One-Pot Synthesis of pH-Responsive PEGylated Nanogels Containing Gold Nanoparticles by Autoreduction of Chloroaurate Ions within Nanoreactors

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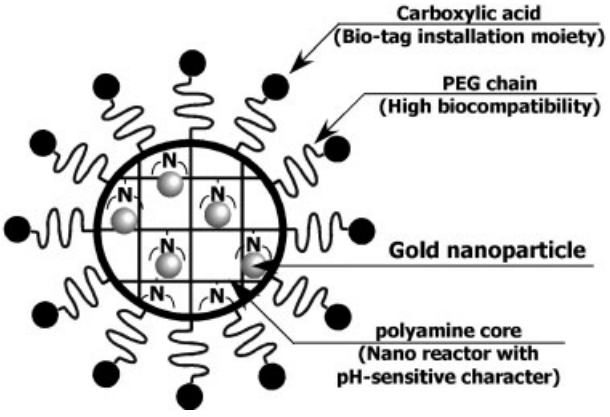
One-pot synthesis of pH-responsive PEGylated nanogels (diameter <100 nm) containing gold nanoparticles (AuNPs) was successfully carried out through the autoreduction of $HAuCl_4$ with PEGylated nanogels constructed from cross-linked poly[2-(*N*,*N*-diethylamino)ethyl methacrylate] (PDEAMA) core and tethered PEG chains. Transmission electron microscopy image of the nanogel containing AuNPs prepared at N/Au ratio = 8 revealed that the average number of AuNPs in a single nanogel and average diameter of the AuNPs were about 10 particles/nanogel and 6 nm, respectively. The surface plasmon band of the PEGylated nanogel containing AuNPs was shifted in response to pH, indicating that the cross-linked PDEAMA core of the nanogels acts as not only nanoreactor but also pH-sensitive matrix.



Introduction

Small clusters of metals[1] and semiconductors[2] have received considerable attention and interest because of their unique mechanical, electronic, magnetic, optical, and chemical properties. Of particular interest is gold nanoparticles (AuNPs),[3,4] which show a very intense surface plasmon band (SPB) in the visible (typically around

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520 nm: bright-pinkish color). They are useful for biomedical applications such as biological marker,[5] DNA sensor,[6] immunoassay,[7] drug delivery systems,[8] and molecular recognition systems.[9] Nevertheless, AuNPs dispersed by the electrostatic repulsion force of the absorbed ions on their surfaces tend to show coagulation themselves in high ionic strength milieu as well as non-specific absorption of biomolecules such as protein and DNA, resulting in reduced sensitivity and selectivity.[10]

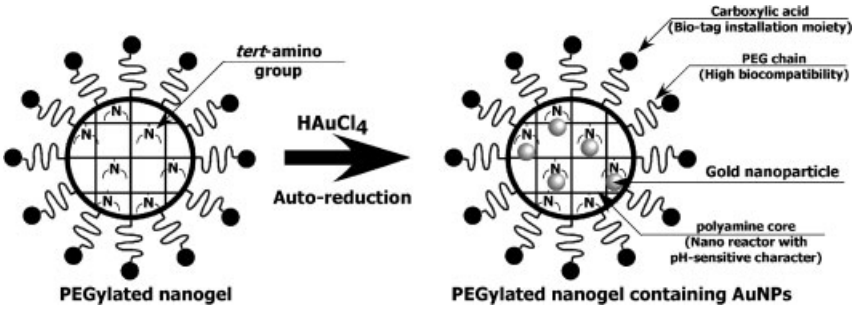

Figure 1. Schematic illustration of the pH-responsive PEGylated nanogel containing AuNPs.

