OPTICAL PROPERTIES OF GOLD-CONTAINING POLY (ACRYLIC ACID) COMPOSITES

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ABSTRACT

There is strong interest in the research & development of the particle/polymer composite technology for functional applications. Current activities are directed towards polymer assisted synthesis of ultrafine metal or semiconductor particles in solution, with an ultimate goal to arrange the particles in a matrix in well-controlled fashion, for possible electro-optical applications. In the present work the optical properties of poly(acrylic acid) polymers containing gold chloride have been investigated. This material system permits synthesis of gold nanoparticles by the reduction of gold chloride. The polyelectrolyte initially forming upon mixture of the reagents shows a gelating behavior. In-situ reduction into gold clusters can be achieved by several ways. Rheological properties, optical absorption/extinction spectra as well as photoluminescence and photoluminescence excitation spectra will be presented and discussed. Different possible combinations of gold ligands and co-ordinations states will be considered in the discussion. Gold may be present in the form of complexes, to the polyelectrolytes, or in form of nanoparticles or larger aggregates depending on the relative concentrations of the reagents and polymer molecular weight.

1. INTRODUCTION

The interaction of gold particles and nanoparticles with polymer matrices has been subject to investigations for numerous reasons, ranging from photographic technology and geochemistry to more recent topics such as gold particle immobilization for catalytic purposes [1] and exploration of new optical data storage media [2]. The interaction of gold particles with polymers as well as the gold particle synthesis in polymers and the polymers influence on the synthesis are to be adressed. Recently, we investigated the use of poly(styrene)-poly(acrylic acid) copolymeric micelles as nanoreactors for the synthesis and stabilisation of gold nanoparticles [3]. The gold chloride was incorporated as gold precursor into the poly(acrylic acid) (PAA) forming the core of these micelles, the polymers interaction with the metal salt deserves closer investigation. Here we present our results on the formation and stabilization of gold particles in PAA matrices.

2. EXPERIMENT

Aqueous solutions of poly(acrylic acid) with molecular weights of 2000, 5000, or 90000 Mw were mixed with gold chloride which was added in solution or as a powder. The solutions had a pH of 2.2 to 2.5, which is low enough to stabilize the gold salt and prevent the precipitation of poorly soluble gold hydroxide [4]. Optical transmission spectra were measured at different reaction times on a Perkin Elmer Lambda 6 spectrometer. The dynamic rheologic properties of the samples were measured on a Rheometrics RDA II apparatus. Viscosity and elasticity of solution films with a thickness of approximately 0.5 mm were measured between two polymeric or glass plates. The sample solutions were protected by silicone oil against drying out at the plate edges. The strain was varied at a rate of 10 rad/s, and was kept low enough not to destroy the gels. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured on a Hitachi FL-4500 fluorimeter. All experiments were done at a room temperature of 22°C. Solid films were produced by spreading films on glass substrates and drying in air at a temperature of 80°C.

2. RESULTS AND DISCUSSION

When aqueous solutions of PAA are mixed with gold chloride, they form a gel which then turns slowly from yellow transparent to reddish-brown color. The latter is supposedly associated with the formation of gold nanoparticles. Due to both the high polymer content and the instability of gold chloride under the electron beam, this particle formation cannot be observed directly by transmission electron microscopy. In this paper, the kinetics of this reaction are investigated using various other experimental techniques.

2.1. Optical transmission spectroscopy

Typical evolution of optical transmission spectra for aqueous solutions are shown in figure 1. The different features visible in the spectra can be related to different components which are present in the solutions. A peak found around 450 nm in the initial AuCl3 solution is non-stoichiometric and appears in concentrated solutions only [5].

