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ORIGINAL CONTRIBUTION

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Cobalt nanoparticles in block copolymer micelles: Preparation and properties

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Abstract The preparation and properties of Co nanoparticles in polystyrene(PS)-poly-4-vinyl-pyridine(PVP) micelles were studied. Elementary Co was generated by two methods: (i) by reduction of micelles loaded with $CoCl_2$, and (ii) by thermal decomposition of $Co_2(CO)_8$ in micellar solutions of such block copolymers. Co particles formed by both processes are effectively stabilized by the block copolymer matrix and do not aggregate. For $CoCl_2$ as a Co-source, the formed particles have a size less than 1 nm. Thermal treatment of such dried polymers at 200 °C for 2 h leads to spherical particles of 3–5 nm in size. The polymeric hybrid materials prepared in this way display remarkably high values of magnetization at rather low Co contents in the polymer, i.e., we obtain a tenfold increase of the specific magnetization density. $Co_2(CO)_8$ as a Co source, results in a more complex behavior. $Co_2(CO)_8$ dissolves in the solvent as well as in the micelle core where it is converted to an cationic–anionic complex involving the 4-VP units. The shape and size of the Co nanoparticles formed by thermolysis can be controlled by the balance of 4-VP/Co and can be varied from spherical particles in the limit of lower Co loads being mainly attached to the micelle core to a star-like and cubic morphology in case of excess of $Co_2(CO)_8$. Both superparamagnetic and ferromagnetic materials can be prepared. For ferromagnetic samples coercive force varies from 250 to 475 Oe depending on Co content and polymer sample.

Key words Cobalt nanoparticles – block copolymer micelles

Introduction

The interest of researchers in colloidal metals has grown in the last years causing the appearance of a lot of new controlled methods for colloid metal synthesis. In particular, nanosized face-centred-cubic (f.c.c.) Co particles gain a very special, technologically driven interest, which is due to their high spin density and the resulting extraordinary magnetic properties. For instance, Co particles in a size range of 1–10 nm exhibit superparamagnetic behavior and are highly promising for preparation of "mild" magnets for controlling devices. The synthesis of Co nanoparticles has been improved for many years, and a paramount successful procedure for this was the formation of particles under thermal decomposition of $Co_2(CO)_8$ dissolved in a hydrocarbon solvent containing a suitable polymeric material [1, 2]. This method allowed the preparation of spherical particles or chains of particles, depending on polymer–solvent–metal balance, but did not permit the subtle regulation of shape and size of Co particles which very

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strongly influences the magnetic properties, e.g. coercive force and absorption bandwidth of electromagnetic oscillations. Varying the asymmetry parameters one might move the absorption band position which will, in turn, permit to control the magnetic properties of polymeric materials.

A recent trend in the synthesis of colloidal particles is the process of metal particles formation in the amphiphilic block copolymer micelles. This approach was successfully elaborated recently by some research groups, including the authors [3–8]. These works, however, were related to noble metal colloids or semiconductors, and not a single paper dealt with magnetic particles of less noble metals.

This paper reports the preparation and properties of Co nanoparticles in polystyrene-poly-4-vinylpyridine (PS-b-P4VP) micelles where elementary Co was generated in two ways: (i) by reduction of micelles loaded with $CoCl_2$, in analogy with preparation of noble metal colloid particles, and (ii) by thermal decomposition of $Co_2(CO)_8$ in micellar solutions of such block copolymers.

Experimental

Materials and polymer synthesis

Unhydrated $CoCl_2$ was prepared by drying $CoCl_2{\cdot}6H_2O$ through interaction with $SOCl_2$ [9]. $Co_2(CO)_8$ was purified by crystallization from pentane during cooling. Toluene was refluxed for 4 h under Na and subsequently twice distilled under Na; THF was predried with KOH, then refluxed under Na/benzophenone up to the appearance of violet color and distilled prior to use. Superhydride, $Li(C_2H_5)_3BH$ (1 M solution in THF), was used as the reducing agent as received (Aldrich). The synthesis of PS-b-P4VP block copolymer was carried out by the procedure described in [10]. For preparation of metal colloids two samples of PS-b-P4VP block copolymers were used: PS-1,2 which has $M_n = 127400$, $M_w = 149000$, $U = 1.17$, and a relative 4-VP content of 21 mol%; and PS-3,4, having $M_n = 19400$, $M_w = 22500$, $U = 1.16$, and a relative 4-VP content of 34 mol%.

