

Metal Nanoparticles in the Template of Poly(2-ethyl-2-oxazoline)-*block*-Poly(ϵ -caprolactone) Micelle

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Abstract: The amphiphilic block copolymer (PEtOz-PCL) of poly(2-ethyl-2-oxazoline) (PEtOz) and poly(ϵ -caprolactone) (PCL) formed spherical micellar structures with an average diameter of 26 nm in aqueous phase. Au and Pd nanoparticles with an average diameter of 2~3 nm were prepared by using the PEtOz-PCL micelle consisting of a PEtOz shell and PCL core. The Au nanoparticles of PEtOz-PCL micelles in aqueous phase could be transferred into organic phase by using *n*-dodecanethiol. The use of the Pd-NP/PEtOz-PCL micelle as a nanoreactor for Suzuki cross-coupling reaction was investigated.

Keywords: nanoparticle, micelle, poly(2-ethyl-2-oxazoline).

Introduction

Colloidal nanoparticles have been the focus of an increasing amount of the recent research due to their unique properties.^{1,2} Well-defined nanocrystal and hierarchical assembled structures of nanocrystals can be used as catalyst, biological sensor, biological labeling, light emitting device, and photovoltaic cell.¹ In particular, water-soluble Au nanoparticles have a tremendous demand for biological applications such as nanoparticle carriers, and biological sensors due to their unique surface plasmonic properties, stability, and functionality.^{1,2} Palladium nanoparticles are known as effective catalysts for several reactions.³⁻⁵ Various types of templates such as water-soluble surfactants, polymers, and dendrimers have been utilized to prepare nanoparticles with controlled size.^{3,6,7}

Self-assembly of block copolymers provides an efficient route to fabricate a variety of nanomaterials in a well-defined fashion.⁴ This approach can make it possible to synthesize supramolecular assemblies with precisely controlled geometry and shape. In particular, self-organization of block copolymers in aqueous phase produced a variety of nano-architectures such as spherical micelle, cylindrical micelle, vesicle, and nanotube.^{8,9} These architectures based on block copolymers have been used in numerous scientific fields due to their stability and functionality. In recent reports, we have presented some unique characteristics of block copolymer micelles based on hydrophilic poly(2-ethyl-2-oxazoline) (PEtOz) block and hydrophobic poly(ϵ -caprolactone) (PCL)

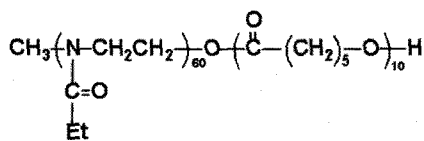
block (Table I).¹⁰⁻¹³ The PEtOz-based block copolymer micelles with a narrow size distribution were highly stable in various conditions without any precipitation for several months. In addition, PEtOz-PCL block copolymer micelles undergo reversible complexation with poly(acrylic acid) or poly(methacrylic acid) in aqueous phase via pH-induced hydrogen bonding.¹⁰⁻¹³

In this work, we report on the preparation of metal nanoparticles at the PEtOz shell by using poly(2-ethyl-2-oxazoline)-poly(ϵ -caprolactone) (PEtOz-PCL) micelle as a template in aqueous phase. The transfer of Au nanoparticles from the template in aqueous to organic media is described as well. In addition, the catalytic property of Pd nanoparticle in the PEtOz-PCL micelle is reported for the Suzuki cross-coupling reaction.

Experimental

Materials and Equipment. 2-Ethyl-2-oxazoline (Aldrich) was dried and distilled over calcium hydride. ϵ -Caprolactone (Aldrich) was vacuum distilled over calcium hydride. Methyl *p*-toluenesulfonate (Aldrich) was purified by vacuum distillation. Stannous octoate, H₂AuCl₄, K₂PdCl₄, and NaBH₄ from Aldrich were used as received. Acetonitrile and chlorobenzene were distilled over calcium hydride and calcium chloride, respectively. Molecular weights and block compositions of the diblock copolymers were determined by the analysis of ¹H NMR spectra. ¹H NMR spectra were obtained on a Bruker AC 250 spectrometer at 250 MHz. Molecular weight distribution were determined using a GPC equipped with a

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Table I. Molecular Structure, Molecular Weight, and Micellar Property of the PEtOz-PCL Block Copolymer

Block Copolymer ^a	M_n^b	Composition Ratio ^c	wt% of PCL ^d	M_w/M_n^e	d (nm) (μ_2/Γ^2) ^g
PEtOz-PCL	8,200	0.14	0.15	1.17	26 (0.12)

^aThe sample was prepared using PEtOz-OH with M_n of 7,000. ^bEstimated by ¹H NMR. ^cMolar composition ratio of the repeating units of PCL to that of PEtOz by ¹H NMR analysis. ^dWeight percentage of PCL block in the block copolymer. ^eEstimated by GPC. ^fMean diameter of micelles in distilled water at 25 °C. ^gPolydispersity factor.

