Synthesis of Gold Nanoparticles Coated with Well-Defined, High-Density Polymer Brushes by Surface-Initiated Living Radical Polymerization

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ABSTRACT: The synthesis of a gold nanoparticle (AuNP) coated with a well-defined polymer is reported. The AuNP coated with an initiator group for living radical polymerization was prepared by the simple one-pot reduction of tetrachloroaurate with sodium borohydrate in the presence of an initiator group-holding disulfide. The surface-initiated living radical polymerization of methyl methacrylate (MMA) mediated by a copper complex was carried out with the initiator-coated AuNP in the presence of a "sacrificial" free initiator. Living polymerization proceeded exhibiting a first-order kinetics of monomer consumption and an evolution of molecular weight of the graft polymer proportional to monomer conversion, thus providing well-defined, low-polydispersity graft polymers with an approximate graft density of 0.3 chains/nm^2. Transmission electron microscopic observations of as-cast films of the AuNPs coated with PMMAs (PMMA−AuNPs) revealed that the particles were well dispersed in the polymer matrix without forming aggregates and that the interparticle distance increased with increasing graft chain length. Absorption spectra of the PMMA−AuNPs dissolved in an organic solvent exhibited an intense surface plasmon absorption band peaked at 525−535 nm with a weak blue shift becoming more significant with increasing PMMA chain length.

Introduction

As nanoscopic science, technology, and engineering have been rapidly developed in recent years, nanoparticles, particles in the nanometer size range, have attracted much attention due to their fascinating electronic, optical, magnetic, and/or catalytic properties associated with their nano- or quantum-scale dimensions.[1] In particular, ever since the establishment of reliable methods for the synthesis of gold nanoparticles (AuNPs),[2] they have been extensively studied, and numerous important findings on their properties have been reported.[3] Much effort has been made for surface-modifying AuNP by various organic compounds ranging from alkyl chains to macromolecules in order to develop new building blocks for optical, electrical, and biomedical applications.

Strategies have been developed to tailor AuNP surfaces by polymers.[4−9] AuNPs featuring thymine functionality were assembled into spherical aggregates by diaminotriazine-functionalized random and block copolymers. The use of a diblock copolymer allowed size-controlled formation of AuNP aggregates of several tens of nanometers in solution as well as in thin film.[4a] Dendrimers uniformly dispersed in a hydrophilic polymer network was used as a template for the formation of AuNP.[5a] As the network was swollen in aqueous solution of gold salt, the ions were attached to the dendrimer, where they were reduced forming AuNPs in the dendrimer. AuNPs were also formed in the confined reaction spaces of polymeric micelles composed of amphiphilic block copolymers.[4b,c] Moreover, amphiphilic star-block copolymers had advantages over polymeric micelle systems, serving as a confined reaction vessel to prepare single AuNPs.[4d] Size-controlled synthesis of AuNP was conducted by using the inorganic polymer, poly(methylphenylphosphazene), in which the nitrogen lone pair electrons acted as interaction points to stabilize the formed AuNP.[5d] Attempts were made to graft preformed functionalized polymers onto AuNP surfaces: Kataoka et al.[7a] modified AuNP by poly(ethylene glycol)-based glycopolymer for the investigation of quantitative and reversible lectin-induced association of AuNPs in order to construct a colloidal sensor system applicable to bioassay and biorecognition. Lennox et al.[7b] reported the synthesis of AuNPs decorated with covalently bound thiol-capped polystyrene and the successful incorporation of the AuNPs into presynthesized polystyrene matrix. In general, the methodologies described above, however, are only useful for producing polymer layers with a relatively low graft density.

