

Gold Nanoparticles Functionalized with Block Copolymers Displaying
Either LCST or UCST Thermosensitivity in Aqueous Solution

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Gold nanoparticles (AuNPs) coated with a diblock copolymer composed of poly(ethylene oxide) (PEO) and poly(*N,N*-dimethylaminoethyl methacrylate) (PEO-*b*-PDMAEMA) were prepared, while their reaction with 1,3-propane sultone gave rise to quaternized PEO-*b*-PDMAEMA chains on AuNPs. Using pyrene as a probe equilibrated with polymer-coated AuNP aqueous solutions, the fluorescence measurement results show that the diblock copolymers tethered to AuNP surfaces could undergo a thermally induced solubility change characterized by either a LCST (with PEO-*b*-PDMAEMA) or a UCST (with quaternized PEO-*b*-PDMAEMA). In both solutions, the use of a water-soluble PEO outer block helps preventing aggregation of AuNPs upon dehydration (decreased solubility) of either PDMAEMA chains at $T > \text{LCST}$ or quaternized PDMAEMA chains at $T < \text{UCST}$. Moreover, the reversible solubility change of block copolymer chains on AuNPs could be induced not only by heating the bulk solution but also, to some extent, by illuminating the solution at wavelengths close to the surface plasmon resonance (SPR) band of AuNPs due to a photothermal effect. The method presented is an easy way to prepare polymer-coated AuNPs that can have a stable dispersion in aqueous solution while exhibiting either LCST or UCST thermosensitivity.

Introduction

Grafting stimuli-responsive polymers to gold nanoparticles (AuNPs) is a convenient way to render them responsive to changes in environmental conditions such as pH and temperature.^{1,2} With a water-soluble polymer ligand tethered to the surface of AuNPs, a stable dispersion in water can be obtained. Recent studies found that if the polymer chains become insoluble due to either a temperature change or a pH change, aggregation of AuNPs can occur, resulting in a reduced optical transmittance of the solution and a shift of the surface plasmon resonance (SPR) mainly as a result of closer distances between the surfaces of AuNPs.^{1,2} In view of the importance of AuNPs in many emerging applications such as sensing, delivery, and cancer therapy,³ developing new stimuli-responsive AuNPs is of interest. To our knowledge, all thermosensitive polymer-coated AuNPs reported thus far display a lower critical solution temperature (LCST), meaning that the polymer becomes insoluble in water when solution temperature is raised to $T > \text{LCST}$. To make polymer-coated AuNPs respond to temperature change in the opposite way, i.e., with a polymer that becomes insoluble in water upon lowering temperature, the coated polymer should exhibit an upper critical solution temperature (UCST). We report herein the design, synthesis, and characterization of AuNPs functionalized with diblock copolymers that impart both LCST and UCST thermosensitivity to AuNPs. Combined with a stable

dispersion in water regardless of the polymer phase transition, these new polymer-functionalized AuNPs may also promise for thermally and optically controlled delivery of guest molecules trapped by polymer chains on the surface of AuNPs.

As shown in Figure 1, the starting polymer used to coat AuNPs is a diblock copolymer composed of poly(ethylene oxide) (PEO) and poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA), with the PDMAEMA block grafted to AuNPs. The design rationale is as follows. First, PDMAEMA, which bears tertiary amine groups, is known to have a LCST,⁴ whereas after reaction with 1,3-propane sultone converting nonionic PDMAEMA to a zwitterionic moiety, the quaternized PDMAEMA displays a UCST.⁵ Therefore, with the use of a same diblock copolymer PEO-*b*-PDMAEMA tethered to AuNPs, both LCST and UCST thermosensitive AuNPs could be obtained. Second, since the thermosensitive PDMAEMA chains form the inner layer on the surface of AuNPs while PEO chains form the outer corona, either with PDMAEMA becoming insoluble in water upon temperature increase to $T > \text{LCST}$ or with its quaternized form becoming insoluble upon temperature decrease to $T < \text{UCST}$, the outer corona of PEO would keep AuNPs soluble in water and thus prevent aggregation of AuNPs into large particles. In other words, the change in water solubility of polymer chains on surface in response to temperature variation in both ways would not affect the colloidal stability of the polymer-coated AuNPs. As discussed below, our characterization results confirmed this design, showing that polymer chains on AuNP surface could exhibit solubility change upon solution temperature variation, via either LCST or UCST, while AuNPs remained soluble. Moreover, a photothermal effect was observed by illuminating the solution at wavelengths close to the SPR of AuNPs.

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(1) See, for example: (a) Zhu, M.-Q.; Qang, L.-Q.; Exarhory, G. J.; Li, A. D. Q. *J. Am. Chem. Soc.* **2004**, *126*, 2656. (b) Shan, J.; Chen, J.; Nuopponen, M.; Viitala, T.; Jiang, H.; Peltonen, J.; Kauppinen, E.; Tenhu, H. *Langmuir* **2006**, *22*, 794. (c) Edwards, E. W.; Chanana, M.; Wang, D.; Mohwald, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 320. (d) Li, D.; He, Q.; Li, J. *Adv. Colloid Interface Sci.* **2009**, *149*, 28.

(2) See, for example: (a) Li, D.; He, Q.; Yang, Y.; Mohwald, H.; Li, J. *Macromolecules* **2008**, *41*, 7254. (b) Shen, Y.; Kuang, M.; Shen, Z.; Nieberle, J.; Duan, H.; Frey, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 2227. (c) Qian, X.; Li, J.; Nie, S. *J. Am. Chem. Soc.* **2009**, *131*, 7540.