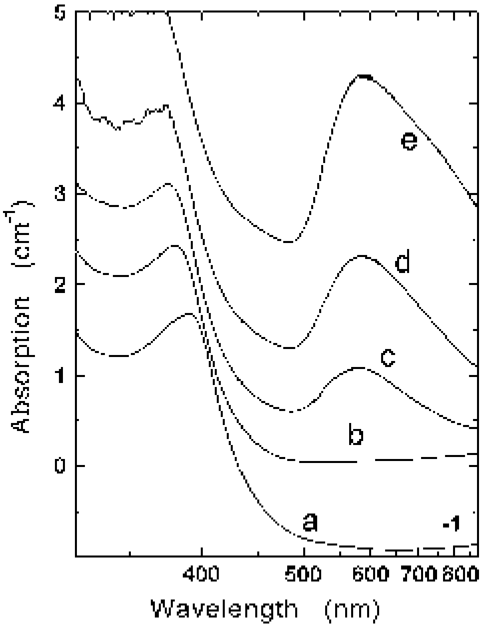

Figure 1: Absorption spectra of 25 wt.% 90000 Mw PAA solutions after different times after addition of 2.6 mg/ml AuCl3. The spectra were taken after 30 s (a), 7000 s (b), 22000 s (c), 133000 s (d), and 390000 s (e). Spectrum (a) is rigidly shifted downwards by one unit. The peak associated with high AuCl3 concentrations is continously shifting towards the blue with time, indicating a decrease of AuCl3 concentration (b). The gold plasmon peak is appearing after two to three hours (c). The subsequent increase of the absorption coefficient, which is almost independent of the wavelength (d,e), is due to particle aggregation.

It is decreasing in intensity and shifting rapidly to 400 nm upon mixing with polymer solution and lateron continues shifting to shorter wavelengths, indicating a continous decrease of AuCl3 concentration in the samples(see figure 1a,b). The formation of gold nanoparticles can be observed by optical transmission spectroscopy (see figure 1c) due to the appearance of the surface plasmon absorption line which is characteristic for gold nanoparticles [6]. The spectra then start to show an increase of absorption which is almost independent of the wavelength (figure 1d,e). This is due to absorption and screening of light by larger aggregates of gold particles which are found to grow over several days or even weeks. In dried, solid samples the formation of the particles generally took longer, and the aggregation-induced shift was negligible. The evolution can also be seen by plotting the absorption as a function of time a in figure 2. Here the different phases can be distinguished more easily. The initial decrease of the intensity around 500 nm is best seen in the difference spectra (figure 2b). The decrease is less pronounced at 600 nm, where the plasmon absorption peak grows as the second step of the reaction. The third phase is the wavelength-independent incrementation of the absorption caused by the aggregation (figure 2a).

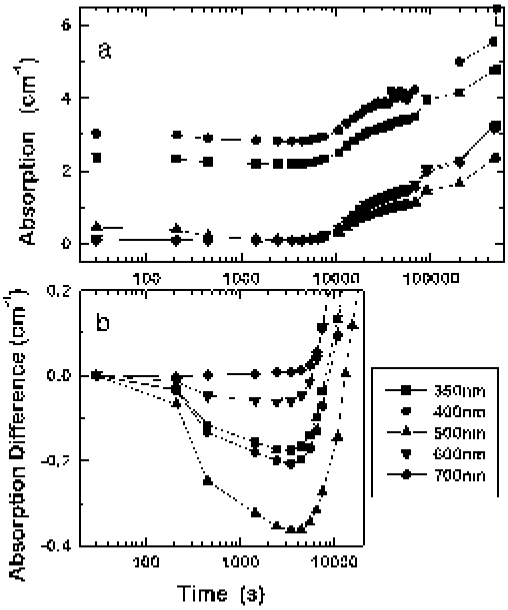

Figure 2: (a) Evolution of the absorbance at various wavelengths for the 25 wt.% 90000 Mw PAA solutions after different times after addition of 8.3 mg/ml AuCl3. (b) The difference spectra are normalized for same absorbance for the first spectrum which was taken 30 seconds after mixing the reagents.

The wavelength of the plasmon peaks is between 580 and 650 nm. The wavelength is close to the one observed by Nagayama et al. [2]. It is longer than the approximately 530 nm expected for particles in the nanometer size range from theory [6], which is close to what was observed in similar systems before [7,8]. Several possible reasons can be envisaged to account for this in theory. The particles may either be larger than 80 nm in diameter; this can be ruled out because they would nevertheless have to have a narrow size distribution to produce a pronounced peak. Also the volume concentration of gold particles can not be around 50 %, which would be necessary to explain the peak positions; the amount of gold added to the samples is not sufficient. For the same reasons the refractive index of the solution can not be significantly raised by the addition of gold chloride. The shift is also too large to be explained by an adsorbate-induced reduced electron density in the clusters as discussed in [9], except if the clusters are very small (< 1 nm). The question will be answered when electron microscopy reveals the particle sizes.

