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ORIGINAL CONTRIBUTION

A.B.R. Mayer
J.E. Mark

Transition metal nanoparticles protected by amphiphilic block copolymers as tailored catalyst systems

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A.B.R. Mayer · J.E. Mark (✉)
Department of Chemistry
and the Polymer Research Center
The University of Cincinnati
Cincinnati, Ohio 45221-0172, USA

Abstract Several stable palladium, platinum, silver, and gold colloids were prepared by reducing the corresponding metal precursors in the presence of protective amphiphilic block copolymers. Some palladium and platinum precursors with different hydrophobicities, namely palladium chloride $PdCl_2$, palladium acetate $Pd(CH_3COO)_2$, hexachloroplatinic acid H_2PtCl_6, and platinum acetylacetonate $Pt(CH_3COCH=C(O-)CH_3)_2$, have been used in order to investigate differences in their catalytic activity. The polymers investigated for their ability to stabilize such transition metal colloids were polystyrene-b-poly(ethylene oxide) and polystyrene-b-poly(methacrylic acid). The metal particle sizes and morphologies were determined by transmission electron microscopy and found to be in the nanometer range. The catalytic activity of the palladium and platinum colloids was tested by the hydrogenation of cyclohexene as a model reaction. The protected palladium and platinum nanoparticles were found to be catalytically active, and final conversions up to 100% cyclohexane could be obtained. Depending on the choice of polymer block types and lengths, the precursor type, and the reduction method, different nanoparticle morphologies and catalytic activities could be obtained. These novel catalytically active metal–polymer systems are thus promising candidates for the development of tailored catalyst systems.

Key words Metal nanoparticles – block copolymers – catalysis – hydrogenation

Introduction

Colloidal transition metals are recently receiving increased attention. For instance, colloidal gold and silver can exhibit different colors depending on particle size, shape, and agglomeration, and this variability has been used for coloring glass for a long time [1]. In addition to interesting optical properties exhibited due to their nanometer size, several transition metal nanoparticles are interesting for catalytic applications. For example, due to their high surface area and special morphologies (amorphous or crystalline), very active and selective metallic or bimetallic catalytic systems can be obtained [2, 3]. Furthermore, colloidal nanosized semiconductive or magnetic materials are also of high technological interest [4]. Usually, such colloidal nanoparticles are stabilized by various protective polymers.

Polymer-protected transition metal colloids are usually prepared by various *in situ* reactions from a suitable metal precursor, such as chemical reductions, photoreductions, or thermal decompositions [3]. The goal is to obtain small particle sizes and narrow size distributions.

Generally, the polymers used for the stabilization of a metal colloid should fulfill some, or possibly all, of the following requirements:

(i) Of course, they should be soluble in the solvents and thermally stable at the temperatures used during preparation, and/or technical application, of the resulting colloids.

(ii) They should have a good protective function, that is, a small "gold number", for the stabilization of metal colloids [2] and thus have good interactions with the metal surface. Often, this interaction is based on hydrophobic affinities.

(iii) Ideally, there should also be the possibility of interacting with the metal precursor, e.g., by ion-pair or complex formation, or by hydrophobic interactions.

(iv) Finally, various types of polymers should be suitable as protective agents, since they can also be important in tailoring metal–polymer systems for certain applications, e.g., influencing the selectivity of catalytic reactions.

Based on these considerations, various polymer types can be chosen, depending on the special function they are required to fulfill in combination with the nanometal:

(i) Two options are water-soluble homopolymers and random copolymers possessing a hydrophobic backbone to interact with the hydrophobic metal surface, and hydrophilic side groups to interact with the dispersion medium [2]. The stabilization of the metal colloids by polymers is based on steric stabilization [3, 5]. Due to the steric hindrance provided by the polymer to reactants attempting to approach the catalytically active metal surface, selective catalytic reactions can be achieved [3]. This has already been shown by several groups [6–8].

(ii) Cationic polyelectrolytes provide another option and offer the advantage of combining both steric and electrostatic stabilization of the metal colloid [5]. Also, for certain metal precursors, such as H_2PtCl_6 or $HAuCl_4$, there can be good interactions with the precursor through ion-pair formation [9]. In fact, palladium and platinum nanoparticles stabilized by several cationic polyelectrolytes have already been investigated as active hydrogenation catalysts [10–13]. For further catalytic applications it can be expected that this "cloud of charges" surrounding the catalytically active metal can also influence the selectivity of reactions involving charged or polar species [2].

