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Synthesis of platinum colloids sterically stabilized by poly(*N*-vinylformamide) or poly(*N*-vinylalkylamide) and their stability towards salt

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This is part IX in the series of the study on synthesis and functionalities of poly(*N*-vinylalkylamide).

Abstract Colloidal dispersions of nanometer-sized platinum colloids were prepared by ethanol reduction of $PtCl_6^{2-}$ in the presence of poly(*N*-vinylformamide) (PNVF), poly(*N*-vinylacetamide) (PNVA) or poly(*N*-vinylisobutyramide) (PNVIBA) and analyzed by UV-vis spectroscopy and transmission electron microscopy. The dispersion stability of each colloid to the presence of added KCl was determined by a stirring and centrifugation procedure. The platinum colloid stabilized by PNVF (PNVF-Pt) was the most stable and its critical flocculation concentration was not observed up to the highest electrolyte concentration employed (4.0 M). The stability of the platinum colloids stabilized by poly(*N*-isopropylacrylamide) (PNIPAAm) and poly(vinylpyrrolidone) (PVP) was also examined. The sequence of polymer-stabilized platinum colloids in increasing order of dispersion stability was found to be PNIPAAm-Pt < PNVIBA-Pt < PVP-Pt < PNVA-Pt < PNVF-Pt.

Key words Poly(*N*-vinylformamide) – Poly(*N*-vinylalkylamide) – Dispersion stability – Colloidal platinum nanoparticles – Critical flocculation concentration

Introduction

Ever since Dunworth and Nord [1] reported the synthesis of catalytically active metal sols via the reduction of a noble metal ion by molecular hydrogen in the presence of poly(vinylalcohol), numerous studies have been performed to prepare metallic colloids stabilized by synthetic polymers and to characterize their physicochemical properties [2–6]. The production of metal sols by aqueous methanol reduction of metal salts in the presence of a polymeric stabilizer was first reported by Hirai et al. [2]. In this novel metal-polymer system, the protective polymer cannot only influence metal particle sizes and morphologies but can also have a tremendous influence on the catalytic activity and selectivity. To our knowledge, only a few synthetic polymers, such as poly(vinylalcohol) [2], poly(vinylpyrrolidone) (PVP) [3], sodium poly(acrylate) [4] etc., have been studied so far with respect to their utility in the metal-polymer system. Mayer and Mark [6] described the use of several cationic polyelectrolytes for the preparation of Pt and Pd nanoparticles. They found that cationic polyelectrolytes create a strong electrostatic "environment" surrounding the catalytically active metal particle which, in turn, has a large effect on the catalytic activity of such systems. Recently, we reported that poly(*N*-isopropylacrylamide)-stabilized colloidal Pt nanoparticles showed a cloud-point temperature of 34.2 °C in aqueous solution and the temperature-dependent catalytic activity was not at all Arrhenius-like [7].

The aim of this work was to produce colloidal dispersions of Pt nanoparticles using poly(*N*-vinylformamide) (PNVF), poly(*N*-vinylacetamide) (PNVA) and poly(*N*-vinylisobutyramide) (PNVIBA) as the protective polymer, respectively. PNVF or PNVA undergo acid- or base-catalyzed hydrolysis to form poly(vinylamine), a commercially important polymer which has been used in many areas of science and technology including wastewater treatment, paper coatings, textiles, personal care products, and adhesives [8–10]. PNVIBA is a novel water-soluble polymer and exhibits a well-defined lower critical solution temperature (LCST) in water [11]. A major focus of this study was to investigate the particle sizes and size distributions under various conditions needed to synthesize catalytically active Pt particles.