To construct a highly dense polymer brush, the so-called "grafting from" techniques should be used.[9−19] The surface-initiated polymerization in conjunction with a living polymerization technique is among the most useful synthetic routes to precisely design and functionalize the surfaces of various solid materials by well-defined polymers and copolymers.[9,11−19] Above all, surface-initiated living radical polymerization (LRP) is particularly promising due to its simplicity and versatility.[12−19] It has been widely applied to the surface modification of various organic and inorganic solids. We previously reported the synthesis of high-density polymer brushes by surface-initiated LRP. Those high-density brushes showed extremely interesting physical properties such as a strong resistance against compression and an increased glass transition temperature.[13]

In this work, we have applied the surface-initiated LRP technique to the synthesis of a gold nanoparticle coated with a well-defined, high-density polymer brush. In this regard, the previous reports from two different groups should be noted: In the method used by Hallensleben et al.,[9b] a dodecanthiol-protected AuNP was

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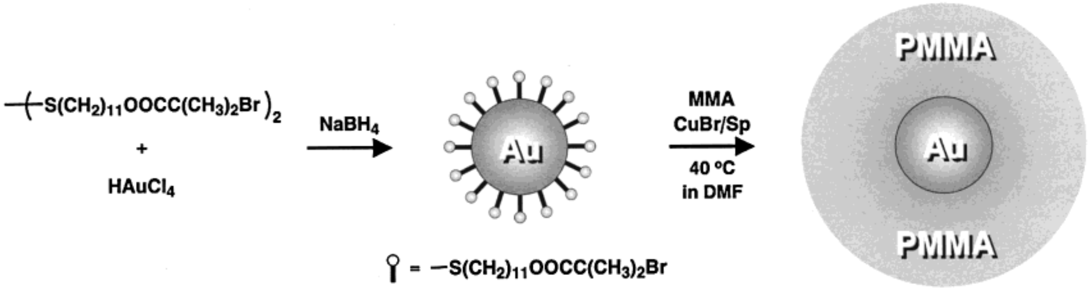
Scheme 1. Schematic Representation for the Synthesis of Polymer-Coated AuNP by Surface-Initiated LRP



first prepared, followed by the site exchange reaction with an initiator-carrying thiol synthesized by reduction of the corresponding disulfide. In the one used by Walt et al.,[9c] an undecanol monolayer-coated AuNP was first prepared, followed by the acylation of the AuNP with an initiation site-carrying acid bromide. In these previous studies, the graft densities were not evaluated accurately enough to confirm the formation of high-density brushes. Here we will propose a simple one-pot reaction for the synthesis of an initiator-modifed AuNP. We will also follow the LRP process by conducting a series of polymerization experiments and precisely evaluate the graft densities to confirm the establishment of high-density graft layers on the AuNP.

Experimental Section

Materials. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Wako Pure Chemicals, Osaka, Japan. Ethyl 2-bromoisobutylate (2-(EiB)Br) was used as received from Nacalai Tesque Inc., Osaka, Japan. (−)-Sparteine (Sp) was purchased from Aldrich and used without further purification. *N*,*N*-Dimethylformamide (DMF) was dried over molecular sieves (4 Å) for several days. Initiator-carrying disulfide (DSBr) was prepared by acylation of the corresponding hydroxyl group-terminated disulfide with 2-bromoisobutyryl bromide according to the literature.[12a] Methyl methacrylate (MMA) was obtained from Nacalai Tesque Inc. and purified by distillation under reduced pressure over calcium hydride. Water was purified by a Milli-Q system (Nihon Millipore Ltd., Tokyo, Japan) to have a specific resistivity of ca. 18 MΩ·cm. All other reagents were purchased from commercial sources and used as received.

Measurements. Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a Tosoh GPC-8020 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30 cm mixed columns (Shodex GPC KF-804L), and a Tosoh differential refractometer RI-8020. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the GPC system. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a JEOL/AL400 400 MHz spectrometer. Transmission electron microscopic (TEM) observation was made on a JEOL transmission electron microscope JEM-1010 operated at 100 kV.

