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Synthesis and Properties of Selective Metal-Complexing Nanoparticles

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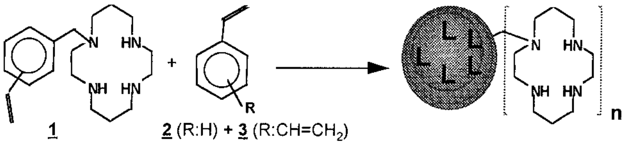
The concept of immobilizing reagents onto polymer supports for use in organic reactions and combinatorial chemistry has received a great deal of attention. Polymers as metal ion complexing agents have also been proposed for an extensive variety of purposes as diverse as separation and recovery of metal ions, catalysis, chromatography, and dioxygen transport.[1,2] Although much progress has been documented in recent years, the development of new selective materials with high functionality and reagent accessibility as well as suitable solubility properties is a challenging endeavor. Furthermore, a wide range of applications require polymeric materials which are applicable in aqueous media. The technique of polymerization in microemulsion offers new opportunities since it allows one to produce stable aqueous suspensions of polymer particles in the nanometer-size range (<30 nm), which exhibit a very large specific area, not attainable with classical polymerization process.[3−5] Moreover, the well-defined structure of the microemulsions affords a means to synthesize special polymer materials, such as copolymers with high surface functionality, which are not accessible by other techniques.

In this communication, we report the one-step synthesis of ultrafine metal-complexing particles containing high densities of the well-known 1,4,8,11-tetraazacyclotetradecane (cyclam) ligand and the study of their complexation properties. These nanoparticles exhibit a high metal-binding ability as well as a high selectivity for cupric ions and give access to "bimetallic" polymer materials with adjustable solubility.

Thus, stable translucent aqueous suspensions of cyclam-functionalized nanoparticles are readily obtained, in a one-step procedure, by copolymerizing mixtures of polymerizable ligand (**1**), styrene (**2**), and divinylbenzene (**3**) (cross-linking agent) in oil-in-water microemulsions prepared using a cationic surfactant (dodecyltrimethylammonium bromide, DTAB).[6] Complete polymerization of all monomers is achieved at room temperature using an oil-soluble radical initiator[5] so that the amount of cyclam in the resulting particles can easily be modulated: polymeric particles (P1 and P2) containing 0.35−0.63 mequiv of cyclam/g (determined from elemental analysis) have thus been obtained from microemulsions containing 5−10% molar ratio of **1** (Scheme 1). Whatever the functionality, quasielastic light scattering studies indicate that the nanoparticles are very small and quite monodispersed with mean diameters of 12−13 nm (Figure 1). It is worth noticing that, in microemulsion polymerization processes,[3−6] the particle size is mainly controlled by the surfactant per monomer ratio so that, for a given ratio, the particle size does not depend on the amount of cyclam in contrast to other functionalization reactions described in the literature.

Scheme 1



Molar ratio 1 / 2 / 3 : 10 / 45 / 45 — **P1** : D=13nm, n~430 (0.63meq/g)
5 / 47.5 / 47.5 — **P2** : D=12nm, n~200 (0.35meq/g)

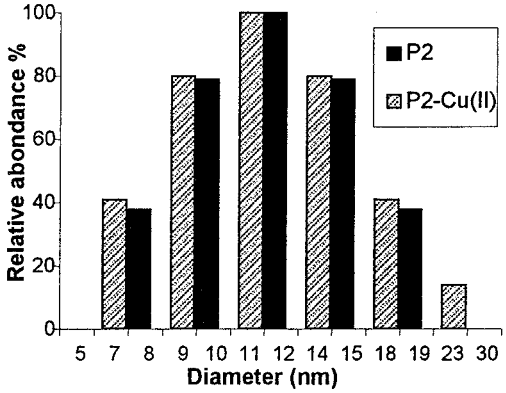


Figure 1. Particle size distribution of suspension P2 and suspension P2 + Cu^{II}.

