Formation and Stabilization in Water of Metal Nanoparticles by a Hyperbranched Polymer Chemically Analogous to PAMAM Dendrimers

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Successful one-pot preparation of a hyperbranched polymer chemically analogous to PAMAM dendrimers was achieved and its use for metal nanocluster stabilization is reported. When compared to PAMAM, such experiments demonstrate clearly the effect of the macromolecular architecture on the formation of the inorganic nanoparticles.

Small metal particles have quite unique optical, electronic, and catalytic properties that result from size, shape, and size distribution effects.The preparation of such metal colloids requires the use of stabilizers which prevent the thermodynamically favored aggregation of the nanoparticles in solution. Various well-known compounds (e.g., water-soluble polymers, surfactants, etc.) have been employed as stabilizers.[1] Dendrimers have also been used as nanoreactors in which metal cations are localized before reduction leading to stabilized metal nanoparticles of a few nanometers,[2] this small size being presumably related to the unique structure of the dendrimers. However, the costly synthesis of dendrimers is prohibitive for many applications. In contrast to those perfectly branched monodisperse dendrimers, randomly branched (i.e., hyperbranched) polymers can be easily accessible[3] and they can effectively stabilize metal nanoparticles in organic solvents.[4] To our knowledge, no attempt has been made, up to now, to compare nanoparticles obtained from reduction of metal salts complexed with dendrimer and hyperbranched polymer.

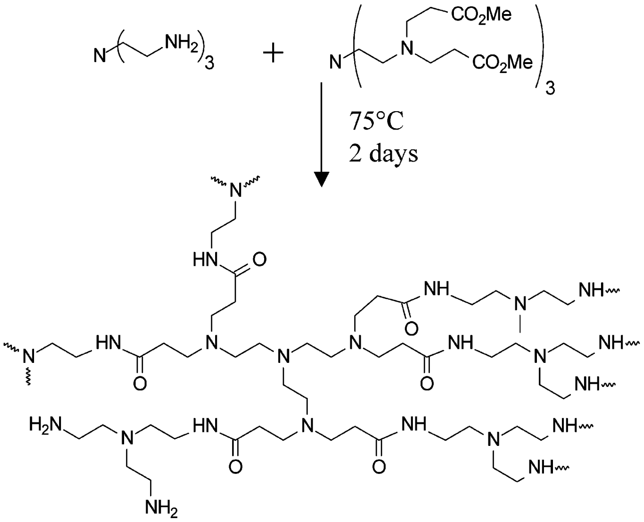

Figure 1. Schematic representation of the synthesis and structure of the HYPAM hyperbranched polymer.

In this work, we present the synthesis and characterization of a hyperbranched polymer that is chemically analogous and close in molecular weight to the 4th generation of PAMAM dendrimers (noted PAMAM4). Because of this similarity in the molecular weights, this hyperbranched polymer was noted HYPAM4. Characterization of gold nanoparticles prepared using these polymers is also described.

Polymer Synthesis[5] and Characterization. The synthesis of hyperbranched polyamidoamines with a structure similar to the one of PAMAM dendrimers was based on a method described by Dvornic,[6] where a hexaester was reacted with a triamine (Figure 1).

This method has the strong advantage of leading to hyperbranched architectures in a single step and can be carried out in large quantities. By adjusting the mole ratio between the hexaester and the triamine for the polymer synthesis, control of the final molar mass of the hyperbranched polymer can be experimentally achieved. We have focused our work on the samples obtained when a triamine/hexaester mixture of 10:1 ratio was used for the synthesis. Clearly, the characterization of this polymer demonstrates that HYPAM4 is quite comparable to the highly used PAMAM dendrimer of the 4th generation. Molar masses are very close for both compounds, as are the numbers of primary and tertiary amines (see Table 1) (by construction, HYPAM4 has, however, less amide functions when compared to PAMAM4). Indeed, to check the chemistry of the hyperbranched polymer, the quantification of amine groups was carried out by several methods. The most reliable results were obtained by quantitative ^{13}C NMR experiments in the presence of a calibration

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(5) For HYPAM4, 2.5 g of tris(2-aminoethyl)amine (17.1 mmol) was mixed with 1.13 g of tris(2-di(methylacrylate)aminoethyl)amine (1.7 mmol). The solution was stirred under argon at 75 °C during 2 days, at which time the products were dissolved in 5 mL of CH_2Cl_2 and precipitated into 200 mL of THF at 0 °C. A 2.05 g portion of precipitated polymer was obtained as a yellow gum.

