pt}(\text{AcAc})_2$ diffuses together with the styrene to the polymerization loci, as the solubility of the metal complex in the continuous phase is comparable with that of the monomer. A more detailed discussion on the precise mechanism of this modified emulsion methodology will be given in a forthcoming paper.

By adjusting the amount of surfactant from 0.5 to 4 wt % (related to the monomer), the particle size can be easily controlled in a range between 150 and 260 nm (see Table 3 and Figure 7). As a control for the efficiency of the seeding process, the particle number density was determined before and after the seeding process, revealing strongly scattering values between 0.5 and 2.5 for the ratio of both densities. Those differences are attributed to (i) significant amounts of coagulate and (ii) the uncertainty of the size measurement; however, for certain samples, the ideal value of 1.0 is reached.

To determine the absolute value of the metal content in the latexes, a plasma etching process followed by an annealing step, as in ref 21, is performed. During the isotropic oxygen plasma, the diameter of the polystyrene particles can be systematically reduced until the etching rate approaches

zero, indicating that the final diameter has been reached. During the diameter reduction, the positions of the polystyrene particles are conserved, forming a hexagonal pattern (Figure 8).

Annealing of such hexagonal particle arrays, where the residues of the loaded PS particles contain platinum (sample ES_EM_Pt_1), leads to platinum particles with a diameter of 13.5 nm and interparticle distances of 230 nm (Figure 9).

The expected value as calculated from the loading of the polystyrene particles with platinum complex is 14.5 nm. The size distribution of these particles is comparable to that of the original polystyrene particles and shows a standard deviation between 10 and 13% (Figure 10).

This implies that the loading with platinum(II)acetylacetonate is almost complete and homogeneously distributed and that the particles finally obtained after plasma treatment are practically of pure platinum. It should be mentioned that the higher standard deviation of the resulting particles could be a result of the plasma and annealing steps. When these platinum particles are used as masks during anisotropic etching of silicon in a CF_4/CHF_3 plasma in order to fabricate nanopillars,²¹ the observed etching rate of the particles is in

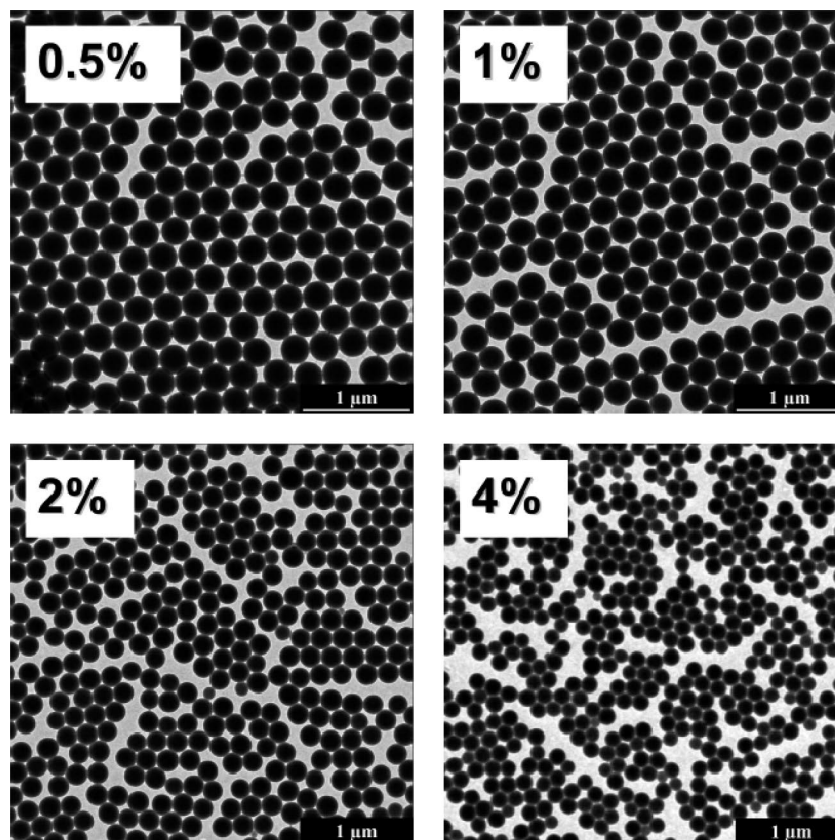


Figure 6. TEM images of platinum containing PS latexes prepared by emulsion polymerization with different amounts of surfactant (SDS) in wt % with respect to dispersed phase and 20 wt % ethanol content (see also Table 3).