2.2. Rheology measurements

The rheologic properties of the samples were measured as a function of time after mixing of the two components. Tests were made to make sure that the rheometry does not affect the gel formation. The evolution of viscosity and elasticity for a 90000 Mw PAA sample are shown in figure 3.

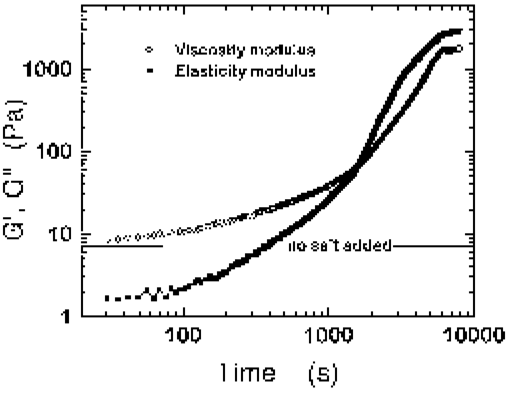

Figure 3: Viscosity and elasticity moduli of a 25 wt. % PAA aqueous solution with 90000 Mw after mixing with 8.3 mg/ml AuCl3 at t=0. The viscosity modulus of the initial solution with no salt added is indicated by a horizontal bar.

Both the viscous and the elastic moduli are increasing by several orders of magnitude with respect to the pure PAA solution. This is due to crosslinking between chains. The linking mechanism is supposed to be substitution of the hydroxyl or chlorine ligands by the polymerÕs carboxylic group. Tossell proposed the formation of larger complexes by p-bonding of additional ligands to the square-planar gold complex [10]. Comparison with the optical data of figure 2 shows, that the gelating process starts with the formation of the first gold-PAA complexes. 1500 s after mixing the two components, the crosslinking or gelling point is reached. The gel viscosity saturates after 6000 s. This happens when all ligands are substituted by carboxylic groups. As shown by the optical data, at the same time the nanoparticle formation starts. This and - lateron - the concentration of the gold in aggregates destabilizes the gel at longer times, by consuming the gold which thus is not any more available for chain interlinking. Therefore, after approximately one week, samples with lower gold salt content become liquid again. The situation is different for shorter polymer chainlengths. Here, much higher salt concentrations are necessary to build enough links between chains until a gel is formed. However, for a 5000 Mw PAA solution the viscosity even decreased, which is probably due to electroviscous effects [11]. For shorter chains, also the entropy gain by adsorption to nanoparticles is larger, making them less efficient for steric stabilisation of the colloid.

2.3. Photoluminescence

On solid samples with high contents of gold chloride photoluminescence was observed (see figure 4). The PL emission is on the long-wavelength side of the gold nanoparticle plasmon peak, but it is improbable to have PL emission from gold particles. Also a pronounced peak at 450 nm is observed in the absorption spectrum; it is tentatively assigned to gold monochloride which has a similar absorption spectrum [12] and may be complexed with the polymer. Gold monochloride has been found to be photoluminescent at an emission wavelength of 635 nm [12]. Gold monochloride is therefore a by-product of the stepwise recution of AuCl3.

