Photochromism and Optical Property of Gold Nanoparticles Covered with Low-Polydispersity Diarylethene Polymers

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ABSTRACT: Gold nanoparticles covered with photochromic diarylethene polymers or block copolymers with styrene were prepared according to Brust's method. These nanoparticles expressed a bright red color because of their surface plasmon resonance absorption, and exhibited reversible photochromism upon alternate irradiation with ultraviolet and visible light in the solid state as well as in solution. The photocyclization reactivity of the diarylethenes around the gold nanoparticles decreased by shortening the distance between the surface of the gold nanoparticles and the diarylethene chromophore. Some effects of the gold nanoparticles on the optical properties of the diarylethene chromophores were evaluated by comparison of the difference spectra between the UV–visible absorption spectra in the photostationary state and in the initial state under various conditions. The effect was found to appear as a bathochromic shift in the absorption maximum of the diarylethene closed-ring form, which is related to the local electric field generated by the surface plasmon resonance of the gold nanoparticles.

Introduction

Photochromism is referred to as a photoreversible transformation process between two isomers having different absorption spectra.[1] Photochromic compounds exhibit various chemical and physical property changes, not only in their absorption spectra but also in the refractive indices, dielectric constants, oxidation–reduction potentials, and geometrical structures, because of their molecular structure changes.[2] Among various photochromic compounds, diarylethenes have excellent characteristics,[2,3] such as thermal stability of both isomers, fatigue resistance, high sensitivity,[4] high response,[5] and response in various states.[6–9] Hence, the optical properties of these compounds can be used for optical memories,[10,11] for photoswitching,[12–14] for image recording,[15] and in photomechanical devices and photomechanical devices.[16,17]

On the other hand, nanometer-size metal particles are known to show specific properties that are different from those in the bulk solid state. In particular, gold nanoparticles exhibit a strong optical absorption in the visible region (around 520 nm) and express a bright red color due to their surface plasmon resonance.[18] These have been extensively studied in various research fields, for example, physical chemistry, photochemistry, and biochemistry, because the surface plasmon resonance has a high sensitivity to particle size, shape, interparticle distance, and the ambient environment.[18–24] In addition, the surface of the gold nanoparticle is a specific reaction field. For example, the Raman intensity of a molecule adsorbed to the surface of a gold nanoparticle is strongly enhanced by surface-enhanced Raman scattering (SERS).[25]

Generally, in order to functionalize gold nanoparticles, strategies employing the sulfur−gold bond have often been used in many research studies since the thiol group and sulfur atom bind to the gold surface and form a strong combination. As a result, these particles can be covered and protected with various functionalized molecules, for instance, various dye molecules,[26–28] various polymers,[29–36] biomolecules,[37,38] and photochromic compounds,[39–42] which we utilized in this study.

Recently, gold nanoparticles covered with photochromic compounds have been reported and applied to various switching devices. For example, the photoresponsive interparticle spacing of the gold nanoparticles induced by the photoisomerization of azobenzene linker molecules,[43] the light-induced modulation of the self-assembly on spiropyran-capped gold nanoparticles,[44] the photoswitching of the conductance of a diarylethene-gold nanoparticle network,[45] and the switching of the tunneling current of a single molecule diarylethene on a gold surface[46] have been reported. Theoretical studies of the electronic and optical properties of diarylethenes connected to gold clusters have also been reported.[47] Photochromic molecules very close to the surface of the gold nanoparticle in the excited-state are quenched.[41] However, the interaction between the nanoparticle and the photochromic compound far from the surface of the gold nanoparticle has not been discussed. The gold nanoparticle generates a local electric field on the surface. In order to investigate the electric field interaction far from the gold surface, the distance between the gold surface and the photochromic compound should be controlled. Therefore, new synthetic approaches of gold nanoparticle-photochromic compound complexes are required.

In this study, we developed a new type of diarylethene−gold nanoparticle complex to evaluate the electric field interaction between the gold nanoparticle and the photochromic diarylethene far from the gold surface. In this system, the diarylethene moieties can be introduced in a high density around the gold nanoparticle. The interaction between the gold nanoparticle and the diarylethene moiety was evaluated by an absorption spectral analysis. Block copolymers with styrene were also synthesized in order to evaluate the interaction in detail.