In this regard, a variety of polymer systems interacting with AuNPs have been used so far as a means of stabilization, particle size control and organization.[3] We recently reported a simple and effective approach to the concomitant stabilization and functionalization of AuNPs based on the autoreduction of the chloroaurate ions ($AuCl_4^-$) in the presence of poly(ethylene glycol)-*block*-poly[2-(*N*,*N*-dimethylamino)ethyl methacrylate] (PEG-PDMAMA) copolymer bearing a reactive acetal group (bio-tag installation moiety) at the PEG end.[11] Note that formation of the PEGylated AuNPs spontaneously occurred through an ion exchange process between $AuCl_4^-H^+$ and protonated PDMAMA segment ($-N^+Me_2HCl^-$), followed by the reduction of Au(III) ions to Au(0) particles by PDMAMA segment without any additional reducing agents, viz. tertiary amino groups in the PDMAMA segment play a crucial role in the autoreduction of Au(III) ions as well as the binding of the AuNPs.[12,13] Due to the steric stabilization of tethered PEG chains surrounding the AuNPs through multivalent coordination between the gold surface and the tertiary amino groups of the PDMAMA segment, bio-tag installed and PEGylated AuNPs formed from PEG-PDMAMA copolymer showed excellent stability under physiological conditions, minimal interaction with biological components, and specific molecular recognition, compared to the other conventional polymer-stabilized AuNPs systems. However, the PEGylated AuNPs formed from PEG-PDMAMA copolymer is lack of the specified properties and functions such as stimuli sensitivity.

More recently, next generation of AuNPs with specified properties and functions can have a significant impact on the nanoscale bio-tools and bio-device. A major key to the construction of next generation of AuNPs is the incorporating of the AuNPs into smart polymer matrix that can be triggered to significant change in the characteristics of the matrix in response to the stimuli such as pH and temperature,[14–18] because the exact position and intensity of SPB is known to be extremely sensitive to not only the size and shape, but also to the optical and electronic properties of the environments surrounding the particles.[19] Worth noting in this regard is a new class of nano-sized (<100 nm), pH-sensitive, PEGylated nanogels constructed from a cross-linked, pH-sensitive poly[2-(*N*,*N*-diethylamino)ethyl methacrylate] (PDEAMA) core and tethered PEG chains that possess a carboxylic acid group as a platform moiety for the installation of bio-tag.[20] Indeed, the PEGylated nanogels showed extremely high dispersion stability as well as reversible volume phase transition (swelling) in response to the pH due to the protonation of the cross-linked PDEAMA core surrounded by the tethered PEG chains,[21] but the pH of the phase transition point depends on the ionic strength and temperature. This indicates that the cross-linked PDEAMA core of the nanogels acts as both nanoreactor and stimuli-sensitive matrix to produce and stabilize the AuNPs through the autoreduction process (Figure 1).

A unique finding, which we would like to describe here, is one-pot synthesis of pH-responsive PEGylated nanogel containing AuNPs through an autoreduction of chloroaurate ions within the cross-linked PDEAMA core. Note that shift of the SPB of the PEGylated nanogel containing AuNPs was observed synchronizing with reversible volume phase transition of PDEAMA core in response to the pH. Thus, we believe that the use of environmentally sensitive, PEGylated nanogel containing AuNPs represents a promising strategy for the biosensor systems.

Experimental Part

Materials

Ethylene glycol dimethacrylate (EGDMA; Wako) and 2-(*N*,*N*-diethylamino)ethyl methacrylate (DEAMA, Wako) were distilled over CaH_2 under reduced pressure. Potassium persulfate (KPS; Wako) was purified by recrystallization from water and then dried *in vacuo*. Tetrachloroauric acid ($HAuCl_4$, Wako) was used without further purification. Water was purified using the Milli-Q system (Millipore).

Synthesis of pH-Responsive PEGylated Nanogel

The α-vinylbenzyl-ω-carboxylpoly(ethylene glycol) (CH_2=CH–Ph–PEG–COOK, $\overline{M}_n = 3\,500$, $\overline{M}_w/\overline{M}_n = 1.04$) macromonomer was

synthesized as described in our previous report.[20] The vacuum and argon purging cycles of the reactor containing CH_2=CH–Ph–PEG–COOH (1.0 g, 286 μmol) and KPS (60.5 mg, 222 μmol) were repeated three times, followed by the successive addition of deionized-distilled water (25 mL), DEAMA (4.0 g, 21.6 mmol), and EGDMA (41.75 μL, 0.219 μmol, 0.1 mol-%). Emulsion copolymerization was carried out at room temperature for 24 h.