Synthesis of Initiator-Coated AuNP for Surface-Initiated LRP (Scheme 1). To DSBr (1.53 g, 2.17 mmol) dissolved in methanol (MeOH, 770 mL) was added $HAuCl_4 \cdot 4H_2O$ (3.6 g, 8.74 mmol) dissolved in pure water (19 mL). After 10 min, a freshly prepared 0.5 M aqueous sodium borohydrate solution (192 mL) was added at a dropping rate of 5 mL/min with vigorous stirring. The mixture turned dark brown immediately after the addition of the reductant. After further vigorous stirring for 15 h at room temperature, the resultant precipitate was collected by centrifugation (9000 rpm, 5 min). The crude product was suspended in a mixture of 2:1 MeOH/water (200 mL), briefly sonicated to ensure complete dissolution of byproducts, and collected by centrifugation, and this cycle was repeated twice mainly to remove inorganic impurities. The same process was carried out five times with a mixture of 1:1 ethyl acetate/*n*-hexane (5 × 200 mL) to give product free of organic impurities. The final precipitate was dried in vacuo at room temperature, giving 3 g of a waxy compound of dark brown in color. The average size of the obtained AuNPs was determined by observing the TEM image of about 700 particles. The TEM sample was made by mounting a drop of the solution on a carbon-coated copper grid and drying in air for at least 30 min.

General Procedure for Surface-Initiated LRP on the AuNP (Scheme 1). A Pyrex glass tube was charged with a magnetic stirring bar and a predetermined amount of Cu(I)Br, to which was quickly added a mixture of MMA (50 wt %) and DMF containing a prescribed concentration of 2-(EiB)Br, Sp (ligand for copper complexation), and the initiator-coated AuNPs (1.25 wt %). The system was immediately degassed by three freeze−pump−thaw cycles and subsequently sealed off under vacuum. The polymerization was carried out in a water bath thermostated at 40 °C with magnetic stirring and, after a prescribed time *t*, quenched to room temperature. An aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molar mass and molecular weight distribution. The rest of the reaction mixture was diluted by THF and precipitated in an excess of *n*-hexane to obtain a mixture of free polymer and polymer-grafted AuNP. A fractional reprecipitation technique was carried out to remove the free polymer from the mixture: namely, the mixture was dissolved in acetone, to which pure water was added dropwise until a purple solid was precipitated from the solution.[20] This fractional reprecipitation was repeated three times to obtain polymer-grafted AuNPs perfectly free of the free polymer. To determine the molecular weight of the graft polymer, PMMA chains were cleaved from the surface as follows: 20 mg of the polymer-grafted AuNP was dissolved in a 5 mM iodine solution in dichloromethane (3 mL) and stirred for 12 h. The mixture was evaporated and redissolved in THF. The solution was centrifuged to remove an insoluble component. The supernatant was filtrated and then subjected to the GPC measurement.

Results and Discussion

Preparation of Initiator-Coated AuNP. We developed here the novel, facile synthetic route of the AuNP bearing 2-bromoisobutyryl groups suitable for copper-mediated LRP (Scheme 1). In contrast to the previous methods in which multistep reactions were required to prepare the initiator-coated AuNPs,[9] this route involves a one-pot reduction of $HAuCl_4$ by $NaBH_4$ in the presence of the initiator-carrying disulfide (DSBr). The introduction of the initiator groups onto the AuNPs was confirmed by infrared analysis. As shown in Figure 1, TEM observation reveals that the initiator-coated AuNPs are well dispersed forming no large aggregates. The sizes of the AuNPs range from 0.8 to 7 nm, averaging about 2.7 nm.

Surface-Initiated LRP of MMA on AuNP. The initiator-coated AuNPs were subsequently subjected to

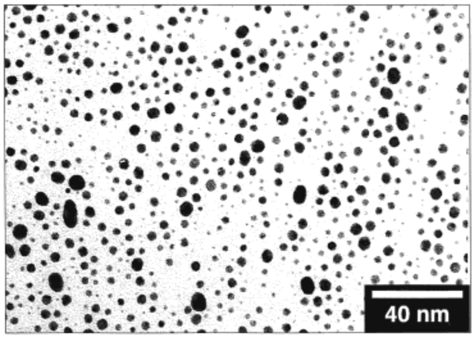


Figure 1. TEM micrograph of initiator-coated AuNP.