(iii) For similar reasons, protection of metal nanocatalysts by chiral polymers, for instance, based on cyclodextrine derivatives, would be highly promising [2]. Such polymers could lead to highly useful enantioselective catalysts.

(iv) Finally, in a possibility which is the main topic of this paper, amphiphilic block copolymers are very interesting since they offer a number of advantages:

(i) They are very good steric stabilizers for metal colloids [5].

(ii) They can provide control of particle size and size distribution of the metal particles [4, 14–22].

(iii) The resulting metal–polymer systems can not only be catalytically active, but it is expected that the catalytic activity and selectivity can be controlled as well [15, 16].

The careful choice of polymer block type and length as well as of the metal precursor type (e.g. more or less hydrophobic) is very important in designing tailored catalytically active systems.

Several metal precursors were used in this work. In the case of palladium and platinum, precursors of different degrees of hydrophobicity were employed since the influences and differences with respect to the catalytic activity of the metal colloids were to be investigated. The block copolymers were chosen from those commercially available. The polystyrene-b-poly(methacrylic acid)(PS-b-PMAA) chosen has a smaller hydrophobic polystyrene (PS) content. It has also been selected since its hydrophilic block poly(methacrylic acid) alone is a stabilizer for palladium and platinum colloids. In contrast, poly(ethylene oxide) (PEO) has been chosen as hydrophilic partner for the second block copolymer polystyrene-b-poly(ethylene oxide) (PS-b-PEO), and is known to be a poor stabilizer for metal colloids. Also, the PS-b-PEO employed here has been selected with a larger hydrophobic polystyrene content for investigation of this influence on the catalytic activity.

Several metal colloids in the presence of these block copolymers have been prepared by various reduction methods, such as refluxing alcholic solutions, photoreduction by UV irradiation, or reduction by potassium borohydride, depending on the metal. The particle sizes and size distributions were investigated by transmission electron microscopy (TEM), and the catalytic activity of the palladium and platinum colloids was tested by the hydrogenation of cyclohexene as a model reaction. Significant differences in catalytic activity, depending on metal precursor hydrophobicity and PS block lengths, have been found.

Experimental part

Chemicals and reagents

The metal precursors hydrogen tetrachloroauric acid $HAuCl_4$, silver nitrate $AgNO_3$, palladium chloride $PdCl_2$,

Table 1 Metal nanoparticles stabilized by PS-b-PMAA[a]

Precursor	Reduction method	Color of colloid	Average particle size (nm)
$HAuCl_4$	KBH_4	Deep red	~3
$HAuCl_4$	UV irradiation	Purple	~6
$PdCl_2$	KBH_4	Light brown	2.1
$PdCl_2$	Refluxing EtOH	Light brown	7.8
$Pd(ac)_2$	KBH_4	Light brown	1.3
$Pd(ac)_2$	Refluxing EtOH	Light brown	3.4
H_2PtCl_6	KBH_4	Brown	3.2
H_2PtCl_6	Refluxing EtOH	Brown	~2
$Pt(acac)_2$	Refluxing EtOH	Pale brown	2.7

[a] Ethanol was used as solvent in all cases.

Table 2 Metal nanoparticles stabilized by PS-b-PEO

Precursor	Reduction method	Color of colloid	Average particle size (nm)
$HAuCl_4$	KBH_4	Red[a]	5
$HAuCl_4$	UV irradiation	Purple[a]	~6
$AgNO_3$	KBH_4	Yellow[b]	3.3
$AgNO_3$	UV irradiation	Yellow[b]	~4
$PdCl_2$	KBH_4	Light brown[a]	3.4
$PdCl_2$	Refluxing EtOH	Light brown[a]	6.8
$Pd(ac)_2$	KBH_4	Light brown[a]	~5
$Pd(ac)_2$	Refluxing EtOH	Light brown[a]	~5
H_2PtCl_6	KBH_4	Brown[a]	2.9
H_2PtCl_6	Refluxing EtOH	Brown[a]	2.1

[a] Ethanol : tetrahydrofuran = 3 : 1 was used as solvent.
[b] Ethanol : tetrahydrofuran : water = 3 : 1 : 4 was used as solvent.

