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Communications

Synthesis of Poly(oxyethylene)-Grafted Palladium Clusters

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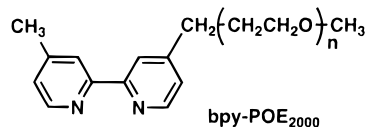
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Current interest in metal clusters and colloids in the size range 1–10 nm is increasing because of their actual and potential use as catalysts and as advanced materials in electronics such as quantum dots.¹ To prevent agglomeration with the formation of large particles or powders, these nanostructured particles usually need to be protected by stabilizers such as polymers² or surfactants.³ Much recent effort has been directed toward the fabrication of polymers containing nanometer-sized clusters, which are usually prepared by reduction of metal ions within the polymer matrix. Construction of well-defined polymers containing nanometer-sized clusters is one of the attractive targets for polymer and material chemistry. Here we introduce

a new methodology for constructing well-defined polymers containing metal clusters, i.e., polymer-grafted metal clusters.

To connect a polymer end with a surface of metal cluster, a coordination bond is considered to be the most suitable link. For the past decade ligand-stabilized metal clusters have been reported as a simple method to protect colloidal particles with a skin of ligand molecules which are not removed when the materials are isolated and completely dried.⁴ We speculated that polymer-grafted metal clusters would be simply produced by reduction of metal ions with bipyridyl-terminated polymers. Physical characteristics of metal clusters show a marked dependence on the ligand shell. Attachment of metal clusters to synthetic polymers may add film-forming properties to the metal cluster and also may provide the opportunity for microphase separation between the metal clusters and the polymer matrix.



Bipyridyl-terminated poly(oxyethylene) (bpy-POE₂₀₀₀) was prepared from poly(oxyethylene) monomethyl ether

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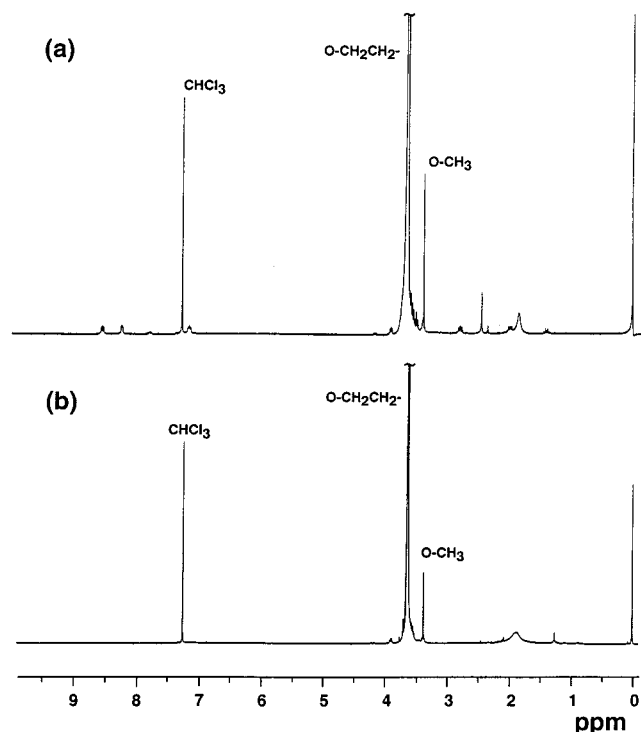


Figure 1. ^1H NMR spectra of bpy-POE₂₀₀₀ (a) and the polymer-grafted palladium cluster (b) at 270 MHz in CDCl_3 as a solvent.

(MW = 2000) according to a previous report.⁵ A palladium cluster was synthesized by stirring an acetic acid solution (24 mL) of palladium(II) acetate (67.5 mg, 3×10^{-4} mol) and bpy-POE₂₀₀₀ (78.9 mg, 3.75×10^{-5} mol) (molar ratio 8:1) under 1 atm hydrogen at room temperature for 18 h. Reduction of palladium ion was monitored by absorption spectrum. After reduction was continued, the homogeneous black reaction mixture gave an unstructured UV-vis spectrum without maximum of typical palladium clusters.⁶ The black solution was then exposed to an oxygen atmosphere for 6 h to oxidize the free surface atoms. After the solvent was removed under reduced pressure, the black residue was dissolved in water and the resulting solution was subjected to dialysis against water for several times to remove free ligand. The aqueous solution of the palladium cluster was evaporated under reduced pressure to give a black powder. The isolated yield was 57 mg.

The obtained palladium cluster was soluble in various solvents such as CH_2Cl_2 , CHCl_3 , MeOH, acetone, and water and was not soluble in Et_2O and *n*-hexane. The solubility of the resulting palladium cluster was the same as that of poly(oxyethylene). These solutions were stable without precipitation for more than half a year at room temperature under air. The sample showed a film-forming property after CHCl_3 solution was cast onto a slide glass. When poly(oxyethylene) (MW = 2000 or 5000) without bipyridyl-terminal was used instead of



Figure 2. TEM of the polymer-grafted palladium cluster deposited on a 200 mesh copper grid covered with colosion.

bpy-POE₂₀₀₀, stable colloids were not formed.⁷ Palladium(II) ion was completely precipitated. Although the formation of palladium cluster was reported when an acetic acid solution of palladium(II) acetate was stirred with a large excess amount of poly(ethylene oxide) (MW 900000) (molar ratio 1:10) under 1 atm hydrogen at room temperature, the precipitation of the metal occurs after a comparably short time (1–2 days).^{2c} These results suggested that the poly(oxyethylene) interacted with the palladium clusters via the terminal bipyridyl ligand.