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Table 1. Polymer Characterization

	$\overline{M_w}$[a]	$I = \overline{M_w}/\overline{M_n}$[b]	primary amines/ tertiary amines/ amide groups (mmol·g^{-1})[c]
PAMAM4	13 000 (14 215)[d]	1.1	3.8/3.9/7.1 (4.5/4.4/8.7)[d]
HYPAM4	13 600	1.4	4.9/5.0/3.3

[a] Molecular weight determined by LS–SEC. [b] Polydispersity index determined by SEC. [c] Results obtained from quantitative ^{13}C NMR experiments. [d] Theoretical values deduced from the chemical structure.

product (Me_4NOH). The attribution of the peaks was carried out by COSY, HSQC, and HMBC experiments and comparison with corresponding spectra of PAMAM dendrimers. The quantity of primary amine groups was obtained by comparison of the CH_2-NH_2 peak at 37.8 ppm to the Me_4NOH peak at 55.2 ppm. Results are presented in Table 1. For PAMAM4, this method gave an experimental value relatively close to the theoretical one. The discrepancy between theoretical and experimental values can be attributed to the limit of accuracy from signal/noise ratio and to defects in PAMAM4 real structure.[7]

Formation of Gold Nanoparticles. Hyperbranched polymer-stabilized nanoparticles were prepared in a two-step process. First, an aqueous solution of HYPAM4 (1.5 10^{-6} M) was mixed with aqueous solutions of $HAuCl_4$ with a controlled molar ratio [Au^{III}]/[HYPAM4]. Second, the ions were chemically reduced by sodium borohydride. Besides a very weak band around 640 nm, the absorption spectrum of a $HAuCl_4$ solution presents a strong absorption band at 226 nm and a shoulder at 290 nm due to charge transfer between the metal and the chloro ligands (see Figure 2A). When adding $HAuCl_4$ to a solution of HYPAM4, the absorbance at 290 nm increases linearly with the number of added Au^{III} ions until the ratio [Au^{III}]/[HYPAM4] reaches ca. 150.

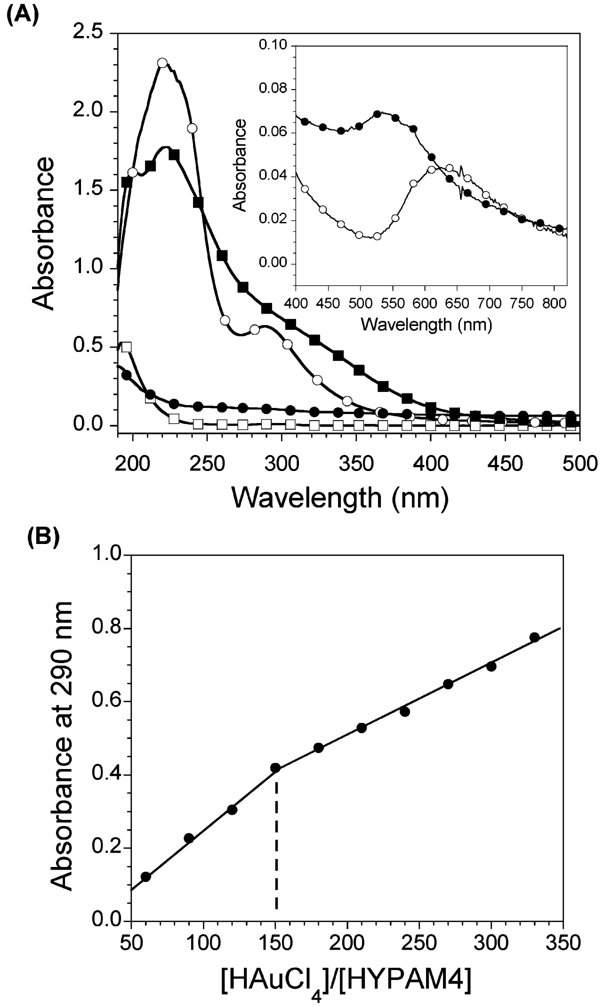

Figure 2. (A) Absorption spectra of aqueous solutions: 1.8 × 10^{-4} M $HAuCl_4$ (open circles); 1.5 × 10^{-6} M of HYPAM4 (open squares); 1.8 × 10^{-4} M $HAuCl_4$ and 1.5 × 10^{-6} M of HYPAM4 before (full squares) and after reduction with a 5-fold molar excess of $NaBH_4$ (full circles). (B) Optical density at 290 nm of a solution 1.5 × 10^{-6} M of HYPAM4 with various amount of Au^{III} (the optical path length is 0.5 cm).