palladium acetate $Pd(CH_3COO)_2$ ($Pd(ac)_2$), dihydrogen hexachloroplatinic acid H_2PtCl_6, and platinum acetylacetonate $Pt(CH_3COCH{=}C(O^-)CH_3)_2$ ($Pt(acac)_2$) were obtained from Aldrich. PS-b-PMAA (molecular weight (M_n) of PS 6500; M_n of PMAA 16 000; M_w/M_n 1.02) and PS-b-PEO (M_n of PS 29 800; M_n of PEO 8400; M_w/M_n 1.03) were purchased from Polymer Source. Potassium borohydride KBH_4 was obtained from Aldrich.

Colloid preparation

(a) *Refluxing the alcoholic solutions*: Palladium and platinum colloids were prepared according to the method described by Hirai et al. [2, 23]. The noble metal precursors were reduced by refluxing alcoholic solutions (6.8×10^{-4} M; oil bath temperature 100 °C) containing the block copolymers in a mass ratio of copolymer:metal of 25:1. For the PS-b-PEO samples a solvent mixture of ethanol:tetrahydrofuran = 3:1 (v/v) was used.

(b) *UV irradiation*: Gold and silver colloids were prepared by photoreduction from their precursors $HAuCl_4$ and $AgNO_3$. The water-cooled solutions (6.8×10^{-4} M; solvent/solvent mixtures used as indicated in Tables 1 and 2) containing the precursors and the block copolymers in a mass ratio of copolymer:metal = 25:1 were UV irradiated with a Hanovia Ultraviolet Quartz Lamp.

(c) *Potassium borohydride*: An aqueous solution of potassium borohydride was prepared just before use and rapidly added to the stirred solutions (6.8×10^{-4} M; sandbath temperature 50 °C; solvent/solvent mixtures used as indicated in Tables 1 and 2) containing the metal precursors ($PdCl_2$, $Pd(CH_3COO)_2$,H_2PtCl_6, $Rh(CH_3COO)_2$, $HAuCl_4$, or $AgNO_3$) and the copolymers in a mass ratio of copolymer:metal = 25:1.

Characterization

Transmission electron microscopy (JEOL-100 CX II electron microscope operated at 80 V) was used to obtain the particle size, morphology, and particle-size distribution of the metal nanoparticles. The samples were prepared by placing a drop of the colloidal solution on a formvar/carbon-coated copper grid and letting the solvent evaporate. The particle sizes were measured with a comparator and the average particle sizes and size distributions were determined based on the measurement of at least 150 particles.

Catalytic hydrogenations

The hydrogenations were carried out with a Parr hydrogenation apparatus at room temperature, with a hydrogen pressure of 35 psi. Cyclohexene (0.1 ml) was added to 20 ml methanol, and the palladium or platinum catalysts were added as a solid after evaporation of the solvent. The PS-b-PEO catalysts were first dissolved in 1 ml tetrahydrofuran (THF) and then 19 ml methanol was added. An amount of catalyst that corresponds to 1 wt% metal (with respect to cyclohexene) was added. The reaction mixtures were analyzed by gas chromatography (SE-30 packed column) with a flame-ionization detector, and helium as a carrier gas.

Results and discussion

Colloid formation

Table 1 shows the results for metal colloids obtained in the presence of PS-b-PMAA. Small particle sizes and colloids stable for months were obtained. Generally, the reduction by potassium borohydride leads to smaller particle sizes, which should be expected since it is a more rapid reduction method in comparison to the others used. With a rapid reduction method more metal nuclei are formed initially which then leads to smaller particle sizes. Similar results were obtained for the metal colloids obtained in the presence of PS-b-PEO, and these are listed in Table 2.

An example of a metal colloid, gold nanoparticles stabilized by PS-b-PEO, is shown in Fig. 1. As expected, the electron micrograph shows that the gold nanoparticles are not located exactly in the micelle core since there is only a small tendency for the gold precursor $HAuCl_4$ to be accumulated inside the hydrophobic micelle core. However, the gold nanoparticles are at least in the vicinity to the hydrophobic core, which leads to stabilization and thus prevents further agglomeration of the gold nanoparticles. The principle for this colloid stabilization is suggested to be similar to the general steric stabilization of colloidal metal nanoparticles achieved by various flexible homopolymers and random copolymers possessing a hydrophobic backbone.

