Polymer Nanocomposites Containing Superstructures of Self-Organized Platinum Colloids

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Colloidal platinum (diameter 1-2 nm) in styrene was prepared in situ by reduction of a platinum(II) compound followed by partial evaporation of styrene. The resulting dispersions were purified from the reaction sideproducts, and ammonium *O*,*O*'-dialkyldithiophosphates of different chain length or octadecanethiol was added. Polymerization was started with a radical initiator. Several parameters were varied and, particularly in the presence of long-chain dialkyldithiophosphates, self-assembled superstructures of metal colloids appeared at certain conditions in the resulting poly(styrene)-platinum nanocomposites. Unusual hollow shell structures of typical diameters of 50-300 nm were found, which phenomenologically resembled bilayer vesicles in aqueous solutions, although the formation mechanism of the bilayers and the superstructures in the nanocomposites is considered to differ. It is supposed that the formation of the superstructures in the nanocomposites is induced by crystallization of alkyl chains adsorbed at the platinum surface below monolayer coverage.

Introduction

Materials consisting of a polymer with incorporated inorganic particles of dimensions below 50-100 nm (nanocomposites) have been described more than 150 years ago;¹ however, they have attracted attention particularly in the past decade. In most cases, the matrix incloses randomly distributed particles or randomly composed aggregates of particles. Comparatively little examples are known so far, in which the particles form regular or anisotropic structures. For instance, uniform silica particles, surface-modified with methacrylate groups, can crystallize in methyl acrylate.²⁻⁵ Upon polymerization, induced by light at room temperature, the regular lattice of the particles is retained. The nanocomposites, which contained 35-45% w/w of silica, are birefringeant and diffract light according to Bragg's equation. An increase in the particle concentrations results in a decrease in the lattice spacings which is connected with a hypsochromic shift of the absorption maximum due to the diffracted light.

Ultrathin nanocomposite films with a regular distribution of inorganic colloids have been obtained with the help of block copolymers in which the blocks segregate into regular structures.^{6–11} In these cases, metal ions or metal complexes show a specific affinity to one of the blocks. The metal entities were then exposed to other reagents in order to prepare the desired particles. For example, Pb^{2+} ions were converted with H_2S to produce PbS, or [AuCl₄]⁻ was reduced to gold. The particles thus obtained remain in the respective blocks, i.e., the particles adopt the patterns formed by the polymer blocks. Lamellar or hexagonal arrangements of particles were achieved in this way.

Between 1890 and 1940, the preparation and characterization of uniaxially oriented arrays of nanoparticles in natural polymers was reported.^{12–21} Typically, plant or animal fibrils were impregnated with various metal salts, which were subsequently reduced in situ to yield metal particles. Gold, silver, platinum, and several other metals were employed. The colors of the resulting nanocomposites observed upon transmission of polarized light depend on the angle between the polarization plane and the orientation axis of the fibrils. It was recognized early that the size of the generated primary particles is in the



C₁₈thiol

Figure 1. Chemical structures and acronymes of the complexing agents used in this work.

nanometer range $(5-14 \text{ nm})^{20}$ and that the particles aggregate to oriented structures, which causes the dichroic behavior of the samples.^{14,17,20,21} More recently, similar effects have been described when dodecanethiol-coated silver or gold colloids were embedded in poly(ethylene), which is subsequently subjected to solid-state drawing at 120 °C.^{22–27} Under appropriate conditions, this process induces an orientation of the metal particles into arrays parallel to the drawing direction.

Here, we describe the preparation of self-assembled superstructures of platinum colloids in poly(styrene) which markedly differ from those mentioned above. The self-organization of the platinum colloids was induced by addition of sulfur-containing compounds (Figure 1), which are assumed to coordinate on the particle surfaces by their sulfur-containing headgroups. The influence of the compounds themselves as well as the influence of other parameters on the formation on the superstructures was investigated.