The difference in the slopes suggested various surroundings for the added gold ions and therefore some interactions between gold ions and the polymer. As already described in the case of chitosan,[8] formation of ion pairs between $AuCl_4^-$ and the protonated amino groups of HYPAM4 (the pK_{NH_2} value in HYPAM4 should be close to the 9.5 estimated for the NH_2 functions in PAMAM4[9] and $HAuCl_4$ has a pK_a lower than 3) could be responsible at least partially for this phenomenon. Whatever the nature of the interaction between $AuCl_4^-$ and the hyperbranched polymer may be, this experiment shows that HYPAM4 can be loaded with a maximum number of ca. 150 Au^{III} ions per macromolecule. This number is larger than the primary amine functions of HYPAM4 (ca 70 as deduced from Table 1) and close to the number of amine and amide functions within the polymer (ca 180). For PAMAM4, the maximum number of loaded metal ions was found to be around 50, i.e., close to the number of external amine functions (see Table 1). This demonstrates that the open structure of the hyperbranched polymer compared to the dendrimer architecture facilitates the interactions of the metal ions with the internal chemical functions, increasing therefore the maximum load of ions per polymer. After reduction with a 5-fold molar excess (respective to gold ions) of $NaBH_4$, the 226 nm band of $AuCl_4^-$ vanished, indicating that $AuCl_4^-$ was completely reduced. Instead, a broad band appeared at around 540 nm which is assigned to a plasmon band of gold particles (see insert in Figure 2). Furthermore, a very weak shoulder was observed at ca. 280 nm and may be due to some irreversible oxidation of the polymer by gold ions.[10] The final solution (pH ca. 8–9) remained stable during a few days (even for weeks if only one equiv of $NaBH_4$ was used for the reduction or if the pH solution was adjusted below ca. 5–6). Figure 3 shows a transmission electron microscopy (TEM) micrograph of the gold nanoparticles. The particles are isolated and quite monodisperse. The mean particle size (see Table 2) was determined to be ca. 4 nm. Electron diffraction micro-

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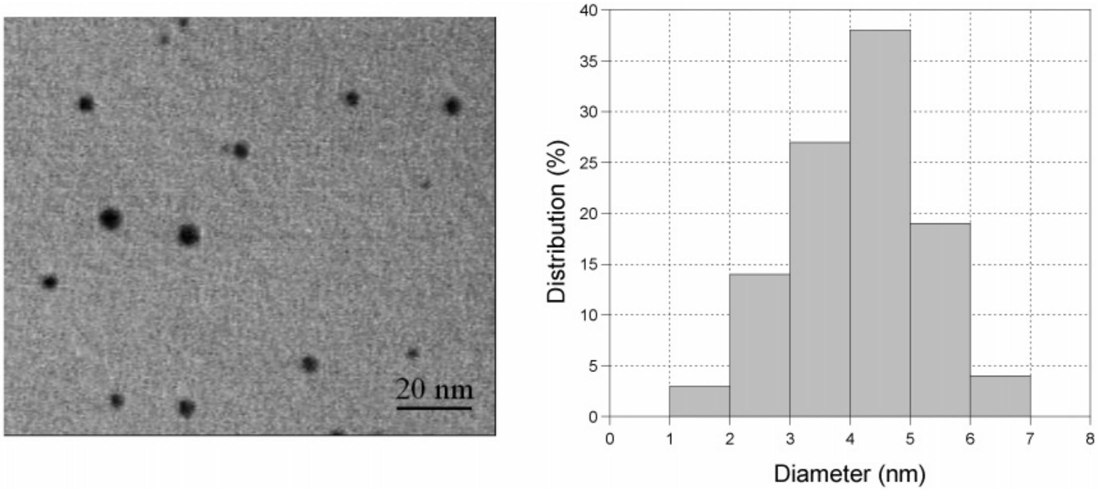

Figure 3. TEM micrograph and histogram (ca 300 nanoparticles analyzed) illustrating the particle size distribution of HYPAM stabilized gold nanoparticles.

Table 2. Complexation and Reduction Characterization

	maximum load of Au^{III} per stabilizer[a]	reduction	
		$[Au^{III}]$/[stabilizer]	size (nm) [b]
HYPAM4	150 ± 10	60	4.0 ± 0.9
		120	4.2 ± 1.0
		240	7.1 ± 2.2
PAMAM4	50 ± 5[c]	60[c]	2.0 ± 0.8[c]

[a] Obtained from UV−visible absorbance [b] Obtained from TEM measurements after reduction by a 5-fold molar excess (respective to Au^{III}) of $NaBH_4$. [c] Value in agreement with literature data[2g].

graphs obtained by TEM fitted well with expected pattern associated with Au metal. In view of these observed cluster sizes and assuming that the HYPAM4 gyration radius is comparable to the one of PAMAM4 dendrimer (i.e., 4.5 nm[11]), the nanoparticles should be stabilized by more than one macromolecule. Below the maximum load of HYPAM4, the quantity of loaded gold ions had no noticeable effect on the nanocluster size. Above this limit, an increase in size but mainly in polydispersity was observed.

These results are therefore quite similar to those obtained with PAMAM. The difference between the two systems is the slightly larger average diameters (respectively, ca. 4 and 2 nm) of the nanoparticles.

In conclusion, the open architecture of the HYPAM hyperbranched polymers facilitates the interactions between metal ions and polymer functional groups. Nevertheless, it maintains the possibility to use such a polymer as a nanoreactor like PAMAM. Experiments are underway to compare dendrimers of higher generation with other HYPAM polymers and to analyze the effect of pH on the nanoparticle stability.

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Supporting Information Available: Experimental details of the synthesis, description of apparatus used, NMR spectra, and TEM data (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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