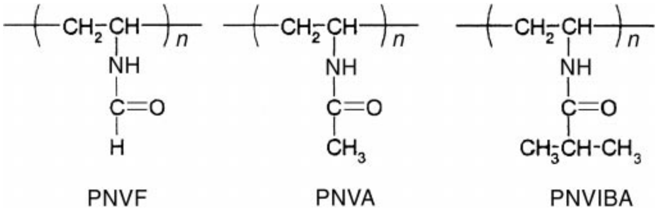
Another aim of this study was to investigate the flocculation behavior of such Pt sols in aqueous electrolyte solutions. Aqueous dispersions of colloidal Pt particles have been widely used as redox catalysts for the solar photolysis of water [12]. Besides the catalyst, other charged components, such as electron donors and pH buffers, are often involved in photolysis systems. The catalytic activity of the catalyst depends strongly on its dispersion stability in such mixtures. The electrolyte-induced coagulation of small Pt particles stabilized by surface adsorption of anions was studied by Furlong et al. [13]; however, little has been reported on the flocculation behavior of polymer-stabilized Pt colloids in aqueous electrolyte solutions.

In this paper we present for the first time UV-vis spectroscopy and transmission electron microscopy (TEM) evidence for the formation of well-dispersed Pt colloids stabilized by PNVF, PNVA or PNVIBA. The influence of preparation parameters on the particle size and size distribution is also discussed. A stirring and centrifugation procedure was used to investigate the aggregation behavior of such Pt colloids in aqueous KCl solution.

Experimental

Synthesis of PNVF, PNVA and PNVIBA

Scheme 1



These homopolymers with different mean molecular weights were obtained by radical polymerization at 60 °C under a nitrogen atmosphere according to the previously reported method [10, 11], as shown in **Scheme 1**. The number-average molecular weights of the polymers were evaluated by gel permeation chromatographic measurements. The NVF monomer was a generous gift from Mitsubishi Chemical Cooperation.

Preparation of aqueous colloidal Pt dispersions stabilized by these polymers

The Pt particles were prepared by refluxing a solution of chloroplatinic acid and protective polymers in ethanol/water as previously reported [7]. For example, $H_2PtCl_6 \cdot 6H_2O$ (0.03 mmol Pt) and PNVF (mean molecular weight 60 000, 85.2 mg, 1.2 mmol as monomeric unit) were dissolved in an ethanol/water mixed solvent (4/6, v/v, 75 ml), and the solution was then refluxed at 90 °C in an oil bath. After an induction period of 15 min, the color of the mixture changed suddenly from pale yellow to dark brown. The reaction mixture was boiled for 60 min before being allowed to cool. The molar ratio of the monomeric unit/Pt was therefore 40 for the colloidal Pt dispersion stabilized by PNVF (PNVF-Pt). Evaporating the solvent from the dispersion solutions and then redissolving the residues in 50 ml distilled water gave stable aqueous dispersions of PNVF-stabilized Pt colloids. The preparation of Pt colloids stabilized by PNVA, PNVIBA and poly(*N*-isopropylacrylamide) (PNIPAAm) was carried out in 50 ml ethanol/water mixtures with an ethanol volume fraction of 0.6 because of their different solubility from that of PNVF.

Physical measurements

The formation of Pt nanoparticles was followed by recording the UV-vis absorption spectra on a JASCO model V-550 recording spectrophotometer as a function of refluxing time and the data were corrected for ethanol/water background absorption. TEM images were obtained with a Hitachi H-700H microscope operating at an acceleration voltage of 150 kV at a magnification of 200 000. Specimens of the various Pt colloids were prepared by slow evaporation of a drop of the appropriately diluted solution deposited onto a collodium-coated copper mesh grid. We measured the size distributions of the particles from enlarged photographs of the TEM images.

Dispersion stability

The stability of each Pt colloid to the presence of added KCl was determined by a method similar to that employed by Furlong et al. [13]. The relative particle concentration of a Pt sol was assessed by measurement of sol turbidity at 500 nm (JASCO V-550 spectrophotometer). The concentration when expressed relative to the initial particle concentration gives the quantity stability. The Pt sols at different electrolyte levels ([Pt] = 9.8 mg dm^{-3}, 15 ml) were agitated by a magnetic stirrer at about 1000 rpm for 4 h, after which time they were centrifuged at 7000 rpm using a TOMY refrigerated centrifuge for 15 min. The supernatant on the top 5 cm^3 was withdrawn for the absorption measurement. The critical flocculation concentration (CFC) was taken as the initial break point in the resulting stability versus logarithm of KCl concentration curve.