To confirm the interaction of terminal bipyridyl ligand with the palladium cluster, ^1H NMR of the sample was measured in CDCl_3 . ^1H NMR spectrum of the prepolymer (bpy-POE₂₀₀₀) showed aromatic protons of the ω -terminal bipyridyl ring at 7.0–8.5 ppm as well as α -terminal methoxy protons at 3.3 ppm (Figure 1a). In contrast, the ^1H NMR spectrum of the resulting palladium cluster showed only poly(oxyethylene) protons at 3.6 ppm and α -terminal methoxy protons at 3.3 ppm (Figure 1b). ω -Terminal bipyridyl protons were hardly recognized compared with α -terminal methoxy protons. Disappearance of the signals indicated the restricted motion of these protons. Therefore, these results indicate that the terminal bipyridyl ligand was fixed at the surface of the palladium cluster and was a very rigid structure. The α -terminal end of the poly(oxyethylene) chain was a relatively mobile shell.

Quantitative size information of metal particles can be obtained using transmission electron microscopy (TEM). TEM investigation of the obtained clusters, deposited on a grid from an aqueous solution, indicated

(5) We recently reported the preparation of star-shaped polymers with metal-bipyridyl complexes as cores by complexation of bipyridyl-terminated poly(oxyethylene) prepolymers with metal ions, see: (a) Chujo, Y.; Naka, A.; Krämer, M.; Sada, K.; Saegusa, T. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *32*, 1213. (b) Naka, K.; Kobayashi, A.; Chujo, Y. *Macromol. Rapid. Commun.* **1997**, *18*, 1025.

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(7) An acetic acid solution of palladium(II) acetate and poly(oxyethylene) (MW = 2000 or 5000) without terminal bipyridyl (molar ratio = 8:1) was stirred for 18 h under 1 atm hydrogen at room temperature.

narrow particle size distribution with a diameter of 3.6 ± 1.1 nm⁸ (Figure 2). The average particle size of 3.6 nm was correspond to so-called "magic atom number" of 2057 atoms, i.e., eight-shell clusters.^{4b} A recent example of a ligand-stabilized palladium cluster showed sizes of 3.2 and 3.6 nm, and another 10% were smaller or bigger by electron micrographic analysis.^{4b} The core size obtained from our approach was the same as that of ligand-stabilized palladium clusters.

Hydrodynamic diameter of the polymer-grafted palladium cluster was determined by dynamic light scattering (DLS). A solution was passed through membrane filters with a nominal pore size of $0.45 \mu\text{m}$ before measurement. The DLS study of an aqueous solution of the sample indicated a narrow size distribution for the diameter of 22 ± 5 nm. These data indicated an actual colloidal material. The fully extended length of the prepolymer was calculated to be approximately 15 nm. The difference between the mean diameters determined by each of these methods, DLS and TEM, was derived from the thickness of the ligand layer. The core size obtained from TEM image was found to be 3.6 nm. Therefore the thickness of the ligand layer was approximately 9 nm. This value was in good agreement with the fully extended length of the ligand polymer chain.

The elemental analysis and inductively coupled plasma (ICP) spectroscopy of the polymer-grafted palladium

cluster gave values as follows: C, 38.24; H, 6.17; N, 1.10; O, 27.74; Pd, 19.9. This corresponded to a molar ratio of Pd:bpy-POE₂₀₀₀ of 4.8:1. The calculated formula for the polymer-grafted palladium cluster was, accordingly, Pd₂₀₅₇(bpy-POE₂₀₀₀)₄₂₈O_{ca.2000} as eight-shell clusters. Although the ligand content in the present palladium cluster was higher than those of the previous ligand-stabilized palladium clusters,⁹ no free ligand existed in the present cluster by ¹H NMR analysis as described above. The UV-vis spectrum of the polymer-grafted palladium cluster in MeOH showed two π to π^* transition bands corresponding to the 2,2'-bipyridyl moiety at 296 and 309 nm. This observation indicated that the linkage between the bipyridyl ligand with the metal surface existed two kinds of species. We are now investigating of the structure of the polymer-grafted palladium clusters in detail.

In conclusion, we have demonstrated a simple preparation of the polymer-grafted palladium cluster with narrow molecular weight distribution. The polymer-grafted metal cluster was a simple and excellent candidate for constructing well-defined polymeric materials containing nanometer-sized clusters.

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(8) Transmission electron microscopy was performed using a JEOL JEM-100SX operated at 100 kV. One drop of the aqueous solution of the sample (2.0 mg/mL) was placed for 2 min on a 200 mesh copper grid covered with collodion. Then, the drop of the solution was removed with filter paper. The grid was dried in a desiccator overnight and dried in vacuo for 2 h. The particle size distribution analysis were performed on a Macintosh computer using public domain NIH Image program (developed at the U.S. National Institutes of Health).

(9) The reported stoichiometry of the ligand-stabilized palladium clusters, which was prepared by reduction of Pd(OAc)₂ by H₂ in the presence of ligands (L) such as 1,10-phenanthroline and 2,2'-bipyridine, was [Pd₉L(O)₃(OAc)₃]_n.^{4a} In another report,^{4b} idealized formulas for the phenanthroline-stabilized cluster were Pd₅₆₁L₃₆O_{ca. 200} (five-shell clusters), Pd₁₄₁₅L₆₀O_{ca. 1100} (seven-shell clusters), and Pd₂₀₅₇L₈₄O_{ca. 1600} (eight-shell clusters).