Table 3. Different Platinum(II)acetylacetonate-Containing Latexes Prepared by Emulsion Polymerization in 20 wt % Ethanol

sample	SDS amount (concentration wrt dispersed phase)	hydrodynamic diameter (DLS) (nm)
ES_EM_Pt_1	10 mg (0.5%)	262 ± 17
ES_EM_Pt_2	20 mg (1%)	254 ± 20
ES_EM_Pt_3	40 mg (2%)	194 ± 13
ES_EM_Pt_4	80 mg (4%)	149 ± 9

good agreement with that of a pure platinum film, confirming the above implication.

The emulsion technique additionally allows for the incorporation of mixtures of different metal complexes in the particles. Therefore, this approach was extended to platinum-

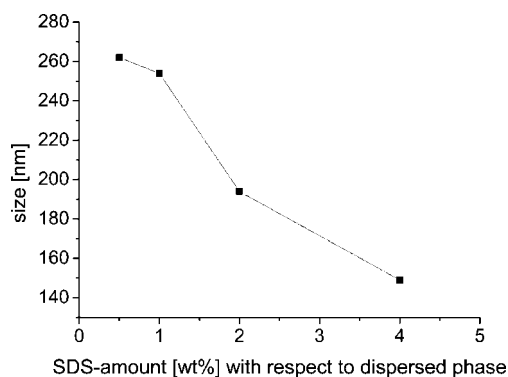


Figure 7. Particle size (hydrodynamic diameter, DLS) versus surfactant concentration of platinum containing particles prepared by emulsion polymerization (dotted lines as a guide for the eyes).

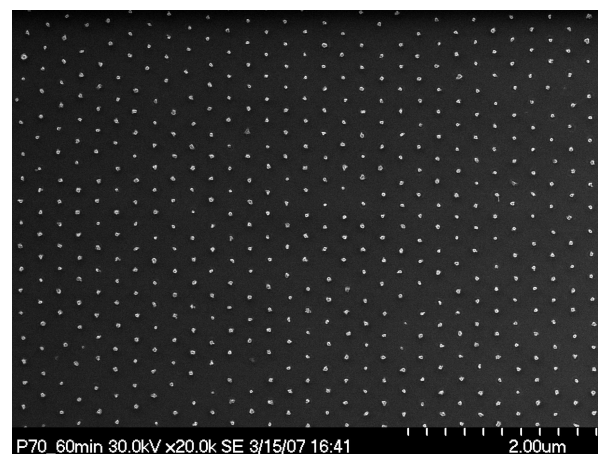


Figure 8. Hexagonal pattern of platinum-complex-containing PS particles on silicon that were etched in oxygen plasma for 60 min. The particles exhibit a final diameter of 40 nm and an interparticle distance of 230 nm.

and iron-containing compounds aiming at the formation of ordered arrays of alloyed FePt clusters after deposition onto a substrate and subsequent plasma etching. In current research, FePt nanoparticles with a molar ratio of ~ 1 raise in interest because of their ability to form ferromagnetic clusters. FePt particles in the face-centered tetragonal $L1_0$ phase, with their high magnetic anisotropy energy, which is advantageous for thermal stability of the magnetic moment, are interesting candidates for future recording media. The adjustment of the ordered $L1_0$ phase as well as the height of the coercivity is decisively dependent on the composition