Synthesis of pH-Responsive PEGylated Nanogel Containing AuNPs

As a typical procedure for the pH-responsive nanogel containing AuNPs at N/Au ratio of 8, $HAuCl_4$ aqueous solution (2.0 mL, 2.86 mg·mL^{-1}, 7.25×10^{-3} M) was added to 2.0 mL of the PEGylated nanogel solution (13.4 mg/mL, [N] = 58.0×10^{-3} M), and the resulting mixture was adjusted to pH = 6.0. The reaction mixture was stirred for 24 h at room temperature.

Characterization of pH-Responsive PEGylated Nanogel Containing AuNPs

To measure the size of pH-responsive nanogel containing AuNPs (>0.5 mg/mL) as a function of pH, dynamic light scattering (DLS) measurements were carried out at 25 °C using a light-scattering spectrometer (DLS-7000, Otsuka Electronics Co. Osaka, Japan) equipped with a vertically polarized incident beam at 488 nm supplied by an argon ion laser at scattering angles of 90°. To determine the pK_a of the pH-responsive nanogel, the pH-responsive nanogel (10 mg) was dissolved in 40 mL 0.0075 M HCl and titrated with 0.01 M NaOH. An automatic titrator (DL-25, METTLER) was used for titration. In this case, the titrant was added in quantities of 0.05 mL after the pH values were stabilized (minimal interval: 30 s). The α/pH curves were determined from the obtained titration curves. To characterize the optical property of the pH-responsive nanogel containing AuNPs, UV-vis spectra were recorded using a Shimadzu UV-2400PC spectrometer with a 1 cm quartz cell. Transmission electron microscope (TEM) samples were prepared by mounting a drop of the solution on carbon-coated Cu grids and allowing them to dry in air. TEM analysis was carried out using Hitachi H800 operating at 200 kV to measure the size of AuNPs in PEGylated nanogels. The average diameter and numbers of AuNP from TEM images were calculated by Scion Image soft.

Results and Discussion

Synthesis of pH-Responsive PEGylated Nanogel

The pH-responsive PEGylated nanogel was prepared at room temperature by emulsion copolymerization of DEAMA with heterobifunctional PEG bearing a 4-vinylbenzyl group at the α-end and a potassium carboxylate group at the ω-end (CH_2=CH–Ph–PEG–COOK; $\overline{M}_n$ 3 500 $\overline{M}_w/\overline{M}_n = 1.04$) in the presence of KPS and EGDMA (0.1 mol-%) as a cross-linker, as described previously.[20]

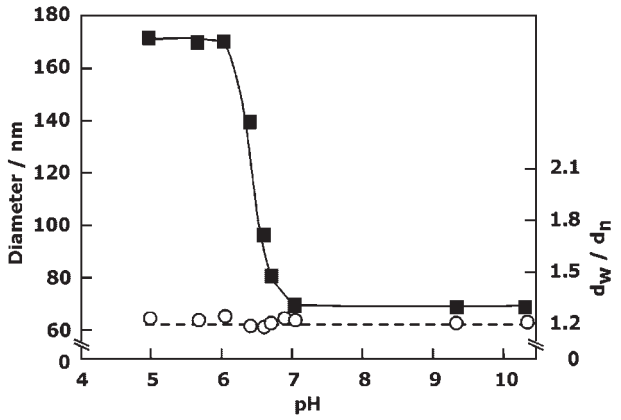

Figure 2. pH dependency of the diameters (closed square) and d_w/d_n (open circle) of the pH-responsive PEGylated nanogel without AuNP (DLS measurement: angle, 90°; temperature, 25 °C).

In the present system, although copolymerization of amine-containing monomer and anionic PEG macromonomer often tends to show a coacervate formation, the emulsion copolymerization smoothly proceeded to form the nanogel with PEG–COOK tethered chains on the surface because of the hydrophobic nature of the DEAMA monomer.[20] The diameter of the obtained nanogel increased proportionally with a unimodal size distribution (weight average of diameter/number average of diameter: $d_w/d_n < 1.25$) with decreasing the pH from 7.0 to 5.0, reaching to a 14.8-fold larger hydrodynamic volume at pH = 5.0 (diameter = 171 nm) compared to that at pH = 7.0 (diameter = 70 nm) (Figure 2), due to an increase in the ion osmotic pressure and solvation of the PDEAMA core caused by the protonation of the tertiary amino groups in the core of the nanogel.

