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Poly(2-hydroxyalkyl methacrylates) as stabilizers for colloidal noble metal nanoparticles

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Abstract

Two poly(2-hydroxyalkyl methacrylates) were investigated as stabilizing matrices for dispersions of colloidal palladium, gold, and silver nanoparticles. The metal colloids were generated by various in-situ reductions from their respective precursors. Transmission electron microscopy was employed to investigate the metal nanoparticle sizes and shapes, and UV–Vis spectroscopy was used to characterize the optical properties of these composites. Very stable dispersions were obtained, especially for gold and silver colloids reduced by potassium borohydride (KBH_4). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(2-hydroxyalkyl methacrylate); Noble metal; Colloid

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1. Introduction

Nanosized colloidal metal nanoparticles protected by polymers exhibit intriguing optical, catalytic, or electronic properties due to the “size effect”, and additionally provide the option of influencing the materials’ properties by selection of the polymeric matrix [1–3]. A large number of preparative methods for these colloidal metal dispersions involve the presence of the polymer during the reduction from the metal precursors. In this way, the polymer can profoundly influence the particle features of the resulting metal colloids, as well as their long-term colloidal stability.

For obtaining small and colloidally well-stabilized metal nanoparticles, several factors with regard to the polymer (constitution and backbone) are influential [1,2,4]:

1. *Hydrophobic character of polymer components:* it has been shown that in many cases the presence of hydrophobic components in the polymer leads to smaller particle sizes with narrow size distributions and high colloidal stability [5,6].
2. *Interactions with the metal precursor and the metal colloid:* equally important is the capability of a polymer to provide groups which can interact with the metal precursor and/or the resulting metal colloid, for instance, by complex or ion-pair formation [4,5,7].

Water-soluble homopolymers, such as poly(*N*-vinyl-2-pyrrolidone) or poly(vinyl alcohol), have been most extensively studied [1,2,4,8,9]. Poly(methyl methacrylate) (PMMA) has been used as protective matrix for noble metal colloids in organic solvents [10,11], or in solid metal sols [12,13]. In our investigations two poly(2-hydroxyalkyl methacrylates) were investigated for their ability to stabilize colloidal palladium, gold, and silver nanoparticles, and their effects on the nanoparticle features. Like PMMA, these polymers are oxygen-containing polymeric ligands, capable of forming complexes with metal species [14]. This effect should be increased by the presence of the hydroxy groups and this, in combination with the improved solubilities in polar media makes these polymers particularly interesting [14].

2. Experimental

2.1. Chemicals and reagents

Palladium chloride, hydrogen tetrachloroaurate, and silver nitrate, as well as potassium borohydride were obtained from Aldrich. Poly(2-hydroxyethyl methacrylate) and poly(2-hydroxypropyl methacrylate) were purchased from Polysciences.

2.2. Colloid preparation

1. Reduction by KBH_4: An aqueous solution of an excess of KBH_4 was freshly prepared and rapidly added to the

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Table 1
Transmission electron microscopy results and UV–Vis spectroscopic data for polymer-protected noble metal colloids

Precursor	Reduction method	Average particle diameter (nm) (std. dev.)	Particle shape	Color	λ_{max} [FWHM] (nm)	Shape
Poly(2-hydroxyethyl methacrylate)						
$PdCl_2$	Refluxing[a]	21.5 (8.4)	Crystalline[b]	Dark brown	–	Unstructured
$PdCl_2$[c]	Refluxing[a]	23.2 (6.8)	Crystalline[b]	Dark brown	–	Unstructured
$HAuCl_4$	KBH_4	4.6 (1.9)[d]	[e]	Deep purple	480–600 [~90]	Broad
$HAuCl_4$	KBH_4, stored	5.4 (2.8)[d]	[e]	Dark red	540 [92]	Broad
Poly(2-hydroxypropyl methacrylate)						
$PdCl_2$	Refluxing[f]	9.1 (5.6)	Crystalline[b]	Dark brown	–	Unstructured
$HAuCl_4$	KBH_4	3.7 (2.3)	[e]	Deep red	480–600 [~85–90]	Broad
$AgNO_3$	KBH_4	8.1 (6.1)	[e]	Dark yellow	405.3 [96]	[g]
$HAuCl_4$	KBH_4, stored	5.4 (2.9)	[e]	Purple-red	535 [81]	Broad
$AgNO_3$	KBH_4, stored	9.5 (1.7)	[e]	Dark yellow	407 [105]	[g]