Waters Associates 410 RI detector, 510 HPLC pump, and μ -Styragel columns with pore sizes of 10², 500, 10³, and 10⁴ Å. The eluent was THF, and the molecular weight was calibrated with polystyrene standards.

Preparation of PEtOz Homopolymer and PEtOz-PCL Block Copolymer. The polymer synthesis and characterization were carried out following the procedure reported previously.¹⁰⁻¹²

Transmission Electron Microscopy. TEM images were obtained on a Philips CM 200, operating at an acceleration voltage of 80 kV. For the observation of size and distribution of micellar particles, a drop of sample solution (1 g/L) was placed onto a carbon coated copper grid. About 2 min after deposition, the grid was tapped with a filter paper to remove surface water, followed by air-drying. Staining was performed by using a droplet of a 2 wt% phosphotungstic acid solution. The samples were air-dried before measurement.

Preparation of Micellar Solutions. To prepare micellar solutions, doubly distilled water (20 mL) was added dropwise to a THF solution of amphiphilic block copolymer (PEtOz-PCL). Then, THF was evaporated at 30 °C under reduced pressure. The concentration of the micellar solution was 0.5 g/L.

Synthesis of Metal Nanoparticles. To produce Au nanoparticles using PEtOz-PCL micelle as a template, HAuCl₄ (150 μ M) was added in the micellar solution (10 μ M) and the mixture was gently stirred for 30 min. After addition of NaBH₄ (5 fold molar excess), stirring was continued for 10 min. Synthesis of Pd nanoparticles was performed by the identical method. Briefly, to the micellar solution (10 μ M) was added K₂PdCl₄ (150 μ M) and then the mixture was gently stirred for 30 min. After addition of NaBH₄ (5 fold molar excess), the mixture was allowed to react for 10 min.

General Procedure for Suzuki Cross-Coupling Reaction. Into the CH₃CN solution (10 mL) of arylhalide (1 mmol) and phenylboronic acid (1.2 mmol), Na₂CO₃ (2.4 mmol) and the aqueous solution (10 mL) of Pd-NP/PEtOz-PCL micelles (0.01 mmol Pd-NP) were added. After deoxygenation for 1 h, the mixture was allowed to react at 50 °C for 12 h under nitrogen. The crude products were purified by column chro-

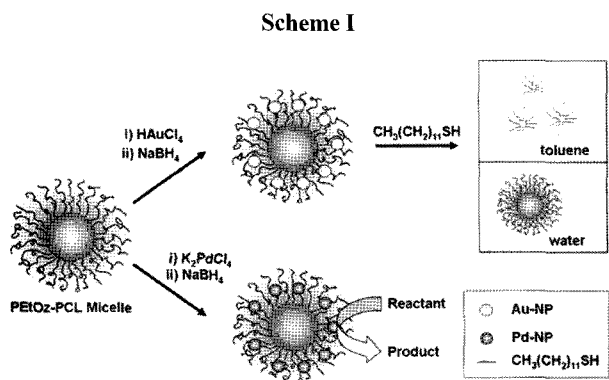
matography over silica gel using *n*-hexane/methylene chloride as an eluent to obtain the isolated products.