Experimental Procedure

Chemical Substances. All chemical substances were purchased from Fluka or Aldrich and used without further purification, if not otherwise indicated. The ammonium O,O'-dialkyldithiophosphates were synthesized according to the literature.²⁸

Synthesis of Tris(styrene)platinum(0). Tris(styrene)platinum-(0) was prepared in situ approximately following a procedure described in the literature.^{29,30} A mixture of *cis*-dichlorobis-(styrene)platinum(II) (3.00 g, 6.3 mmol, synthesized according to the literature³¹) and freshly distilled styrene (120 mL) was exposed to triphenylsilane (3.29 g, 12.6 mmol) and stirred for 30 min. A mixture of concentrated ammonia (30 mL) and water (250 mL) was added, and the two-phase system was vigorously stirred for 90 min. The organic phase was separated in a separatory funnel, vigorously stirred with water (250 mL), separated again, and filtered through 15 cm Alox basic (activity I) which was situated in a pipe of 4 cm diameter. After filtration, the Alox was rinsed with freshly distilled styrene (150 mL), and the eluate was combined with the previous fraction, yielding a total mass of 150 (\pm 10) g.

To determine the concentration of platinum, the solvent of 5 g of tris(styrene)platinum(0) solution was evaporated at room temperature under reduced pressure (ca. 0.01 mbar). The black residue was dissolved in warm aqua regia, and the orange solution was diluted in 0.1 M hydrochloric acid (700 g). The platinum content in these solutions was analyzed by the analytical service of the Laboratory of Inorganic Chemistry at ETH Zürich. Platinum concentrations ranging from 0.47 to 0.58% w/w were found in various tris(styrene) platinum(0) solutions.

Preparation of Colloidal Platinum. Purified tris(styrene)platinum(0) solutions, as described above, were concentrated to a platinum content of ca. 8% w/w at room temperature under reduced pressure (ca. 0.01 mbar). During this process, the individual platinum atoms agglomerate and the originally slightly yellow solutions adopt the brown color of colloidal platinum. The exact concentrations indicated in the text for nanocomposite preparation were obtained by dilution of concentrated solutions with freshly distilled styrene.

Preparation of the Nanocomposites. Azobis(isobutyronitrile) (AIBN, 10 mg, 61 μ mol) and ammonium *O*,*O*'-dialkyldithiophosphate (C_xdtpNH₄) or octadecanethiol (C₁₈thiol) in the quantities indicated in the text were placed in a test tube which had been inserted in a Schlenk tube under argon atmosphere (Figure 2). To this mixture, 1 g of colloidal platinum dispersion in styrene with the platinum concentrations indicated in the text was added under argon and heated to 60 °C, whereupon the reaction mixture slowly solidified. After 3 days, the test tube was removed and broken in order to access the nanocomposite.

Transmission Electron Microscopy (TEM). To prepare the samples for investigations with TEM, the nanocomposites were cut first with a razor blade to a regular tetragonal pyramid. Thin slices of approximate dimensions of 100 nm \times 0.5 mm \times 0.5 mm were cut with a Reichert Ultracut Microtome using a diamond knife. TEM images were recorded with a Philips EM 301 electron microscope operating at an acceleration voltage of 80 keV.

Gel Permeation Chromatography (GPC). For GPC measurements, the nanocomposites were dissolved in tetrahydrofuran, and the molecular weights were determined by the analytical service of the Institute of Polymers of ETH Zürich using poly-(styrene) standards.

Results

The production of the nanocomposites is derived from a method that has been described for the preparation of nano-



Figure 2. Schematic representation of the nanocomposite synthesis.



Figure 3. Reaction scheme for the preparation of the poly(styrene)-platinum nanocomposites.

composite foams consisting of poly(styrene) with randomly dispersed platinum particles²² (Figures 2 and 3). First, tris-(styrene)platinum(0) dissolved in styrene was prepared in situ by quantitative reduction of *cis*-dichlorobis(styrene)platinum-(II) with triphenylsilane in styrene. After removal of the reaction side products, the tris(styrene)platinum(0) was destabilized by partial removal of styrene at room temperature and reduced pressure, inducing an aggregation of the platinum atoms to colloids.