(3) See, for example: (a) Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. *Nano Today* **2007**, *2*, 18. (b) Agasti, S. S.; Chompoosor, A.; You, C.-C.; Ghosh, P.; Kim, C. K.; Rotello, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 5728. (c) Nam, J.; Won, N.; Jin, H.; Chung, H.; Kim, S. *J. Am. Chem. Soc.* **2009**, *131*, 13639.

(4) (a) Butun, V.; Armes, S. P.; Billingham, N. C. *Polymer* **2001**, *42*, 5993. (b) Vamvakaki, M.; Unali, G. F.; Bueten, V.; Boucher, S.; Robinson, K. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2001**, *34*, 6839. (c) Gohy, J.-F.; Antoun, S.; Jerome, R. *Macromolecules* **2001**, *34*, 7435.

(5) Weaver, J. V. M.; Armes, S. P.; Butun, V. *Chem. Commun.* **2002**, 2122–2123.

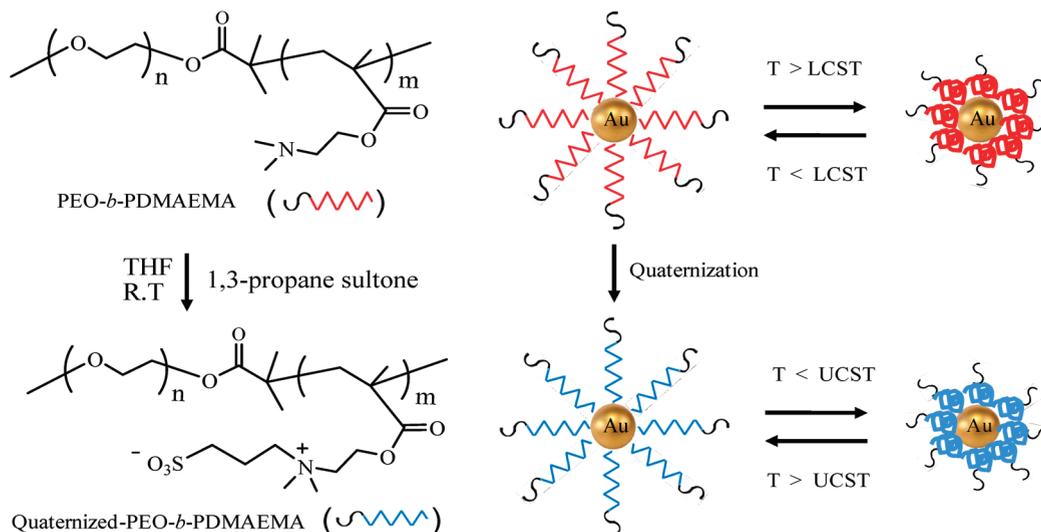


Figure 1. Chemical structures of the diblock copolymers tethered to gold nanoparticles (AuNPs) and schematic of both LCST and UCST thermal phase transitions on AuNP surface.

Experimental Section

1. Synthesis. *Materials.* Poly(ethylene glycol) methyl ether (PEO, 2000 g/mol), *N,N*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (4-DMAP), dichloromethane, dimethylaminoethyl methacrylate (DMAEMA, 98%), 1,3-propane sultone (98%), pyrene (98%), and 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl) ketone (Irgacure-2959) were purchased from Sigma-Aldrich and used without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN) (Polysciences) was recrystallized twice from ethanol before use. Hydrogen tetrachloroaurate tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Alfa Aesar, while the chain transfer agent (CTA), *s*-1-dodecyl- α' -(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate, was synthesized according to a literature method.⁶

*Synthesis of PEO-*b*-PDMAEMA.* The used sample of diblock copolymer PEO-*b*-PDMAEMA was synthesized by using reversible addition–fragmentation chain transfer polymerization (RAFT). PEO-CTA, a macromolecular chain transfer agent, was first prepared using a literature procedure.⁷ To obtain the diblock copolymer, DMEAME (9.8 g, 62 mmol), PEO-CTA (500 mg, 0.25 mmol), and AIBN (5.1 mg, 31 μmol) were dissolved in 10 mL of THF. After three freeze–pump–thaw cycles for degassing the solution, the reaction was carried out at 65 °C for 3 h. The sample was purified by precipitation from THF solution in cold hexane. GPC (polystyrene standards) yielded $M_n = 4.4 \times 10^4 \text{ g mol}^{-1}$ and polydispersity index $\text{PDI} = 1.7$. Using the ^1H NMR spectrum of the sample and knowing the molecular weight of the PEO block, comparison of the integrals of the resonance peaks of PEO and PDMAEMA led to $M_n(\text{NMR}) = 3.8 \times 10^4 \text{ g mol}^{-1}$. The quit large PDI of the sample was likely caused by the chosen chain extension conditions used to obtain a high average molecular weight for the PDMAEMA block. On the basis of the $M_n(\text{NMR})$, the BCP sample has a composition of $\text{PEO}_{45}\text{-}b\text{-PDMAEMA}_{228}$.

*Preparation of PEO-*b*-PDMAEMA-Coated AuNPs.* AuNPs with polymer chains tethered to the surface were prepared following a well-established method.⁸ PEO-*b*-PDMAEMA (340 mg) and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (24 mg) were dissolved in 25 mL of deionized water under stirring for 30 min. Irgacure-2959 (30.5 mM) was dissolved in a mixture of water and MeOH (2:1, v/v), and 5 mL of this initiator solution was added to the HAuCl_4 /polymer mixture (molar ratio of polymer/Au/I-2959 = 0.07:1:3) and stirred for 30 min.

