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## COLLOIDAL GOLD NANOPARTICLES PROTECTED BY CATIONIC POLYELECTROLYTES

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### ABSTRACT

Several stable gold colloids were prepared by the *in-situ* reduction of hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ) in the presence of various cationic polyelectrolytes. Several types of such polyelectrolytes were investigated for their ability to stabilize gold colloids, and UV-VIS spectroscopy was used to follow the *in-situ* reductions and to further characterize the colloids. The particle sizes and size distributions were determined by transmission electron microscopy (TEM). TEM micrographs and UV-VIS spectra were also used to characterize the stability of the colloids after storage for nine months in air at room temperature. Colloids protected by the cationic polyelectrolytes with ammonium side-groups along a hydrophobic polymer backbone frequently exhibited very good stability.

### INTRODUCTION

Noble metal colloids are well known, and have been used in technology for a very long time. The red color of colloidal gold, for instance, has been known as "purple of Cassius" and been used as coloring agent for glass and enamel [1]. Such

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materials have now become increasingly interesting for a variety of technological applications [2-11]. Gold and silver colloids exhibit interesting optical properties; for instance, depending on particle size, shape, and agglomeration, gold colloids can be red, violet, or blue. Furthermore, they are used as electron-dense labeling agents in histochemistry and cytochemistry [12, 13]. Nanosized gold particles stabilized with -in a polymer matrix might also be very interesting for applications in electron-due to the high thermal and electrical conductivity of gold [1]. Finally, another important application for colloidal noble metals is in catalysis. Gold is often used as a component in bimetallic catalyst systems to improve or modify the catalytic activity of catalysts such as palladium or platinum [1]. Small gold particles have also been reported to be useful as electron-transfer catalysts for the formation of hydrogen [14], and to show a high reactivity towards oxygen [15] (which could make such nanoparticles interesting for oxidation catalysis).

Various *in-situ* reactions, such as chemical reductions, photoreductions, or thermal decompositions, are known for the general preparation of polymer-protected noble metal colloids from suitable metal precursors. The usual goal is to obtain small particle sizes, narrow size distributions, and well-stabilized colloids. The preparative methods for gold colloids are mostly based on precursors containing gold complexes such as  $[\text{AuCl}_4]^-$  [1-13], with hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ) being the precursor most commonly used.

The protective polymer used can further influence the technological applicability of such colloidal systems. In catalysis, for instance, the choice of the protective polymer with its specific properties can be extremely important with respect to the modification of the catalytic activity and/or selectivity of the entire metal-polymer system. Therefore, it is necessary to investigate a broad variety of protective polymers and their ability to stabilize noble metal colloids.

These protective polymers employed should fulfill some, or ideally all, of the following requirements. They should:

- (i) Be soluble of course in convenient solvents, and be thermally stable at the temperatures used for the preparation and the technological applications of the colloids
- (ii) Provide good stabilization of the metal colloids through good interactions with the metal surfaces [16]
- (iii) Participate in good interactions with the metal precursors, for example by formation of complexes or ion-pairs

A variety of polymers fulfilling these requirements should be for investigation in order to design metal-polymer systems tailored for specific applications.

Commonly used so far for the stabilization of gold colloids are poly(1-vinylpyrrolidone) and poly(ethylene glycol) [12, 13], and for these flexible polymers the stabilization of the metal colloids is based on steric effects [17, 18]. Several other groups of polymers can be selected based on the above considerations, however, and can be investigated for their usefulness in stabilizing such gold colloids.

One such group is described in the present paper and consists of cationic polyelectrolytes as potential stabilizers for gold nanoparticles. This group is advantageous since they can:

- (i) Combine both steric and electrostatic stabilization of colloidal metal particles.
- (ii) Interact with the metal precursor, here the negatively charged tetrachloroaurate anion  $[\text{AuCl}_4]^-$ , through ion-pair formation [19], which can be expected to result in small particle sizes.
- (iii) Facilitate interactions with the gold particles (with corresponding stabilization), since gold colloids are known to carry a negative surface charge stemming from adsorbed chloride anions from precursors [12, 13].