Preparation of cobalt colloid particles

Samples derived from $Co_2(CO)_8$ were prepared in Schlenk tubes equipped with a Teflon stirring bar, a reflux condenser, and a bubble counter. The polymer solution (0.05 g in 8 ml of toluene) was evacuated under freezing and then inflated by argon. A distinct amount of $Co_2(CO)_8$ to keep the desirable ratio Co:N was added and three-time degassed under freezing. Afterwards, the reaction tube was filled with argon and heated at 110 °C for 1 h.

The incorporation of $CoCl_2$ into PS-1,2 micelles in toluene of THF solution was carried out by procedure described in [3, 4] for other salts. Polymer solution (0.05 g in 8 ml of toluene or THF) was prepared in a two-neck flask containing stopcock, rubber septum, and a Teflon stir bar. Oxygen removal was achieved by a three-time degassing procedure and storage under argon. $CoCl_2$ (0.0133 g, loading molar ratio Co:N = 1:1) was added in argon counterflow.

After stirring for two weeks at room temperature, a blue solution was obtained finally, which was filtered through 0.45 μm Millipore filter units. After an additional degassing procedure, the salt was reduced by $Li(C_2H_5)_3BH$ (5 mol excess). Handling with degassed samples during reduction provides the further stability of metal colloids under air because the interaction of Co particles formed with air or water leads only to the formation of thin oxide film on the particle surface. The presence of air or water during reduction or thermolysis results in the complete Co oxidation.

For FTIR and elemental analysis examination, an aliquot of the final solution after filtration and before reduction was precipitated in petroleum ether, washed and dried in a vacuum dessicator under paraffin and P_2O_5.

Ferromagnetic resonance (FMR) examination

Measurements were performed in ampoules filled by solutions of the samples studied in a special argon box (to prevent the surface oxidation of nanoparticles which could influence the FMR line width), then frozen and sealed under vacuum. FMR was carried out with a Varian E-12 spectrometer. The whole examination includes several operations: the recording of FMR spectra of liquid, frozen and solid samples at room and at liquid nitrogen temperatures.

The qualitative data of coercive force of Co-particles were obtained by a set of FMR recording in low fields. The beginning of the first record exhibits a zero level of resonator breakdown because of absence of the macroscopic magnetization. The second record is produced in the opposite direction of magnetic field change. The end level of the second record usually does not coincide with the beginning of first one as the result of a magnetic hysteresis loop. The next operation is the rotation of a sample through 180° in zero magnetic field. The recording pen registers the resonator breakdown due to the rotation of the macroscopic magnetic orientation of the sample. The value of the magnetic field strength is equal to the coercive force when the pen marks zero level again in the third record in the direction of magnetic field increase.

Symmetric positions with respect to zero level of the second and third circles are important for the correct definition of the coercive force. Measurements were usually performed at 77 K in the frozen magnetic liquids.

Transmission electron microscopy and X-ray fluorescence

Samples were prepared by evaporation of 10^{-4} mol/L toluene solutions under air. A drop of solution was placed on a copper sample grid of the electron microscope. After drying, electron micrographs of the sample were prepared with a Zeiss 912 Omega electron microscope. A magnification of 125 000 was used. Particle sizes were determined by processing from the photographs.

Co content was examined by XRF measurements employing a VRA-30 spectrometer (Carl Zeiss Jena) with a Mo anode, a LiF crystal analyzer and a SZ detector. The line used for analysis was Co-Kα. Samples (for comparison and for analysis) were prepared by mixing 1 g of polystyrene with 10–20 mg of standard substances. The time of calculation was 10 s.