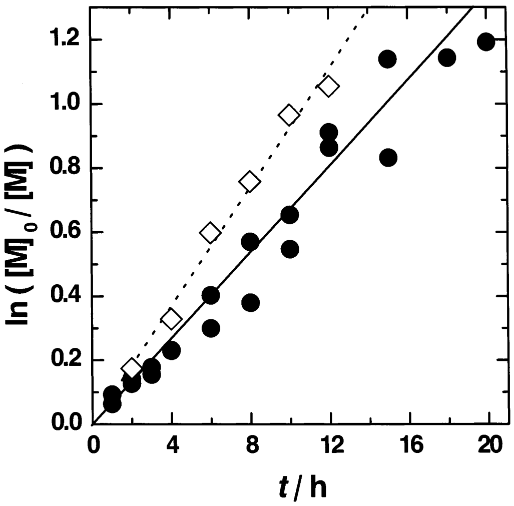


Figure 2. Plot of ln($[M]_0/[M]$) vs *t* for the solution polymerization of MMA (50 wt %) in DMF at 40 °C with (●) and without (◇) initiator-coated AuNP (1.25 wt %): $[MMA]_0/[2\text{-(EiB)Br}]_0/[Cu(I)Br]_0/[Sp]_0$ = 300/1/1.5/3.

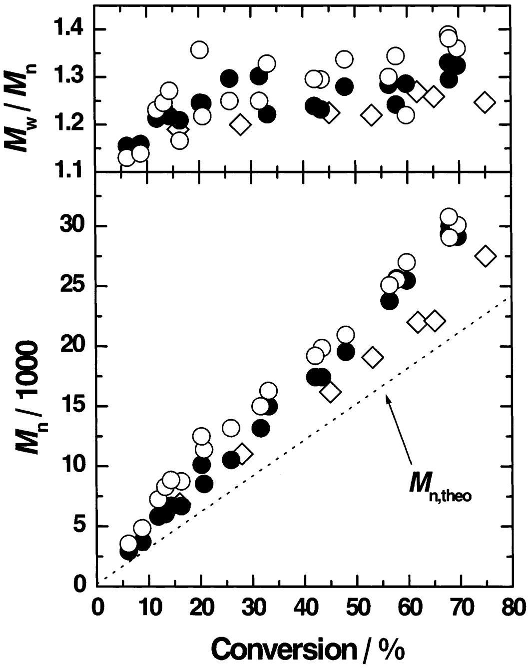


Figure 3. Evolution of M_n and M_w/M_n of the graft (○) and free (●) polymers as a function of monomer conversion for the solution polymerization of MMA (50 wt %) in DMF at 40 °C with initiator-coated AuNP (1.25 wt %): $[MMA]_0/[2\text{-(EiB)Br}]_0/[Cu(I)Br]_0/[Sp]_0$ = 300/1/1.5/3. The open diamond symbol (◇) represents the results for an AuNP free system.

the copper-mediated LRP of MMA. To obtain a satisfactory result, we paid particular attention to the following three points: first, since the S−Au bond is known to be unstable at high temperatures, we used the relatively low polymerization temperature of 40 °C to suppress detachment of the initiator groups from the AuNP surface. Second, we used DMF as a solvent in order to enhance the generally poor solubility of the AuNP. Third, we carried out the polymerization in the presence of the "sacrificial" free initiator of 2-(EiB)Br. The free initiator plays an important role in the surface-initiated LRP to allow the polymerization to proceed in a controlled fashion, as described elsewhere.[13a]

Figure 2 shows the first-order kinetic plots of monomer conversion for the polymerization of MMA with and without the initiator-coated AuNPs under the specified condition. In both cases, the plots can be approximated by a straight line, thus giving first-order kinetics with respect to monomer conversion. The linear relationship reveals that the concentration of the propagating species is constant throughout the course of polymerization. It is also evident that the rate of polymerization, as estimated from the slope of the figure, in the presence of the AuNP is slightly smaller than that in the absence of the AuNP. This may be due to the interactions of the AuNPs with copper complexes and/or monomer that could bring about the subtle divergence in the kinetics.

