Stabilization of colloidal palladium particles by a block copolymer of polystyrene and a block containing amide sidegroups

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A block copolymer of polystyrene and poly(tert-butylmethacrylate) was prepared by anionic polymerization. The ester groups of the poly(tert-butylmethacrylate) were hydrolyzed, after which the remaining carboxyl groups were reacted with pyrrolidine. The resulting block copolymer with amide sidegroups was used for stabilization of a palladium colloid in toluene.

1. Introduction

Reduction of a noble metal salt in a polymer solution is the most common method in order to prepare polymer-protected noble metal colloids [1, 2]. Block copolymers have been shown to be effective stabilizers for colloidal gold [3–6]. Additionally, reduction of gold and palladium(II) salts in the presence of polystyrene-block-poly(2-vinylpyridine) and polystyrene-block-polyethyleneoxide have been described [7, 8]. The functional blocks of these block copolymers can either undergo rather strong (poly(2-vinylpyridine)) or weak interaction (polyethyleneoxide) with metal surfaces. Although the number of monomers which can be linked by anionic polymerization to block copolymers is rather limited, modification of the blocks provides a route to versatile alternative block copolymers.

The work described here is directed towards the synthesis of a functional block with amide side groups, and its utilization for the preparation of palladium colloids.

2. Experimental

2.1. Preparation of the polymer

Polymerization

A block copolymer consisting of blocks of 375 styrene units and 25 t-BMA units (PS(375)-b-PtBMA(25)) was synthesized by means of anionic polymerization in inert gas atmosphere, with use of high vacuum cleaning techniques as described before [9].

Modification of the t-butylmethacrylate block

a. Hydrolysis: 0.74 g KI and 0.9 ml trimethylchlorosilane were dissolved in 2 ml of acetonitrile and stirred under argon for 0.5 h. Then, 1 g of PS(375)-b-PtBMA(25) dissolved in 10 ml chloroform was added. The mixture was stirred at room temperature for 2 days. The solution was quenched with 8 ml of an aqueous solution of Na2SO3 (0.1 g/ml). After separation of the phases, the organic layer was concentrated. The residue was dissolved in 5 ml THF, and precipitated in methanol.

b. Preparation of the amide: 0.25 g hydrolyzed polymer was dissolved in 5 ml methylene chloride. To this solution, 90 mg dicyclohexylcarbodiimide (DCC) was added under argon. After stirring for 12 h, 5 mg dimethylaminopropiophenone (DMPA) was added. The opaque solution was stirred for 6 h at room temperature. Finally, 0.5 ml pyrrolidine was injected and allowed to react at room temperature for 48 h. The solution was concentrated and twice precipitated in methanol. The polymer was dried overnight in vacuum at 50 °C (yield 100%).

2.2. Characterization

1H-NMR

Spectra of polymer solutions in deuterated chloroform were recorded on a Bruker AC-200 (200 MHz). Chemical shifts refer to TMS. The following spectra were obtained: PS(375)-b-PtBMA(25): 1.00–1.70: (broad signal, –CH2– in PS and PtBMA backbone), 1.52: (singlet, –CH3 groups in PtBMA block), 1.70–2.32: (br. signal, –CH(C6H5)– in PS block), 6.28–6.86: (br. signal, arom. protons in meta position in PS block), 6.86–7.29: br. signal, arom. protons in ortho and para position in PS block).

Polymer after hydrolysis: comparable to the spectrum of PS(375)-b-PtBMA(25), with a reduced singlet at 1.52.

Polymer after hydrolysis and amide formation (PS(375)-b-PAM(25)): comparable to the spectrum of the hydrolyzed polymer, with an additional broad signal between 2.60 and 3.40 ppm (–NC2H4 in functional block). The conversion was calculated from the integral of this broad signal and the integral of the broad signal of the styrene sidegroup between 6.28 and 7.29 ppm.

FTIR spectroscopy

Diluted polymer solutions in chloroform were put on thin (0.5 mm) KBr plates. After evaporation of the solvent and drying in vacuum at room temperature for 1 h, spectra of samples in vacuum were recorded on a Bruker IFS 66 V.