In this investigation, several gold colloids protected by cationic polyelectrolytes were prepared from the  $\text{HAuCl}_4$  precursor. Two reduction methods with different rate were chosen for comparison, i.e. the rapid reduction by potassium borohydride and the somewhat slower photoreduction by UV irradiation. The formation of the gold colloids could be followed by UV-VIS spectroscopy, and the particle sizes and particle-size distributions were investigated by transmission electron microscopy (TEM). UV-VIS spectra and TEM micrographs were also taken of the stable gold colloids after storage in air at room temperature for nine months, in order to investigate their stabilities.

Specifically, four groups of cationic polyelectrolytes were investigated, namely, those based on:

- (i) Quaternary ammonium side groups
- (ii) Primary ammonium side groups
- (iii) Side groups carrying a nitrogen with a partial positive charge
- (iv) Positively charged nitrogen atoms along the polymer backbone, for reducing hydrophobic character

The first three groups of cationic polyelectrolytes were of particular interest since they resulted in red, clear colloids that had particle sizes below 10 nm, and were stable for months.

## EXPERIMENTAL

### Chemicals and Reagents

The gold precursor hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ), the reducing agent potassium borohydride ( $\text{KBH}_4$ ), the polymers poly(diallyldimethyl ammonium chloride) and poly(allylamine hydrochloride), and some hexadimethrine bromide were obtained from Aldrich. Poly(2-hydroxy-3-methacryloxypropyl-trimethyl ammonium chloride), poly(2-vinyl-1-methylpyridinium bromide), and poly(4-vinylpyridine-N-oxide) were purchased from Polysciences, and poly(methacrylamidopropyl-trimethyl ammonium chloride) and poly(3-chloro-2-hydroxypropyl-2-methacryl-oxyethyl-dimethyl ammonium chloride) from Monomer-Polymer & Dajac Laboratories.

### Colloid Preparations

#### *UV Irradiation*

Water-cooled solutions of  $\text{HAuCl}_4$  ( $6.8 \times 10^{-4}$  M, ethanol: water = 1:1, v/v) containing the polyelectrolytes in a mass ratio of polyelectrolyte: gold = 25:1 were UV irradiated with a Hanovia Ultraviolet Quartz Lamp. The formation of the colloidal gold nanoparticles was followed by UV-VIS spectroscopy, by the decrease and final disappearance of the ligand-to-metal charge transfer (LMCT) band of the  $[\text{AuCl}_4]^-$  ion centered at approximately  $\lambda_{\text{max}} = 319$  nm [15]. For the cationic polyelectrolytes possessing bromide as counteranions, ligand exchange with the  $[\text{AuCl}_4]^-$  anion takes place. In these cases, the formation of the colloidal gold can be followed by the decrease and disappearance of the LMCT band centered at approximately  $\lambda_{\text{max}} = 400$  nm.

#### *Potassium Borohydride*

An aqueous solution of  $\text{KBH}_4$  was prepared just before use and rapidly added to the stirred solutions ( $6.8 \times 10^{-4}$  M, ethanol: water = 1:1, v/v) containing  $\text{HAuCl}_4$  and the polyelectrolytes in a mass ratio of polyelectrolyte: gold = 25:1. UV-VIS spectra were taken before and after the reduction. In both approaches, all glassware was cleaned with aqua regia before use.

### Characterization

Transmission electron micrographs were taken with a JEOL-100 CX II transmission electron microscope (operated at 80 kV) in order to obtain the particle sizes, morphologies, and particle-size distributions of the gold nanoparticles. The

samples were prepared by placing a drop of the colloid on a formvar/carbon-coated copper grid (placed on a filter paper) 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 measurements of at least 150 particles. UV-VIS spectra were taken with a Milton Roy Spectronic 3000 Array instrument before, during (if possible), and after the reductions, as well as after the storage of the gold colloids under parafilm, in air at room temperature for nine months.

