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Dendritic Polymers with a Core−Multishell Architecture: A Versatile Tool for the Stabilization of Nanoparticles

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Potential applications of nanomaterials induced a tremendous amount of studies, to control size and shape of the nano-objects and/or to stabilize them in solution.[1] This last objective may be reached by adsorption or grafting of a stabilizer (ions, molecules, or polymers) on the nanoparticles (NPs) surface.[1] Two main drawbacks are generally found: (1) the modified colloids are stable in a limited range of experimental parameters: pH, ionic strength, nature of the solvent, temperature, and so forth, and (2) the "recipies" for the chemical surface modification can be applied to a limited type of NPs. In particular, only a few cases of stabilizers working in both, organic solvent and water, were reported.[2–4] To go beyond these strong limitations, we propose using a hyperbranched polymer with a core−multishell architecture. As discussed in this paper, we can take advantage of the different parts of this structure to control the formation and/or the stabilization of NPs in different media. For this purpose, a hyperbranched poly(ethylene imine) core (PEI, mean molar mass in weight: 5000 $g \cdot mol^{-1}$) surrounded by a double layered shell, composed of hydrophobic alkyl groups (C_{18}) linked to a hydrophilic monomethyl poly(ethylene oxide) chain (PEO with an average of 14 glycol units) which forms the outer shell (Figure 1) was prepared and fully characterized as previously described.[5] In brief, the mean molar mass in weight of this polymer (PEI−C_{18}−PEO) and polydispersity index, determined by size exclusion chromatography, were estimated as 44 000 $g \cdot mol^{-1}$ and 1.2, respectively. The degree of functionalization of the amino groups was found to be 100% by ^1H NMR.

This polymer was first used to control the formation of gold NPs (AuNPs) as follows. After addition of $HAuCl_4$ to a PEI−C_{18}−PEO solution, a band around 524 nm appeared in the UV spectrum after a short time of induction (less than 1 h) and was growing and narrowing with time (see Supporting Information). These changes were completed within two days. This band at 524 nm and the red color of the solution are characteristic for the formation of AuNPs. A similar behavior was observed with similar kinetics in the case of pure PEI. Moreover, the substitution of the PEI core by a hyperbranched polyglycerol core induced the disappearance of this phenomenon. These facts confirm, as

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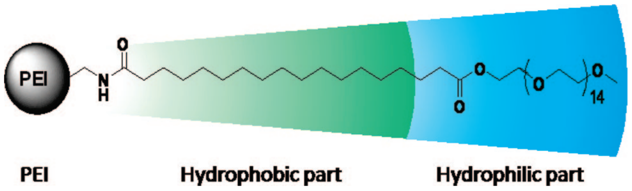

Figure 1. Structure of the modified hyperbranched polymer PEI−C_{18}−PEO.

described in literature for linear PEI,[6] that the hyperbranched PEI core promotes the reduction of gold ions. Under the applied conditions (pH between 7 and 3 and low ionic strength), both solutions remained stable for months. The mean particle diameter was determined by transmission electronic microscopy to be 6.2 ± 2.5 nm for an initial [$HAuCl_4$]/[PEI−C_{18}−PEO] ratio of approximately 17. When the quantity of added gold ions was higher than 17, size and polydispersity of the NPs increased strongly. This suggests that one polymer can load a maximum number of ions. To confirm this, we studied the addition of copper sulfate to a PEI−C_{18}−PEO solution (no reduction phenomenon occurs in that case). The absorbance around 290 nm increased linearly[7–9] with the number of Cu^{II} ions until a maximum loading ratio was reached at approximately 20 ± 5 (ca. 40 ± 5 for PEI). Such a behavior is typical for a dendrimer or hyperbranched structure which can be used to get size controlled NPs. As the hydrodynamic radius of the hyperbranched structure was found[5] around 5 nm, the NPs obtained are too large to be contained in a single hyperbranched polymer. These particles are most likely to be capped by multiple polymer chains.[8]