One-Pot Synthesis of pH-Responsive PEGylated Nanogels Containing AuNPs

The PEGylated nanogel composed of PDEAMA core and the tethered PEG chains seems to act as both nanoreactor and stabilizer of the AuNPs formed from autoreduction of tetrachloroauric acid ($HAuCl_4$). Figure 3 shows UV-vis spectra of reaction mixture of $HAuCl_4$ and PEGylated nanogel in the molar ratio of tertiary amino group: $HAuCl_4$ of 8 (N/Au = 8) under the several pH conditions. The reaction solutions at pH 6.0 and 7.0 gradually changed in color from yellow to pinkish-red, especially, significant increase in the absorbance at 523 nm attributed to the SPB was observed at pH = 6.0, strongly indicating that formation of AuNPs occurred through the autoreduction of $HAuCl_4$.[11] In sharp contrast, increase in the absorbance at SPB and color change were not observed in the reaction

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Macromolecular Journals

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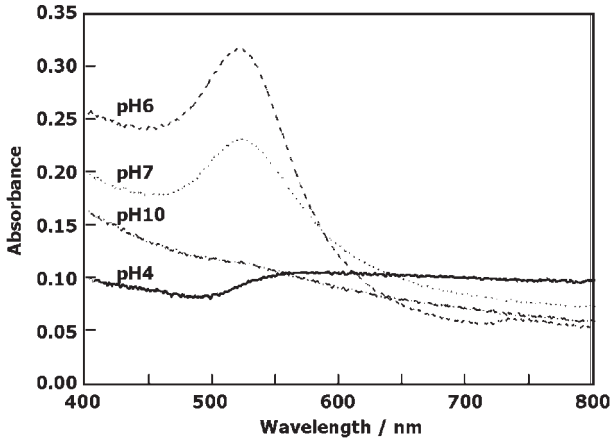

Figure 3. UV-vis absorption spectra of the pH-responsive PEGylated nanogel containing AuNPs (N/Au = 8) synthesized at pH 4.0, 6.0, 7.0, and 10.

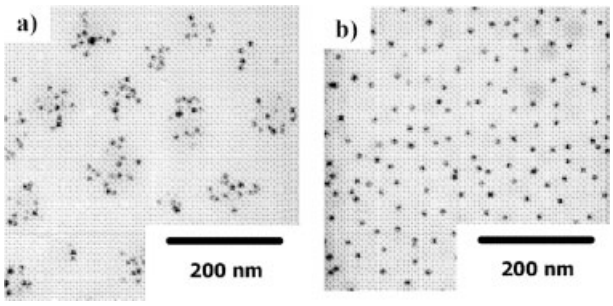

Figure 4. TEM image of the a) pH-responsive PEGylated nanogel containing AuNPs synthesized at N/Au = 8 at pH 6.0 and b) AuNPs synthesized by PEG-PDMAMA block copolymer at pH 6.0.

solution at pH = 10.0, where the cross-linked PDEAMA core ($pK_a = 7.1$) was deprotonated and hydrophobic, viz. ion exchange reaction between $AuCl_4^-$ and deprotonated PDEAMA core was completely inhibited. Furthermore, the reaction solution at pH = 4.0 showed no absorbance at SPB, but the color of the solution changed to purple, leading to the coagulation as well as precipitation of AuNPs. This is presumably due to the low coordination ability of protonated PDEAMA core under low pH (high proton concentration) conditions. Transmission electron microscopy (TEM) image of the PEGylated nanogel containing AuNPs synthesized at pH = 6.0 shows that AuNP clusters were clearly observed, where the TEM shows not only AuNPs (high contrast) but also the PDEAMA core of the nanogel (lower contrast; < 100 nm),[14] as shown in Figure 4a. The average number of AuNP in a single nanogel (cluster) and average diameter of the AuNPs were about 9.6 particles/nanogel and 6 nm with a unimodal size distribution ($d_w/d_n <$ 1.15), respectively. In sharp contrast, any AuNP clusters were not observed for AuNPs (diameter = 8.4 nm, $d_w/d_n <$ 1.08) prepared by the autoreduction of $HAuCl_4$ in the presence of PEG-PDMAMA block copolymer, as shown in Figure 4b. In addition, the observed SPB of the PEGylated nanogel containing AuNPs (Figure 3) is somewhat longer wavelength ($\lambda_{max} = 523$ nm) compared to the commercially available citrate-stabilized AuNPs with same size (≈10 nm, $\lambda_{max} = 518$ nm), suggesting the coordination of the amino groups on the surface of