## RESULTS AND DISCUSSION

Table 1 shows some results for the borohydride reduction method in the presence of various cationic polyelectrolytes. The color of the colloids, the UV-VIS spectroscopic data, and the average diameters (and standard deviations) of the resulting gold nanoparticles as determined by TEM are listed. Figure 1 shows the structures for some of the cationic polyelectrolytes investigated. Usually, stable gold colloids with small particle sizes and no agglomeration are red. Any color change to violet or blue indicates incipient agglomeration and subsequently, in many cases, particle precipitation [12, 13]. As can be seen from Table 1, the rapid borohydride reduction in most cases gave brownish-red, clear colloids having spherical particles with average diameters below 5 nm. The fact that the particle sizes are small also can be deduced from the UV-VIS spectra. A representative example for gold colloids protected by poly(diallyldimethyl ammonium chloride) and reduced by borohydride is shown in Figure 2. The absorption usually centered about 545 nm in the UV-VIS spectrum is broadened to shoulders between approximately 470-600 nm, indicating very small particle sizes [3, 16, 20, 21]. Generally, for such small particles the plasmon absorption bands decrease and broaden and no distinct absorption maxima are obtained [2, 3, 21]. Additionally, a broadening of the absorption bands occurs if there are strong interactions with the surrounding medium, in this case with the sorbed protective polyelectrolytes that can polarize the gold surface.

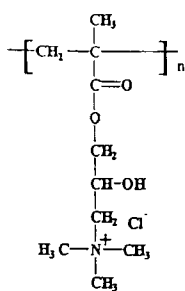
Thus, stable red gold colloids could be obtained in the presence of cationic polyelectrolytes based on quaternary ammonium side groups, primary ammonium side groups, and side groups containing a nitrogen atom with a partial positive charge.

It is interesting to note that in the case of poly(3-chloro-2-hydroxypropyl-2-methacryloxyethyl dimethyl ammonium chloride), somewhat larger particle sizes are obtained, as estimated from the TEM measurements. This can also be seen from

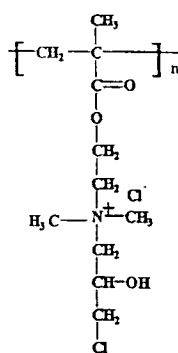
TABLE 1. Gold Nanoparticles Protected by Cationic Polyelectrolytes,  $\text{KBH}_4$  Reduction, Freshly Prepared

Polyelectrolyte	Color of colloid	UV-VIS $\lambda_{\text{max}}$ (nm)	$A_v$ particle diameter (nm) (standard deviation)
Poly(diallyldimethyl ammonium chloride)	Brownish-red	Shoulder 470-600	1.6 (0.97)
Poly(2-hydroxy-3-methacryloxy-propyltrimethyl ammonium chloride)	Brownish-red	Shoulder 470-600	1.5 (1.0)
Poly(methacrylamidopropyl-trimethyl ammonium chloride)	Brownish-red	Shoulder 470-600	3.1 (1.2)
Poly(3-chloro-2-hydroxypropyl-2-methacryloxyethyl dimethyl ammonium chloride)	Deep red	Broad $\approx 530$ (470-600)	3.5 (1.4)
Poly(2-vinyl-1-methylpyridinium bromide)	Brownish-red	Shoulder (weak)	1.1 (0.43)
Poly(4-vinylpyridine-N-oxide)	Brownish-red	Shoulder (very weak)	1.5 (0.61)
Poly(allylamine hydrochloride)	Brownish-red	Shoulder (very weak)	2.3 (1.0)
Hexadimethrine bromide	Violet	Very broad 460 - >600	6.2 (6.8) (agglomerates)