To induce superstructures of self-organized colloids, alkyl compounds with a sulfur headgroup (Figure 1) were added to the platinum-styrene dispersions. We expect that such compounds are able to attach to platinum colloids via their sulfur atoms.^{32,33} The compounds employed were mainly ammonium-O,O'-dialkyldithiophosphates, termed C_xdtpNH₄, where *x* denotes the number of carbon atoms in the alkyl chains. These substances were prepared according to the literature.²⁸ We assume that the ammonium groups are coadsorbed upon coordination of the dithiophosphate groups to the platinum

 TABLE 1: Overview of the Experiments and the Structures Observed in the Nanocomposites

| | | M/L^a | | | | | | | |
|----|------------|------------------------------------|------------------|------------------------------------|------------------|------------------------------------|------|------------------------------------|------|
| | | 1:1 | | 2:1 | | 3:1 | | 4:1 | |
| С | no L, type | L | type | L | type | L | type | L | type |
| 1% | A^b | C ₁₈ dtpNH ₄ | А | C ₁₈ dtpNH ₄ | \mathbf{B}^{c} | C ₁₈ dtpNH ₄ | А | C ₁₈ dtpNH ₄ | А |
| 2% | А | C ₁₈ dtpNH ₄ | А | C ₁₈ dtpNH ₄ | В | C ₁₈ dtpNH ₄ | В | C ₁₈ dtpNH ₄ | А |
| 4% | А | $C_2 dtpNH_4$ | \mathbf{D}^{e} | $C_2 dtpNH_4$ | D | C_2 dtpNH ₄ | D | $C_2 dtpNH_4$ | D |
| | | C ₆ dtpNH ₄ | А | C ₆ dtpNH ₄ | \mathbf{C}^d | C ₆ dtpNH ₄ | С | C ₆ dtpNH ₄ | D |
| | | C ₁₂ dtpNH ₄ | А | C ₁₂ dtpNH ₄ | В | C ₁₂ dtpNH ₄ | В | C ₁₂ dtpNH ₄ | А |
| | | C_{18} dtpNH ₄ | B, C | C_{18} dtpNH ₄ | В | C_{18} dtpNH ₄ | В | C ₁₈ dtpNH ₄ | В |
| | | C ₁₈ thiol | \mathbf{E}^{f} | C ₁₈ thiol | Е | C ₁₈ thiol | Е | C ₁₈ thiol | Е |
| 8% | А | C ₁₈ dtpNH ₄ | В | C ₁₈ dtpNH ₄ | В | C ₁₈ dtpNH ₄ | Е | C ₁₈ dtpNH ₄ | Е |
| | | C ₁₈ hiolt | Е | C ₁₈ thiol | Е | C ₁₈ thiol | Е | C ₁₈ thiol | Е |

^{*a*} M/L denotes the molar ratio between platinum atoms and complexing agent molecules, *c* the platinum concentration [w/w] in the initial styrene solution, C_xdtpNH₄ the ammonium *O*,*O*'-dialkyldithiophosphates with the number of carbon atoms *x* in the alkyl chains, and C₁₈thiol, octadecanethiol. ^{*b*} Type A: no superstructures or exceptional features. ^{*c*} Type B: hollow shells and networks. ^{*d*} Type C: large disks or thick-walled shells. ^{*e*} Type D: disklike structures with irregular shape. ^{*f*} Type E: mainly connected shells and stringlike objects.

surfaces. For comparison, experiments with octadecanethiol (C₁₈thiol) have also been performed. The adsorption of alkanethiols on noble-metal colloids is well established.^{22–27,32–36}