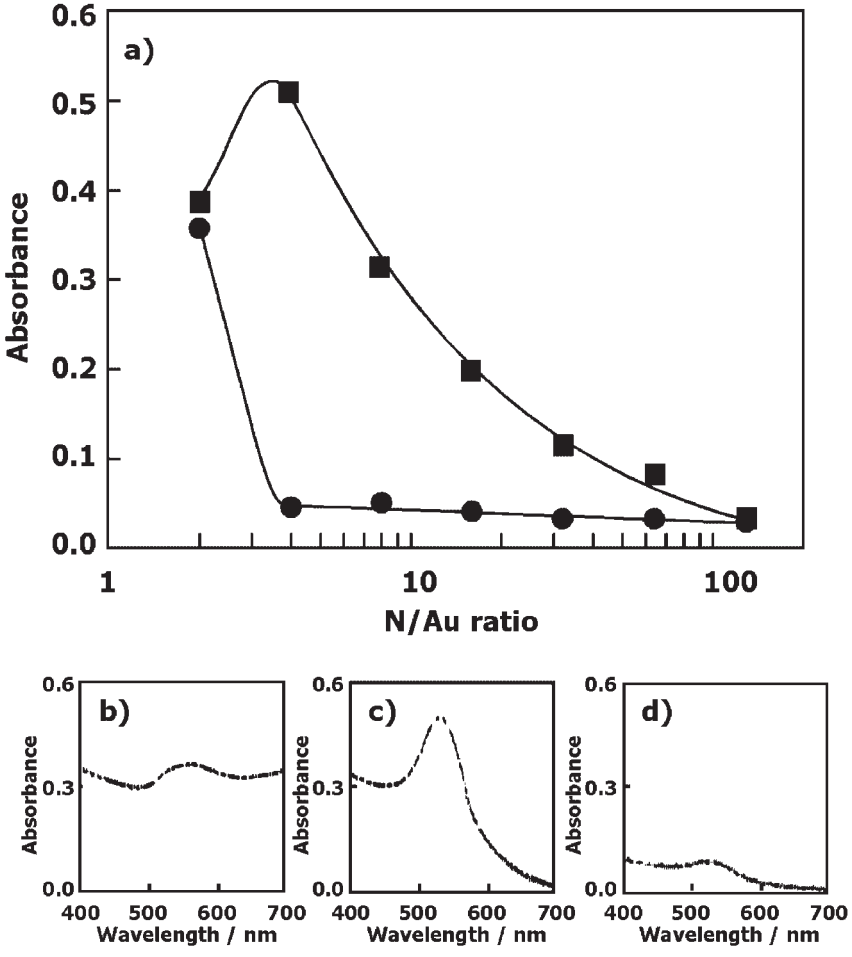

Figure 5. a) Absorbance at λ_{max} (square) and at 650 nm (circle) of the pH-responsive PEGylated nanogel containing AuNPs synthesized by various N/Au ratios. Typical UV-vis absorption spectra of pH-responsive PEGylated nanogel containing AuNPs synthesized at b) N/Au = 2, c) N/Au = 4, and d) N/Au = 64.

the AuNPs.[18] These findings give direct proof that AuNPs have been formed within the PDEAMA core of the PEGylated nanogel through the autoreduction process, that is, in the "nanoreactors".

Figure 5 shows UV-vis spectra and absorbance at both λ_{max} (SPB) and 650 nm (coagulation) of the reaction solution of the $HAuCl_4$ and PEGylated nanogels at pH = 6.0 at various N/Au ratios (2, 4, 8, 16, 32, 64, and 128). The final concentration of the PEGylated nanogel in all reaction solutions was constant ([N] = 58 mM). The absorbance at SPB of the PEGylated nanogel containing AuNPs decreased with increasing N/Au ratios from 4 to 128 due to the decrease in the concentration of $HAuCl_4$, although the no shift of the SPB (523 nm) and no change in absorbance at 650 nm were observed. On the other hand, significant shift of the SPB (ca. 560 nm) and increasing in absorbance at 650 nm were observed at N/Au ratio of 2, and the resulting color of the solution changed to purple, indicating that excess $HAuCl_4$ led to the coagulation of the AuNPs in the PDEAMA core. This result suggests that each Au(III) presumably interacts with at least 4 amino groups to form stable PEGylated nanogel containing AuNPs.