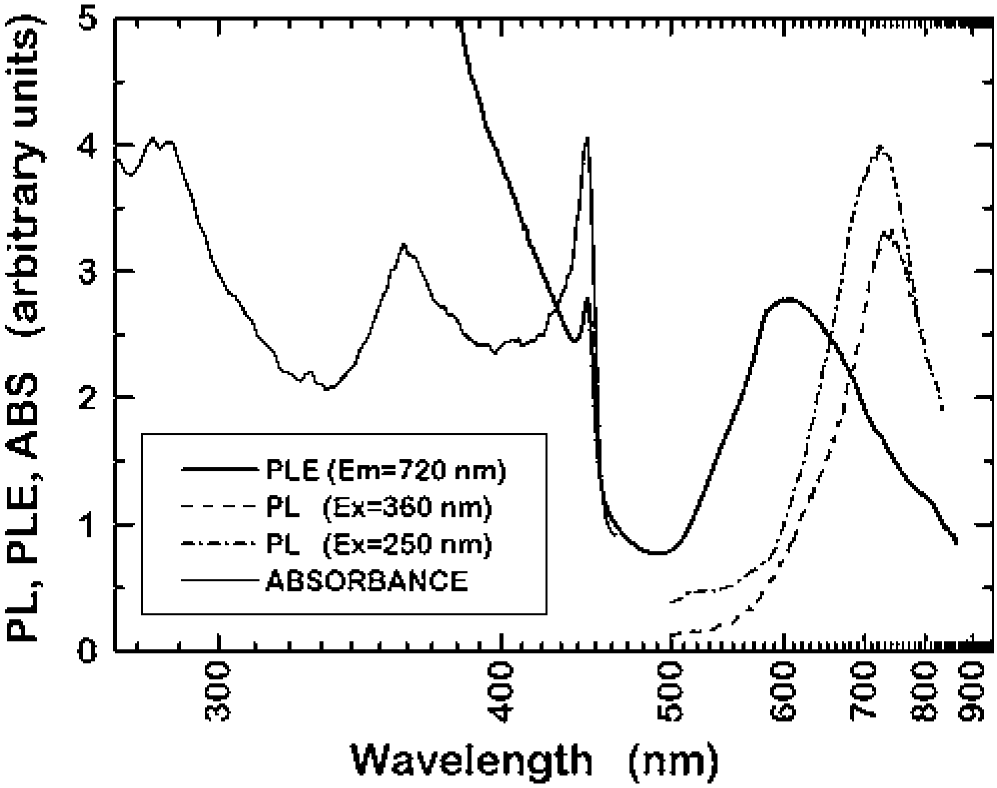

Figure 4: Absorption (thick solid line), Photo-luminescence spectra (dotted and dot-dashed lines) and excitation spectrum (thin solid line) for a dried solid film of 5000 Mw PAA with a concentration of AuCl3 of 20 % weight fraction.

3. CONCLUSIONS

The formation of gold nanoparticles in PAA matrices takes place in several steps. These depend critically on the relative and absolute concentration of the involved species. In the following we will develop a model for the mechanisms of nanoparticle formation.

- Gold chloride is predominantly dissolved in water in the form of square-planar complexes of the form AuCl4- or AuCl3OH- [4]. In concentrated AuCl3 aqueous solutions, deviations from Lambert-BeerÕs law are observed in the optical absorption [5], with the chloride ligands being replaced by OH- ligand groups with time and depending on the pH. In a first step after addition of the concentrated solution to the polymer solution, the optical spectra shown in figure 1 are undergoing this transition from a saturated gold chloride solution to complexes. These complexes are probably forming by replacing the -OH group of the AuCl3OH- complex by a hydrolysed carboxylate group of the acid.
- The next step of the process is gel formation by chain crosslinking, which can be observed by rheology measurements. It is speculated that the link between two polymer chains is across an AuCln complex; Cl ligands in the gold complex may be exchanged by acrylic acid ligands, which are far more abundant under the experimental conditions. The gelation process can only take place if the number of gold atoms is larger than the number of polymer chains. It saturates when all gold ligands are replaced by acrylic acid groups.
- The step by step formation of intermediate complexes, replacing hydrolyzed chlorine ions by carboxylic groups, is supposed to facilitate the reduction of the gold chloride. The carboxylic ligands make - due to their lower redox-potential - the gold atom easier to reduce to Au0, from which the nanoparticles are built. Therefore, the formation of nanoparticles starts at the same time as the saturation of the gelation process. Particle formation is seen in the optical spectra by the appearance of the nanoparticle plasmon absorption, though the peak position is shifted from the wavelength predicted by theory.
- With increasing number of gold nanoparticles, they start to agglomerate to large aggregates. These aggregates lead to an increased opacity of the samples which is independent of the light wavelength; it is caused by the large particles screening the light proportional to their geometric cross-section. The gel is destabilized since the gold needed to link the chains is concentrated in particles and aggregates, the viscosity is diminuished visibly and the gel becomes liquid again. At the limit, this is leading to a phase-separation into one phase which is rich of aggregated gold particles, and a second phase with clear polymer solution. In the gels utilized in this study, this process takes several days. The kinetics depend on the viscosity of the solutions or gels. For diluted solutions, high diffusion leads to immediate aggregation and sedimentation of gold particles. In dried films, however, the diffusion of gold particles is inhibited by the solid matrix, and aggregation remains negligible.

In conclusion, it has been shown that PAA can be utilized for the synthesis of gold nanoparticles. These are mainly stabilized by kinetic effects, making the rheological properties of the matrix the key factor for particle stabilization.

4. ACKNOWLEDGEMENTS

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