Polymerization of styrene-platinum dispersions was actuated in the presence and absence of the above-mentioned complexing agents by addition of a radical initiator, azobis(isobutyronitrile) (AIBN) at 60 °C. According to preliminary experiments, nanocomposites were produced predominantly in the presence of C_{18} dtpNH₄ at different platinum concentrations (1-8% w/w) and different ratios of metal atoms and complexing agent molecules (M/L ratio, varying from 1:1 to 4:1). Ammonium O,O'-dialkyldithiophosphates with alkyl chains containing less than 18 carbon atoms or octadecanethiol were also employed. A survey of the experiments is presented in Table 1. The number-average molecular weights (M_n) of the poly(styrene) matrix, measured by gel permeation chromatography (GPC), are not significantly affected by the presence of platinum and complexing agents. Typical M_n between 30 000 and 40 000 with $M_{\rm w}/M_{\rm n}$ around 5–7 ($M_{\rm w}$ = weight-average molecular weight) were found in numerous materials with C18dtpNH4; these values do not differ significantly from those of pure poly(styrene) prepared under the same conditions or polymer containing only platinum colloids but no complexing agent. The samples prepared with M/L ratios of 1:1 are hard, and the specimens become more and more brittle with increasing M/L ratio. In the absence of a complexing agent, the nanocomposites tend to become brittle as the platinum concentration increases, with the exception of the 8% platinum sample, which consists of a gumlike product. As evident from TEM images, the individual platinum colloids are 1-2 nm in size in all experiments. The TEM pictures also show that the particles' dimensions are established upon formation of the pristine platinum dispersion and the partial evaporation of the liquid before addition of the stabilizer, i.e., the particles do not grow anymore upon treatment with stabilizer or polymerization of styrene. The platinum colloids thus obtained have the same dimensions as the reported Pt₃₀₉ clusters³⁷ and the colloids in the poly(styrene)-platinum nanocomposite foams, in which the platinum particles were prepared according to the same chemical reactions.²² The extent of the individual platinum clusters do not change significantly in the presence of a complexing agent.

As indicated in Table 1 and as described below in more detail, several types of arrangements of platinum colloids were observed in the nanocomposites, depending on the type of complexing agent, the ratio between platinum atoms and complexing agent molecules, and the platinum concentration. In absence of a complexing agent, no superstructures or exceptional features appear in transmission electron microscopy (TEM) images obtained from thin nanocomposite sections, and such "featureless" nanocomposites are termed here type A. Type A structures also dominated the micrographs of some materials prepared in the presence of C_{18} dtpNH₄ at low platinum concentrations (1 or 2% w/w) and of most C_x dtpNH₄ compounds at the lowest *M/L* ratio (1:1).

Onionlike structures of several shells as well as single shells of platinum colloids emerge in TEM micrographs of a number of nanocomposites fabricated in the presence of ammonium O,O'-dialkyldithiophosphates (Figure 4a-d). These structures, defined as type B, seem to be favored at intermediate M/L ratios (in particular 2:1 but also 3:1) and long alkyl chains (C₁₈dtpNH₄ and C₁₂dtpNH₄), as evident from Table 1. The type B patterns appear as "rings" of typical diameters of 50-300 nm and thickness of the borderline of 5-15 nm. These rings consist of hundreds or thousands of colloidal platinum particles. The cross sections of the borderlines comprehend several particles, as evident from TEM pictures at high magnifications (Figure 4b). Features composed of connected shells are also visible (Figure 4a), and complex multilayer structures appear with C₁₈dtpNH₄ at platinum concentrations of 4 and 8% w/w and M/L of 2:1, and at 8% w/w and M/L of 1:1 (Figure 4d). Finally, concentric shells emerge occasionally; the diameters of the outermost rings attained, for instance, $1-2 \ \mu m$ (Figure 4c).

When the alkyl chain length in C_x dtpNH₄ complexes decreases at a platinum concentration of 4% w/w and *M/L* of 2:1 and 3:1, objects other than the above-described type B structures dominate the TEM pictures. In the case of C₆dtpNH₄, large disks or shells with thick walls of diameters around 5 μ m (defined as type C, Figure 5a) or, when C₂dtpNH₄ is used, disklike entities (or thick-walled shells) with irregular shape and diameters of 100 nm-2 μ m are found (defined as type D, Figure 5b). Obviously, the formation of superstructures of platinum colloids in the presence of C_xdtpNH₄ is governed by the alkyl chains. Type D structures also appear with C₂dtpNH₄ and C₆dtpNH₄ at *M/L* = 4:1 and with C₂dtpNH₄ at *M/L* = 1:1. Hence, it seems that a certain length of the alkyl chains is required to obtain self-organization.