We have previously found that the size of the AuNPs can be controlled by the N/Au ratio when PEG-PDMAMA block copolymer was used for the autoreduction of $HAuCl_4$ (N/Au = 18, diameter = 11 nm; N/Au = 36, diameter = 7 nm).[22] The same phenomenon was observed by using nanogel as a nanoreactor. From the TEM images of the typical PEGylated nanogel containing AuNPs (Figure 4a and 6), the average diameter of the AuNPs in the PEGylated nanogels containing AuNPs synthesized at N/Au = 8 and 4 was found to be 6 ($d_w/d_n = 1.15$) and 9 nm ($d_w/d_n = 1.12$), respectively, though the position of SPB ($\lambda_{max} = 523$ nm) and average number of AuNPs in a nanogel were almost the same regardless of the N/Au ratio (9.6 particles/nanogel for N/Au = 8, 10.4 particles/nanogel for N/Au = 4). Furthermore, the size of AuNPs prepared at above N/Au > 8 was almost similar to that of AuNP prepared at N/Au = 8 (≈6 nm). These findings suggest that increasing in absorbance at SPB of PEGylated nanogel containing AuNPs with the decreasing N/Au ratio in the range of N/Au = 4–8 is due to the increase in the size of the AuNPs formed in the PDEAMA core of the nanogel, because the absorption of SPB is known to increase with the increasing size of the particle.[23] Thus, the control of the AuNP size is possible by varying the N/Au ratio, with increased concentration of PEGylated nanogels favoring smaller AuNP size.

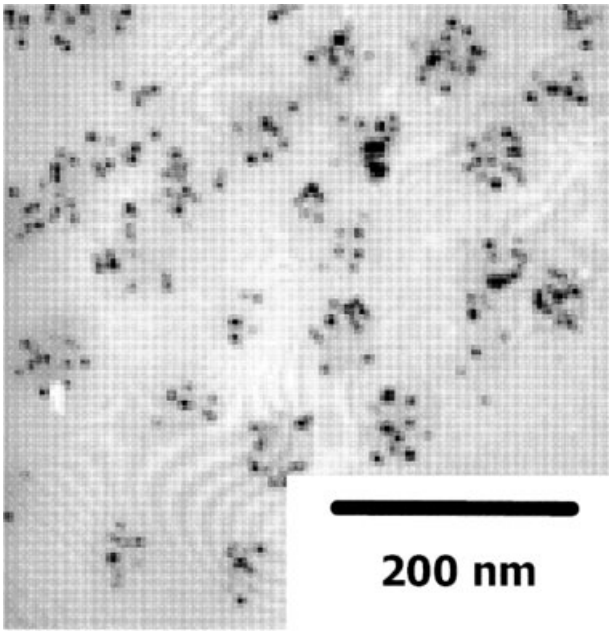

Figure 6. TEM image of the pH-responsive PEGylated nanogel containing AuNPs synthesized at N/Au = 4 at pH 6.0.

Characterization of pH-Responsive PEGylated Nanogels Containing AuNPs

In order to evaluate the pH-sensitivity of the PEGylated nanogel containing AuNPs prepared in this study, the DLS measurements were carried out as a function of the environmental pH. As can be seen in Figure 7, PEGylated nanogel containing AuNPs (N/Au = 64) showed almost similar reversible volume phase transition phenomenon of the PEGylated nanogel without AuNP, indicating that the gold nanoparticle in nanogel did not affect phase transition of the PDEAMA core. Note that d_w/d_n of the PEGylated nanogel containing AuNPs is still low value (<1.2) even at both low and high pH, indicating that coagulation of the PEGylated nanogel containing AuNPs did not cause, viz. PEGylated nanogel containing AuNPs is stable under both low and high pH conditions. Figure 8 shows the pH-sensitivity of the PEGylated nanogel