The yellow solution was then irradiated for 30 min inside a Luzchem photoreactor (L2C-4X) equipped with 14 UV lamps of 75 W at $\lambda = 300 \text{ nm}$. The solution turned wine-colored, indicating the formation of AuNPs. The reaction solution was stirred at room temperature for another 48 h to ensure the dispersion of AuNPs functionalized with PEO-*b*-PDMAEMA. The pH of the as-obtained colloidal solution was about 2.3. Free polymer chains were removed from PEO-*b*-PDMAEMA-coated AuNP dispersion by means of three consecutive cycles of centrifugal precipitation at 25 000 rpm for 3 h followed by redispersion in fresh water. From the TGA result and using the NMR-based M_n , the density of PEO-*b*-PDMAEMA chains on AuNP surface was estimated to be about 2 chains per nm^2 . The PDMAEMA block bearing the CTA chain end group was tethered to the AuNP surface through either the dithioester moiety⁹ or thiol groups arising from reduction of *S*-1-dodecyl moieties.¹⁰ Purified polymer-coated AuNPs were stored in water at room temperature; the dispersion had a very good colloidal stability over several months. For all measurements, the solution was diluted to reach a polymer-coated AuNP concentration of about 0.7 mg mL^{-1} and its pH adjusted to 10 using 0.1 M NaOH solution.

*Quaternization of PEO-*b*-PDMAEMA-Coated AuNPs.* A 50 mL round-bottom flask was charged with 10 mL of dry THF, 110 mg of PEO-*b*-PDMAEMA-coated AuNPs, and 0.5 mL (5.6 mmol) of 1,3-propane sultone. The solution was stirred overnight at room temperature, and an insoluble residue was collected by filtration, washed several times with dry THF, and dried at 40 °C in a vacuum oven. Dried quaternized PEO-*b*-PDMAEMA-coated AuNPs could readily be dispersed in water; for the measurements, diluted solutions (0.7 mg mL^{-1}) with pH adjusted to 10 were utilized.

2. Characterizations. Gel permeation chromatography (GPC) analysis was conducted on a Waters system equipped with a refractive index detector (RI 410) and a photodiode array detector (PDA 996), with THF as eluent (flow rate: 1.0 mL min^{-1}) and polystyrene (PS) standards for calibration. Transmission electron microscopy (TEM) observations were performed on a Hitachi H-7500 operating at 100 kV. Sample were prepared by casting 2–5 μL of the AuNP solution on a carbon-coated copper grid, followed by either air-drying at room temperature or heating at 60 °C in order to have the solution below or above the thermal phase transition temperature of the polymer. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA system under a nitrogen atmosphere, which allowed the amount of

(6) Lai, J.-T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754–6756.

(7) Raula, J.; Shan, J.; Nuopponen, M.; Niskanen, A.; Jiang, H.; Kauppinen, E.-I.; Tenhu, H. *Langmuir* **2003**, *19*, 3499–3504.

(8) McGilvray, K. L.; Decan, M. R.; Wang, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **2006**, *128*, 15980–15981.

(9) Boyer, C.; Whittaker, M.-R.; Luzon, M.; Davis, T.-P. *Macromolecules* **2009**, *42*, 6917–6926.

(10) Vazquez-Dorbatt, V.; Tolstyka, Z. P.; Maynard, H. D. *Macromolecules* **2009**, *42*, 7650–7656.