Experiments performed with C₁₈dtpNH₄ at platinum concentrations of 8% w/w and *M/L* ratios of 1:3 and 1:4 result in nanocomposites that typically contain flattened shells of a length up to 1 μ m, some regular shells and stringlike objects (defined as type E, Figure 5c). A mixture of similar structures was also observed with C₁₈thiol at a platinum concentration of 8% w/w and *M/L* = 2:1 (Figure 5d). The other nanocomposites containing C₁₈thiol at platinum concentrations of 4 and 8% w/w also



Figure 4. Typical examples of Type B structures observed in poly-(styrene)-platinum nanocomposites in the presence of C_{18} dtpNH₄. (a) and (b) M/L = 2:1, platinum concentration 1% w/w, (c) M/L = 3:1, platinum concentration 2% w/w, (d) M/L = 2:1, platinum concentration 8% w/w.

show type E structures, in which, however, chainlike assemblies of colloids dominate.

Discussion

From the above-described structures, the unusual type B patterns attract most attention. At first glance, the related TEM images highly resemble those of the superstructures of bilayer



Figure 5. Typical examples of: (a) type C structure, C₆dtpNH₄, M/L = 2:1, platinum concentration 4% w/w, (b) type D structure, C₂dtpNH₄, M/L = 1:1, platinum concentration 4% w/w, (c) type E structure, C₁₈-dtpNH₄, M/L = 3:1, platinum concentration 8% w/w, (d) type E structure, C₁₈-thiol, M/L = 2:1, platinum concentration 8% w/w.

membranes (vesicles) formed by self-organization in solution (note that such spheric structures appear as circles in the projections represented by the TEM pictures).^{38–42} Such membranes can conjoin to assemblies such as networks,³⁹ as also observed in type B features. In fact, the molecules forming bilayer membranes typically consist of a polar headgroup which

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is connected to two alkyl chains with typically 12–18 carbon atoms, i.e., these molecules are of the same type as the longchain dialkyldithiophosphates used in this study. Even more, complexation of the headgroup by metal atoms can stabilize bilayer aggregates.³⁸ However, there are striking differences between bilayer membranes and the structures described here: typical bilayer membranes are essentially formed in aqueous solutions as a consequence of a balance between hydrophilic and hydrophobic interactions, and the thickness of the walls is molecularly controlled. In the systems described here, the medium is apolar and the walls of the structures vary somewhat in thickness, which extends over a few particle diameters.

As mentioned in the Introduction, compounds with sulfur atoms show a high affinity to platinum. Hence, C_xdtpNH₄ molecules are expected to coordinate to the colloids' surfaces, in equilibrium with C₁dtpNH₄ molecules dissolved in the matrix. If the platinum surfaces were saturated with C_xdtpNH₄ molecules at all M/L ratios applied here, the interaction of the C_vdtpNH₄modified particles with each other and the matrix was the same for all M/L ratios and, as a consequence, we would expect the types of structure to be independent of the M/L ratios, which, however, does not agree with the observations, where differences in the structures prepared at M/L of 1:1 and 2:1 are common. Therefore, we assume that the surfaces are saturated with complexing agent molecules at most at the lowest M/L ratio (1:1), if at all, and that the surface coverage with C_x dtpNH₄ tends to decrease with increasing M/L. In fact, it is not clear if there are sufficient C_x dtpNH₄ molecules in the system at M/L= 4:1 to cover the colloids completely because the particles are so small that most of the atoms could be exposed to the surface and hence be capable to coordinate with C_rdtpNH₄. If the surface coverage decreases with increasing M/L, the packing density of the attached molecules also decreases.