Dynamic Light Scattering Measurements. Dynamic light scattering measurements were performed using a Brookhaven BI-200SM goniometer and BI-9000AT autocorrelator. All the measurements were carried out at 25 °C. The sample solutions were filtered through 0.45 μ m filters from Millipore. The scattered light of a vertically polarized He-Ne laser (632.8 nm) was measured at an angle of 90° and was collected on an autocorrelator. The hydrodynamic diameters (d) of micelles were calculated by using the Stokes-Einstein equation $d = k_B T / 3 \pi \eta D$, where k_B is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and D is the diffusion coefficient. The polydispersity factor of micelles, represented as μ_2/Γ^2 , where μ_2 is the second cumulant of the decay function and Γ is the average characteristic line width, was calculated from the cumulant method.^{14,15} CONTIN algorithms were used in the Laplace inversion of the autocorrelation function to obtain micelle size distribution.¹⁶

Results and Discussion

The synthesis of PEtOz-PCL block copolymer was carried out following a reference procedure.¹⁰⁻¹³ The structural characterizations were performed by using NMR and ¹H NMR. The M_n value of the polymer, based on the ¹H NMR analysis, was 8,200 ($M_w/M_n = 1.17$). The molar composition ratio of the repeating units of PCL to that of PEtOz block was estimated to be 0.14 by ¹H NMR analysis. The amphiphilicity due to the hydrophilic PEtOz block and hydrophobic PCL block provides an opportunity for the block copolymer to form spherical micelles consisting of PEtOz shell and PCL core in aqueous phase. The hydrodynamic diameter of the micelle of PEtOz-PCL measured by dynamic light scattering (DLS) was 26 nm (polydispersity factor, $\mu_2/\Gamma^2 = 0.12$) (Table I).

In order to produce Au nanoparticles in the PEtOz outer shell of the PEtOz-PCL micelle (Au-NP/PEtOz-PCL), as described in Scheme I, HAuCl₄ was added into the aqueous



solution of PEtOz-PCL micelle followed by addition of NaBH_4 . The reduction of the Au ions in the PEtOz-PCL micelle to zerovalent Au nanoparticle was easily monitored as the color changes from yellow to brown purple. In this process, Au ions are adsorbed at amido coordination sites of PEtOz,¹⁷ and then the reductant, NaBH_4 , initiates the particle growth, which is eventually quenched by limited void of PEtOz shell.

Figure 1 shows the UV-vis absorption spectra of the block copolymer micelle and the Au-NP/PEtOz-PCL solutions. The PEtOz-PCL micelle did not show any absorption between 350 and 800 nm (Figure 1(a)). In Figure 1(b), for the aqueous solution of Au-NP/PEtOz-PCL-micelle, the surface plasmon resonance arising from Au nanoparticles was observed at 500-550 nm. In DLS experiment, the mean diameter of the micelles measured before and after addition of Au salt and the reducing agent was almost identical (~ 26 nm). The TEM image of the Au-NP/PEtOz-PCL micelle solution in Figure 2(a) clearly showed that Au nanoparticles were formed in the PEtOz-PCL micelle. The average diameter of

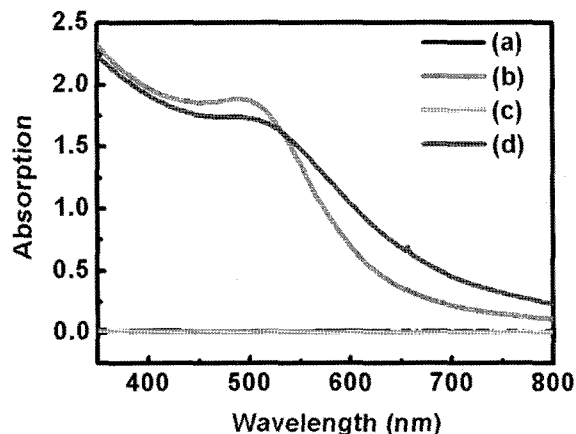


Figure 1. UV-vis spectra of (a) PEtOz-PCL micelle, (b) Au-NP/PEtOz-PCL micelle, (c) aqueous phase after extraction, and (d) organic phase after extraction.

Au nanoparticles was 2.6 ± 0.5 nm (Figure 2(b)). The Au-NP/PEtOz-PCL micelle solution was stable in an ambient condition for over 5 months without any aggregation or decomposition. The energy dispersive spectroscopy (EDS) analysis showed an additional evidence for the formation of Au nanoparticles on PEtOz-PCL micelle. The EDS spectrum showed the presence of Au, N, O, and C for Au-NP/PEtOz-PCL micelle (Figure 2(c)).