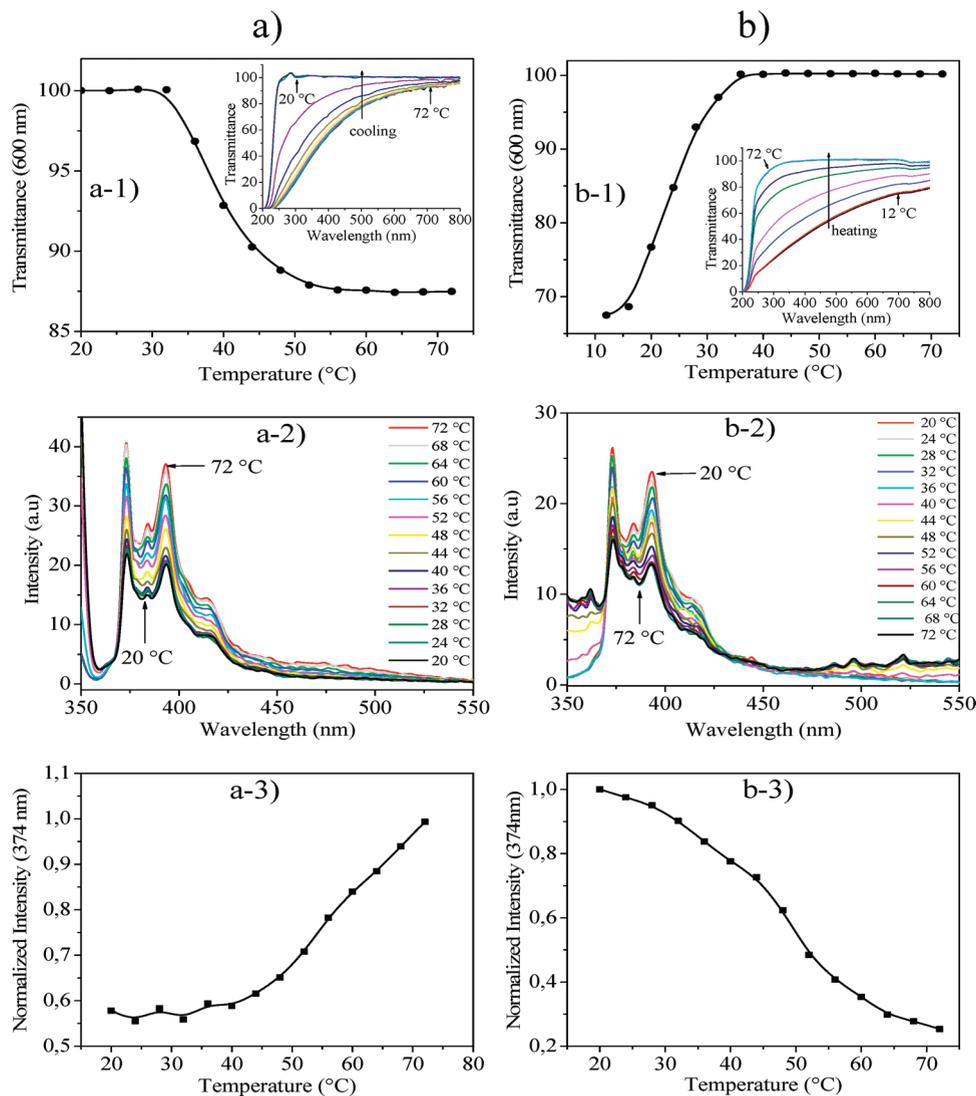


Figure 2. Results for aqueous solutions of (a) PEO-*b*-PDMAEMA and (b) quaternized PEO-*b*-PDMAEMA (0.4 mg mL^{-1} , $\text{pH} = 10$) equilibrated with pyrene probe: (a-1, b-1) transmittance (measured at 600 nm) vs temperature, the insets show the absorption spectra; (a-2, b-2) variable-temperature fluorescence emission spectra of pyrene ($\lambda_{\text{ex}} = 335 \text{ nm}$); (a-3, b-3) changes in normalized fluorescence intensity measured at 374 nm as a function of temperature.

the polymer ligand on AuNP surface to be determined. Samples were heated from 25 to 800 °C at a heating rate of 5 °C/min. UV-vis spectra were recorded with a Varian 50 Bio spectrophotometer with a temperature controlling sample holder (a single Peltier cell). Transmittance at 600 nm was used to measure the solution turbidity change associated with LCST or UCST (solution filtered through a $0.45 \mu\text{m}$ pore size membrane before measurement), the solution temperature being generally varied between 12 and 72 °C with a heating and cooling rate of $\sim 0.4 \text{ }^\circ\text{C/min}$. Fluorescence emission spectra of polymer or polymer-coated AuNP solutions equilibrated with a pyrene probe were recorded on a Varian Cary Eclipse fluorescence spectrophotometer, with an excitation wavelength of 335 nm. To prepare a pyrene-equilibrated solution, $5 \mu\text{L}$ of a pyrene solution ($98 \mu\text{M}$, in acetone) was added in 3 mL of block copolymer or polymer-coated AuNP solution under rigorous stirring; acetone was removed by evaporation at 40 °C under vacuum. Pyrene is a highly hydrophobic molecule; the presence of a polymer in aqueous solution could increase its solubility. Pyrene molecules solubilized in the polymer or polymer-coated AuNP solution under the used conditions were considered to be equilibrated with the polymer. For all fluorescence measurements, a solution volume of 3 mL was utilized with a standard quartz cuvette (1 cm optical path). Dynamic light scattering (DLS)

measurements were carried out at a detection angle of 90° , using a Brookhaven goniometer (BI-200) equipped with a highly sensitive avalanche photodiode detector (Brookhaven, BI-APD), a digital correlator (Brookhaven, TurboCorr), a helium-neon laser ($\lambda = 632.8 \text{ nm}$), and a thermostat sample holder. At each temperature the solution was equilibrated for 10 min; cumulant and CONTIN analysis were applied to determine the hydrodynamic diameter (D_H). For the test of photothermal effect, the irradiation light centered at 550 nm was generated by using a UV-vis curing system (Novacure 2100) and an interference filter ($550 \pm 10 \text{ nm}$, Oriel). The irradiation intensity reaching the solution was about 20 mW/cm^2 .

Results and Discussion

Before coating AuNPs with the water-soluble diblock copolymers PEO-*b*-PDMAEMA and its quaternized form, the thermosensitivity of the two polymers in water was first investigated. Part of the PEO-*b*-PDMAEMA sample was converted to quaternized PEO-*b*-PDMAEMA by reaction with 1,3-propane sultone. The changes in turbidity of their aqueous solutions were monitored by measuring the solution transmittance at 600 nm as a function of temperature. The turbidity measurement allows the possible