Results and discussion

The dissolution of metal salts in the solution of PS-b-P4VP micelles which are otherwise insoluble in the solvent means the incorporation of these salts only in micelle cores, as described in our previous papers [3, 4]. The uptake of most of the salts, besides Au- and Ag-salts, into the micelle core is however very slow, and their content inside the micelles is limited [3]. Solvents in which salts are soluble can be also used to provide a faster uptake. Therefore both toluene and THF solutions of PS-1,2 are employed for the introduction of $CoCl_2$ into micelles. PS-1,2 was chosen because it forms rather large, strongly segregated micelles in both solvents, unlike PS-3,4 which forms micelles only in the poorer solvent for the core block, toluene. It was found that in toluene solutions a significant quantity of $CoCl_2$ remains as undissolved crystals in the reaction flask even after two weeks of stirring. The dissolution of $CoCl_2$ in THF occurs almost immediately after adding.

The FTIR spectrum of the polymer prepared by interaction of PS-1,2 with $CoCl_2$ in toluene (PS-1,2-Co-1) in the ratio Co:N = 1:4.07 (by elemental analysis data) shows the weakening of bands characteristic for pyridine units (1555 and 1415 cm^{-1}) and the appearance of new bands at 1637 and 1615 cm^{-1} which are responsible for stretching of pyridine complexes with metal salts. A similar behavior was observed for the Au-salts [3]. Strong new bands show that the complete metal salt is coordinated with VP units, although the solubilization of $CoCl_2$ in micelle core proceeds very slowly and the metal load of the micelle core is also low. On the contrary, the metallation in THF results in the formation of complex with VP units where the THF is involved as a ligand which is confirmed by FTIR data [11]. Because $CoCl_2$ is soluble in THF, the salt is at first present both inside and outside of the micelles. However, with time (about two weeks), the major part of Co salt becomes a coordinated with VP units of the micelles cores: the precipitation of polymer and elemental analysis of the precipitate confirms that 85 mol% of the Co salt is inside the micelles.

The reduction of Co^{2+} ions in block copolymer micelles derived from PS-1,2 both in toluene and THF was carried out by super-hydride. As found previously for Au and Pd colloids [3, 4], super-hydride reduction of $CoCl_2$ provides the formation of very small, non-ferromagnetic particles. As discussed above, the magnetic properties of Co particles are strongly influenced by their size, and *vice versa*, ferromagnetic resonance (FMR) allows examination of particle size, especially as a correlation exists between FMR line width and the particle size [12, 13]. Particles smaller than 1 nm exhibit magnetic disorder [10], and are thus undetectable by FMR. The data of elementary analysis and FMR for the Co nanocrystals derived from PS-1,2 and $CoCl_2$ are summarized in Table 1.

PS-1,2-Co-1 containing 2.34 wt% Co includes Co particles with size less than 1 nm. For the sample PS-1,2-Co-2 prepared in THF and containing 8.26 wt% Co (in dried state), reduction by super-hydride leads to the appearance of a very weak and broad signal in the FMR spectrum. The position of the absorption maximum H_0 (about 2550 Oe) and FMR line width ($\Delta H = 1250$ Oe) are characteristic for the formation of some large, slightly asymmetric particles. Both PS-1,2-Co-1 and PS-1,2-Co-2 were precipitated after reduction in petroleum ether. Dried Co-containing polymers were heated in vacuum-sealed ampoules for 2 h at 200 °C which exceeds the glass transition temperature T_g of both blocks ($T_g^{PS} = 93\,°C$; $T_g^{PVP} = 142\,°C$). After this heating cycle, the samples were reexamined by FMR. In both cases such heating leads to the formation of spherical particles ($H_0 = 2950$ Oe; a value of 2975 Oe is typical for spherical particles [12]) with a size of about 3–5 nm for PS-1,2-Co-1 and PS-1,2-Co-2. Table 1 shows very high values of coercive force for these samples. Similar values of H_c have been described for Co particles prepared in stabilizing polymers at a tenfold higher Co content (75 wt%) when Co particles form chains of 20 nm Co particles [2]. In this paper it was speculated that the high coercive force was provided by the specific small distance of separation between the primary particles (about 2 nm). For the present case of Co particles in PS-b-P4VP micelles, the spherical Co particles formed in solid micelle