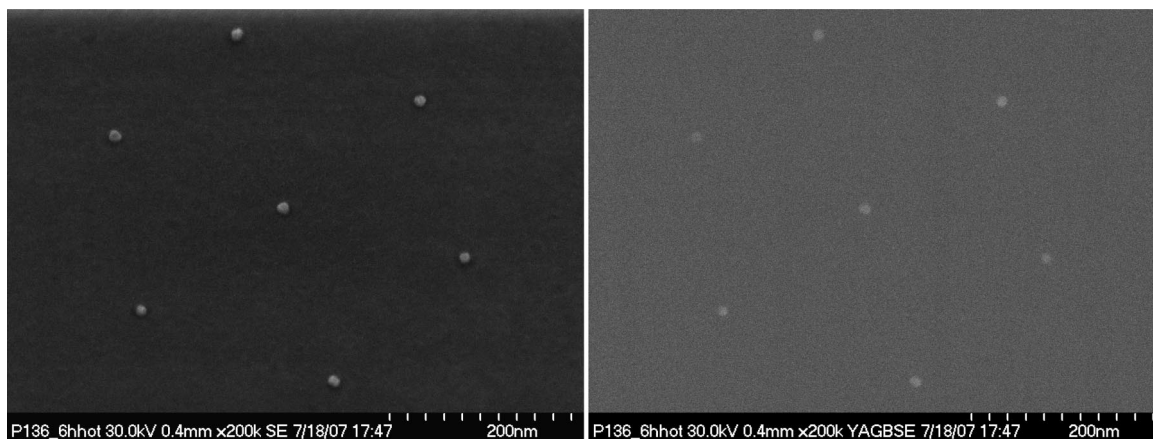


Figure 9. SEM images of platinum particles with a diameter of about 13.5 nm and an interparticle distance of 230 nm on silicon. Left: Signal from secondary electrons. Right: Signal from backscattered electrons.

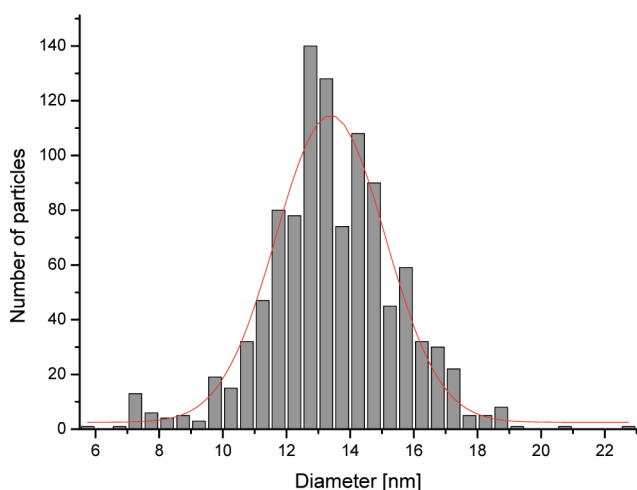


Figure 10. Size distribution of particles as shown in Figure 9. Solid curve: Gaussian fit. The standard deviation is 1.6 nm.

and ordering degree of the FePt-nanoparticles, respectively. High coercitivity can mainly be obtained for molar Fe/Pt-ratios near 1:1.^{26,27} For this purpose, a combination of platinum(II)acetylacetonate and Fe(TMDH)₃ was added to the monomer phase (see Table 4). Besides SDS, ammonium laurate and Lutensol AT50 were used as surfactants. Ammonium laurate has similar properties and a comparable structure as SDS but is metal-free. Therefore, no residues are expected after plasma etching. Lutensol AT50 is also a purely organic but nonionic surfactant. Thus, destabilizing effects by metal ions during the miniemulsion process can be excluded.

For low iron contents, the results are comparable to those obtained by emulsion polymerization techniques for particles containing only platinum (see Figure 11).

In contrast to the miniemulsion process, in emulsion polymerizations net diffusion generally takes place which can lead to concentration differences in the single droplets. Therefore, to qualitatively prove the incorporation of plati-

num and iron, energy-dispersive X-ray spectroscopy (EDX) was applied in combination with SEM. Taking corresponding X-ray maps delivers a spatially resolved image of the distribution of both elements.

An annealed multilayer of polymer particles loaded with platinum and iron complexes is presented in Figure 12a. The X-ray maps of this film (Figure 12b for platinum and Figure 12c for iron) verify the incorporation of the metal complexes. Figure 12d shows single polymer particles of the same type as above. The metal content of the single particles seems to be distributed uniformly, as can be seen on the X-ray maps (Figure 12e for platinum and Figure 12f for iron).