Experimental Section

Measurements. The solvents used were of spectroscopic grade and purified by distillation. The ^{1}H NMR spectra were recorded using a Jeol A-400 NMR spectrometer at 400 MHz. The absorption spectra were measured by a Jasco V-560 spectrophotometer. Photoirradiation was carried out using a 200 W mercury−xenon lamp (Moritex MUV-202) as a light source. Monochromic light was obtained by passing the light through a monochromator and a UV filter. The transmission electron microscope (TEM) images were obtained using a Hitachi H-7000 at 75 kV. The TEM samples were prepared by dropping a toluene solution of gold nanoparticles on a carbon-coated copper grid. The atomic force microscopy (AFM)

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utilized a Digital Instruments NanoScope IIIa scanning probe microscope in the tapping mode.

Materials. All reagents, 2,2′-azobis(2,4,4-trimethylpentane) (ATMP), styrene (St), tetraoctylammonium bromide (TOAB), sodium borohydride, and hydrogen tetrachloroaurate tetrahydrate were commercially available from Wako Chemicals. ATMP was recrystallized from hexane. St was purified by distillation under reduced pressure before use. All other reagents were used without further purification.

Synthesis of Low-Polydispersity Diarylethene Polymer Having Dithiobenzoate Group (Poly(DE)). The diarylethene monomer (DE) was synthesized according to a method described in our previous paper.[48] The dithiobenzoate-terminated diarylethene polymer (poly(DE)) was synthesized by a reversible addition-fragmentation chain transfer (RAFT) radical polymerization using 1-phenylethyl dithiobenzoate (PEDB)[49] and ATMP as the RAFT agent and the azoinitiator, respectively, in toluene at 100 °C ([DE] = 2.9 mol dm^{-3}, [ATMP] = 1.0×10^{-3} mol dm^{-3}, [PEDB] = 0.03–0.06 mol dm^{-3}). The polymerizations were run in glass tubes sealed under vacuum. After the polymerization for 60 h, the polymer was obtained by precipitation in methanol. The polymer was purified by reprecipitation. The number- and weight-average molecular weights (M_n and M_w) of the polymers were determined by gel-permeation chromatography (GPC) at 40 °C in THF as the eluent. GPC was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns. Standard polystyrenes were used as the calibration standard. The molecular weight of the polymer was also determined by a ^{1}H NMR spectroscopic analysis of an end group of the polymer. The degree of polymerization (n(NMR)) and M_n(NMR) were determined by comparing the peak intensities of the signals of the methylene protons in the repeating unit of the polymer at 5.3 ppm and a methine proton bound to the dithiobenzoate end group at 4.5–5.0 ppm.[50]

Synthesis of Poly(DE)-*block*-poly(St). Poly(DE)-*block*-poly(St) was also synthesized by the RAFT radical polymerization of St using poly(DE) (n = 25) as a macro-RAFT agent in toluene for 60 h at 100 °C ([St] = 3.0 mol dm^{-3}, [ATMP] = 1.0×10^{-3} mol dm^{-3}, [poly(DE) (n = 25)] = 0.029 mol dm^{-3}). The molecular weight of the resulting block copolymer was determined by a ^{1}H NMR spectroscopic analysis of an end group of the block copolymer (M_n(NMR) = 22100). The polydispersity of the block copolymer was determined to be M_w/M_n(GPC) = 1.16 by GPC. The content of DE and St in the block copolymer was determined to be 35:65 by the ^{1}H NMR spectroscopic analysis.

Reduction of Dithiobenzoate Group to an −SH Group. Poly(DE) (n = 42) (380 mg; 1.3×10^{-2} mmol) was dissolved in a toluene solution (3.0 mL) of TOAB (76 mg; 0.14 mmol). To the toluene solution was added an aqueous solution (3.0 mL) of sodium borohydride (40 mg; 1.1 mmol), and the mixture was stirred overnight. When the solution no longer produced any gas and the red decoloration disappeared, the solution was added to methanol and worked up. The resulting polymer (poly(DE)−SH) was obtained as a colorless powder in 98% yield. Disappearance of the dithiobenzoate group was confirmed by ^{1}H NMR and IR spectroscopy.[50,51] Poly(DE)-*block*-poly(St)−SH was also prepared by a similar method.