Table 1 The data of elemental analysis and FMR for f.c.c. Co species derived from PS-1,2 and $CoCl_2$*)

Sample	Co in solid polymer [wt%]	N:Co (mol) in solid polymer	H_o, [Oe]	ΔH, [Oe]	H_c, [Oe]	Solvent	Aggregate state
PS-1,2-Co-1	2.34	4.07:1	—	—	0	Toluene	Liquid
	2.34	4.07:1	2975	650	425	Toluene	Solid
PS-1,2-Co-2	8.26	1.15:1	2550	1250	0	THF	Liquid
	8.26	1.15:1	2950	500	675	THF	Solid

*)According to loading Co:N = 1:1 (mol).

Table 2 Elemental analysis and FMR data for f.c.c. Co-containing PS-b-P4VP toluene solutions prepared from $Co_2(CO)_8$

N:Co [mol] according to loading	Co in solid polymer [wt%]	H_o, [Oe]	ΔH, [Oe]	H_c, [Oe]
PS-3,4				
2:1	6.55	—	No signal	0
1.5:1	8.42	2950	1250	0
1.75:1	7.23	2950	700	0
1:1	10.22	1945	825	250
1:2	12.56	2275	625	250
PS-1,2				
1.5:1	5.83	2950	1125	0
1:1	6.58	2200	1250	300
1:2	7.23	2425	550	350
1:3	7.89	2263	700	475

cores are not arranged in chains, as confirmed by the values of the position of the absorption maximum H_0. In addition, the low content of Co in polymer (especially for PS-1,2-Co-1) in combination with the high stabilization power of block copolymers prevent the aggregation of Co particles.

By analogy with the approach described in [1, 2], the formation of Co colloids by thermal decomposition of $Co_2(CO)_8$ in the PS-b-P4VP toluene solutions was also studied. $Co_2(CO)_8$ is soluble in toluene, and it is straightforward to assume that it is present both inside and outside the micelles. FTIR spectra of PS-b-P4VP after adding $Co_2(CO)_8$ in carbonyl region does not correspond to $Co_2(CO)_8$ [15] and shows mainly one wide band at 1884 cm^{-1} which is characteristic of anionic species $Co(CO)_4^-$ of cationic–anionic complexes which can form in DMF [16] and pyridine [17]. Therefore, on the basis of the FTIR data we suggest that dissolution of $Co_2(CO)_8$ in block copolymer solution leads to the formation of a similar cationic–anionic complex with VP units with the structure $[Co(VP)_6]^{2+}[Co(CO)_4]_2^-$, where – due to the sterically demanding polymeric ligands involved – the complex is not expected to be perfect. Since P4VP is localized in the micelle core, such a complexation does not lead to the precipitation of polymer, but provides the interaction of Co compound with polymer molecules which, in turn, can furnish the size and shape control during Co particle formation.

Table 2 summarizes the elemental analysis and FMR data on Co particles prepared from $Co_2(CO)_8$ and PS-b-P4VP. It is seen that at feeding ratios PVP:Co equal to 15:1 and 1.75:1, spherical particles are formed: the position of absorption maximum H_0 corresponds exactly to that observed for spheres. Moreover, such molar ratios also provide the preparation of superparamagnetic particles, since $H_c = 0$.

For a feeding ratio N:Co = 2:1 (for PS-3,4) the formed Co particles are neither ferromagnetic nor superparamagnetic (i.e., particle size is less than 1 nm), and only after 2 h heating at 200 °C in the solid state, a FMR signal appears characterized by the parameters $H_0 = 2970$ Oe, $\Delta H = 275$ Oe, which is an evidence of the formation of spherical particles of 1–3 nm in size [16].

