Mineralization of Gold Nanoparticles in a Block Copolymer Microemulsion

Joachim P. Spatz, Stefan Mößmer, and Martin Möller*

Abstract: Controlled mineralization of gold nanoparticles has been performed in a microemulsion of polystyrene-*block*-poly(2-vinylpyridine). The starting point was the formation of a thermodynamically stable dispersion of $HAuCl_4$ in inverse micelles of the block copolymer in toluene, which became metastable when the gold was reduced. Kinetic control of the transformation allowed the following stages of the mineralization/coagulation process to be stabilized: 1) one gold particle per micelle, 2) aggregated micelles containing two or three gold particles, and 3) a state in which empty micelles coexist with larger polymer-stabilized gold particles. Distinctive variations in the spectra were observed dependending on the particle size and whether two particles had formed a couple with orientation-dependent dipolar interactions.

Keywords
block copolymers · micelles · mineralization · nanostructures · thin films

Introduction

Regular metal or semiconductor nanocrystals of well-defined size that are sterically stabilized, either in solution or in the bulk, are of great potential interest, for example, in optical applications, because of quantum size effects and the enormous oscillation strength of metal particles, and also for catalysis, because of the large active surface.[1, 2]

A new concept for the control of the particle formation utilizes diblock copolymers.[3–10] These form micelles in a solvent, which is selective for one of the constituent blocks, and organize in a microdomain structure in the bulk state.[11] If the blocks that form the core of the micelle or the dispersed domains are polar and able to interact with a transition metal compound, the latter can be selectively incorporated within the micelles or the domains.[3–5, 10] The nano-sized compartments formed in this way can serve as reactors for the mineralization of inorganic crystallites or clusters, and the particle size and interparticle distance can thus be controlled exclusively through the choice of block copolymer. Problems that are encountered with this concept are the formation of several particles per compartment or the transfer of the inorganic species between the micelles causing loss of control over the particle formation.[3, 5–8, 12, 13]

Only recently we have shown that it is possible to prepare monomicellar films of polystyrene-*block*-poly(ethylene oxide) with exactly one monocrystal of gold in each micelle. In this case the mineralization step was achieved in the dry film, where the glassy state of the block copolymer efficiently inhibited any intermicellar transport.[4]

It would, however, be much more attractive if the mineralization step could be executed inside dissolved micelles. It would then be possible to add further components, to mix different micelle-stabilized particles, and to cast bulk materials of arbitrary shape without restriction on size. Attempts to prepare monodisperse nanoparticles with surface-active low molecular weight compounds are based on strong chemisorption or complexation of the surfactant on the particle surface, affecting the particle properties significantly.[14, 15] In the present report, we describe a first successful attempt at the kinetically controlled formation of gold nanoparticles in a microemulsion of polystyrene-*block*-poly(2-vinylpyridine) in toluene.

Results and Discussions

For the mineralization within diblock copolymer micelles, three different steps have to be considered: 1) The micelles are loaded with the inorganic precursor compound forming a thermodynamically stable microemulsion. 2) The precursor compound is converted chemically to an insoluble species that mineralizes. 3) The nanoparticles are stabilized by a shell of the block copolymers, which must efficiently prohibit any Ostwald ripening.

The stability of the microemulsion is significantly disturbed by the mineralization step because of 1) the addition of a chemical reagent necessary to induce mineralization (in the case of metal particle formation this is a reducing agent such as hydrazine or $NaBH_4$), 2) the contribution of the surface energy of the newly formed particle to the total free energy of the system, and 3) the conformational reorganization and changes in the interaction parameters of the block copolymer.