The purified AuNP after the polymerization was treated with iodine to cleave the graft polymer from the AuNP surface, and the cleaved polymer was subjected to GPC to determine the molecular weight and its distribution. Figure 3 shows the evolution of number-average molecular weight M_n and the polydispersity index M_w/M_n of the cleaved graft polymer and of the free polymer simultaneously produced from the free initiator. It can be seen that the M_n's of the graft and free polymers are nearly the same, both increasing with increasing monomer conversion. These M_n values, however, are slightly larger than the theoretical values, $M_{n,theo}$, for a still unclear reason. The M_w/M_n ratio remains fairly low, smaller than 1.3 for most samples. All these results confirm that the polymerization of MMA initiated from the AuNP surface proceeds in a living fashion, giving AuNPs coated with well-defined PMMA (PMMA−AuNP).

Determination of Graft Density of PMMA−AuNP. Elemental analysis for the PMMA−AuNPs was carried out in order to estimate the amount of the graft polymer on the AuNP, with which the graft density was calculated using the known density and surface area of the AuNP and the M_n of the graft polymer. As can be seen in Figure 4, the graft density is nearly constant independent of time and approximately equal to 0.3 chains/nm^2. This figure is apparently larger than those of the polymer brushes formed by the "grafting to" methods or by the surface-initiated conventional radical polymerization.[10] It is comparable to the surface densities previously attained by the surface-initiated LRP on the surfaces of silicone wafer or silica particles.[13]

Characterization of PMMA−AuNP. The PMMA−AuNP obtained here is soluble in most common good solvents for PMMA. In contrast to the fact that alkanethiol-based self-assembled monolayers on gold surfaces are not very stable in organic solvent, the PMMA−AuNPs were stably dispersed at room temperature in organic solvents such as THF, acetone, and benzene at least for 1 month. The neat PMMA−AuNPs could be easily redissolved in the organic solvents even

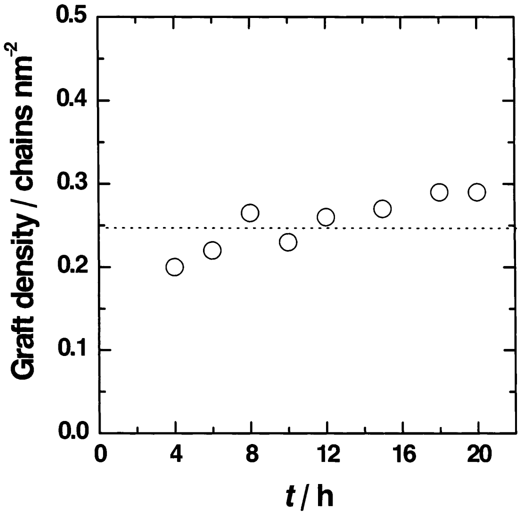


Figure 4. Time dependence of the graft density of PMMA grown from the AuNP surface.

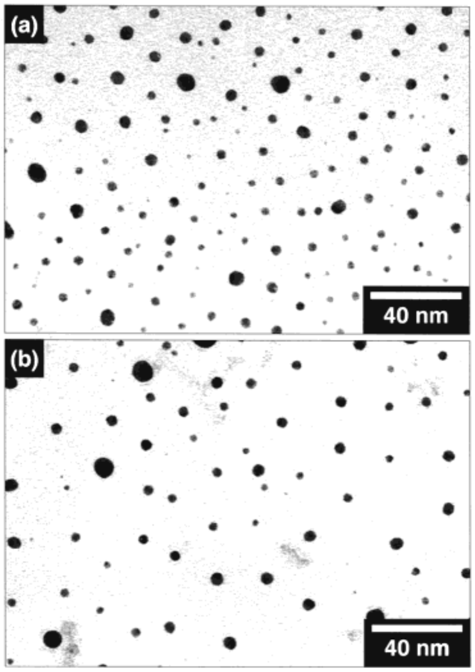


Figure 5. TEM micrographs of PMMA–AuNPs: M_n's of the graft polymers are (a) 15 000 and (b) 25 000.