Beside this effect, we expected that the PEI−C_{18}−PEO polymer may also interact with and stabilize preformed hydrophilic or hydrophobic NPs. To test this hypothesis, we have chosen hydrophobic NPs covered by 1-hexadecanethiol which have been obtained by the Brust−Schiffrin method.[10] These hydrophobic AuNPs had a mean diameter of 1.5 ± 0.5 nm and presented a weak surface plasmon extinction band.[10,11] They were stable in organic solvents but not dispersable in water. After mixing these NPs with PEI−C_{18}−PEO, it was possible to dissolve them in water as shown by the "brown" color of the aqueous phase (see Figure 2). Decreasing the length of the PEO part from 14 to 5 greatly increased the transfer into water, suggesting that the hydrophobic part plays the main role in the interaction between polymer and hydrophobic AuNPs. Similar tests were performed with hydrophilic AuNPs. In that case, we have chosen AuNPs formed by reduction of $HAuCl_4$ with sodium borohydride[12,13] in water at pH = 8 (AuNps formed by reduction by citrate led to similar results). When PEI−C_{18}−PEO and toluene were added and after shaking the biphasic system, one observed that the organic phase was slightly colored (see Figure 2). Therefore, the PEI−C_{18}−PEO polymer did interact with hydrophilic NPs and allowed partial transfer of the NPs into the organic solvent (the weak color of the toluene phase in the Figure 2 is related to the partition coefficient of PEI−C_{18}−PEO between water and toluene, the partition coefficient being clearly in favor of the solubilization in water). To avoid any misinterpretation due to the formation of emulsion in toluene with the PEI−C_{18}−PEO polymer, we have made complementary experiments by drying aqueous solutions of hydrophilic AuNPs in the presence of PEI−C_{18}−PEO. The resulting red powder was easily redispersed in a wide range of concentrations and solvents (see Figure 3): water, toluene, methanol, dichloromethane, tetrahydrofurane, acetonitrile, ethyl acetate, and dimethylformamide (but not in hexane, due to the insolubility of the polymer). The integrity (in particular the size) of the NPs was maintained in all solvents as demonstrated by TEM measurements. Except for the slight shift of the plasmon band due to the change of the refractive index of the solvent,[14] no significant change in absorbance was observed over a 6-month period.

Those experiments demonstrate clearly that the capping of these hydrophilic or hydrophobic NPs was successfully

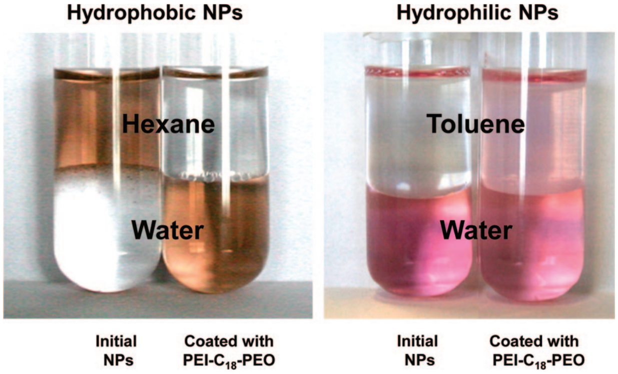

Figure 2. Left: phase transfer of hydrophobic AuNPs from hexane to water before and after capping with PEI−C_{18}−PEO. Right: partial phase transfer of hydrophilic AuNPs from water to toluene before and after capping with PEI−C_{18}−PEO.

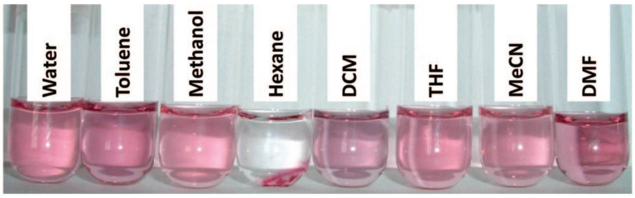

Figure 3. Solution of hydrophilic AuNPs stabilized by PEI−C_{18}−PEO redispersed in different solvents ([PEI−C_{18}−PEO] ~ 1.5 × 10^{-5} mol·L^{-1}, [Au]/[PEI−C_{18}−PEO] = 7). DCM, THF, MeCN, and DMF stand for dichloromethane, tetrahydrofurane, acetonitrile, and dimethylformamide.