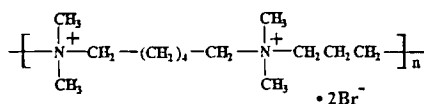
the slightly more distinct UV-VIS spectrum (broad absorption bands versus shoulders). When comparing the structures shown in Figure 1, it is suggested that in this case the interaction with the tetrachloroaurate anion  $[\text{AuCl}_4]^-$  by ion-pair formation is slightly reduced due to both the slightly higher hydrophobic character and the larger steric hindrances of the side groups. In the other cases, the positively charged nitrogen is only substituted by methyl groups, thus facilitating the ion-pair formation with the precursor anion. A similar exception for poly(3-chloro-2-hydroxypropyl-2-methacryloxyethyl dimethyl ammonium chloride) has also been observed by us when investigating palladium colloids protected by various cationic polyelectrolytes and their use in catalysis [11].



Poly(2-hydroxy-3-methacryloxy-propyltrimethyl ammonium chloride)



Poly(3-chloro-2-hydroxypropyl-2-methacryl-oxethyltrimethyl ammonium chloride)



Hexadimethrine bromide

Figure 1. Structures of the cationic polyelectrolytes.

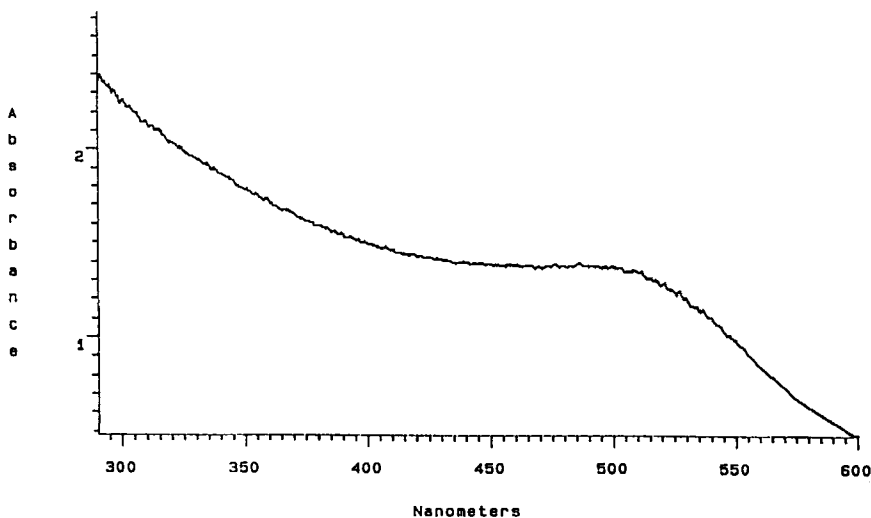


Figure 2. UV-VIS spectrum of gold nanoparticles protected by poly(diallyl-dimethyl ammonium chloride);  $\text{KBH}_4$  reduction; freshly prepared .



TABLE 2. Gold Nanoparticles Protected by Cationic Polyelectrolytes, Photoreduction, Freshly Prepared

Polyelectrolyte	Color of colloid	UV-VIS $\lambda_{\max}$ (nm)	$A_v$ particle diameter (nm) (standard deviation)
Poly(diallyldimethyl ammonium chloride)	Purple-red	Broad $\approx 540$	4.0 (4.9)
Poly(2-hydroxy-3-methacryloxy-propyltrimethyl ammonium chloride)	Purple-red	Broad $\approx 550$	8.2 (10.6)
Poly(3-chloro-2-hydroxypropyl-2-methacryloxyethyl dimethyl ammonium chloride)	Deep purple (Violet)	Broad 568.6	8.8 (4.1)