[a] Reflux time: 25 h.
[b] Separate particles and small agglomerates.
[c] Mass ratio polymer: Pd = 10:1.
[d] Only the measurable “non-fused” particles are considered in this value.
[e] Spherical and elongated particles, coexisting with “fused” particles.
[f] Reflux time: 20 min.
[g] Slightly asymmetric in the red, slight shoulder in the blue region.

stirred solutions containing $HAuCl_4$ or $AgNO_3$ (6.8×10^{-4} M) and the polymer in a mass ratio of polymer:metal = 25:1. The solvents used were ethanol (EtOH) for the poly(2-hydroxypropyl methacrylate)–gold samples, and methanol (MeOH):EtOH = 1:1 (v/v) for the poly(2-hydroxyethyl methacrylate)–gold samples. For the silver colloids the solvent used was EtOH:water = 1:1 (v/v).

2. Alcohol reduction [4]: $PdCl_2$ was reduced by refluxing the solutions (6.8×10^{-4} M) containing $PdCl_2$ and the polymer in a mass ratio of polymer:metal = 25:1 (oil-bath temperature: 100–110°C). The solvents were EtOH:water = 3:2 (v/v) for the poly(2-hydroxyethyl methacrylate) samples, and EtOH:water = 4:1 (v/v) for the poly(2-hydroxypropyl methacrylate) samples.
3. Reduction by UV irradiation: The water-cooled solutions of $HAuCl_4$ or $AgNO_3$ (6.8×10^{-4} M) containing the polymers in a mass ratio of polymer:metal = 25:1 were UV irradiated with a Hanovia Ultraviolet Quartz Lamp, using solvents as described under (1).

UV–Vis spectra were taken immediately after the reduction. For the stable gold and silver samples reduced by KBH_4, additional spectra were recorded after storage in air and in the dark for several months. All glassware was cleaned with concentrated nitric acid (for the silver and palladium samples) or aqua regia (for the gold samples).

2.3. Characterization

Transmission electron micrographs were taken with a JEOL-100 CX II and a Philips EM 400 (for the stored silver samples) transmission electron microscope (operating at 80 kV). The samples were prepared by placing a drop of the colloidal dispersion on a carbon/formvar-coated copper grid and allowing the solvent to evaporate. The particle sizes were measured with a comparator and the number-average particle sizes and size distributions were determined based on the measurement of at least 150 particles. UV–Vis spectra were recorded with a Milton Roy Spectronic 3000 Array instrument (10 mm pathlength quartz cuvettes).

3. Results and discussion

Table 1 summarizes the results obtained by transmission electron microscopy (TEM) for the stable colloids, that is, the particle diameters (and standard deviations) and nanoparticle shapes. The UV–Vis spectroscopic data are presented as well.

Dark brown colloidal palladium dispersions were obtained, exhibiting average diameters of about 10 or 20 nm. The differences in size can be mainly attributed to different reflux times, with the shorter reflux time resulting in smaller particle sizes [15]. A small influence on the particle size may also stem from slight differences in the hydrophobic character of the protective polymers; however, they should be negligible here in comparison to the influence from the reflux time. The colloidal stability of the poly(2-hydroxyalkyl methacrylate) samples seems to depend to a large extent on the nanoparticle sizes. The samples incorporating the larger 20 nm particles showed precipitation after several weeks, whereas the sample containing the 10 nm particles was colloidally stable for several months. The formation of nanosized single crystals was observed for all three palladium samples. Various shapes and geometric

