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Preparation of Catalytically Active Palladium Nanoclusters in Compartments of Amphiphilic Hyperbranched Polyglycerols

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Transition metal clusters and colloids of narrow particle size distributions in the range 1–10 nm are currently subject to intense research efforts.¹ From a fundamental perspective, the transition from the properties of the bulk to those of molecular clusters is expected to occur in this size range. A transition metal cluster of 2 nm diameter consists of a few hundred atoms, a large portion of which are located at the surface of the cluster. In view of potential applications, such materials are of interest with regard to for example catalysis^{2,3a,f,4c,5b,6d} or microelectronics.^{1a,b} However, increasing the control of particle size and the stability of the metal colloid solutions remain key challenges. Recent approaches to the controlled preparation of metal or semiconductor nanoparticles have utilized surfactants^{2l,3} or the self-assembled nanostructures of block copolymer micelles,^{2t,4} achieving an unprecedented control of particle size and also spatial organization in thin films by the latter method. However, such template structures self-assembled from a larger number of individual molecules are by their very nature dynamic in solution. Thus, their size and aggregation numbers are subject to fluctuations, and such structures can be shear-sensitive. To stabilize micelle-like structures, polymerized micelles⁵ and very recently dendrimers⁶ have been employed as molecular compartments for the preparation of metal particles. Whereas dendrimers⁷ offer the advantage of a well-defined structure, their syntheses are usually tedious. By contrast to the perfectly branched structure of dendrimers, hyperbranched polymers⁸ possess a randomly branched structure. They can be prepared conveniently in one-pot procedures; however, usually polymers of extremely broad molecular weight distributions are obtained. In a recent approach, amphiphilic hyperbranched poly(glycerols) of low polydispersity ($M_w/M_n < 1.7$) were prepared by anionic multibranching polymerization of glycidol,⁹ followed by partial esterification of the OH functions with long chain fatty acids (Scheme 1).¹⁰ Such amphiphilic macromolecules function as nanocapsules, incorporating individual hydrophilic dye molecules as guests.¹⁰ We now report on the application of these easily accessible, well-defined amphiphilic molecules for the preparation of nanometer-size stable palladium colloids and their application in catalysis.

In the following experiments, amphiphilic polymers prepared by esterification of 60–67% of the OH functions of poly(glycerol) scaffolds of different molecular weights with palmitoyl chloride were employed.¹¹ Solutions of these polymers in apolar organic solvents, such

as toluene or chloroform, solubilize PdCl_2 to yield yellow solutions of the otherwise insoluble metal salt. Exposure of such toluene solutions to hydrogen (1 atm) or heating to 60 °C for several hours resulted in a slow reduction,¹² ultimately yielding clear dark, brownish metal colloid solutions.²⁰ Employing $\text{Pd}(\text{OAc})_2$ as a precursor, similar results were obtained. In all cases, no deposition of metallic palladium was observed. By comparison, in the absence of the amphiphilic polyglycerol, reduction was accompanied by immediate precipitation of palladium black. A molar ratio $\text{Pd}(\text{II})$ salt/polymer corresponding to as low as ca. 2 OH groups of the polymer/Pd was employed. The nanometer-sized palladium particles formed were visualized by transmission electron microscopy¹³ (TEM). Employing an amphiphilic polymer prepared from a poly(glycerol) scaffold of $\text{DP}_n = 63$ at a high metal loading (4 OH/Pd), a colloid of 5.2 ± 1.8 nm average particle size was obtained (Figure 1a). Utilization of a *smaller amphiphilic polyglycerol* ($\text{DP}_n = 23$) under otherwise identical conditions resulted in a *decrease in metal cluster size* to 2.1 ± 0.6 nm (Figure 1b). In view of these observed cluster particle sizes, some of the clusters may be stabilized by more than one amphiphilic polymer molecule in both cases.^{14,15} However, upon reducing the high metal-to-polymer ratios 10-fold, much smaller metal particles were obtained, meeting the limit of resolution (ca. 1 nm) of TEM analysis. Such particle sizes are clearly in the range expected for stabilization of a cluster in a unimolecular micelle-type structure. The colloidal solutions were found to be stable in air for at least several months at room temperature. Complete evaporation of solvent and drying in vacuo resulted in formation of dark oils, which could be redissolved (e.g., in olefinic substrates; vide infra) to yield clear dark solutions again.

Dendrimers⁶ or block copolymers⁴ used in previous related studies usually contain nitrogen donor atoms to enable initial coordination of metal salt precursors prior to reduction as well as subsequent stabilization of metal clusters formed by reduction of the metal salt. The presence of such coordinating moieties can be disadvantageous, e.g., by blocking of active sites in catalysis. By contrast, the polyglycerol-based system reported contains highly polar, but weakly coordinating, OH functions. As a first probe for the applicability of these polymer-stabilized colloids in catalysis, the hydrogenation of cyclohexene was investigated. Well-behaved kinetics were observed, a high rate¹⁶ of olefin consumption being sustained throughout the course of the reaction. For example, 75% conversion $\equiv 22,000$ TO corresponded to an overall average rate of $700 \text{ TO h}^{-1} \text{ atm (H}_2\text{)}^{-1}$ (cf. Supporting Information). These turnover numbers (i.e., combination of high rate and catalyst stability) compare favorably to previous reports on hydrogenation of cyclohexene by solutions of palladium colloids.^{21,4c,17} A commercially available Pd/activated charcoal catalyst was found to display a somewhat lower activity under identical conditions. These results clearly demonstrate good accessibility of the colloidal metal for the substrate in our system. Recycling the catalyst, no significant decrease in activity was observed. Also, no deposition of palladium was observed in repeated runs, evidencing the stability of the metal colloids during catalysis. As for the stability of the amphiphilic polymer

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- (11) Poly(glycerol) scaffolds were prepared using trimethylolpropane as an initiator,⁹ amphiphilic modification by partial esterification as previously described.¹⁰ All samples employed displayed a low polydispersity of $M_w/M_n < 1.5$.
- (12) In the reduction upon heating, the –OH moieties of the polymer may function as a reducing agent. Cf. Hirai, H.; Nakao, Y.; Toshima, N. *J. Macromol. Sci., Chem.* **1979**, *A13*, 727–50.
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- (14) Roughly estimating the size of a single amphiphilic molecule for comparison, for the $DP_n = 63$ polymer a diameter of 4 nm is calculated for a spherical, nonswollen molecule.
- (15) Due to a certain flexibility of the branched polyether backbone, an organization of several molecules around a cluster is possible.
- (16) TO = turnovers, i.e., moles of cyclohexane formed per mole of palladium (calculated with respect to the entire amount of Pd present in the clusters, i.e., activity of the significant surface atoms will be higher).
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- (20) Reduction with carbon monoxide occurred much faster, affording clear dark colloid solutions within minutes.

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