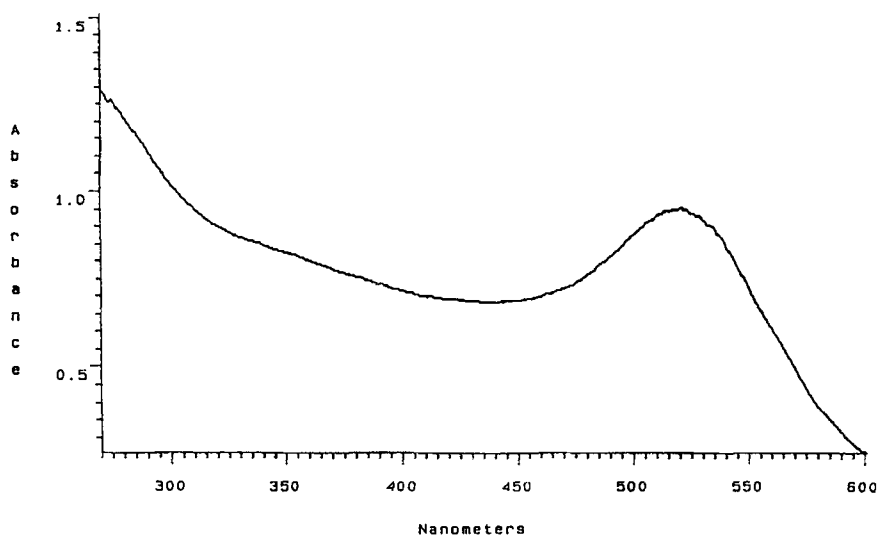
In the case of hexadimethrine bromide (1,5-dimethyl-1,5-diazaundecamethylene polymethobromide), which carries positively charged nitrogen atoms along the polymer backbone, an unstable, violet colloid was obtained. This is both due to the low molecular weight of this polyelectrolyte ( $M_w = 4,000-6,000$ ) and, even more, to the restricted hydrophobic character of its back-bone (which allows only poor interactions with the gold surfaces).

For some selected examples, photoreduction by UV irradiation was performed as well, and these results are given in Table 2. Somewhat larger particle sizes and broader size distributions were obtained, and partial precipitation of the metal usually started after several days/weeks. For larger particles the intensity of the plasmon bands increases and the bandwidth decreases, giving a better defined absorption spectrum [20]. Thus, the broad absorption bands obtained for the colloids prepared by the photoreduction approach indicate larger particle sizes for these cases. In addition to the fact that slower reductions usually result in larger particle sizes, a chemical reversibility of the photoreduction, especially in the presence of oxygen (which can act as electron scavenger) [3, 14] could be responsible for this increase in particle size. Thus, it might be interesting for future work to perform the photoreductions in the absence of oxygen. This method could also be expected to result in more stable colloids. It was not employed here, however, in order to permit better comparisons with the samples reduced by borohydride.

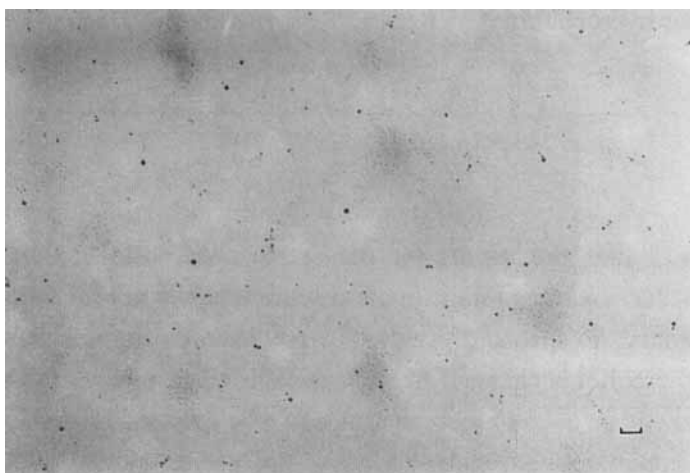
TABLE 3. Gold Nanoparticles Protected by Cationic Polyelectrolytes,  $\text{KBH}_4$  Reduction, After Storage of Nine Months.