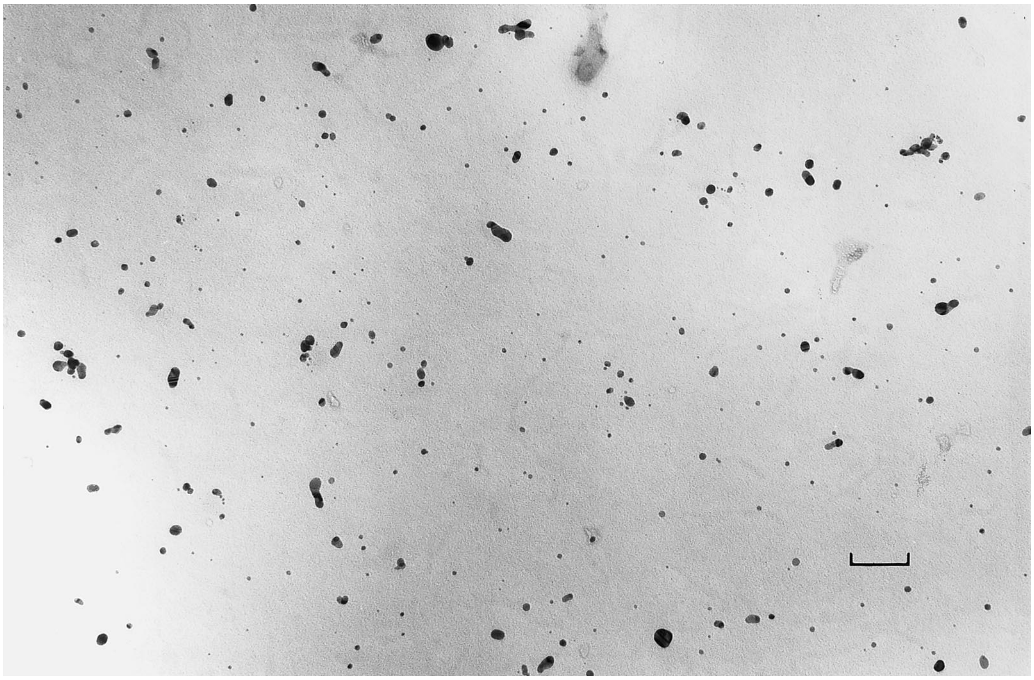

Fig. 1. TEM micrograph of silver nanoparticles generated in the presence of poly(2-hydroxypropyl methacrylate) by the reduction with KBH_4, mass ratio polymer:silver = 25:1 (bar = 110 nm).

features, including triangular, pentagonal, or hexagonal profiles are found, which are typical for multiple-twinning of an f.c.c. metal, such as palladium [8,9]. Such formation of crystalline palladium nanoparticles was already observed for the use of poly(*N*-vinyl-2-pyrrolidone) [8,9] and poly(*N*-vinyl-2-pyrrolidone-*co*-acrylic acid) [6], and was attributed to the formation of complexes between the palladium species and the polymer. The polymers investigated here are oxygen-containing macroligands, capable of forming complexes with metal species [14]. In addition, the formation of oxonium complexes with palladium and hydroxy groups has been reported [8]. The completeness of the reduction of the palladium colloids could be followed by UV–Vis spectroscopy, specifically by the disappearance of the absorption bands of $PdCl_2$ at about 320 and 425 nm. The final UV–Vis spectra show an unstructured, continuous absorption without any peaks in the visible range, which is typical for nanosized palladium colloids [16].

Two reduction methods were employed for the gold samples, namely the rapid reduction with potassium borohydride, and the somewhat slower photoreduction by UV irradiation in air. The reduction by UV irradiation resulted in very unstable samples, with precipitation occurring after only a few hours or days. With the reduction by KBH_4 deep red/purple and clear gold dispersions were obtained, which were colloidally stable for several months. The TEM investigations reveal particle diameters for the gold colloids of less than 10 nm. The stabilization of the colloidal dispersions is obviously achieved both with the use of a borohydride as rapid reducing agent and the formation of very small particle sizes in the presence of these poly(2-hydroxyalkyl methacrylates). Separate spherical and elongated particles are found, in coexistence with agglomerates consisting of "fused" gold particles. The tendency to form such fused particle shapes is found to be clearly smaller for the sample employing poly(2-hydroxypropyl methacrylate). It is possible that the formation of the fused particles indicates the beginning of agglomeration (due to initially lower interactions of the polymer, and "delayed" protective action). This is then "frozen" by the presence of the polymer once its protective function starts to become effective, preventing further agglomeration and precipitation. The finding that the sample involving the slightly more hydrophobic poly(2-hydroxypropyl methacrylate) exhibits a lower tendency for the formation of such fused particle shapes indicates that the stabilizing ability and protective function of the polymer is influenced by the hydrophobic character of its backbone or polymer comonomers. The UV–Vis spectra reveal a broad plasmon absorption band at about 540 nm, typical for nanosized gold particles. The broad bandwidth is due to the variations in the particle features and matrix interactions [17–19]. These gold sols were colloidally very stable, and after nine months storage in air and in the dark both samples were still of a deep red color and clear, with no trace of precipitation. UV–Vis spectra were recorded after this storage period, and the spectra remained essentially unchanged, indicating only little change in the nanoparticle features. To confirm this, TEM micrographs were obtained as well. Considering the long storage time only little change was found, with the average particle diameters being only slightly larger, due to ripening processes.