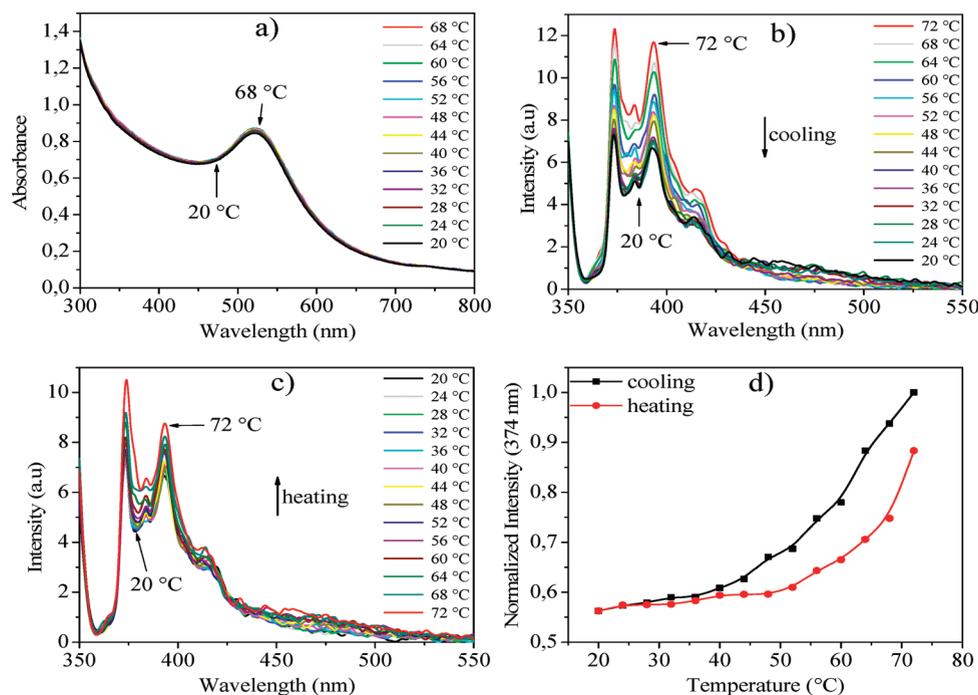


Figure 3. Results for aqueous solution of AuNPs coated with PEO-*b*-PDMAEMA (0.7 mg mL^{-1} , $\text{pH} = 10$) equilibrated with pyrene: (a) variable-temperature UV-vis absorption spectra; (b) variable-temperature fluorescence emission spectra of pyrene ($\lambda_{\text{ex}} = 335 \text{ nm}$) upon cooling of the solution; (c) emission spectra upon subsequent heating of the solution; (d) changes in normalized fluorescence intensity measured at 374 nm as a function of temperature.

“cloud point” arising from the aggregation of the polymers to be determined. Furthermore, we wanted to obtain a fluorescent probe whose emission spectral variations could be related to the polymer solubility changes. The reasoning is as follows. The appearance of a “cloud point” requires the formation of aggregates through inter-chain aggregation. This may not happen with the polymers tethered to AuNPs, since as mentioned above (Figure 1), with the outer PEO chains, the diblock copolymer was designed to afford a good colloidal stability of AuNPs even when the inner polymer layer (PDMAEMA or its quaternized form) becomes dehydrated and tends to collapse in response to temperature change. To this end, we tested the use of pyrene as the fluorescent probe. An aliquot of the polymer solution equilibrated with pyrene was used to record the UV-vis spectra (for the turbidity measurement), while the other part was used to record the fluorescence emission spectra of pyrene (excitation 335 nm) as a function of temperature. The results obtained are shown in Figure 2 (Figure 2a for PEO-*b*-PDMAEMA and Figure 2b for quaternized PEO-*b*-PDMAEMA).

For PEO-*b*-PDMAEMA, the solution at $\text{pH} = 10$ displayed clearly a LCST at about $35 \text{ }^\circ\text{C}$, as can be seen from the plot of transmittance at 600 nm vs temperature (a-1); the inset shows the actual spectral variation, displaying greater transmittance changes for shorter wavelengths. Concomitantly, the fluorescence emission of pyrene increased with increasing the temperature (a-2). By plotting the normalized emission intensity at 374 nm as a function of temperature (a-3), it appears that the emission intensity rose sharply around the LCST of the polymer. For quaternized PEO-*b*-PDMAEMA, the temperature-dependent transmittance indeed changed in the opposite way (b-1), showing a UCST at about $30 \text{ }^\circ\text{C}$. The fluorescence emission of pyrene also changed in the opposite way; it increased as the solution was cooled (b-2 and b-3). However, in this case, the emission spectra recorded at higher temperatures were distorted by an apparent scattering effect. We found that this was caused by quaternized PEO-*b*-PDMAEMA, for which we have no explanation at this time. A baseline correction was

applied in measuring the relative intensity of the pyrene peak at 374 nm for those higher temperatures (b-3). Despite this, it is clear that the fluorescence of pyrene probe equilibrated with quaternized PEO-*b*-PDMAEMA exhibited an opposite variation upon temperature change as compared to aqueous solution of PEO-*b*-PDMAEMA. The results in Figures 2 thus confirm that the diblock copolymer PEO-*b*-PDMAEMA and its quaternized counterpart exhibit the LCST and UCST type solubility change in aqueous solution, respectively. And the fluorescence emission of pyrene equilibrated with the polymers could be related to the polymer solubility. The emission intensity increases at both $T > \text{LCST}$ and $T < \text{UCST}$, where pyrene molecules should be surrounded by less hydrated polymer chains, whereas it decreases when the polymers are hydrated (soluble) in water. The lower emission intensity is likely to be caused by fluorescence quenching of pyrene by tertiary amines in PDMAEMA or ionic groups in quaternized PDMAEMA,¹¹ which might be enhanced with hydrated polymers chains that favor collision or contacts between pyrene molecules and the quencher sites. It can also be noticed that in the case of PEO-*b*-PDMAEMA the increased fluorescence emission at $T > \text{LCST}$ is accompanied by an increased pyrene excimer emission at $\sim 480 \text{ nm}$ (Figure 2a-2).