The X-ray maps in Figure 12h and Figure 12i show the final state after plasma etching for polystyrene particles loaded with platinum and iron complexes, respectively.

To quantitatively determine the metal content in the polymer latexes, we performed additional ICP and EDX measurements (see Table 5). The EDX results were averaged over 10 measurements (relative standard deviation of a single measurement <5%). Comparison of the EDX data to the ICP results (relative standard deviation of a single measurement <1%) gives an excellent agreement. This indicates that EDX can be routinely employed for a precise determination of the metal concentration within the latexes. The results for the miniemulsion (sample ES_miniFePt2) also show a very good correlation between the weighted sample and the measured metal content. Thus, for the miniemulsion, a molar Fe/Pt ratio of 1:1 can be achieved. In contrast, the metal content in the emulsions differ from the theoretically expected values. Although the platinum content corresponds to almost 100% of the weighted amount, the iron content is less than 20% for MS_36 and less than 10% for ES_EM_FePt3, respectively. The enhancement of the weighted amount of iron in sample ES_EM_FePt3 does not lead to higher iron content within the latex. Obviously, the iron incorporation is limited for this specific iron complex. Because the emulsion polymerization is dependent on diffusion processes, this limitation may be explained by different diffusion properties of the platinum and iron complexes. To raise the iron content further, experiments with different iron-complexes are under way.

(26) Sun, S.; Fullerton, E.; Weller, D.; Murray, C. *IEEE Trans. Magn.* **2001**, 37, 1239–1243.

(27) Li, B.-H.; Feng, C.; Yang, T.; Teng, J.; Zhai, Z.-H.; Yu, G.-H.; Zhu, F.-W. *J. Phys. D: Appl. Phys.* **2006**, 39, 1018–1021.

Table 4. Different Platinum(II)acetylacetonate- and Iron(III)TMHD₃-Containing Latexes Prepared by (Mini)-Emulsion Polymerization in 20 wt % Ethanol

sample	surfactant	platinum(II)-acetylacetonate	iron(III)TMHD ₃	hydrodynamic diameter (DLS) (nm)	PDI
ES_EM_FePt_3 (emulsion)	20 mg ammonium laurate	20 mg (1%)	46 mg (2.3%)	285 ± 21	0.021
MS_36 (emulsion)	20 mg SDS	20 mg (1%)	31 mg (1.5%)	273 ± 31	0.002
ES_MiniFePt_2 (miniemulsion)	100 mg Lutensol AT50	20 mg (1%)	31 mg (1.5%)	211 ± 24	0.021

It is possible to obtain FePt particles after annealing the hybrid particles (see Figure 13). In this case, a diameter of 18 nm is expected as opposed to the experimental result of about 14 nm. This value corresponds to the theoretical value for pure platinum particles, which is consistent with the

observed low iron content. Similar results were obtained with other iron- or platinum-containing latexes.

From these results, one concludes that miniemulsions are preferable if a precise control of the metal contents is required, whereas emulsion polymerization delivers more