Experimental results published to date have shown that a stable dispersion of small particles in a nonpolar solvent can be achieved relatively easily by means of the block copolymer concept.[6–9] However, formation of the crystallites or clusters was not directly controlled by the block copolymer micelles. Typically, in addition to empty micelles, particles of different size were formed. Apparently, the transformation runs out of control during the second step. In order to overcome the problems

---

[*] Prof. Dr. M. Möller, Dipl.-Phys. J. P. Spatz, Dipl.-Chem. S. Mößmer
Universität Ulm, Organische Chemie III, Makromolekulare Chemie
Albert Einstein Allee 11, D-89069 Ulm (Germany)
Fax: Int. code +(731)502-2883
e-mail: martin.moeller@chemie.uni-ulm.de

0947-6539/96/0212-1552 $ 15.00+.25/0

caused by the instability of the microemulsion, we focused in our approach on the kinetic stability of the micellar associations.

A micellar solution of the block copolymer, with blocks each consisting of 190 monomer units, was mixed with half an equivalent of $HAuCl_4$ per pyridine unit. The solid auric acid was easily taken up by the vigorously stirred solution as the pyridine units became protonated.[5] Reduction to elemental gold was achieved by addition of anhydrous hydrazine dissolved in absolute toluene. Anhydrous hydrazine was employed in order to avoid the microemulsion being affected by the addition of water. Similar attempts described in the literature with aqueous hydrazine suffered from the fact that small water droplets were formed, which could take up gold and block copolymer.[6–9]

The reduction/mineralization process could be monitored by the time dependence of the UV/Vis absorbance of the colloidal solution. $HAuCl_4$ showed an absorbance band at 325 nm, which disappeared after the addition of hydrazine. Formation of the gold particles was indicated by the appearance of a band at 525 nm, which is caused by the surface plasmon resonance of the metal.[14]

When the hydrazine was added in small portions, far less than was needed for complete reduction of the $HAuCl_4$ solubilized by the polymer, the stepwise reduction process could be followed (Fig. 1). The decrease in the intensity of the $HAuCl_4$ peak at around 325 nm was accompanied by an increase in the gold plasmon resonace peak at around 550 nm. Clearly, the plasmon resonance shifted to longer wavelengths with increasing amounts of hydrazine added; this indicates that the gold particles increased in size as more gold was reduced.[14] However, when the addition of hyrazine was stopped, each stage appeared to be stable, as the corresponding spectrum did not change over several hours.

Figure 2a shows a transmission electron micrograph (TEM) of a thin film cast from a solution to which sufficient hydrazine had been added to reduce 70% of the auric acid (corresponding to spectrum E in Fig. 1). The dark spots in the TEM indicate gold particles with a diameter of about 30 nm. The gray disks mark the cores of block copolymer micelles containing the residual $HAuCl_4$. Obviously, the particles are larger than the original cores and also than the remaining micelles. The size of the gold particles (≈30 nm) corresponds to the plasmon resonance with a maximum at around 550 nm (Fig. 1E).[5]

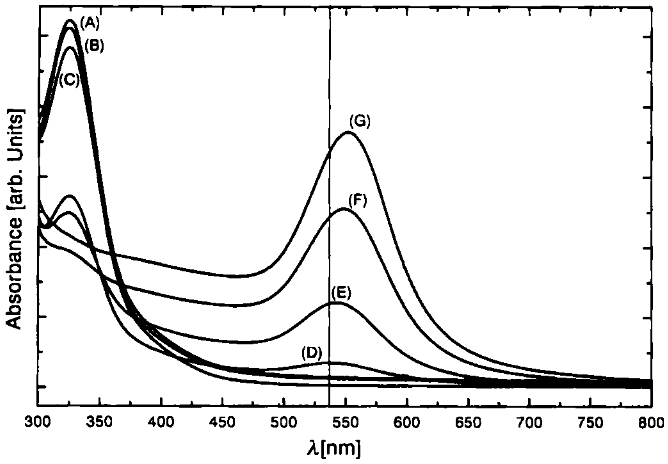


Fig. 1. UV/Vis absorbance spectra of a solution of polystyrene-*block*-poly(2-vinylpyridine) treated with 0.5 equiv $HAuCl_4$ per pyridine unit. The reduction process was initiated stepwise; percentage of gold reduced: A) ≈0, B) ≈2, C) ≈10, D) ≈60, E) ≈70, F) ≈95, G) ≈100.