The pyrene fluorescence emission ratio I_1/I_3 , measured from the absorbance of the emission peaks at 374 nm (I_1) and 384 nm (I_3), is known to be sensitive to the polarity of the environment in which pyrene molecules are located.¹² Quite surprisingly, Figure 2 shows that in both solutions, within experimental error, the emission ratio I_1/I_3 did not change significantly as a function of temperature.

(11) (a) Winnik, M. A.; Bystryak, S. M.; Liu, Z.; Siddiqui, J. *Macromolecules* **1998**, *31*, 6855–6864. (b) Engebretson, R. R.; von Wandruszka, R. *Environ. Sci. Technol.* **1994**, *28*, 1934–1941.

(12) (a) Ringsdorf, H.; Venzmer, J.; Winnik, F. *Macromolecules* **1991**, *24*, 1678–1686. (b) Winnik, F. *Chem. Rev.* **1993**, *93*, 587–614. (c) Dong, D. C.; Winnik, M. A. *Photochem. Photobiol.* **1982**, *35*, 17–21. (d) Dong, D. C.; Winnik, M. A. *Can. J. Chem.* **1984**, *62*, 2560–2565. (e) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039–2044.

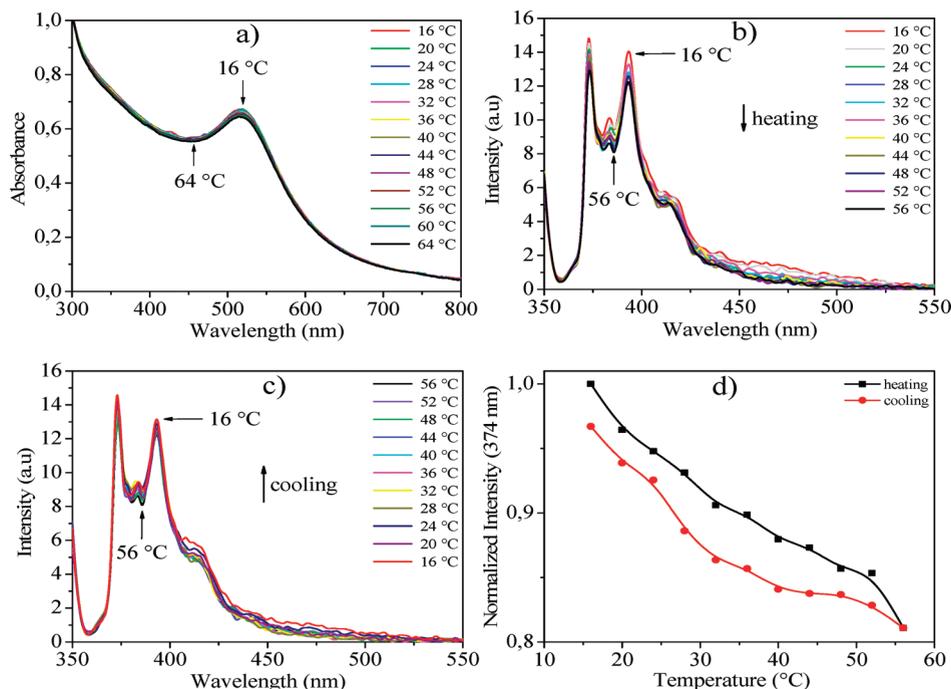


Figure 4. Results for aqueous solution of AuNPs coated with quaternized PEO-*b*-PDMAEMA (0.7 mg mL^{-1} , $\text{pH} = 10$) equilibrated with pyrene: (a) variable-temperature UV-vis absorption spectra; (b) variable-temperature fluorescence emission spectra of pyrene ($\lambda_{\text{ex}} = 335 \text{ nm}$) upon heating of the solution; (c) emission spectra upon subsequent cooling of the solution; (d) changes in normalized fluorescence intensity measured at 374 nm as a function of temperature.

The ratio was around 1.5, which is much lower than ~ 1.9 in water. This indicates that pyrene molecules were solubilized by polymer chains and located in a polymer environment. The fact that the I_1/I_3 ratio remained essentially the same with the polymer undergoing the LCST or UCST phase transition suggests that the micropolarity experienced by pyrene molecules was determined by the polymer environment and did not change much upon changes of the polymer hydration degree related to the LCST or UCST. As a matter of fact, dehydrated polymer chains upon a thermal phase transition could still retain a significant amount of water molecules, as it was reported that a highly collapsed globule of poly(*N*-isopropylacrylamide) (PNIPAM) could contain $\sim 80\%$ of water in its hydrodynamic volume.¹³ Between PDMAEMA and quaternized PDMAEMA, it should be expected that the zwitterionic side group in the latter would increase the polarity, but the longer hydrophobic aliphatic chain introduced in the side group could compensate this effect, which might account for their similar I_1/I_3 ratios.

Aqueous solutions of AuNPs coated with PEO-*b*-PDMAEMA and its quaternized form, equilibrated with pyrene, were then investigated using UV-vis and fluorescence spectroscopic measurements under the same conditions as for the diblock copolymers alone. The results are summarized in Figures 3 and 4. For the solution of AuNPs functionalized with PEO-*b*-PDMAEMA (Figure 3), at pH 10 and over the range of temperatures investigated, the absorption spectra showed little changes, with no noticeable shift of the SPR band of AuNPs centered at 524 nm and with a similar transmittance at 600 nm and longer wavelengths (Figure 3a). This indicates that no aggregation of AuNPs occurred upon temperature change. However, pyrene exhibited a similar fluorescence spectral change to the solution of PEO-*b*-PDMAEMA alone (Figure 2), the emission intensity being reduced upon cooling of the solution (Figure 3b) and increased upon heating (Figure 3c).