Results and discussion

Preparation and characterization of colloidal Pt dispersions

Several examples of the sol characteristics of the polymer-stabilized Pt colloids as well as the preparation conditions are summarized in Table 1. The ethanol serves as the reducing agent for the reduction of $PtCl_6^{2-}$. Several previous metal sol preparations have required the addition of water in alcohol to obtained a colloidal dispersion of the metal [14, 15]. For example, the Rh(III)-methanol reaction is thought to involve the formation of hydride species in which the hydridic hydrogen is oxidized by the metal ion to H^+ instead of H_2 [14]. Further oxidation of aldehyde, which is formed in the principal reaction, to a carboxylic acid can occur

Table 1 Formation of colloidal Pt sols by means of the ethanol-reduction method in the presence of protective polymers[a]

Protective polymer	$M_n \times 10^{-4}$	Induction period (min)	Boiling duration (h)	Color	Average diameter (Å)	Standard deviation (Å)	Critical flocculation concentration (M)
PNVF	6.0	15	1.0	Yellow-brown	22.5	6.9	/
PNVA	1.0	17	1.0	Dark brown	24.1	6.1	2.0
PVP	1.0	10	1.0	Dark brown	28.1	7.7	1.4
PNVIBA	0.9	14	1.0	Yellow brown	19.0	6.2	1.0
PNIPAAm[b]	0.6	12	1.1	Dark brown	23.8	6.3	0.4

[a] Molar ratio of monomeric unit/Pt is 40/1 for each sol. For details see Experimental section

[b] From Ref. [7]

in the presence of water. In addition, Teranishi et al. [16] recently found that the precise particle size and distribution critically depend on the volume ratio of ethanol/water in the preparation of PVP-stabilized Pd nanoparticles. Therefore, the ethanol volume fraction should be selected properly in order to protect the polymer against precipitating upon refluxing the reaction mixture and to obtain the well-dispersed metal colloids.

PNVIBA is a thermoreversible water soluble polymer, whereby aqueous solutions of this polymer exhibit a LCST (about 39 °C) [11, 17]. Although the chemical structure of the polymer is different from that of PNIPAAm, the total hydrophobic and hydrophilic balances of the two polymers are quite similar [17]. Both ethanol and water are solvents for PNIPAAm at room temperature; yet mixtures of the aqueous solutions in certain proportions result in immiscibility. This phenomenon has been termed "cononsolvency", and is also observed in aqueous solutions of PNIPAAm with methanol as the second solvent [18]. When the ethanol volume fractions ranged from 0.6 to 0.9, well-dispersed PNIPAAm-Pt colloids were obtained [7]. The observed solution behavior of PNVIBA was similar to that PNIPAAm in the same binary solvent. At volume fractions of ethanol higher than 0.56, the LCST of PNVIBA exceeds the boiling point of the mixture. Therefore, well-dispersed PNVIBA-Pt colloids with a mean diameter of 19.0 Å and a narrow size distribution can be obtained in the ethanol-water mixture at a volume fraction of ethanol of 0.6. In the case of PNVA, the polymer is soluble to the boiling point of the mixture of water and ethanol in all proportions. Thus, PNVA-Pt colloids with a mean diameter of 24.1 Å were synthesized successfully at a volume fraction of ethanol of 0.6.

In contrast to PNVIBA and PNVA, the water-soluble PNVF will precipitate from aqueous mixtures above an ethanol volume fraction of 0.5 on raising the temperature to the boiling point. In these preparation experiments 35 ml ethanol was added to a 40-ml aqueous solution of PNVF containing 0.03 mmol Pt (in the form of chloroplatinic acid) and the mixture was refluxed for 1 h. At this ethanol content a homogeneous PNVF-stabilized Pt dispersion was obtained. As shown (SD) in Table 1, the average diameter and standard deviation of the PNVF-Pt colloids in water were 22.5 and 6.9 Å, respectively.