2.3. Preparation of PS-b-PAm protected palladium colloids in toluene

2 ml Pd(OAc)2 solution in toluene was added to 5 ml (1 wt.-%) polymer solution in toluene (0.2 mol Pd(OAc)2 per mole amide groups) and stirred overnight. Reduction of the polymer/salt complex was performed at 60 °C after addition of 0.25 ml methanol.

Transmission electron microscopy (TEM)

A drop of the polymer-stabilized palladium colloid was put on a 400 mesh carbon-coated copper grid. The solution immediately soaked into a paper on which the grid was lying, leaving a thin polymer film behind on the grid. Pictures were made on a Philips EM 401 operating at 80 keV.

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UV/vis spectroscopy

Spectra of solutions in quartz glass cuvettes were recorded at a rate of 480 nm/min on a Perkin Elmer Lambda 16 spectrophotometer, equipped with PECSS software.

Scanning force microscopy

The block copolymer surface was investigated using a Nanoscope III (Digital Instruments) using the tapping mode, at a frequency of ca. 360 KHz. A mica substrate was dipped in a 0.5 mg/ml solution of the polymer in toluene. This solution was prepared by dilution of a 25 mg/ml solution directly before the film casting.

3. Results and discussion

3.1. Synthesis

A block copolymer of polystyrene and poly(tert-butylmethacrylate) was prepared by anionic polymerization with sec-BuLi in THF as described before. Molecular weights and monomer composition were analyzed by GPC and 1H-NMR. The length of the blocks turned out to be 375 units (polystyrene) and 25 units for the poly(tert-butylmethacrylate), which is in good agreement with the expectations from the monomer-to-initiator ratio.

The t-butylmethacrylate groups of the polystyrene-block-poly(t-butylmethacrylate) block copolymer were hydrolyzed and then reacted with pyrrolidine (Scheme 1).

Scheme 1.

In the first step, the ester was hydrolyzed by trimethylchlorosilane in acetonitrile [10-13]. After reaction with water, the carboxylic acid group was formed. Next, the amide group was introduced by reaction with pyrrolidine in the presence of DCC and DMAP [14].

The interaction of the polyamide block with metal surfaces might be comparable with that of polyvinylpyrrolidone, which was reported to be an efficient stabilizer for colloidal noble metal catalysts in aqueous solution [1].

Comparison of the 1H-NMR spectra of PS(375)-b-PtBMA(25) and the hydrolyzed product demonstrated elimination of the t-butyl group by reduced intensity of the signal at 1.52 ppm. The remaining signal intensity originates from the methyl groups attached to the backbone of the polymethacrylate.

When a sample was taken from the mixture after the reaction with pyrrolidine, GPC revealed that a large amount of the block copolymer had been crosslinked (Fig. 1). This crosslinking can be explained by anhydride formation during the amidation reaction with DCC. From this it follows that the reaction with pyrrolidine does not proceed completely.

Fig. 1. GPC spectra of the polymer after the amidation reaction, before (a) and after (b) contact with traces of water.

When the polymer had been worked up (precipitation from THF in methanol), the crosslinked products had disappeared. The THF and methanol apparently contained enough water in order to hydrolyze the anhydride bridges between the different block copolymer molecules.

Incorporation of the pyrrolidine in the block copolymer was indicated by a new broad signal in the 1H-NMR spectrum between 2.60 and 3.40 ppm. The formation of the amide linkage could be observed more clearly in the FTIR spectrum. The spectrum of the final product (PS-b-PAm) showed a pronounced shoulder at 1620 cm⁻¹ in comparison to the spectrum of the hydrolyzed block copolymer, which can be ascribed to the presence of the amide bond (Fig. 2).

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Fig. 2. IR spectra of the polymer after hydrolysis, and after amidation (PS(375)-b-PAm(25)).