This suggests that PEO-*b*-PDMAEMA chains on AuNP surface underwent a LCST-type solubility change, with PDMAEMA chains becoming more hydrated at lower temperature. The thermal phase transition of polymer chains on AuNPs appeared to be reversible as revealed by the partly reversible fluorescence change (Figure 3d). Further heating-cooling cycles resulted in a diminished fluorescence intensity of pyrene. As argued above, even when PDMAEMA chains become dehydrated at $T > \text{LCST}$, the outer PEO chains could retain the dispersion of AuNPs and prevent the aggregation of AuNPs from occurring.

Likewise, for AuNPs coated with quaternized PEO-*b*-PDMAEMA (Figure 4), the stability of AuNPs over the entire temperature range can be seen from the unchanged absorption spectra (Figure 4a). In this case, however, quaternized PDMAEMA should impart a UCST-type solubility change of the polymer chains on the surface of AuNPs. Indeed, contrarily to PEO-*b*-PDMAEMA-coated AuNPs, as quaternized PDMAEMA chains become increasingly hydrated upon heating of the solution, the fluorescence emission intensity of pyrene decreased (Figure 4b), while when the solution was cooled down, the fluorescence intensity was greatly recovered (Figure 4c,d). Although in this case the fluorescence intensity variation was less important than the solution of PEO-*b*-PDMAEMA-coated AuNPs, the reversed change implies a UCST-type solubility change for quaternized PEO-*b*-PDMAEMA chains on AuNPs. The reversible variation of fluorescence emission suggests that pyrene molecules remained essentially dispersed in the polymer chains on AuNP surfaces regardless of the polymer solubility state.

The above analysis was made based on the assumption that the change in fluorescence emission intensity of the pyrene probe in polymer-coated AuNP solutions reflected the changing polymer solubility in the same way as in polymer solutions without AuNPs. In other words, there was neither quenching nor enhancement of pyrene fluorescence caused by AuNPs, which are known phenomena for fluorophores located on or in a close vicinity to

(13) Wu, C.; Zhou, S. *Macromolecules* **1995**, *28*, 8381–8387.

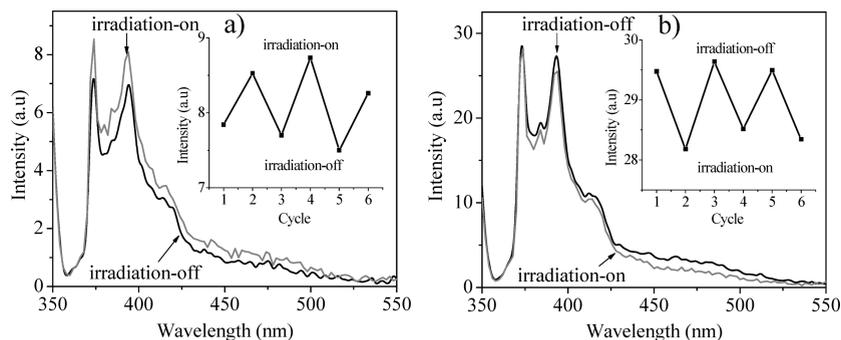


Figure 5. Fluorescence emission spectra of pyrene equilibrated with (a) AuNPs coated with PEO-*b*-PDMAEMA and (b) AuNPs coated with quaternized PEO-*b*-PDMAEMA at 32 °C subjected to 6 min illumination centered at 550 nm (spectra labeled “irradiation-on”) and after turning off the irradiation (spectra labeled “irradiation-off”). The insets show the reversible changes recorded with three cycles of illumination on and off.

the surface of AuNPs.^{14,15} This assumption should be reasonable for the following reasons. On the one hand, although the fluorescence emission wavelengths of pyrene (around 400 nm) overlap with some absorption of AuNPs, they are well below the SPR of AuNPs (524 nm) (the apparent strong absorption at low wavelengths is due to scattering by the nanoparticles in solution). Under this condition, the fluorescence quenching requires the fluorophore to be adsorbed or bound to the metallic surface,¹⁴ which is not the case here. In the present study, pyrene molecules are solubilized by polymer chains tethered to AuNP surface, while from the BCP composition (PEO₄₅-*b*-PDMAEMA₂₂₈), polymer chains should form a layer with a thickness in the order of several nanometers even in the dehydrated state.¹³ Therefore, pyrene molecules entrapped in the polymer layer are too distant from the AuNP surface to undergo a fluorescence quenching effect. On the other hand, the fluorescence enhancement, which was generally observed for a single fluorophore molecule placed at a close vicinity to AuNP surface,¹⁵ could not occur because the used excitation wavelength (335 nm) is far below the SPR of AuNPs, and there is no overlap between the excitation wavelength of pyrene and the absorption wavelengths of AuNPs.