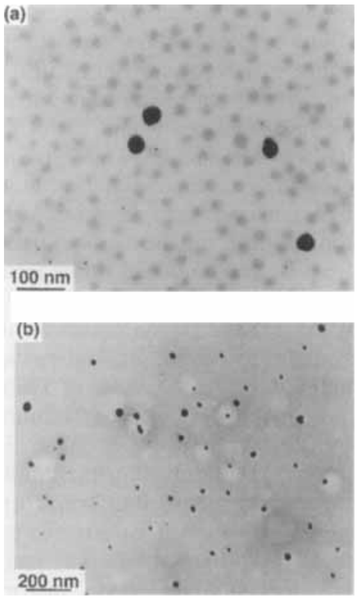


Fig. 2. Transmission electron micrographs of the solution after stepwise reduction as described in the legend of Fig. 1. a) A polymer film obtained from a solution in which 70% of the $HAuCl_4$ had been reduced. Besides the micelles that still contain $HAuCl_4$, particles of 30 nm in diameter are formed. B) A polymer film from a solution in which all $HAuCl_4$ had been reduced.

Figure 2b shows the TEM of a polymer film from a solution with all the acid reduced by hydrazine (corresponding to spectrum G in Fig. 1). The micelles cannot be seen any more because of the lack of contrast. While in Figure 2a the particles are rather uniform in size, a larger distribution of particle sizes is found in Figure 2b.

In a first summary, it can be stated that the stepwise reduction process led to particles whose sizes did not correlate with the size of the original micelles. Apparently, particle formation was not constrained to the micellar compartment. Stepwise addition of hydrazine resulted in uneven formation of gold nuclei throughout the solution. Exchange of $HAuCl_4$ between the different centers was sufficiently rapid to allow the micelles in which no gold nucleus was initially formed to serve as an auric acid reservoir for the growing particles.

In order to initiate reduction/mineralization simultaneously in all micelles, the micellar solution was poured into a toluene solution containing a 35-fold excess of anhydrous N_2H_4. In the first stage, the yellowish solution turned orange-purple, then bluish, and finally a deep purple. The development of the plasmon resonance is depicted in Figure 3. While the absorbance of the $PyH^+ \cdot AuCl_4^-$ ions disappeared almost instantaneously, the band at 525 nm characteristic for the formation of small gold particles arose within about a minute and broadened slowly towards larger wavelengths. Spectrum A gives the absorbance of the initially formed gold particles recorded one minute after

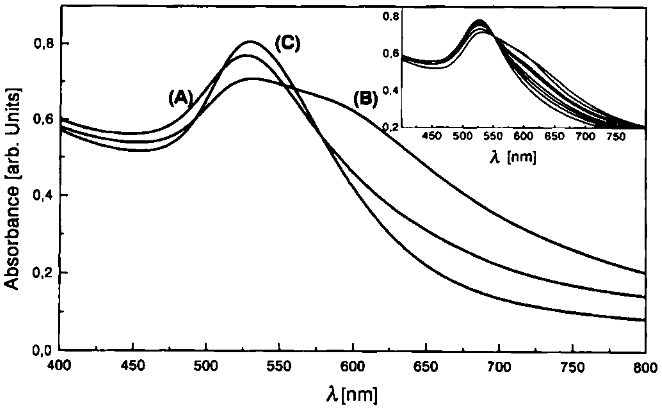


Fig. 3. UV/Vis absorbance spectra of a solution of polystyrene-*block*-poly(2-vinylpyridine) treated with 0.5 equiv $HAuCl_4$ per pyridine unit after reduction with anhydrous hydrazine: A) plasmon resonance of the initially formed gold particles 1 min after reduction, B) after 30 min, and C) after 2 d (final state). The inset shows a series of spectra measured during the first 30 min. The isosbestic point indicates the transformation between two states.