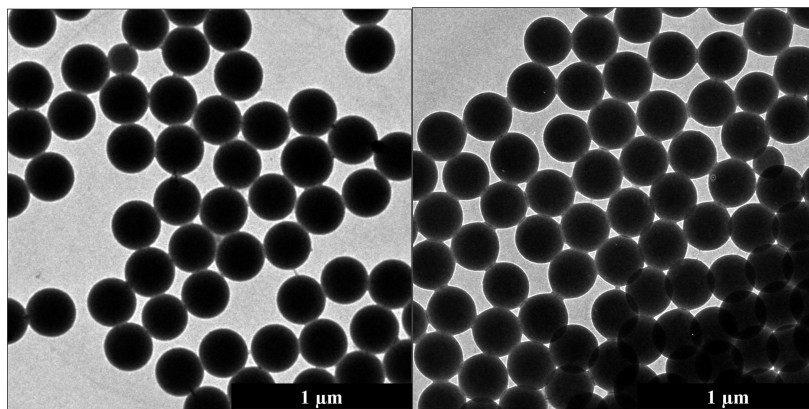
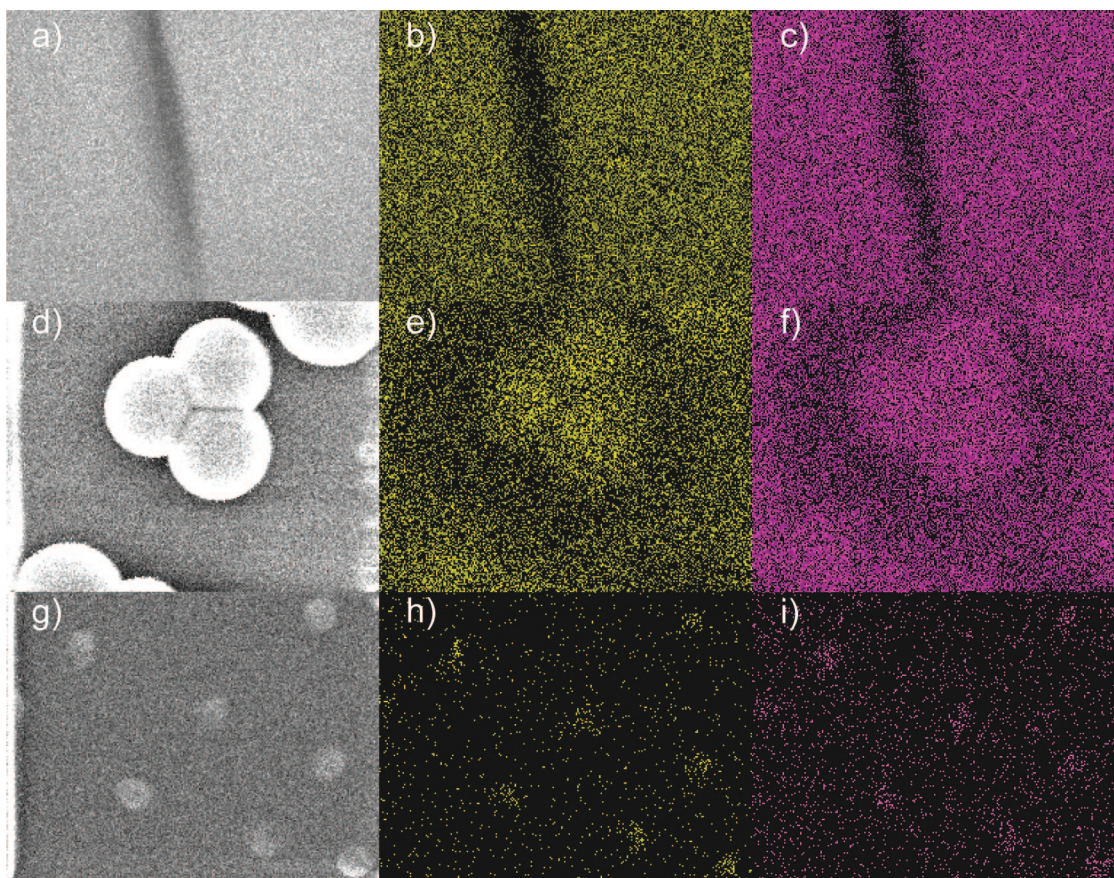
**Figure 11.** Polymer particles containing platinum(II)acetylacetonate and Fe(TMHD)₃ (ES_EM_Pt_3 (left) and MS_36 (right)).**Figure 12.** First column shows SEM images of (a) a film of an annealed and ripped multilayer (sample ES_FePt_3), (d) single particles (diameter ≈ 250 nm, sample MS_36), and (g) single particles etched in an oxygen plasma of PS particles (diameter ≈ 40 nm, sample MS_36) containing a platinum and an iron complex. The second and third columns represent the X-ray maps of these images for platinum (b, e, h) and iron (c, f, i), respectively.