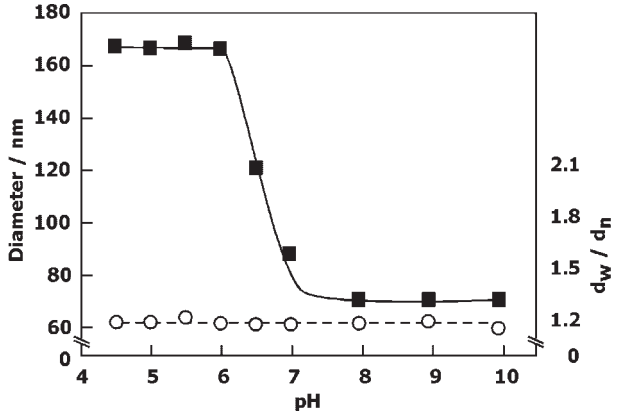

Figure 7. pH dependency of the diameters (closed square) and d_w/d_n (open circle) of the pH-responsive PEGylated nanogel containing AuNPs synthesized at N/Au = 64 (DLS measurement: angle, 90°; temperature, 25 °C).

Macromol. Chem. Phys. **2007**, *208*, 1176–1182

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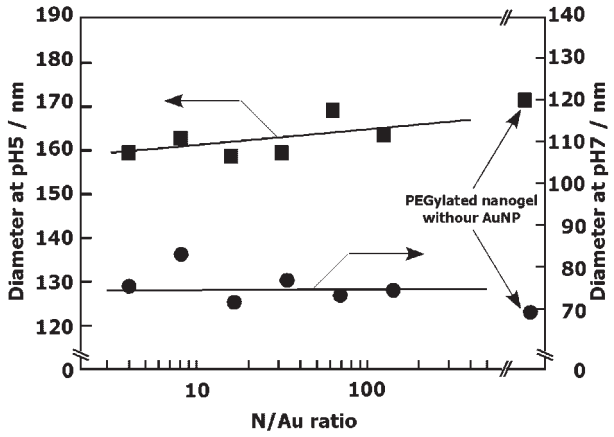

Figure 8. Diameters of the swelling-state at pH = 5 (square) and deswelling state at pH = 7 (circle) for the pH-responsive PEGylated nanogel containing AuNPs synthesized by various N/Au ratios (DLS measurement: angle, 90°; temperature, 25 °C).

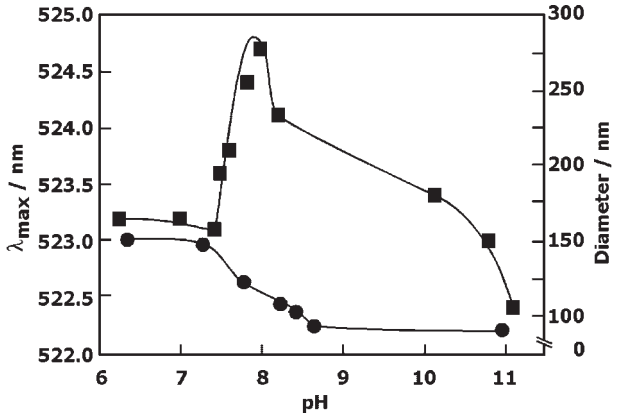

Figure 10. Plots of the variation of the SPB (square) and diameter (circle) of the pH-responsive PEGylated nanogel containing AuNPs (N/Au = 8) at various pH values under 0.15 M ionic strength conditions (DLS measurement: angle, 90°; temperature, 25 °C).

containing AuNPs synthesized at various N/Au ratios. The pH-sensitivity of all PEGylated nanogels containing AuNPs did not influence by the N/Au ratio, although the appearance cross-linking density (non-covalent cross-linkage) constructed from the AuNP and amino group increased with decreasing N/Au ratio. This is most likely that protonation of the coordinated amino groups occurred decrease in pH, leading to the weak coordination of the protonated amino groups to AuNP.