the start of reduction. Spectrum B shows the same colloidal solution after half an hour without stirring. The broad resonance can be deconvoluted into two bands with a maximum around 525 nm and a maximum around 620 nm. After two days we measured spectrum C, which is significantly narrower and has a maximum at 530 nm; this indicates that the gold particles grew in size compared to the initial state.[14] When the excess of hydrazine was reduced by 60%, the development in the color of the solution did not proceed beyond the bluish stage (spectrum B) and remained stable for weeks.

Clearly, the variation in the UV/Vis spectra shown in Figure 3 is not related to the reduction itself, but must involve some structural variation of gold particles. Moreover, the isosbestic point shown in the inset of Figure 3 for the series of spectra measured during the first 24 hours demonstrates that the initial transformation involves two distinct species.

Owing to the high kinetic stability of the ionomer micelles and the corresponding slow transformation of an off-equilibrium state,[5, 17] it has been possible to prepare monomicellar films from the different solutions (stages 1–3) and to observe the gold-loaded diblock copolymer micelles formed in solution by transmission electron microscopy. Figure 4a shows a monomicellar film cast from the solution that gave the spectrum of the initial state (Fig. 3A). The gold particles are uniform in diameter ($d \approx 9$ nm) and are assembled in a two-dimensional hexagonal arrangement with a particle separation of 30 nm. This distance corresponds to the diameter of the $HAuCl_4$-loaded block copolymer micelles.[5] This is confirmed by the scanning force microscopy image in Figure 5a in which the outer contour of the micelles can be discerned.

Figure 4b shows the transmission electron micrograph of a thin film cast from a solution 30 minutes after reduction. The gold particles are arranged in pairs and sometimes in triplets, which themselves form a distorted hexagonal superlattice. The periodicity of the arrangement of about 50 nm demonstrates that the film consists of spherical aggregates with a diameter of 50 nm inside which the gold particles are embedded. The grayish shadow around the gold particles in Figure 4b marks the ionized poly(2-vinylpyridine) core of the polymer spheres.

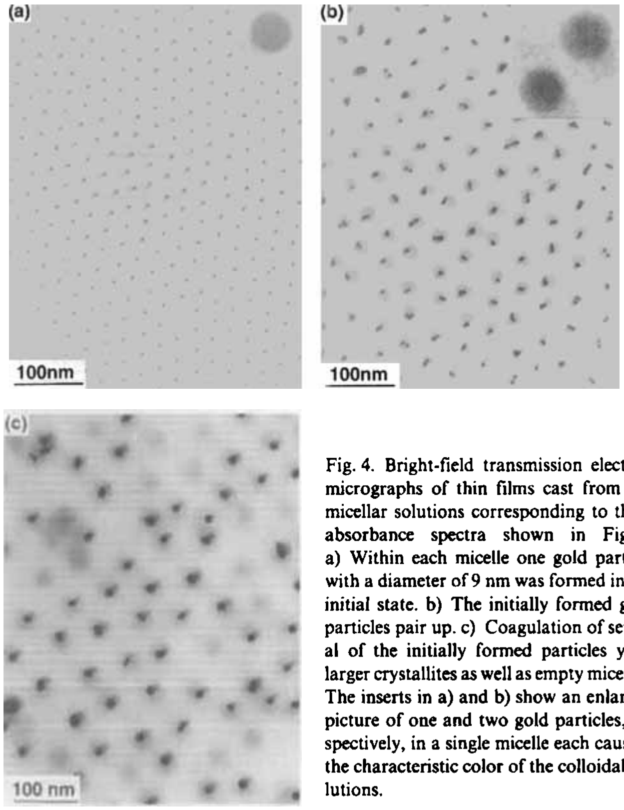


Fig. 4. Bright-field transmission electron micrographs of thin films cast from the micellar solutions corresponding to three absorbance spectra shown in Fig. 3: a) Within each micelle one gold particle with a diameter of 9 nm was formed in the initial state. b) The initially formed gold particles pair up. c) Coagulation of several of the initially formed particles yield larger crystallites as well as empty micelles. The inserts in a) and b) show an enlarged picture of one and two gold particles, respectively, in a single micelle each causing the characteristic color of the colloidal solutions.