Owing to the well-known high affinity of cyclam for cupric ions,[7] copper elemental analysis and direct spectrophotometric measurements were used to evaluate the metal binding ability of the particles. Upon addition of Cu^{II}, the cyclam-functionalized suspensions instantaneously turn violet with an absorption at 536 nm very close to the monomeric Cu^{II}/**1** complex (537 nm), indicating that the binding to the nanoparticles does not modify the structure of the complex. The amount of cyclam−copper complex is easily determined spectrophotometrically, and we obtain quantitative and reproducible measurements, in good agreement with copper elemental analysis, by using an integrating sphere to collect and integrate the scattered light. As can be seen in Figure 2a, the absorbance linearly increases upon progressive addition of a dilute solution of copper nitrate, demonstrating that complete Cu^{II} complexation does instantaneously take place even at very low copper concentration in agreement with a very high complexation constant. The absorbance increases up to a maximum value which corresponds to the complexation of all the accessible cyclam moieties in dilute medium. For both suspensions, P1 and P2, complexation of about 70−75% of the whole cyclam residues contained in the polymeric particles is reached in the dilute medium on the minute time scale, indicating a very high ligand accessibility of such nanomaterials. On the other hand, in the presence of an excess of cupric ions, the complexation rate reaches up to 85% of the whole cyclam residues in a few hours (molar ratio Cu/cyclam >10, 3−4 h). Two complexation processes may thus be proposed: a rapid, "solution-like", complexation process involving the cyclam residues located near the surface (so-called "cyclam surface end groups") and a slow, diffusion-limited, complexation process involving the cyclam

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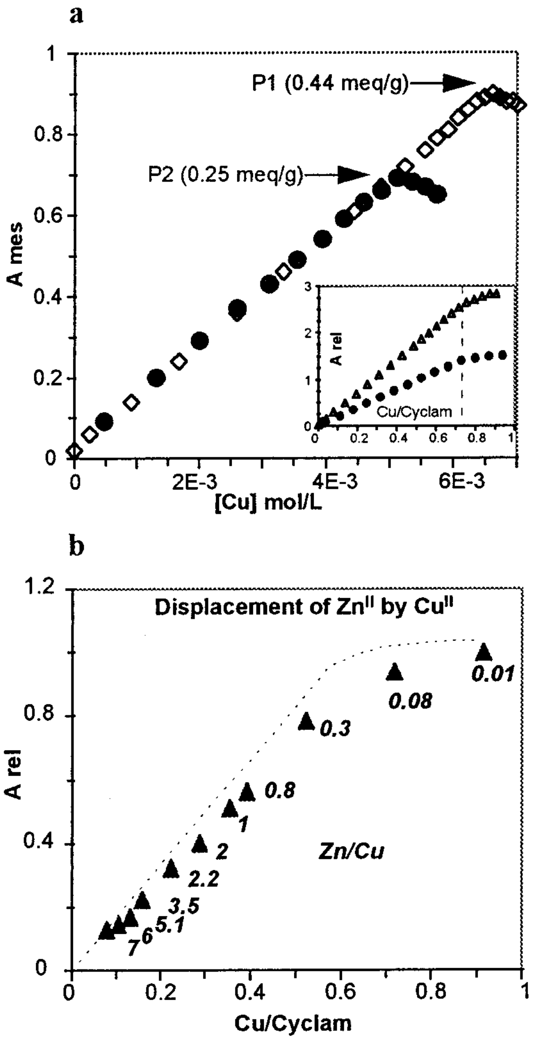

Figure 2. Spectrophotometric titration of Cu−cyclam complex at 536 nm upon progressive addition of a dilute copper nitrate solution (0.01 M). (a) Absorbance vs copper concentration upon addition of Cu^{II} to suspensions P1 (◇) and P2 (●). Inset: relative absorbance vs equiv of Cu added/equiv of cyclam. (b) Relative absorbance (for 1 g of suspension) vs molar ratio of Cu added/cyclam upon addition of copper to suspension P1−Zn^{II} (initial composition given in table). Italic numbers: Zn/Cu ratio per particle. Dotted line: variation of absorbance starting from the metal-free suspension P1. The equilibrium is reached after 5 h except for the last two points Cu/cyclam = 0.75 (24 h) and 0.95 (12 days).