The increase of the Co content in the reaction medium to the extent of balancing or even increasing the ratio of N:Co leads to the change of the position of absorption maximum H_0 which indicates the formation of anisometric particles. These samples exhibit ferromagnetic behavior: their coercive force varies from 250 to 475 Oe depending on Co content and polymer sample. These values are almost in the range of the magnetic Co particles reported in [2], but those data were obtained for dried samples with Co content 75 wt% in solids, as compared to the magnetic liquids (in frozen state) where the highest Co content is 12.56 wt%. Dried samples obtained after precipitation of the reaction solutions of PS-1,2 (Co:N = 1:1) and PS-3,4 (Co:N = 1:1) do not show a change of FMR line widths after 2 h heating at 200 °C. This means that the large Co particles formed in these samples are effectively stabilized by the block copolymer matrix and do not aggregate. From the analysis of the H_c values given in Table 2 it is concluded that the molecular weight of

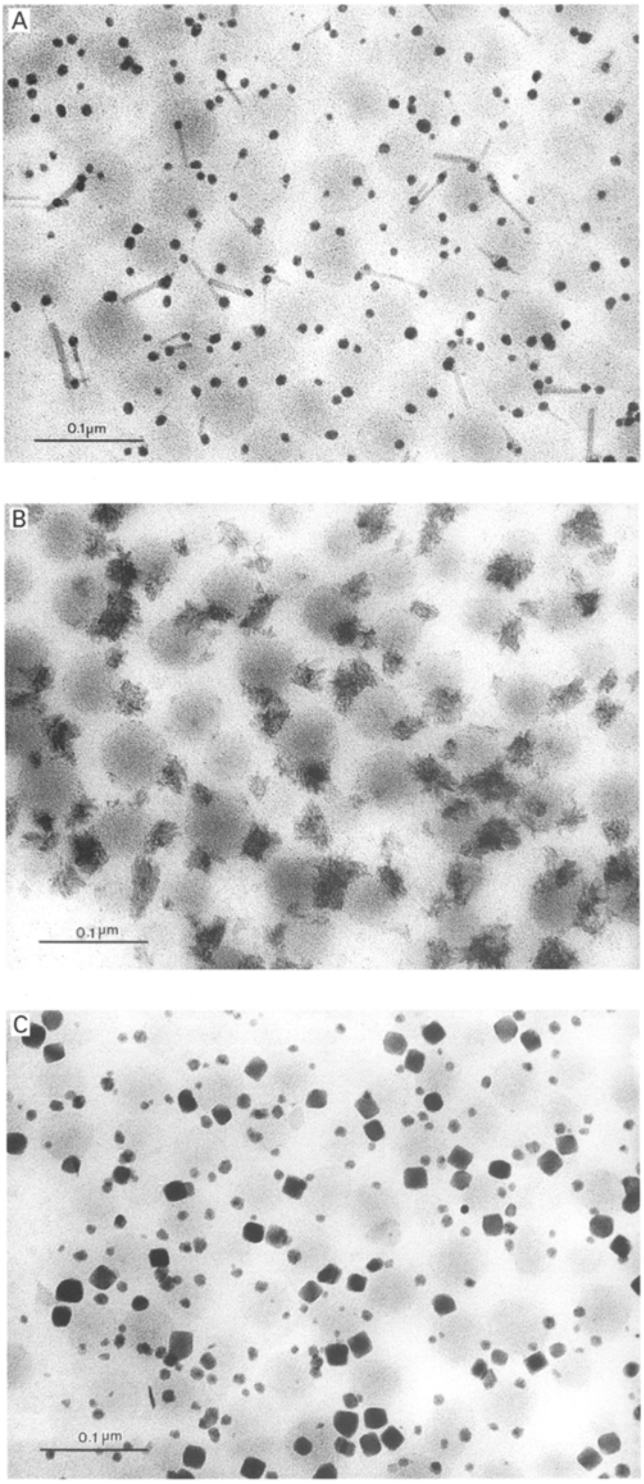

Fig. 1 TEM micrographs of Co nanoparticles prepared in PS-1,2 at molar ratios N:Co = 1:1 **A**, 1:2 **B**, 1:3 **C**

the stabilizing polymer (or micelle size) only marginally influences the magnetic properties of formed Co nanoparticles.