Figure 5b shows tapping-mode scanning force micrograph (SFM) of the film that was used for the TEM in Figure 4b. The picture depicts globuli of equal size with a diameter of about 50 nm. Since the 50 nm spheres shown in Figure 5b develop out of the 30 nm micelles each containing one gold particle (Fig. 4a and Fig. 5a), they must form by coagulation of the original micelles. Thus, the formation of the relatively large polymer aggregates containing two or three 9 nm gold particles separated by less than 2 nm can be explained by the coalescence of two or three of the original micelles (Scheme 1).

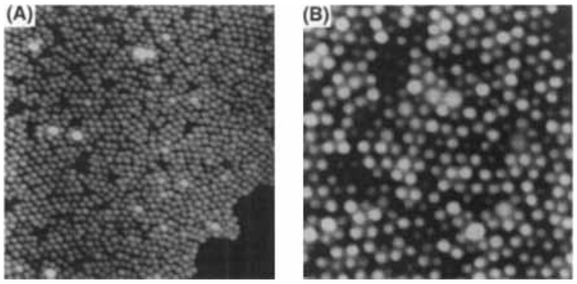
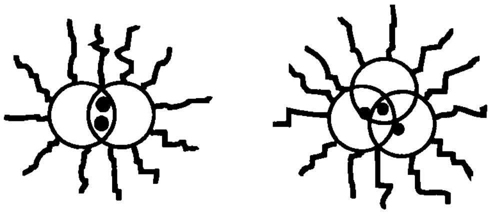


Fig. 5. Scanning force micrographs of the monomicellar films shown in Fig. 4 (scale: image width corresponds to 1 µm): a) Globular micelles with a uniform diameter of 30 nm are observed in the initial stage. b) After 30 min, the original micelles coagulated to nanospheres with a diameter of ≈50 nm.



Scheme 1. Coalescence of two and three micelles.

Figure 4c shows the TEM of a thin film prepared from a solution two days after reduction. Most of the gold particles are coagulated to larger ones with a diameter of up to 13 nm. The grayish shadow around the particles demonstrates that these are still protected by a shell of the block copolymer. This was confirmed by SFM showing that this film also consisted of spherical polymer aggregates. The picture in Figure 4c also shows that empty micelles are present. This is expected because reduced numbers of gold particles are stabilized by significantly fewer block copolymer chains.

So far the data demonstrate that the actual mineralization step of gold in the block copolymer micelle can be subdivided into three different stages. The first stage is the reduction, which can be effected within a few seconds inside the micelles provided that the reducing agent can be added quickly and in excess without destroying the original microemulsion, as was possible in our case. The second stage is the mineralization of one gold particle per micelle, which occurs within a minute and results in the formation of gold particles with a size distribution controlled by the micelles. The third stage is the coagulation of the originally formed micelles. We were able to record the structures shown in Figures 4a and b because the mineralization in each micelle could be performed quickly and independently from the slow coagulation process, which leads to the heterogeneous dispersion shown in Figure 4c.

If the kinetic stability of the block copolymer micelles could be increased, the rate of the coagulation step might be slowed down further. The kinetic and thermodynamic stability of the block copolymer micelles depends primarily on the molecular weight of the block copolymer, N, and the unfavorable interaction parameter, χ, of the core block with the solution (i.e., χN).[18, 19] In the system described here, the incompatibility of the core block is particularly large because of the ionic nature of the protonated pyridine units. Excess hydrazine, however, deprotonates the pyridine units (Scheme 2) and thus destabilizes the micelles; the rate of rearrangement is expected to increase as a result. In addition, the polar hydrazine is selectively solubilized inside the core of the micelles causing swelling. The increased surface cannot be covered by the same number of block copolymer as in the case of the original micelles, and coagulation is the inevitable consequence.