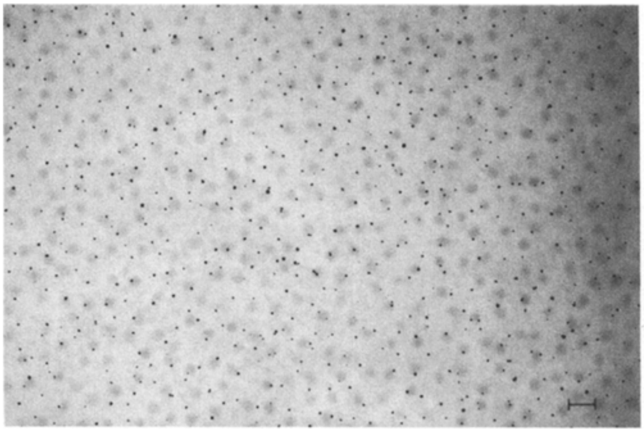

Fig. 1 TEM micrograph of gold nanoparticles in PS-b-PEO; KBH_4 reduction (Bar = 85 nm)

However, the use of block copolymers has one further advantage: for the storage of the metal nanocatalysts especially in air for a long period of time. For example, in the case of the solids after evaporation of the solvent, protective polymers with low diffusion coefficients (for e.g. oxygen or water vapour) are desirable in order to prevent deactivation of the metal catalyst. When using the usual water-soluble homopolymers and random copolymers a compromise has to be made in this regard, especially for the application of the catalysts in aqueous or alcoholic media. The requirement for the solubility of the polymers in these media has to be fulfilled for full catalytic activity of these systems. Some block copolymers can offer a good solution to this problem, i.e., combining good solubility in polar solvents, such as water and lower alcohols, and lower diffusion coefficients (for e.g. water vapor).

An interesting feature comes up when comparing the TEM pictures for the platinum nanoparticles in the two block copolymers PS-b-PMAA and PS-b-PEO, in both cases reduced by the rapid borohydride method. As mentioned before, it is also important to look at the surface morphologies of the catalyst nanoparticles. For some applications small crystalline nanoparticles are desired. However, there is also a considerable interest in amorphous metal nanoparticles as catalysts since they are expected to show very high activities [24, 25]. Often it is difficult to stabilize such nanoparticles and prevent further agglomeration. Block copolymers seem to provide a good solution for this problem, depending on the protective ability of both blocks, of the metal precursor type, and of the reduction method. Figure 2 shows platinum nanoparticles in the presence of PS-b-PMAA, i.e. a copolymer consisting of the hydrophobic PS block and a hydrophilic block which by itself is a moderate to good stabilizer for metal colloids. Dihydrogen hexachloroplatinic acid has

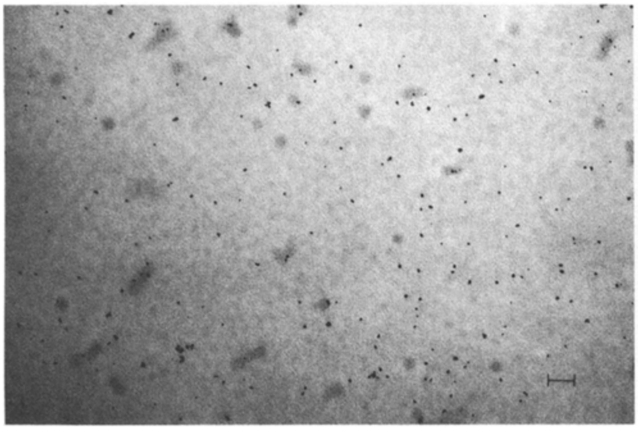

Fig. 2 TEM micrograph of platinum nanoparticles in PS-b-PMAA; KBH_4 reduction (Bar = 40 nm)