Aqueous solutions of Pt colloids stabilized by PNVF, PNVA and PNVIBA are stable for months in air and can be isolated and redispersed without changing their colloidal properties. TEM images and size distributions of well-dispersed Pt colloids stabilized by these protective polymers are shown in Fig. 1. By varying the molecular weight of the protective polymer and the monomeric unit/Pt molar ratio, the particle size and size distribution can be changed, as will be described at a later date.

The formation of PNVF-Pt colloids via ethanol reduction of $PtCl_6^{2-}$ was studied by UV-vis spectroscopy. The absorption spectra of the samples quenched at various intervals of time are shown in Fig. 2. As can be observed, at the beginning of the reflux, there are two different peaks at 260 nm and 220 nm, characteristic of $PtCl_6^{2-}$ and $PtCl_4^{2-}$, respectively [3, 5]. The absorbance at 260 nm decays markedly during the first 12 min; the absorbance of Pt sol, which can be monitored at 500 nm, is not observed. The characteristic absorption band for $PtCl_4^{2-}$ only changed little in its intensity. A two-step reaction mechanism has been proposed for the reduction of $PtCl_6^{2-}$ by ethanol, where $PtCl_4^{2-}$ serves as the intermediate [7]. Also, the reduction of $PtCl_4^{2-}$ is more rapid than that of $PtCl_6^{2-}$, as would be expected from the standard redox potential of the two ions, i.e., 0.68 V for $PtCl_6^{2-}$/ $PtCl_4^{2-}$ and 0.755 V for $PtCl_4^{2-}$/Pt(0) (vs the normal hydrogen electrode) [19]. Then, a high concentration of Pt(II) would be required to give sufficient Pt(0) atoms for nucleation to occur according to classical nucleation theories [20]. After an induction period of 15 min, the absorption at 260 nm decreases rapidly; the absorbance of Pt(0) at 500 nm appears and grows with time. At this time, the solution changed color from light yellow to dark brown and the absorption maximum of $PtCl_4^{2-}$ at 220 nm disappeared. A new absorption band at 215 nm appeared and increased in intensity with time, which is a characteristic of the colloidal Pt predicted by calculations of Creighton and Eadon [21] according to Mie theory. This was the only peak in the spectrum of the PNVF-Pt sol when the reaction was complete after 20 min, and no further changes were observed even after several weeks.