Table 1. Competition Experiments[a]

	$M^b = Ni^{2+}$	$M^b = Zn^{2+}$	$M^b = Co^{2+}$	$M^b = Mn^{2+}$
	Polymer Composition[c]			
% Cu (mequiv/g)	0.51 (0.08)	0.33 (0.05)	0.30 (0.05)	0.36 (0.06)
% M (mequiv/g)	2.30 (0.39)	2.39 (0.37)	2.33 (0.39)	0.15 (0.003)
% M/L[d]	67	63	68	0.5
% M + Cu/L[d]	81	72	76.5	10.5
% Cu comp	>98%	>98%	>98%	>98%
n Cu/particle[e]	55	35	35	40
n M/particle[e]	270	255	270	2
M/Cu	5	7	7.8	0.05

[a] The procedure is detailed in the Experimental Section. [b] M: competing ion. [c] From elemental analysis, composition of the starting particles is as follows: C, 82.8; H, 7.84; N, 3.52. [d] L: cyclam. [e] Number of Cu or M residues per particle calculated from the particle diameter assuming a density of 1.

residues entrapped within the core of the particles. It is noteworthy that the particle size remains constant upon copper complexation (Figure 1) so that we get aqueous suspensions of nanoparticles of 120−130 Å diameter range containing up to 350−400 copper residues per particles.

The binding ability for other metals and the selectivity of the nanoparticles were studied by performing competition experiments with various metallic cations (Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}). The results given in Table 1 demonstrate the very high selectivity of the cyclam-functionalized nanoparticles for copper since, whatever the competing cation, elemental analyses of the resulting particles show that complete complexation of Cu^{II} does take place even under highly unfavorable conditions (substoichiometric amounts of Cu^{2+} and a very large excess of competing ion: Cu/cyclam ∼ 0.1, M/Cu = 1000). The nanoparticles also exhibit high binding abilities for Ni^{2+}, Co^{2+}, and Zn^{2+} with complexation rates reaching about 60−70% of the remaining free-cyclam moieties thus leading to an overall (M + Cu) complexation yield of 70 to 80% of the whole cyclam residues. On the contrary, the particles show a very poor affinity for Mn^{2+}, making them valuable supports for selective removal of Cu(II) toward Mn(II). The excess of competing ion in the aqueous phase is readily removed upon dialysis without destabilization so that competition experiments with Ni^{2+}, Co^{2+}, and Zn^{2+} give access to aqueous suspensions of "bimetallic" nanoparticles containing about 300 metallic residues. Moreover, taking advantage of the very high stability constant of the copper−cyclam complex, the competing cation can be gradually replaced by copper and, as shown in Figure 2b, the cation exchange is easily monitored by measuring the absorbance of the copper−cyclam complex. For example, replacement of Zn^{II} by Cu^{II} readily occurs upon addition of a dilute solution of cupric ions leading to bimetallic particles with modulatable Zn/Cu ratio. Owing to the diffusion-limited complexation process, it is expected that, in such a dilute medium, the substitution would take place first at the surface resulting in the production of core−shell type nanoparticles with a Cu-rich shell and a Zn-rich core.Finally, the copper containing nanoparticles are readily and quantitatively extracted in organic solvents (such as ethyl acetate or ether) upon addition of an anionic lipophilic surfactant (sodium bis(octyl sulfosuccinate)). The extraction process relies on the formation of ion pairs between the cationic Cu^{2+}−cyclam surface end groups and the lipophilic anions which makes the surface hydrophobic and allows the transfer in a nonaqueous medium. Interestingly, the resulting hydrophobized particles can be dried and redispersed later on.