To clarify the stability of the PEGylated nanogel containing AuNPs, time course of the change in the absorbance at SPB of the PEGylated nanogel containing AuNPs synthesized at N/Au = 8 was monitored under very high salt concentrations (1.0 M NaCl), as shown in Figure 9. Note

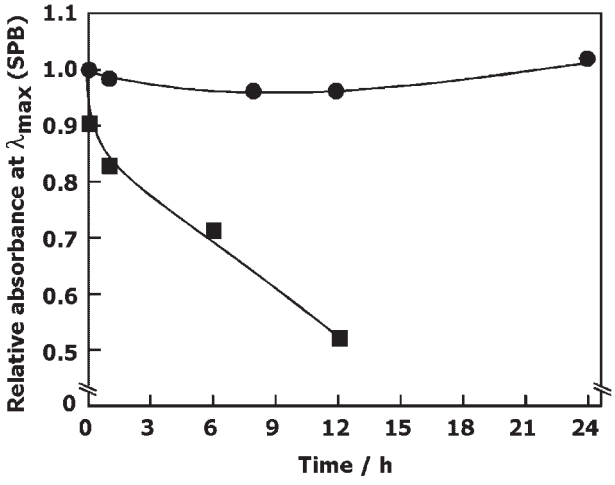

Figure 9. Relative absorbance at λ_{max} of the commercially available citrate-stabilized AuNPs (square) in 0.1 M $NaCl_{aq}$ at pH = 6 and the pH-responsive PEGylated nanogel containing AuNPs (N/Au = 8) (circle) in 1.0 M $NaCl_{aq}$ at pH = 6.

that commercially available citrate-stabilized AuNPs immediately showed the coagulation arisen from the inhibition of electrostatic repulsion force even under lower salt concentrations (0.1 M NaCl), whereas the PEGylated nanogel containing AuNPs showed almost no changing in the shift and absorbance of SPB. The appreciable stability of the PEGylated nanogel containing AuNPs is due to the steric stabilization of the hydrophilic PEG palisade tethered from the surface of the PDEAMA core.

Figure 10 shows plots of the position of the SPB and diameter of the PEGylated nanogel containing AuNPs synthesized at N/Au = 8 under 0.15 M ionic strength conditions. The SPB of the PEGylated nanogel containing AuNPs (pH < 7: λ_{max} = 523.2 nm) was slightly red-shifted with increasing the pH of the medium from 7.0 to 8.0, reaching to the λ_{max} = 524.8 nm. Note that shift of the SPB of the PEGylated nanogel containing AuNPs was observed synchronizing with reversible volume phase transition of PDEAMA core in response to the pH (data not shown). This indicates that coordination between deprotonated amino groups and AuNPs proceeds along with the conversion of the protonated amino groups ($-N^+Me_2HCl^-$) to deprotonated amino groups ($-NMe_2$), probably leading to the change in the electronic environments on the surface of AuNPs. In contrast, blue shift of the SPB was observed at pH above 8, because the environments surrounding the AuNPs becomes less hydrophilic arising from the volume phase transition of the PDEAMA core.[17]

Conclusion

In conclusion, one-pot synthesis of pH-responsive nanogel containing AuNPs was successfully carried out through the autoreduction of $HAuCl_4$ with PEGylated nanogel (dia-

meter < 100 nm) composed of a cross-linked pH-sensitive PDEAMA core and tethered PEG chains. Transmission electron microscopy image of the PEGylated nanogel containing AuNPs synthesized at N/Au ratio of 8 revealed that the average number of AuNPs in a single nanogel and average diameter of the AuNPs were about 9.6 particles/nanogel and 6 nm with a unimodal size distribution ($d_w/d_n < 1.15$), respectively, indicating that these findings give direct proof that AuNPs have been formed within the PDEAMA core of the PEGylated nanogel through the autoreduction process. In addition, the size of the AuNPs in the nanogel (9 nm) increased with decrease in the N/Au ratio from 8 to 4, suggesting that the control of the AuNP size is possible by varying the N/Au ratio, with increased concentration of PEGylated nanogels favoring smaller AuNP size. The SPB of the PEGylated nanogel containing AuNPs was shifted in response to pH region of the volume phase transition of the PEGylated nanogel. The cross-linked PDEAMA core of the PEGylated nanogels acts as not only nanoreactor but also pH-sensitive matrix to produce new class of AuNPs. We anticipate that the pH-responsive and PEGylated nanogel can be used to synthesize colloidal particles such as Pt particles, Pd particles, CdS particles, and magnetic Fe_2O_3 particles, and the resultant pH-responsive PEGylated nanogel containing AuNPs may have very important applications such as biosensor tools.

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