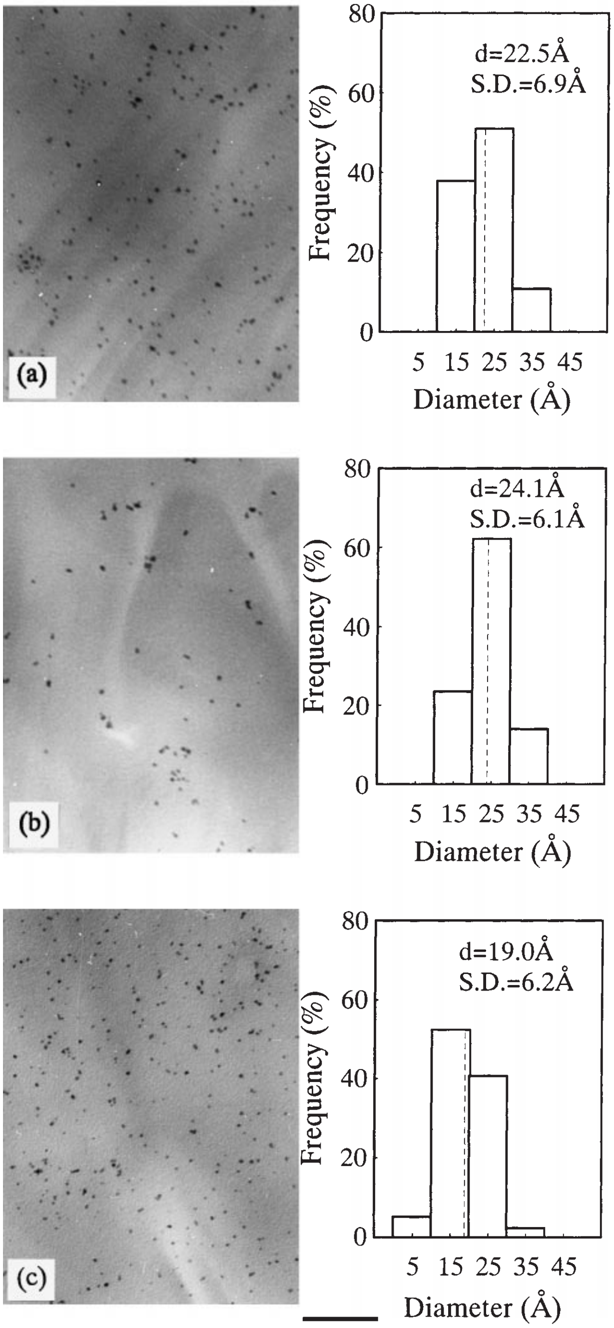


Fig. 1 Transmission electron microscope images and size distributions of **a** poly(*N*-vinylformamide) (*PNVF*)-Pt, **b** poly(*N*-vinylacetamide) (*PNVA*)-Pt, and **c** poly(*N*-vinylisobutyramide) (*PNVIBA*)-Pt colloids. The *scale bar* represents 500 Å for all parts of the figure

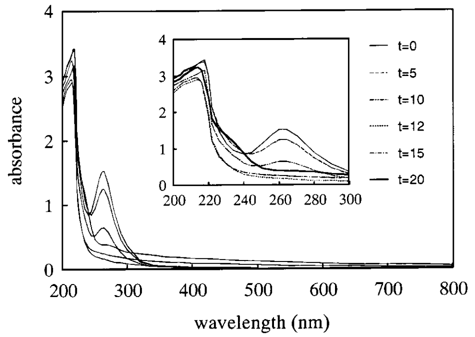


Fig. 2 UV-visible spectrum of a solution containing 2.0 × 10^{-4} M H_2PtCl_6, 1.0 × 10^{-5} M PNVF, and ethanol/water (4/6, v/v) at various reduction times

Dispersion stability of polymer-stabilized Pt colloids

The protective action by the neutral polymers is generally referred to as steric stabilization [22]. The conformation of polymers adsorbed on the surface of metal particles is often described by the train-loop-tail model [23], where trains are the segments in actual contact with the surface, loops are those in-between and extending into the solution, and tails are the free ends of the polymer also extending into the solution. Steric stabilization essentially acts by preventing the approach of the particle cores to a separation where their mutual van der Waals attraction would be sufficient for aggregation to occur. The interaction between the surface of the metal particles and the train parts of the polymers is considered to be hydrophobic. For the protective polymers used in this work, however, the coordination interaction of the amide group in the side chain is also confirmed to contribute to the adsorption of polymer on the surface [24]. Consequently, the dispersion stability of the Pt colloids formed turned out to be very high in pure water at room temperature, as described in the previous section.

The solvent power of the dispersion medium for the protective polymers is another important item. By reducing the solvency conditions of the polymer chains, the dispersion stability of the colloidal metal particles decreases. The flocculation behavior of the series of Pt colloids stabilized by PNIPAAm, PNVIBA, PNVA, PNVF or PVP in aqueous solutions of KCl is illustrated in Fig. 3. The CFC values for these Pt colloids are summarized in Table 1. Above the CFC of KCl for a certain Pt colloid, the solution becomes a poor solvent for the protective polymer; thereby, one can expect the polymer chains to collapse onto the particle surface and the steric stabilizing effect to vanish. The PNIPAAm-Pt and PNVIBA-Pt colloids are clearly unstable to added electrolyte and have a CFC of 0.4 and 1.0 M KCl, respectively. PNIPAAm and PNVIBA are well-known temperature-sensitive polymers [7, 11], showing LCSTs in water at 34 and 39 °C, respectively, in the absence of salt. At higher temperatures than the LCST, the chain backbone changes from hydrophilic to hydrophobic and collapses into a molecular globule. One would expect the flocculation of PNIPAAm-Pt and PNVIBA-Pt colloids to occur on raising the temperature of the systems,