Polyelectrolyte	Color of colloid	UV-VIS $\lambda_{\text{max}}$ (nm)	Av particle diameter (nm) (standard deviation)
Poly(diallyldimethyl ammonium chloride)	Red	Broad 520.6	4.5 (1.4)
Poly(2-hydroxy-3-methacryloxy-propyltrimethyl ammonium chloride)	Red	Broad 524.0	5.0 (1.8)
Poly(methacrylamidopropyl-trimethyl ammonium chloride)	Red	Broad 522.6	3.4 (1.7)
Poly(3-chloro-2-hydroxypropyl-2-methacryloxyethyl dimethyl ammonium chloride)	Red	(Less) broad 530.9	9.9 (4.7)
Poly(2-vinyl-1-methylpyridinium bromide)	Wine-red	Broad 539.1	5.7 (2.8)
Poly(4-vinylpyridine-N-oxide)	Red	Broad 527.4	3.3 (2.4)
Poly(allylamine hydrochloride)	Red	Broad 527.1	3.2 (4.4)

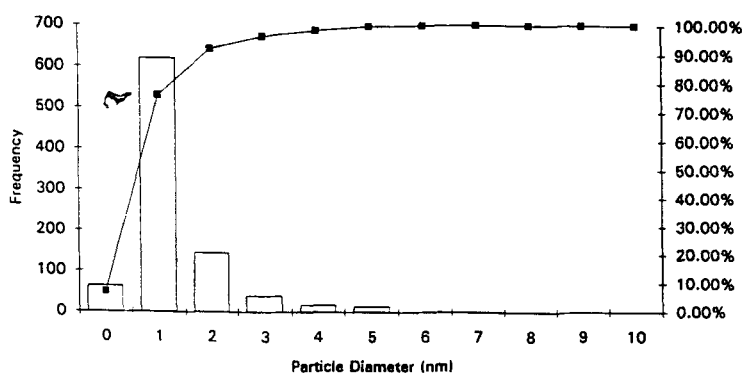
Table 3 lists the results for the stable gold colloids obtained by the borohydride reduction after storage in air at room temperature for nine months. As already mentioned, no special precautions were taken during this storage time. In most cases, the colloids changed from brownish-red to intense red, but they all remained clear and no trace of precipitation could be detected. The UV-VIS spectra are slightly better defined, showing broad absorption bands, which indicates ripening to some extent during storage. Figure 3 shows a particular example, namely gold colloids protected by poly(diallyldimethyl ammonium chloride and reduced by borohydride, after storage for nine months. The TEM investigations confirm these results by showing some particle growth and broadening of the size distributions, but only to a limited extent. The particles still have diameters below 10 nm and are well-stabilized, as can be seen from the corresponding histograms.



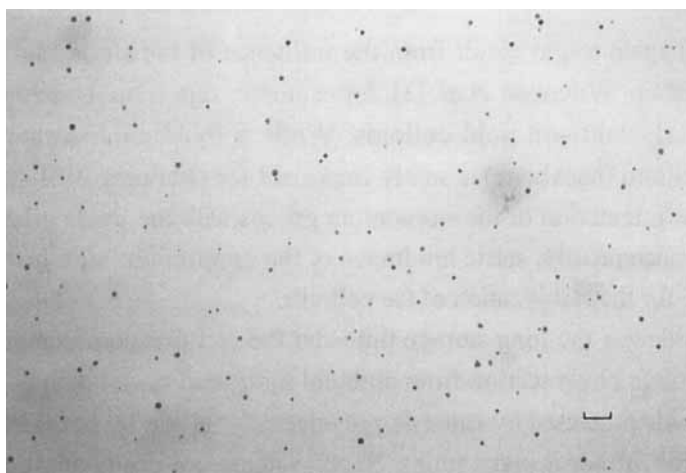
**Figure 3.** UV-VIS spectrum of gold nanoparticles protected by poly(diallyl-dimethyl ammonium chloride);  $\text{KBH}_4$  reduction; stored for nine months.



**Figure 4.** TEM micrograph of gold nanoparticles protected by poly(diallyl-dimethyl ammonium chloride);  $\text{KBH}_4$  reduction; freshly prepared (bar = 30 nm).