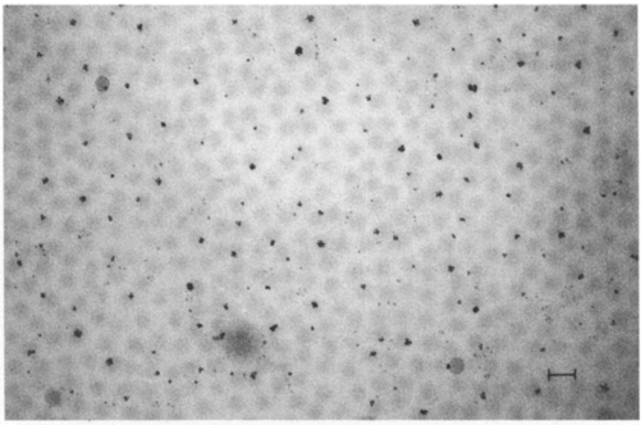

Fig. 4 TEM micrograph of platinum nanoparticles in PS-b-PEO; KBH_4 reduction (Bar = 40 nm)

been used as a precursor in this case, and has only a restricted tendency to become incorporated in the hydrophobic micelle core. Thus, the reduction of this precursor takes place outside the core. However, since both the hydrophobic and the hydrophilic block in this particular copolymer have a protective ability for metal colloids, no excessive agglomeration is observed. The corresponding histogram of particle diameters is shown in Fig. 3 and indicates a relatively narrow unimodal distribution. Figure 4 shows platinum nanoparticles protected by PS-b-PEO, also prepared from the H_2PtCl_6 precursor by borohydride reduction. Here, the hydrophilic block is a poor stabilizer for metal colloids. Since the reduction takes place outside the hydrophobic micelle core, the presence of a poor metal colloid stabilizer leads to some agglomeration of the initially formed smaller platinum nanoparticles. However, these agglomerates lie within certain size limits. The corresponding histogram shown in Fig. 5 can be interpreted as follows: Smaller particles are initially formed due to the rapid reduction method by the borohydride employed. Some of them then form small, amorphous agglomerates due to the presence of the poor stabilizer PEO. Further agglomeration is then prevented and the small amorphous aggregates are stabilized due to the overall good protective function of the block copolymer. This good protective function stems from the hydrophobic PS block, which can interact very well with the hydrophobic metal surface.

This is an example for how block copolymers can be used to control not only particle size but also the particle morphologies of metal nanocatalysts. Of course, further optimization is still necessary for each metal. But the basic idea of creating a balance between initial destabilization and subsequent stabilization controlled by the selection of the polymer blocks seems very promising.