Table 5. ICP and EDX Analysis of Fe/Pt-Containing Latexes.

sample	weighted sample			EDX			ICP			method of preparation
	Fe (wt%)	Pt (wt%)	Fe/Pt (molar)	Fe (wt%)	Pt (wt%)	Fe/Pt (molar)	Fe (wt%)	Pt (wt%)	Fe/Pt (molar)	
ES_miniFePt2	0.13	0.45	1	0.14	0.50	1.02	0.16	0.53	1.04	mini-em.
MS_36	0.14	0.47	1	0.03	0.43	0.24	0.03	0.44	0.22	emulsion
ES_EM_FePt3	0.19	0.45	1.5	0.02	0.40	0.18	0.02	0.40	0.19	emulsion

homogeneous size distribution of the hybrid metal/polymer particles. By exploiting their self-assembly into highly ordered monolayers, the latter case is especially attractive for nanolithographic applications.

Conclusion

In the present work, the incorporation of several commercially available or synthesized hydrophobic metal complexes in latexes and their influence on the particle stability and size distribution after polymerization was shown. Mini-emulsion polymerization reactions with added hydrophobic metal complexes were performed, leading to particles with defined sizes in the range of 100–260 nm. Additionally to the miniemulsion approach emulsion techniques were employed, allowing the encapsulation of platinum and iron complexes.

It could be shown that with the technique of miniemulsion polymerization, metal-containing polymer latexes can be

easily obtained. An encapsulation of metal compounds is possible if a stable oil-soluble metal complex with low water solubility is available. Styrene proved a suitable monomer, but we expect that acrylates or monomer mixtures can be successfully employed as well. It could also be shown that the used complexes can have a major influence on emulsion stability, particle size, and size distribution.

The most homogeneous particle sizes were prepared by the emulsion technique. Homogeneous platinum- or iron-containing particles in the size between 100 and 300 nm were successfully prepared with a very narrow size distribution in 20 wt % ethanol solution.

The emulsion technique could be also employed to obtain larger particle sizes by core/shell techniques applied to existing seed latexes from miniemulsion techniques. The added shell can contain different polymer compositions and even dissolved metal complexes. Particle sizes of 370 nm were reached without any problems. The best results occurred in a 15–20 wt % ethanol/water mixture as continuous phase.

It should be pointed out that for the first time, alloyed particles from iron and platinum precursors were successfully prepared by the (mini)emulsion technique.

Ordered arrays of these narrowly size distributed particles can be deposited onto various substrates and applied for the production of etching masks.²¹ In summary, the type of metal complexes incorporated determines the type of finally obtained metal nanoparticle, the amount of metal complex determines the nanoparticle size, and the starting size of the polymeric particles defines the distance of the resulting metal nanoparticles after plasma etching.

Acknowledgment. We thank Professor Dr. Paul Walther and PD Dr. A. Ziegler (ZE Electron Microscopy, University of Ulm) for advising us in the use of HRSEM and EDX. The support by Deutsche Forschungsgemeinschaft (DFG) within the Cooperative Research Center SFB 569 is gratefully acknowledged.

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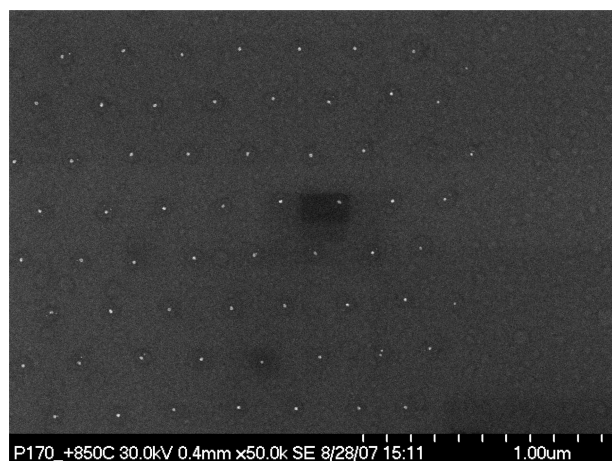


Figure 13. Sample MS_36 after depositing a monolayer onto a silicon substrate, exposing the latexes to an isotropic oxygen plasma for 2 h, and subsequently annealing the sample up to 850 °C for a short period of time. The initial diameter of the latexes is 250 nm; the final diameter of the FePt-nanoparticles 14 nm.