The functionalization of monolayer-protected clusters (MPCs) is a rapidly emerging field in nanomaterials research.⁶ These functional nanoparticles have potential applications for electronic devices, biosensors, and catalysts. MPCs are generally prepared by mixing metal salts, reducing agent, and thiolated ligands. Crooks *et al.* recently reported that

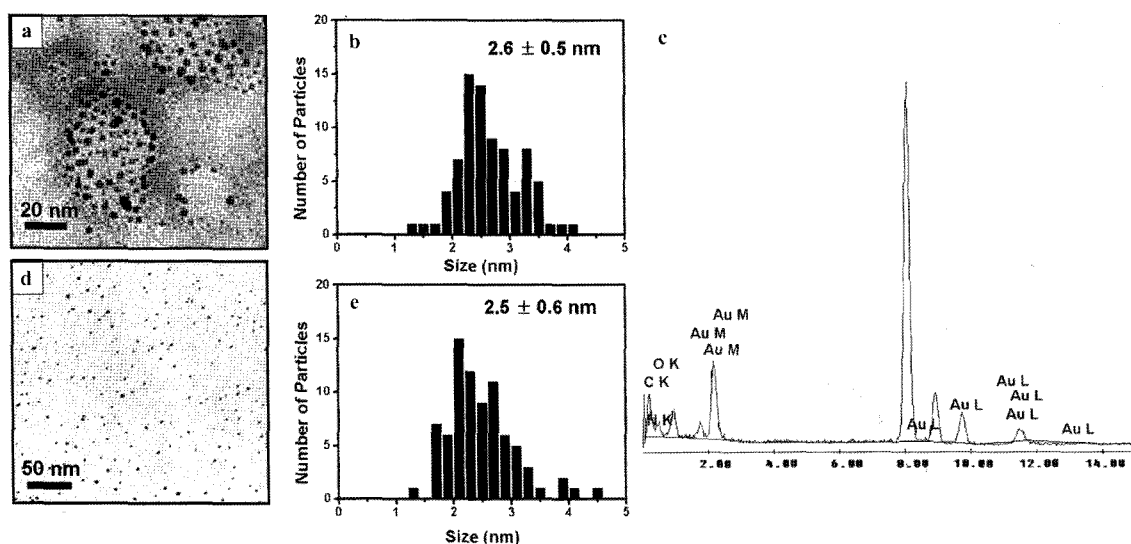


Figure 2. TEM image (a) and histogram (b) of Au nanoparticles in Au-NP/PEtOz-PCL micelle. EDS spectrum (c) of Au-NP/PEtOz-PCL micelle. TEM image (d) and size distribution histogram (e) of Au nanoparticles in toluene after extraction from the micelle in aqueous phase.

Au nanoparticles could be extracted from within the interior of PAMAM dendrimers using *n*-alkanethiol.¹⁸⁻²⁰ The dendrimer templating approach provided reproducible results for controlling the size and composition of MPCs without the need of purification. In this work, we utilized PEtOz-PCL micelle as a template for the preparation of MPCs. The Au nanoparticles are adsorbed in the PEtOz shell of the micelle by the spatial confinement of shell and the interaction with the tertiary amine moiety of the PEtOz block. The Au nanoparticles formed in the aqueous solution of PEtOz-PCL micelle could be extracted into organic phase by using *n*-dodecanethiol in organic solvent such as toluene. After shaking the two-phase system (water/toluene) in the presence of *n*-dodecanethiol for 3 min, the aqueous phase turned from brown purple to colorless and the toluene phase turned from colorless to brown purple, indicating that the Au nanoparticles in aqueous phase were extracted from the micelle into the organic phase (Scheme I). Figures 1(c) and (d) show the UV-vis absorption spectra of the aqueous and organic phases after extraction of Au nanoparticles from the micelle. The UV-vis spectrum of the Au nanoparticles passivated with *n*-dodecanethiol in toluene after extraction from the aqueous phase is similar to that of the aqueous Au-NP/PEtOz-PCL micelle solution prior to extraction. A slight spectral variation probably could result from the differences in nanoparticle concentration, solvent properties, and refractive index.^{21,22} The TEM image (Figure 2(d)) of the Au nanoparticle in toluene strongly suggests that the Au nanoparticles were extracted from the micelle without noticeable aggregation. Before extraction from the micelle, the average diameter of the Au nanoparticle was 2.6 ± 0.5 nm, and after extraction the diameter of the particle in toluene was 2.5 ± 0.6 nm. The Crooks group reported the transfer of Au nanoparticles from PAMAM dendrimer in aqueous phase into organic layer by using *n*-alkanethiol.¹⁸⁻²⁰ In that case, to extract nanoparticles from the PAMAM dendrimer into organic phase, ionic salts were needed to increase the ionic strength of the extraction