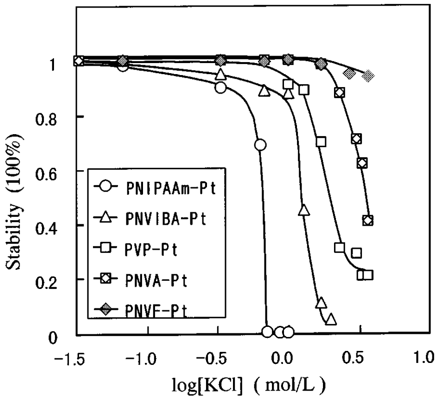


Fig. 3 Plots of dispersion stability of polymer-stabilized Pt colloids against the logarithm of the KCl concentration

reflecting the fact that aqueous solutions of PNIPAAm and PNVIBA phase-separate on heating. We refer to the temperature at which the flocculation of Pt colloids first becomes observable as a critical flocculation temperature (CFT). Similar to the effects of added salts on the LCSTs of PNIPAAm [18] and PNVIBA [25], the addition of KCl depresses the CFTs of the two Pt colloids to temperatures even lower than room temperature. Therefore, the lower CFC values of the PNIPAAm-Pt and PNVIBA-Pt colloids are attributed to the sensitive "coil-to-globule" transitions of the two protective polymers induced by the addition of salt.

It is also evident that the PNVF-Pt colloid is stable to added KCl up to the highest electrolyte concentration (4.0 M) owing to the highly hydrophilic chain backbone of PNVF. The PVP-Pt and PNVA-Pt colloids have CFCs of 1.4 and 2.0 M KCl, respectively, indicating that they have a degree of steric stabilization that is insufficient to confer stability at the higher electrolyte concentrations. Both PNVA and PVP show no LCST in water in the absence of salts [26, 27], and the enhancement of the hydrophilic-to-hydrophobic transition in the presence of KCl is related to the salting-out effect. Even up to the highest KCl concentration, however, both PVP-Pt and PNVA-Pt colloids cannot be flocculated completely. These results confirm the view that the flocculation of the polymer-stabilized Pt colloids only occurs when the solvency of the water for the protective polymer chains is considerably reduced by the added electrolyte. At a certain molar ratio of monomeric unit/Pt, the dispersion stability of the polymer-stabilized Pt colloids is found to be independent of chain length. Six samples of PVP-Pt colloids varying in molecular weight (*M*) from 1.0×10^4 to 3.6×10^5 were examined. Changes in the molecular weight of the stabilizing polymer scarcely altered the measured CFC. It is worthwhile noting that the CFC values are far in excess of the those in Ref. [13] for Pt colloids stabilized by the adsorption of anions (0.01 M KCl), indicating a significant advantage of polymer-stabilized Pt colloids compared to charge-stabilized Pt colloids.

Conclusion and outlook

We have demonstrated the use of PNVF, PNVA and PNVIBA as protective polymers to provide steric stabilization for well-dispersed Pt colloids in water. Flocculation experiments using the electrolyte KCl showed that the sequence of polymer-stabilized Pt colloids in increasing order of dispersion stability is PNIPAAm-Pt < PNVIBA-Pt < PVP-Pt < PNVA-Pt < PNVF-Pt. The Pt colloid stabilized by PNVF is stable to added KCl up to the highest electrolyte concentration employed.

In the future, we want to investigate in detail the effect of reducing the solvency conditions of the polymer chains on the dispersion stability of Pt colloids. For example, ethanol is a nonsolvent for PNVF and a cononsolvent for PNIPAAm or PNVIBA; thereby, the addition of ethanol to the Pt colloids stabilized by these polymers in water will rapidly change the stability behavior over a narrow range of the ethanol volume fraction. These observations regarding the sensitivity of the CFCs of polymer-stabilized Pt colloids to different electrolytes will also have an impact on their potential applications as catalysts for chemical and photochemical reactions.

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