after having been kept in a refrigerator for 1 year. In view of the fact that the initiator-coated AuNP forms a visible precipitate when kept in the solution only for a few days, the high stability of the PMMA–AuNP may be ascribed to the effective protection of AuNP against aggregation by the high-density polymer brushes. This result will give a new option for the improvement of the stability of colloidal particles, one of the most important issues in the area of colloid science and technology.

We have carried out TEM observation for the PMMA–AuNPs. The sample was made by casting a THF solution of the PMMA–AuNP onto a carbon-coated copper microgrid. Figure 5 shows the TEM micrographs of the PMMA–AuNPs with different PMMA chain lengths. Clearly, the AuNPs are uniformly dispersed without forming any aggregate. The average interparticle distance is much larger than that of the initiator-coated AuNP shown in Figure 1, and more importantly, it increases with increasing chain length of the graft polymer. This result forms a sharp contrast to those in the previous studies on surface-initiated LRPs on AuNPs, in which the interparticle distances of the polymer-coated AuNPs were found to be hardly different from those of the corresponding initiator-coated AuNPs as observed by TEM.[9b,c] There is no doubt that our synthetic method for preparing the initiator-coated AuNPs is highly effective to form high-density brush surfaces, which produce the large interparticle distances due to the steric interaction forces among the grafted particles. This finding will give a new possibility to produce an array of AuNPs with a controlled spacing in polymer film. In fact, we have currently succeeded in constructing a two-dimensional ordered array of monodisperse AuNPs coated with highly dense polymer brushes. This will be reported in a forthcoming paper.

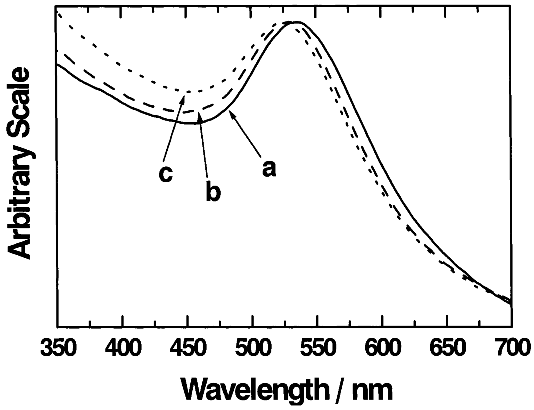


Figure 6. Absorption spectra of PMMA–AuNPs dissolved in THF at room temperature: M_n's of the graft polymers are (a) 6000, (b) 12 000, and (c) 29 000.

Figure 6 shows the absorption spectra of the PMMA–AuNPs of differing PMMA chain lengths dissolved in THF at room temperature. All the spectra exhibit a broad absorption at around 530 nm characteristic of a surface plasmon absorption band of gold particles, indicating the formation of AuNP with a diameter of several nanometers. There is observed a weak but increasing tendency for the spectra to blue shift with increasing chain length of the graft polymer. The surface plasmon absorption of gold particle is known to be sensitive to the surrounding environment.[21] The PMMA chain length may be responsible for a subtle change of the AuNP surface state to give rise to this spectral shift.

Conclusions

It was demonstrated that AuNPs carrying suitable initiator groups for LRP can be readily synthesized by the one-pot reduction of gold salt in the presence of initiator-carrying disulfide. Surface-initiated LRP of MMA using these functionalized AuNP proceeded in a living fashion, yielding structurally controlled hybrid nanoparticles with an AuNP core of several nanometers in diameter and a shell of variable thickness composed of well-defined, high-density polymer brushes. Because of the simplicity of the AuNP preparation method developed here and the versatility of LRP, this chemistry should be highly useful and can be extended to, for example, the synthesis of AuNPs having functional polymer brushes applicable as building blocks for the construction of nanoscale architectures.

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