Scheme 2.

Based on the above consideration, the number of micelles that coagulate must depend on how much hydrazine is added to the original microemulsion. In addition it should be possible to slow down the coagulation process or even inhibit it if the excess hydrazine could be removed in time. Indeed, by reducing the excess hydrazine to 7-fold, we were able to prepare a stable solution with two Au particles per micelle structure (Fig. 4b), corresponding to the spectrum B in Figure 3. The UV/Vis absorption spectrum did not change significantly even after keeping the solution for several months at ambient temperature. It was, however, not possible to permanently stabilize an earlier stage by reducing the excess of hydrazine further. With less than a 7-fold excess of hydrazine there was an increase in particle size distribution relative to that obtained when hydrazine was employed in a larger excess, which ensures that mineralization occurs simultaneously in all micelles.

A solution to this dilemma requires controlled removal of the excess hydrazine after the mineralization step or at any desired stage of the coagulation process. This was achieved by adding HCl, which reacts with excess hydrazine to form hydrazine monohydrochloride. The addition of HCl also stabilizes the block copolymer micelles by increasing the degree of protonation of the pyridine units.

All three stages and also further intermediates could be easily trapped by this procedure, which resulted in the formation of solutions that remained stable for weeks. Hydrazine monohydrochloride precipitated and was finally removed by flushing the heated solution with nitrogen. Thus, a third stabilization stage, after the dispersion and mineralization steps, also enabled us to prepare stable solutions with particle structures corresponding to those shown in the bulk films in Figure 4.

Finally, we want to come back to the structure dependence of the plasmon resonance of the gold particles shown in Figure 3. The spectra demonstrate two main points: 1) The spectrum of the monodisperse 9 nm gold particles initially formed shows a maximum (525 nm) which is slightly blue-shifted and a resonance which is broadened compared to that of the larger globular particles in the final state. 2) The UV/Vis spectrum of the intermediate state shows an additional component of the plasmon resonance absorption shifted to longer wavelengths relative to the initial and final states. This can be explained by the electromagnetic interaction between dipole pairs of gold particles isolated within the block copolymer micelles as depicted in Figure 4b. Because of the close proximity of the paired particles, there is a distinct electromagnetic coupling of the dipole oscillations. Theoretically, counting only the in-phase excitation modes, we expect a longitudinal (at around 620 nm) and a transverse mode (at around 525 nm).[14]

It may be anticipated that the interesting structural variations present in the thin films shown in Figure 4b could form the basis for novel functional materials. For example, the pairwise interaction of the dipole scattering fields of gold particles could be used to pole the otherwise isotropic nanospheres by means of electromagnetic forces.

Experimental Procedure

Sample preparation: Polystyrene-*block*-poly(2-vinylpyridine) was synthesized by anionic polymerization [21]. A 0.5 wt% solution of the block copolymer in dry toluene was mixed with 0.5 equiv of $HAuCl_4 \cdot H_2O$ per pyridine unit. The mixture was stirred for at least 24 h to allow complete dissolution of the gold salt in the cores of the block copolymer micelles. The solution was diluted to 1 mg mL^{-1} by adding further toluene. An aliquot of this solution (2.5 mL) was added to 0.1 vol% anhydrous N_2H_4 in toluene (5 mL) under vigorous stirring (the anhydrous hydrazine was prepared by thermolysis of hydrazine cyanurate on a high-vacuum line [16]). If desired for colloidal stability, HCl (15 µL, 38 wt%, analytically pure) was added to the solution after reduction. Hydrazinium chloride (N_2H_5Cl) precipitated and was finally removed by flushing the heated solution with nitrogen. Thin films were prepared by putting a drop of the solution onto an electron microscopy grid which was coated with a thin layer of carbon and which was in direct contact with a soaking tissue to remove the solution immediately. The film thickness was controlled by varying the concentration.