The interest of the polymer-coated AuNPs reported herein is that through rational design tethered polymer chains can ensure the colloidal stability of AuNPs in aqueous solution while, at the same time, responding to temperature variation by changing the solubility either upon heating (LCST) or cooling of the solution (UCST). Such thermosensitive systems could eventually be used to solubilize hydrophobic compounds through the dehydrated domains (above LCST of PDMAEMA or below UCST of quaternized PDMAEMA) and to release them upon temperature decrease or increase. Moreover, since the thermosensitive block is on the surface of AuNPs, absorption of light by AuNP could also generate heat that changes the temperature of solution close to the nanoparticles surface. Since such a photothermal effect could have the advantage of being more spatially and temporally selective than heating or cooling of the bulk solution, it has been exploited in many studies including, for example, its use to induce the release of a fluorophore attached to a silica–gold core–shell nanoparticle via a thermally labile bond¹⁶ and the release of a

drug from a gold nanocage mediated by the LCST phase transition of PNIPAM chains grafted to gold surface.¹⁷ In those studies, a laser was utilized to generate a significant amount of heat, and the event induced by the photothermal effect (such as the release of molecules) could be monitored after turning off the laser.^{16,17} In the present study, we thought that a photothermal effect could also induce a heating of the solution in the proximity of AuNPs and thus trigger a solubility change for PDMAEMA or quaternized PDMAEMA chains, which could be probed by pyrene. However, with a dilute solution of polymer-coated AuNPs, the heat generated by absorption of AuNPs should dissipate quickly once the illumination is turned off. This means that if there is any heating of the solution, it is likely to be a local effect, in a region close to the AuNP surface. This also made it impossible to use a laser since we could not record the fluorescence emission of the solution under laser illumination. Nevertheless, we conducted an experiment to test the possible photothermal effect on our polymer-coated AuNPs. A solution in a cuvette was first equilibrated at a temperature in the vicinity of LCST or UCST, with the temperature-controlled sample holder mounted in the compartment of the fluorescence spectrophotometer; then a lamp was used to illuminate the solution from the top of the cuvette through a filter delivering a light beam centered at 550 nm (close to the SPR of AuNPs); the emission spectra of pyrene could be recorded prior to, under, and after turning off the illumination. The results are shown in Figure 5. For the solution of AuNPs coated with PEO-*b*-PDMAEMA at 32 °C, the fluorescence emission increased under illumination (6 min) and came back to the initial level after turning off the light; the inset shows that the changes are repeatable with three cycles of light-on and light-off. By contrast, for the solution of AuNPs coated with quaternized PEO-*b*-PDMAEMA at 32 °C, the fluorescence intensity decreased under illumination and was recovered after turning off the light. The changes were small, which could be expected due to the illumination conditions used, but the reversible and opposite variations at irradiation-on and irradiation-off for AuNPs coated with the two block copolymers indicate that the changes were caused by a photothermal effect. We conducted a control test with pyrene equilibrated with the polymers without AuNPs, PEO-*b*-PDMAEMA, and its quaternized form. Illumination under the same conditions resulted in negligible changes in fluorescence emission of pyrene (Supporting Information). This observation confirmed the contribution of heat generated by SPR of AuNPs upon absorption of photons. Using a laser, such photothermal effect could be much enhanced.

(14) (a) Dulkeith, E.; Morteani, A. C.; Niedereichholz, T.; Klar, T. A.; Feldmann, J.; Levi, S. A.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Moller, M.; Gittins, D. I. *Phys. Rev. Lett.* **2002**, *89*, 203002. (b) Ghosh, S. K.; Pal, A.; Kundu, S.; Nath, S.; Pal, T. *Chem. Phys. Lett.* **2004**, *395*, 366–372.

(15) (a) Bharadwaj, P.; Novotny, L. *Opt. Express* **2007**, *15*, 14266–14274. (b) Kuhn, S.; Hakanson, U.; Rogobete, L.; Sandoghdar, V. *Phys. Rev. Lett.* **2006**, *97*, 017402.

(16) Bakhtiari, A. B. S.; Hsiao, D.; Jin, G.; Gates, B. D.; Branda, N. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 4166–4169.

(17) Yavuz, M.; Cheng, Y.; Chen, J.; Cogley, C. M.; Zhang, Q.; Rycenga, M.; Xie, J.; Kim, C.; Song, K. H.; Schwartz, A. G.; Wang, L. V.; Xia, Y. *Nature Mater.* **2009**, *8*, 935–939.

Conclusions

We presented a method to prepare AuNPs coated with diblock copolymers that exhibit either a LCST or a UCST in aqueous solution in response to temperature change without aggregation of the nanoparticles. This was achieved by using a diblock copolymer PEO-*b*-PDMAEMA with the PDMAEMA block tethered to the surface of AuNPs. On the basis of fluorescence emission spectra of a pyrene probe, PEO-*b*-PDMAEMA chains on AuNPs underwent a LCST-type solubility change upon heating of the solution. By contrast, reaction of PEO-*b*-PDMAEMA-coated AuNPs with 1,3-propane sultone resulted in quaternized PDMAEMA block that displayed a UCST-type solubility change. In both cases, even with polymer chains on AuNPs becoming dehydrated at $T > \text{LCST}$ or $T < \text{UCST}$, the use of water-soluble PEO as the outer block allowed the colloidal stability of AuNPs to be retained. Moreover, in addition to thermally induce the solubility change by heating the bulk solution, the changes could also be induced to some extent by illuminating the solution at wavelengths close to the SPR of AuNPs due to a photothermal effect. The design presented in this paper shows an easy way to prepare

AuNPs coated with polymers that can undergo a hydration–dehydration transition in aqueous solution upon either temperature increase or temperature decrease. This would offer new possibilities for exploring AuNPs functionalized with stimuli-responsive polymers.

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Supporting Information Available: More characterization results of block copolymers and gold nanoparticles (^1H NMR, GPC, UV–vis, fluorescence, DLS, TEM, TGA). This material is available free of charge via the Internet at <http://pubs.acs.org>.