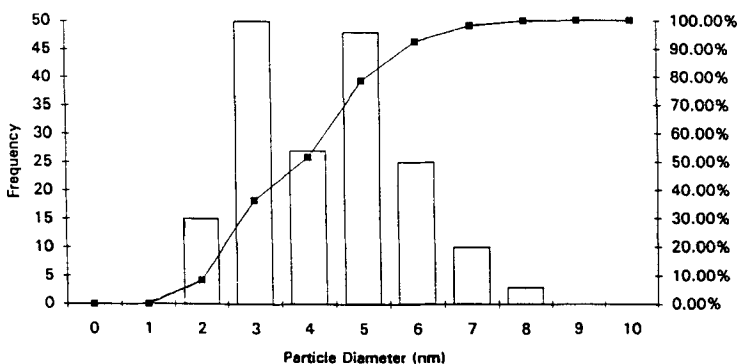


**Figure 5.** Histogram for gold nanoparticles protected by poly(diallyldimethyl ammonium chloride);  $\text{KBH}_4$  reduction; freshly prepared.



**Figure 6.** TEM micrograph of gold nanoparticles protected by poly(diallyldimethyl ammonium chloride);  $\text{KBH}_4$  reduction; stored for nine months (bar = 30 nm).

Such histograms and the corresponding TEM results are shown in Figures 4-7. They are for gold nanoparticles protected by poly(diallyldimethyl ammonium chloride) as a representative example (both for the freshly prepared colloid and after storage for nine months). The larger particle sizes observed for the gold colloids protected by poly(3-chloro-2-hydroxypropyl-2-methacryloxyethyl dimethyl ammon-



**Figure 7.** Histogram for gold nanoparticles protected by poly(diallyldimethyl ammonium chloride);  $\text{KBH}_4$  reduction; stored for nine months.

ium chloride) again might result from the influence of the steric hindrance of the ammonium group. Wilcoxon *et al.* [3], for example, report on the strong adherence of cationic surfactants on gold colloids. While a hydrophobic character of the protective medium (backbone) is surely important for obtaining well-stabilized gold colloids, some interaction of the ammonium groups with the gold colloid could also be desired. Consequently, steric hindrance of the ammonium side group might be less favorable for the stabilization of the colloids.

Considering the long storage time and the fact that no precautions (such as cool temperatures or protection from ambient light) had been taken during storage, the gold colloids protected by cationic polyelectrolytes can be considered as stable and suitable for further investigations. Such systems are promising candidates for applications that require the modification of the "environment" of the metal nanoparticle in particular ways, here by introducing an electrostatic environment surrounding the gold particle. Such systems could be highly useful, for example, in a variety of catalytic applications.

## CONCLUSIONS

A variety of cationic polyelectrolytes was found suitable for the stabilization of colloidal gold nanoparticles, provided the right reduction method was chosen. Faster reduction methods, here by potassium borohydride, are preferable to slower reduction methods in the presence of these efficient stabilizers. Small particle sizes

(below 10 nm) and narrow size distributions can be obtained, and the gold colloids stabilized by such cationic polyelectrolytes were stable in air for several months. A less hydrophobic polyelectrolyte backbone, as in hexadimethrine bromide, results in less-stable colloids. These tendencies correspond well to results obtained by Wilcoxon *et al.* [8] and by us earlier [10], where smaller particle sizes and narrow size distributions were found for gold colloids protected by more hydrophobic media, and from the use of stronger reducing agents. In addition to having hydrophobic backbones, cationic polyelectrolytes having a less sterically-hindered ammonium side group should also be preferred for purposes of stabilization. In this way, additional interactions with the gold colloid surface could occur (possibly from adsorbed chloride anions stemming from the gold precursor).

Also of considerable interest for future investigations would be other cationic polyelectrolytes, for example those carrying phosphonium or sulfonium side groups. In addition, alternative reduction methods should be investigated in order to study options for controlling the sizes and size distributions of the gold nanoparticles.

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