Still, a C=O band of the −COOH groups appears in the spectrum, which is another indication that complete conversion was not obtained. From the NMR spectrum, the conversion could be estimated as 50%, which is still high enough in order to reach reasonable complexation of Pd-salts.

3.2. Preparation of the Pd colloid

When a solution of the block copolymer in toluene was mixed with a Pd(OAc)₂ solution in toluene, the color changed only slightly. UV/vis spectroscopy allowed the in-
teraction of amide groups with palladium(II) acetate to be observed more directly (Fig. 3).

![UV/vis spectra](image)

**Fig. 3.** UV/vis spectra: a - PST-b-PAm, b - Pd(OAc)$_2$, c - complex of PST-b-PAm and Pd(OAc)$_2$ and d - colloidal Pd, protected by PST-b-PAm. All measured in toluene.

Complexation of the palladium(II) by the amide groups caused a shift of the absorbance of the palladium salt from 400 to 388 nm. This shift is not as strong as in the case of complexation of palladium acetate by poly(2-vinylpyridine) (from 400 nm to 380 nm) [7]. The smaller shift can apparently be attributed to a weaker complexation of the amide group with the palladium salt. On the other hand, peak broadening does not appear, which indicates that the palladium acetate is mainly bound to the polymer.

Even in the case of rather concentrated polymer solutions, no micelles could be observed with atomic force microscopy (AFM) when no palladium salt was added to the solution. However, AFM showed that micelles were formed after addition of the complexing salt. Figure 4A shows an AFM picture of a thin polymer film prepared from a polymer solution to which 1 mol Pd(OAc)$_2$ per mole functional polymer groups had been added. Micelles with sizes between 20 and 40 nm can be observed. The rather broad size distribution may be attributed to the film-forming conditions. It appeared necessary to dilute the polymer solutions directly before film casting in order to obtain well-defined films [4]. Although reorganization of salt-loaded micelles on such time-scales is minimal, broadening of the micelle size distribution can be expected in the case of short functional blocks as used in this work.

The core of the salt-loaded micelles could be visualized by transmission electron microscopy (Fig. 4B). Size and size distribution of the micelle cores (between 2 and 5 nm) are in agreement with the size of the micelles as determined by AFM.

When the polymer/Pd(OAc)$_2$ solution was heated to 60 °C, reduction of palladium acetate could be achieved by adding only very small amounts of methanol. This may be explained by the presence of micelles in solution [4]. The micelles act as small micro-reactors in which the palladium acetate and methanol are concentrated. Due to the increased local concentration, the reduction reaction proceeds more easily than in the case of random copolymer solutions [7].

During reduction, a slow discoloration from bright yellow to brown was noticed. The UV/vis spectrum (Fig. 3d)
of the reduced solution was typical for colloidal palladium solutions [15].

Transmission electron micrographs revealed the Pd particles to be rather irregular, as can be seen in Fig. 5. It is likely that particles which were originally formed within the micelles aggregated because of relative weak interaction with the polymer. No significant changes could be observed with TEM over 2 months. This means that the aggregates which were initially formed in the micelles did not aggregate anymore. The size of the particles was determined to be ca. 15 nm.

The size of the particles is too large in order to be related directly to the size of the noble metal salt-loaded micelles as originally present before reduction. Apparently, reorganization of micelles takes place during reduction [8]. Particularly in the case of short functional blocks, this process can be quite pronounced.

4. Conclusions

Modification of a functional block of a diblock copolymer makes it possible to tune the polymer with respect to its stabilizing properties for colloidal metal particles (adsorption strength, micelle formation, etc.). A polystyrene/poly(t-butylmethacrylate) block copolymer was modified by hydrolyzing the methacrylate block, after which the carboxylic acid sidegroups were reacted with pyrrolidine in order to form amide bonds. Although the amidation reaction did not proceed completely, rather stable Pd colloids could be obtained in such polymer solutions. The colloids could easily be formed by reduction of palladium(II) acetate in the modified block copolymer solution in toluene. The formed palladium particles were rather irregular. Nevertheless, even after several months no precipitation or aggregation of particles could be observed.

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References


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