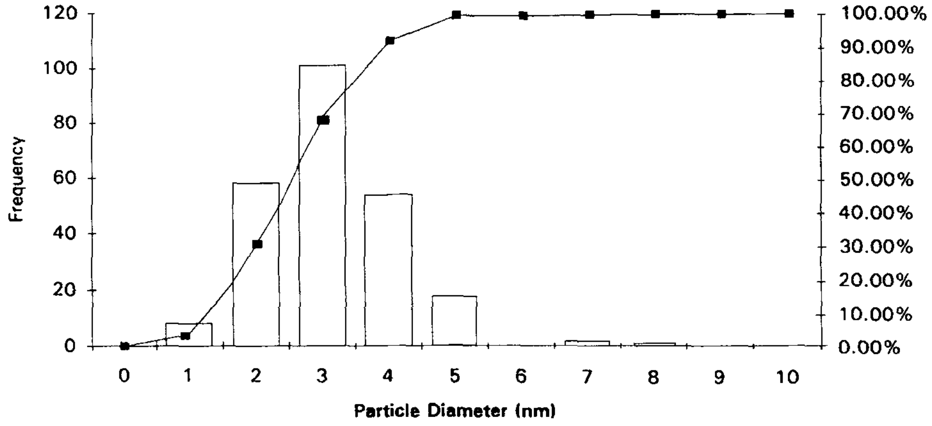

Fig. 3 Histogram for platinum nanoparticles in PS-b-PMAA; KBH_4 reduction

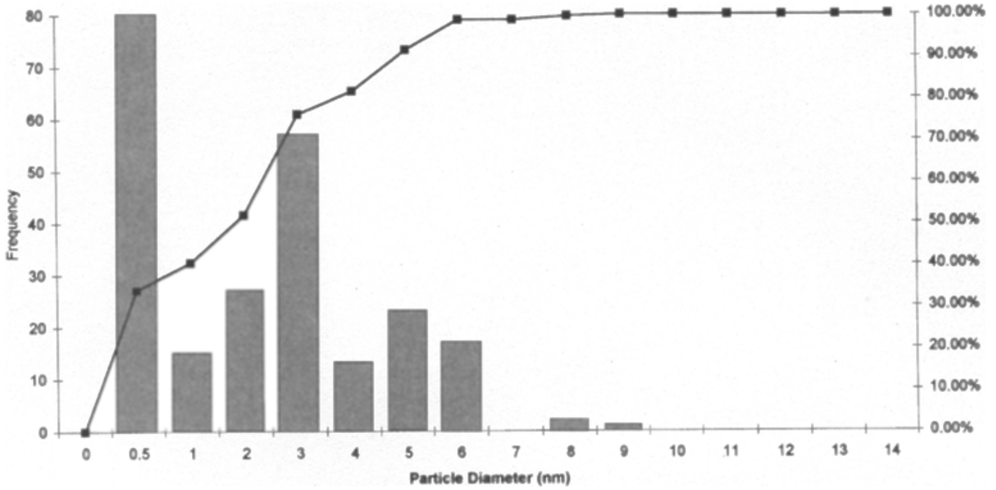

Fig. 5 Histogram for platinum nanoparticles in PS-b-PEO; KBH_4 reduction

Hydrogenations

Some results for the hydrogenation of cyclohexene with platinum and palladium nanoparticles stabilized by PS-b-PMAA are given in Table 3. These metal–polymer systems were all catalytically active, with final conversions of cyclohexene to cyclohexane up to 100%. However, in the case of platinum acetylacetonate ($Pt(acac)_2$) as a precursor there is a slight decrease, and in the case of palladium acetate ($Pd(ac)_2$) as a precursor a larger decrease in catalytic activity. This occurs even though the particle sizes, e.g. for the palladium nanoparticles stemming from the palladium acetate precursor, are smaller than the ones stemming from palladium chloride (see Table 1). In such cases even higher catalytic activities should usually be expected, due to the larger surface area.

This trend is even more obvious for the palladium nanoparticles protected by PS-b-PEO, as shown in Table 4. This block copolymer has larger PS blocks. Here, the conversions are even lower for the palladium nanoparticles generated from the palladium acetate precursor.

An explanation could be found from the catalytic activities obtained, in combination with the transmission electron micrograph in Fig. 6, showing palladium nanoparticles prepared from the palladium acetate precursor and stabilized by PS-b-PMAA. From looking at this

Table 3 Hydrogenation of cyclohexene with metal nanoparticles stabilized by PS-b-PMAA

Metal	Precursor	Reduction method	% Hydrogenation[a]
Pt	H_2PtCl_6	KBH_4	100
Pt	H_2PtCl_6	Refluxing EtOH	100
Pt	$Pt(acac)_2$	Refluxing EtOH	98
Pd	$PdCl_2$	KBH_4	100
Pd	$PdCl_2$	Refluxing EtOH	100
Pd	$Pd(ac)_2$	KBH_4	81
Pd	$Pd(ac)_2$	Refluxing EtOH	82

[a] Hydrogenation time: 20 h.

Table 4 Hydrogenation of cyclohexene with metal nanoparticles stabilized by PS-b-PEO

Metal	Precursor	Reduction method	% Hydrogenation[a]
Pt	H_2PtCl_6	KBH_4	100
Pt	H_2PtCl_6	Refluxing EtOH	100
Pd	$PdCl_2$	KBH_4	100
Pd	$PdCl_2$	Refluxing EtOH	100
Pd	$Pd(ac)_2$	KBH_4	13.1
Pd	$Pd(ac)_2$	Refluxing EtOH	25

[a] Hydrogenation time: 20 h.

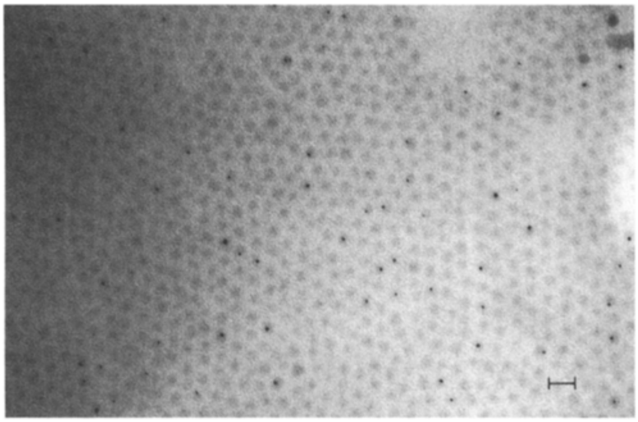

Fig. 6 TEM micrograph of palladium nanoparticles in PS-b-PMAA; refluxed in ethanol; $Pd(ac)_2$ precursor (Bar = 40 nm)