TEM was employed to clarify the shape and size of particles formed. Figure 1 shows TEM images of Co particles prepared in PS-1,2 micelles after $Co_2(CO)_8$ incorporation at three feeding ratios N:Co: 1:1 (A), 1:2 (B), and 1:3 (C). For a feeding ratio of N:Co = 1:1 mainly spherical particles form (a slight asymmetry is seen) with a mean diameter of 10 nm (with a standard deviation of 1.5 nm, from a sample population of 150). Size distribution for this case is narrow. The feeding ratio N:Co = 1:2 brings to the formation of fluffy, star-like aggregates (about 20–23 nm in diameter having an irregular shape), which seem to consist of primary, anisometric clusters. This particle morphology is also supported by the comparably low ΔH-value listed in Table 2. The situation changes again for the feeding ratio N:Co = 1:3 which produces two kinds of particles: smaller spheres and bigger cubes. Evaluation of 150 particles gave a mean diameter of spheres of 10 nm (same size and polydispersity like the spherical particles at the 1:1 feed), and cubes with a mean size of 21 nm (with a standard deviation of 1.5 nm). The size distribution for both kinds of particles is quite narrow. In some pictures it is seen that the cubic particles have a strong tendency to chain or trail formation, lining up a number of cubes. From TEM micrographs it is also seen that the spherical particles (N:Co = 1:1) are mainly located in the micelle cores. Even the larger stars (N:Co = 1:2) seem to start their growth from the cores. At the molar ratio N:Co = 1:3, only the cubic particles are placed outside of micelle cores, while the spherical particles still form in the cores. Obviously, the feeding ratio heavily influences the particle size and shape, but in all cases the polymeric amphiphiles take part in the particles formation, and the following reaction scenario can be given. $Co_2(CO)_8$ is present both in solution and in the micelle core (as a complex). After rapid heating to 110 °C (decomposition starts at 60 °C), elementary Co is formed which quickly aggregates to Co clusters and spherical particles. The formation of such particles is strongly controlled by interaction with 4-VP units: for high relative 4-VP contents, small superparamagnetic particles exhibiting very high coercive forces are obtained. For higher Co-loads, the $Co_2(CO)_8$ being present in the continuous phase acts as a Co-source which feeds further growth of the particles, and either spherical colloids of 10 nm size or star-like clusters are obtained. Only in case of a larger Co-excess, colloids also nucleate in the continuous solvent phase, and cubic colloids are formed.

Conclusions

Reduction of Co salts or thermal decomposition of $Co_2(CO)_8$ in block copolymer micelles of polystyrene-poly-4-vinylpyridine in selective solvents allows the preparation of Co particles with various shapes and sizes. The resulting block copolymer stabilized nanoparticles – as the other systems described in the literature – are very stable, can be handled as a solution or powders or in polymer films, and they display either superparamagnetic or ferromagnetic behavior.

For $CoCl_2$ as a Co-source, the formed particles have a size less than 1 nm in diameter. Thermal treatment of such dried polymers at 200 °C for 2 h leads to spherical particles of 3–5 nm diameter. The polymeric hybrid materials prepared in this way display remarkably high values of magnetization at rather low Co contents in the polymer, i.e., we obtain a tenfold increase of the specific magnetization density. $Co_2(CO)_8$ as a Co source, results in a more complex behavior. $Co_2(CO)_8$ dissolves in the solvent as well as in the micelle core where it is converted to an cationic–anionic complex involving the 4-VP units.

Consequently, the shape and size of the Co nanoparticles formed by thermolysis can be controlled by the balance of 4-VP/Co and can be varied from spherical particles in the limit of lower Co loads being mainly attached to the micelle core to a star-like and cubic morphology in case of excess of $Co_2(CO)_8$.

Due to the extraordinarily high values of coercive force and magnetization, the ability to control particle size, shape and the related type of magnetism, and the possibility to produce both very stable magnetic fluids as well as magnetic polymeric films and coatings, further development of block–copolymer/metal colloid hybrids seems to be a very promising approach to develop materials with high technological relevance.

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