Table II. Results from Suzuki Reactions Catalyzed by Pd-NP/PEtOz-PCL Micelle

Entry	R	X	Time (h)	Yield (%) ^a
1	H	Br	12	64
2	CH=CH ₂	Br	12	72

^aIsolated yield.

solution.¹⁸⁻²⁰ In our system, however, gold nanoparticles adsorbed in the PEtOz-PCL micelle can be extracted without adding any salts possibly because of weak binding between gold nanoparticle and PEtOz shell.

Pd nanoparticles also were prepared by the same method. The average diameter of Pd nanoparticles in the Pd-NP/PEtOz-PCL micelle was 2.0 ± 0.5 nm (Figure 3). The EDS spectrum showed the presence of Pd, N, O, and C for Pd-NP/PEtOz-PCL micelle (Figure 3). We investigated the catalytic property of Pd-NP/PEtOz-PCL micelle for the Suzuki cross-coupling reaction between aryl halides and phenylboronic acid (Table II).²³⁻²⁶ The Suzuki cross-coupling reaction of bromobenzene or 4-bromostyrene with phenylboronic acid was carried out in a mixed solvent (acetonitrile/water, 1:1 v/v) at 50 °C. As shown in Table II, Pd-NP/PEtOz-PCL micelle was catalytically active in Suzuki reaction. For example, Pd-NP/PEtOz-PCL micelle was used to catalyze the reaction between 4-bromostyrene and phenylboronic acid (entry 2 of Table II) for an average 72% yield, which is similar to that of the Pd nanoparticle catalyst in the template of PAMAM dendrimer.²⁶ These results suggest that Pd-NP/PEtOz-PCL micelle can be used as an efficient nanoreactor.

Conclusions

We demonstrated that Au and Pd nanoparticles could be

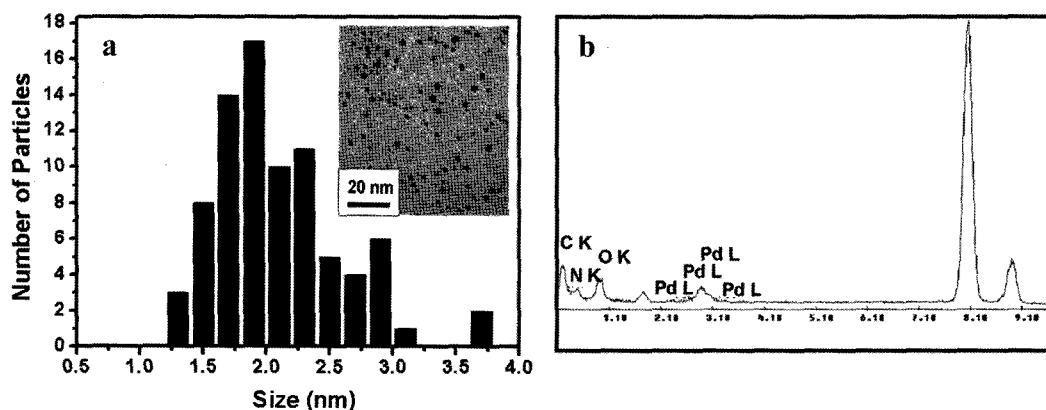


Figure 3. (a) Size distribution histogram and TEM image for Pd-NP/PEtOz-PCL micelle and (b) EDS spectrum of Pd-NP/PEtOz-PCL micelle.

prepared by using the PEtOz-PCL micelle as a template. The UV-vis absorption spectra and TEM images showed that the zerovalent metal nanoparticles formed within the PEtOz outer shell of the block copolymer micelle. This approach provides a simple and efficient method to prepare nanoparticles (< 5 nm) in aqueous solution. The Au nanoparticles formed at the PEtOz-PCL micelles in aqueous phase could be transferred into organic phase by using *n*-dodecanethiol. Therefore, this system will be widely applicable for the preparation of functional MPCs. In addition, the Pd-NP/PEtOz-PCL micelle is found to be an efficient catalyst for Suzuki reaction.

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