micrograph alone it cannot be entirely decided whether the palladium nanoparticles are actually embedded within the hydrophobic micelle core or merely aggregated on the cores. Aggregation outside the micelle core, however, would not explain the reduced catalytic activities found for the metal colloids stemming from the more hydrophobic precursors. Several considerations therefore make particle embedding at least seem possible. In the case of this more hydrophobic precursor (relative to palladium chloride), and with the respective preparation conditions used, the precursor material could be more likely to enter the hydrophobic micelle core and the reduction to the zero valent metal could take place there. The resulting metal nanoparticles would then be embedded within the core. This should be less the case for less hydrophobic precursors based on purely inorganic metal salts. Furthermore, the transmission electron micrographs for this sample (as shown in Fig. 6) show all the palladium nanoparticles within the micelle-core domains. With mere aggregation of the particles on the micelle core at least several particles should be seen clearly being located on the "edge" of the micelle core, considering the random distribution of the sample on the grid which allows views from all sides.

In order to be catalytically active, the catalytic sites on the metal still have to be available and accessible to the reactant to be hydrogenated. This is usually the case with e.g. the flexible, water-soluble homopolymers and random copolymers. If the metal particle is embedded in a larger hydrophobic core, the catalytic activity can become smaller, both due to the larger hydrophobic "cloud" surrounding the catalytically active metal particle and the stronger interaction of the hydrophobic block with the hydrophobic metal surface. However, this can also provide a possibility for increased selectivity of a particular metal–polymer system for certain catalytic reactions. Thus, amphiphilic block copolymers can offer an elegant option for "tuning" the catalyst activity or selectivity for certain applications.

It has to be pointed out that the systems investigated here have been used in low molecular weight alcohol, i.e., polar media. With nonpolar media, such as toluene, the metal precursors can be accumulated for reduction in the micelle core, which in this case is hydrophilic, by the use of the usual purely inorganic, non-hydrophobic salts. Additionally, depending on the precursor, an interaction between non-hydrophobic precursor and hydrophilic micelle core can be achieved, e.g. by ion-pair or complex formation. After the reduction of these precursors the metal is located inside the hydrophilic micelle core and remains there due to the steric hindrance of the surrounding copolymer. The catalytic activity in such cases can be expected to be very high and not diminished since there is little interaction of the hydrophilic micelle core with the hydrophobic metal surface. This has already been demonstrated by others [15, 16].

This fact only adds to the high versatility of the described metal–block copolymer systems. However, which type of micelle is to be used will depend on the special needs for the catalytic reaction, i.e. whether it is desirable to perform this reaction in polar (aqueous or alcoholic) or nonpolar (organic) media. For both cases amphiphilic block copolymers in combination with a metal of suitable morphology, located either inside or at the periphery of the micelle core, offer suitable options for improved catalytic systems.

Conclusions

Amphiphilic block copolymers are very suitable for the preparation of stable metal colloids with small particle sizes and narrow size distributions. They are also highly interesting as parts of catalytically active, colloidal metal–polymer systems since they offer a tremendous variability to design and tune tailored catalysts for special needs. Both the preparation of highly active (either amorphous or crystalline) metal nanocatalysts and less active, embedded nanocatalysts are options. The preparation of the desired catalyst type can be regulated by the choice and combination of polymer block types and lengths, of the metal precursor type, and of the reduction method and conditions. Additional influences for enhanced selectivity of such systems could come with the introduction of further "functions" by the polymer block types. Thus, for instance, the possibility to additionally introduce charges or chiralities make these metal–polymer catalyst systems highly effective materials.

In this context, future investigations of triblock copolymers (ABA or ABC type) is recommended. Also, graft copolymers are interesting, since the degree of hydrophobicity of the main backbone could be varied, e.g. by the introduction of fluorine, offering a further "tuning" opportunity for such catalytic metal–polymer systems.

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