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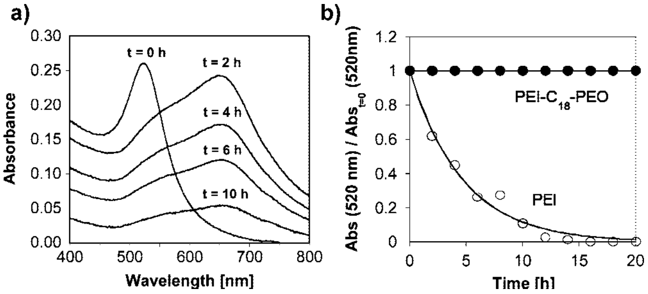

Figure 4. (a) Evolution with time of the UV–visible spectrum of a solution of PEI stabilized AuNPs after changing the ionic strength ([NaCl] = 1 mol$\cdot$L^{-1}, [PEI] = 4 × 10^{-6} mol$\cdot$L^{-1}, [Au(0)]/[PEI] = 17). (b) Evolution of the normalized absorbance at 520 nm as a function of time for hydrophilic AuNPs stabilized by PEI (○) or PEI−C$_{18}$−PEO (●) with [NaCl] = 1 mol$\cdot$L^{-1}.

achieved by the PEI−C$_{18}$−PEO polymer and allows their solubilization in a large variety of solvents. Whatever the type of the initial NPs (formed in presence or in absence of the polymer, hydrophilic or hydrophobic character, etc.) may be, the colloidal stability of the final NPs/polymer system in water was found to be very similar. Here, we report the particular case of hydrophilic AuNPs stabilized by the PEI or PEI−C$_{18}$−PEO polymers in water. In contrary to the initial hydrophilic NPs, the NPs coated by one of these polymers remained stable over time in the initial ionic strength and pH value (i.e., 8) conditions. However, after increasing the ionic strength of the solution by addition of NaCl up to a concentration of 1 mol$\cdot$L^{-1}, a broad absorbance at approximately 650 nm appeared when PEI was used. Its growth was followed after a few hours by a decrease of the whole spectrum which is characteristic for an aggregation−decantation process (Figure 4a).[15] The grafting of the neutral C$_{18}$−PEO shell on the PEI core dramatically increased the stability of AuNPs: with the PEI−C$_{18}$−PEO polymer, no evolution in time was observed in UV spectra over days (Figure 4b) and over months even after drastically increasing the ionic strength (up to ca. 10 mol$\cdot$L^{-1}). A similar behavior was observed, when the pH was increased around 11, which is above the pK_a value of the primary amines (estimated around 9.5). Whereas in case of PEI an aggregation of AuNPs was obtained within a few minutes, no evolution of the AuNPs stabilized with PEI−C$_{18}$−PEO was observed for a wide range of pH values (1–14, see Supporting Information). A flocculation of these NPs was only obtained at very high concentrations of sodium hydroxide. The hydrolysis of ester and amide groups may explain this phenomenon at least partially. Anyway, the increase of stability obtained with the core–shell architecture demonstrates clearly the importance of the multishell structure for the stabilization properties.

In conclusion, whereas the PEI core allows the formation by autoreduction of AuNPs in a controlled way, the neutral structure of the shell significantly increases the stability of aqueous solutions of AuNPs. Moreover, the amphiphilic structure of the shell allows the stabilization of preformed hydrophobic and hydrophilic AuNPs in water and organic solvents. Therefore, we believe that these multishell architectures have an enormous potential as a nanoparticle (of different chemical compositions) stabilizer for catalytic applications, as well as for biological applications. These two points are currently under investigation.

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Supporting Information Available: Experimental details, complexation properties with copper, and kinetics of reduction (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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