Silver colloids were generated in the presence of poly(2-hydroxypropyl methacrylate), employing the two reduction methods by KBH_4 and UV irradiation. Again, the photoreduction resulted in unstable colloids. The silver sample obtained by the KBH_4 reduction resulted in a well-stabilized deep yellow dispersion, which could be stored for several months. The investigations by TEM reveal an average particle diameter of about 8 nm, and various coexisting particle shapes were found (see TEM micrograph shown in Fig. 1). Besides spherical particles, several elongated and partially fused particles were observed, similar to the respective gold sample. For this sample the plasmon peak was located at about 405 nm, with a minimum at about 325 nm and a full-bandwidth at half-maximum (FWHM) of about 96 nm. The spectrum is slightly asymmetric, showing a slight tailing into the higher wavelength region, and exhibiting a slight shoulder in the "blue region". This may stem from the elongated particle shapes found by the TEM investigations for this sample. Elongated nanoparticles should lead to a splitting of the absorption band into two absorption peaks, which is probably indicated here [17]. After storage in air and in the dark for 7–8 months the silver sol was still yellow and clear, and the UV–Vis spectrum obtained after this storage period changed only a little. Merely a slight red-shift towards a longer wavelength and a broadening of about 9 nm of the plasmon absorption band were observed, with the shape of the spectrum remaining the same. The slight observed changes can be assigned to aging effects during storage for this extended period of time, partially due to changes in the particle size and shapes and/or surface oxidation processes on the silver nanoparticles. Since the reduction was performed in air it has to be expected that the silver nanoparticles are partially oxidized, due to the sensitivity of the colloidal silver nanoparticles towards oxidation [20]. Henglein has shown that such oxidation processes are associated with a strong decrease and broadening of the absorption bands [20]. The slight changes of the absorption bands after storage observed here, however, indicate that such oxidation processes either do not have a large influence with this protective polymer, or are completed after a short initial period, with the system then moving into a "stabilized state". TEM micrographs were taken for the stored sample as well, and no drastic change for the average particle diameter and the particle shape was found. Only a slight increase of the average particle diameter of about 1.5 nm is seen, and no significant changes in the particle shape was observed.

4. Conclusions

The results show that certain poly(2-hydroxyalkyl methacrylates) can be useful as stabilizers for gold and silver colloids generated by the KBH_4 reduction. It is proposed that the stabilizing mechanism proceeds in two steps, with an initial period with reduced protective function of the polymer (due to its less-pronounced hydrophobic character) which allows the beginning of agglomeration and the formation of fused nanoparticles, and the initial particle size being dictated by the reduction method and conditions. These particle shapes are subsequently "frozen" by the beginning "delayed" protective action of the polymer (possibly related to a certain particle size), which then acts as a long-term stabilizer for the colloids. The interactions between the polymer components and the metal species can also have an influence on the nanoparticle features. Nanosized single crystals were obtained for the palladium samples, probably due to complex formation with the oxygen-containing polymer repeat units.

Poly(2-hydroxyalkyl methacrylates) not only possess oxygen-containing units, capable of interacting with metallic species. In addition, several properties, such as the hydrophobic character, solubility properties, and the protective function could be subtly varied by variations of the alkyl chain. This could provide an option to "fine-tune" the materials properties of the resulting metal–polymer systems.

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