The smallest cross-sectional area of an alkyl chain in alltrans conformation is 0.19 nm^{2,43} and an area of 0.24 nm² per alkyl chain was estimated for a densely packed alkyl layer of dimethyldioctadecylammonium ions adsorbed on mica;44 hence, the diameter of an idealized alkyl chain is around 0.5 nm, i.e., relatively large compared to the diameter of the platinum colloids of 1-2 nm. Because of the high curvature of the particles, the brushes of alkyl chains are not dense and the chains probably not extended, even at surfaces saturated with C_xdtpNH₄ molecules, and gauche conformations are likely to occur. Nonetheless, organic layers on very small colloidal powders can exhibit crystallization and melting as found in silver colloids with bound dodecanethiol chains.26 If metal surfaces are covered only partially with C_xdtpNH₄ molecules, the alkyl packing is less dense, and hence, the surrounding alkyl layer is probably "liquid". However, crystallization could be induced in an accumulation of particles by interpenetration of alkyl chains of adjacent particles (Figure 6), which may act as the driving force for the formation of superstructures. This balance would depend on many parameters, in particular on the surface coverage, i.e., the M/L ratio, the concentration of the colloids in the matrix, and the length of the alkyl chains. It appears, according to the above discussion, that the platinum colloids in the superstructures observed in this study are covered with C_xdtpNH₄ below saturation. When dispersions of gold colloids, whose surfaces were saturated with a monolayer of dodecanethiol, were dispersed in styrene or methyl methacrylate and converted into nanocomposites under similar conditions as those applied for the experiments above, materials with randomly distributed particles were found,^{45,46} in agreement with the assumption that



Figure 6. Sketch of a possible formation of self-assembled superstructures by crystallization of surface-bound alkyl chains.



Figure 7. Sketch of a possible formation of concentric shells by shape fluctuations.

type B superstructures are favored by a partial coverage of alkanethiols.

Using C_{18} thiol instead of C_{18} dtpNH₄, it has to be considered that the equilibrium constant for the complexation to platinum and the number of alkyl chains per headgroup differ. As a

consequence, different superstructures, if occurring at all, are expected to arise when these two complexing agents are applied under the same reaction conditions, although in both cases alkyl chains surround the platinum surfaces. Indeed, the structures observed in TEM frequently differ when C_{18} thiol and C_{18} dtpNH₄ were used under the same conditions. Although mainly openchain structures have been found when C_{18} thiol was applied, it cannot be excluded that type B objects might be generated upon variation of the reaction conditions, such as platinum concentration, *M/L* ratio, reaction temperature, or matrix composition. The existence of concentric shells, such as shown in Figure 4c, can be explained analogously to related phenomena in bilayer membranes,⁴² since the mechanism is based on shape variations of a given shell with time (Figure 7).

Conclusions

Styrene containing dispersed platinum particles of diameter 1-2 nm was polymerized in the presence of dialkyldithiophosphates, C_xdtpNH₄, and octadecanethiol, C₁₈thiol. The size of the individual particles (1-2 nm) and the degree of polymerization in the formed poly(styrene) (M_n 30,000–40,000) is not significantly affected by the presence of C_xdtpNH₄ or C₁₈thiol under the conditions applied here. It is assumed that C_xdtpNH₄ and C₁₈thiol adsorb at the surfaces of the colloids by complexation with sulfur atoms. As a consequence, a number of the resulting nanocomposites contain superstructures, depending on the type of complexing agent, the length of the alkyl chain, the concentration of platinum, and the ratio between platinum atoms and complexing molecules in the system. Most remarkably, unusual hollow shell structures with a typical diameter of 50-300 nm and a wall thickness of 5-15 nm appear in many examples with C_xdtpNH₄. The formation of these objects is apparently favored by long alkyl chains. With octadecanethiol, C₁₈thiol, chains of such objects were normally observed, but single shells were occasionally also found.

The TEM images of the shells resemble those of bilayer vesicles in aqueous solution; however, the driving force for the superstructures is believed to differ. While a balance of hydrophobic and hydrophilic interactions causes the genesis of typical bilayer structures in aqueous solution, the superstructures in the nanocomposites could be established by a crystallization of alkyl chains on partially covered platinum surfaces in assemblies of particles.

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