Analysis: Bright-field transmission electron microscopy images were recorded with a PHILIPS EM400T microscope operated with 80 kV. In order to minimize the destruction of the polymer by the electron beam, the electron beam intensity was kept as low as possible (second condenser lens: 50 Pt, objective lens: 30 Au). Scanning force microscopy with the same samples (grids) that had been used for electron microscopy were recorded by means of a Nanoscope III from Digital Instruments operating in the tapping mode [20]. UV/Vis absorption spectroscopy was carried out with a 256 array UV/Vis Spectrometer from Carl Zeiss or with a Lambda 16 UV/Vis Absorption Spectrometer from Perkin Elmer.

Acknowledgment: We are thankful for the help of the Abteilung Elektronenmikroskopie, Universität Ulm, for experimentel support in carrying out the EM measurements. The work was supported by the Deutsche Forschungsgemeinschaft (SFB239, Teilprojekt F5) and the Fond der Chemischen Industrie.

Received: June 28, 1996 [F443]

---

[1] D. S. Godovsky, *Advances in Polymer Science* **1995**, *119*, 79.
[2] J. H. Fendler, F. C. Meldrum, *Adv. Mater.* **1995**, *7*, 607.
[3] Y. Ng Cheong Chan, R. R. Schrock, R. E. Cohen, *J. Am. Soc.* **1992**, *114*, 7295.
[4] J. P. Spatz, A. Roescher, M. Möller, *Adv. Mater.* **1996**, *8*, 337.
[5] J. P. Spatz, S. Sheiko, M. Möller, *Macromolecules* **1996**, *29*, 3220.
[6] M. Antonietti, E. Wenz, L. Bronstein, M. Seregina, *Adv. Mater.* **1995**, *7*, 1000.
[7] M. Antonietti, S. Förster, J. Hartmann, S. Oestreich, *Macromolecules* **1996**, *29*, 3800.
[8] A. B. R. Mayer, J. E. Mark, *Polymer Preprint* **1996**, *37*, 459.
[9] A. Roescher, M. Möller in *Nanotechnology*, ACS Symposium Ser. 622 (Eds.: G.-M. Chow and K. E. Gonsalves), Washington **1996**.
[10] M. Moffit, A. Eisenberg, *Chem. Mater.* **1995**, *7*, 1178; *ibid.* 1185.
[11] F. S. Bates, G. H. Frederickson, *Ann. Rev. Phys. Chem.* **1990**, *41*, 525.
[12] M. K. Chow, C. F. Zukski, *J. Coll. Int. Sci.* **1994**, *165*, 97.
[13] J. P. Wilcoxon, R. L. Williamson, R. Baughman, *J. Chem. Phys.* **1993**, *98*, 9933.
[14] U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, Springer **1995**, Heidelberg.
[15] G. Schmid, *Chem. Rev.* **1992**, *92*, 1709.
[16] E. Nachbaur, G. Leiseder, *Monatsh. Chem.* **1971**, *102*, 1718.
[17] D. Nguyen, C. E. Williams, A. Eisenberg, *Macromolecules* **1994**, *27*, 5090.
[18] L. Zhang, A. Eisenberg, *Science* **1995**, *268*, 1728.
[19] J. P. Spatz, M. Mößmer, M. Möller, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1510.
[20] J. P. Spatz, S. Sheiko, M. Möller, R. W. Winkler, P. Reineker, O. Marti, *Nanotechnology* **1995**, *6*, 40.
[21] H. Künstle, *Block Copolymer Composites with Semiconductor Nanocrystals*, Ph.D. Thesis, Holland **1993**.