To conclude, it is worth noticing that this one-step microemulsion polymerization procedure gives access to nanoparticles with the size and the functionalization range of large dendrimers prepared by multistep by step procedures.[8] More, besides their selectivity and their high binding affinity, two of the most outstanding features of these nanoparticles are (1) the complexation of two metallic cation with easily adjustable ratios and (2) their solubility in both aqueous and organic medium easily modulated by surface coverage, making them valuable precursors in material science and valuable supports for chemical processes.

Experimental Section. 1 was prepared from commercial vinylbenzyl chloride according to ref 2a and was isolated as a 60:40 mixture of para and meta isomers (GC−MS analysis). The microemulsions were prepared by adding, upon gentle stirring, the mixture of monomers containing the desired amount of radical initiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA[5]) (P1, **1** 200 mg, **2** 270 mg, **3** 340 mg, DMPA 70 mg; P2 **1** 170 mg, **2** 500 mg, **3** 620 mg, DMPA 100 mg) to a 15 wt % aqueous solution of DTAB (P1, 20 g; P2, 30 g). The polymerization reactions were performed under white light irradiation (60 W lamp) at 20 °C under nitrogen for 15 h and monitored according to the previously described procedures.[5] The composition of the resulting polymer was determined by elemental analysis (C, H, N) after precipitation in methanol, centrifugation, extensive washings in demineralized water at 60 °C, and finally drying at 50 °C until constant weight is reached.[5] Spectrophotometric titrations were performed on a Perkin-Elmer spectrophotometer equipped with a reflection sphere by adding small aliquots (100−300 μL) of a 0.01 M aqueous solution of copper nitrate to the suspension (2 g) placed in a quartz cell. Unless otherwise mentioned, the absorbance at 536 nm was measured 3 min after each addition. Competition experiments: 10^{-2} mol of competing ion (solid Ni or Zn or Mn nitrate salt or Co chloride salt) and then $\sim10^{-5}$ mol of Cu^{II} (as a 0.1 mol/L solution of copper nitrate) were added to ~5 g of suspension P1′ (~200 mg of polymer, 0.58 mequiv of cyclam/g from elemental analysis). The mixtures were allowed to equilibrate for 3 months upon gentle stirring. The suspensions of metal-complexed nanoparticles were then purified by dialysis, using cellulose regenerated membranes of MWCO: 3500, (1) in an aqueous solution of DTAB (0.15 wt %) to remove the excess of metallic cation and (2) in ultrapure water to remove the surfactant. Metallic polymer samples for elemental analysis were obtained after concentration of the purified suspensions to dryness, extensive washings of the resulting powder in water (2 × 500 mL), centrifugation, and final drying: purification yield 90% (110 mg of polymer from 4.7 g of reaction mixture, i.e., 120 mg of starting polymer). Quantitative extraction of copper-containing particles was achieved by adding a solution of sodium bis(octyl sulfosuccinate) (400 mg, 9×10^{-4} mol) in ethyl acetate (6.5 mL) to 500 μL of suspensions of copper-containing particles (20 mg of polymer; Cu/cyclam, 85% or 10%) upon gentle magnetic stirring for 5 min. The deep violet organic phase containing the metal−polymer particles is readily separated from the colorless aqueous phase upon decantation. Traces of water are removed by drying over magnesium sulfate. Quasielastic light-scattering analyses were performed on dilute samples (0.2 mL in 100 mL of water) with a Brookhaven instrument (BI2030AT correlator) equipped with an 2016 Ar laser (514.5 nm), and the data were analyzed by the exponential sampling method or by the nonnegatively constrained least-squares multiple pass method (BI30atn software). P1, 13 nm ($\sigma = 0.169$); P2, 12 nm ($\sigma = 0.007$); P1−Cu, 16 nm ($\sigma = 0.097$); P2−Cu, 12 nm ($\sigma = 0.10$).

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