Synthesis of Gold Nanoparticles Covered with Diarylethene Polymers (Au−Poly(DE), Au−Poly(St)-*block*-poly(DE)). Gold nanoparticles covered with diarylethene polymers were synthesized according to Brust's method.[52] An aqueous solution (1.9 mL) of hydrogen tetrachloroaurate tetrahydrate (24 mg; 5.8×10^{-2} mmol) was mixed with a toluene solution (2.6 mL) of TOAB (71 mg; 0.13 mmol) and stirred vigorously until the tetrachloroaurate was completely transferred into the organic phase. The yellow color in the water phase was decolorized and the colorless organic phase turned brown. Poly(DE)−SH (n = 42) (200 mg; 6.9×10^{-3} mmol) was added to the reaction solution and stirred for several minutes. A freshly prepared aqueous solution (1.5 mL) of sodium borohydride (22 mg; 0.58 mmol) was dropwise added to the reaction mixture with vigorous stirring. After mixing for 27 h at room temperature, the reaction solution was poured into an excess of methanol to remove TOAB and the unreacted reagents, then filtered using a membrane filter (ADVANTEC, H020A025A, pore diameter: 0.2 μm). The resulting residue was collected and dried under vacuum. The solid was added to 20 mL of diethyl ether. The unreacted poly(DE)−SH is soluble in diethyl ether. The cloudy diethyl ether solution was centrifuged at 6000 rpm for several tens of minutes and the precipitate was recollected. After repeating this cycle several times, the product was dried under vacuum. Au−poly(DE) was obtained as a deep purple solid. It was soluble in toluene, chloroform, and tetrahydrofuran. The ^{1}H NMR spectrum of the resulting particles was similar to that of poly(DE). The particle size was determined from the TEM images. Au−poly(St)-*block*-poly(DE) was also prepared by a similar method.

Table 1. RAFT Polymerization of DE and Characterization of the Resulting Polymer (Poly(DE))[a]

[PEDB]/mol dm^{-3}	conv/%	M_n(NMR)[b]	M_w/M_n(GPC)[c]	n(NMR)[b]	n(th)[d]
0.030	76	54000	1.11	79	74
0.030	76	54700	1.16	80	74
0.045	67	28800	1.13	42	44
0.060	55	17300	1.11	25	27
0.060	56	9100	1.15	13	27

[a] [DE] = 2.9 mol dm^{-3}, [ATMP] = 1.0×10^{-3} mol dm^{-3}, in toluene for 60 h at 100 °C. [b] M_n and n determined by ^{1}H NMR spectroscopy (see Experimental Section). Their values include an error of less than 10%. [c] Calibrated by standard polystyrenes. [d] Theoretical degree of polymerization determined from ([DE]/[PEDB] × conv).

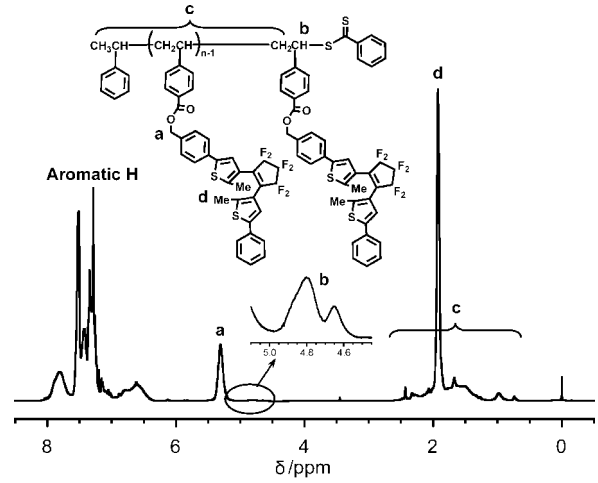


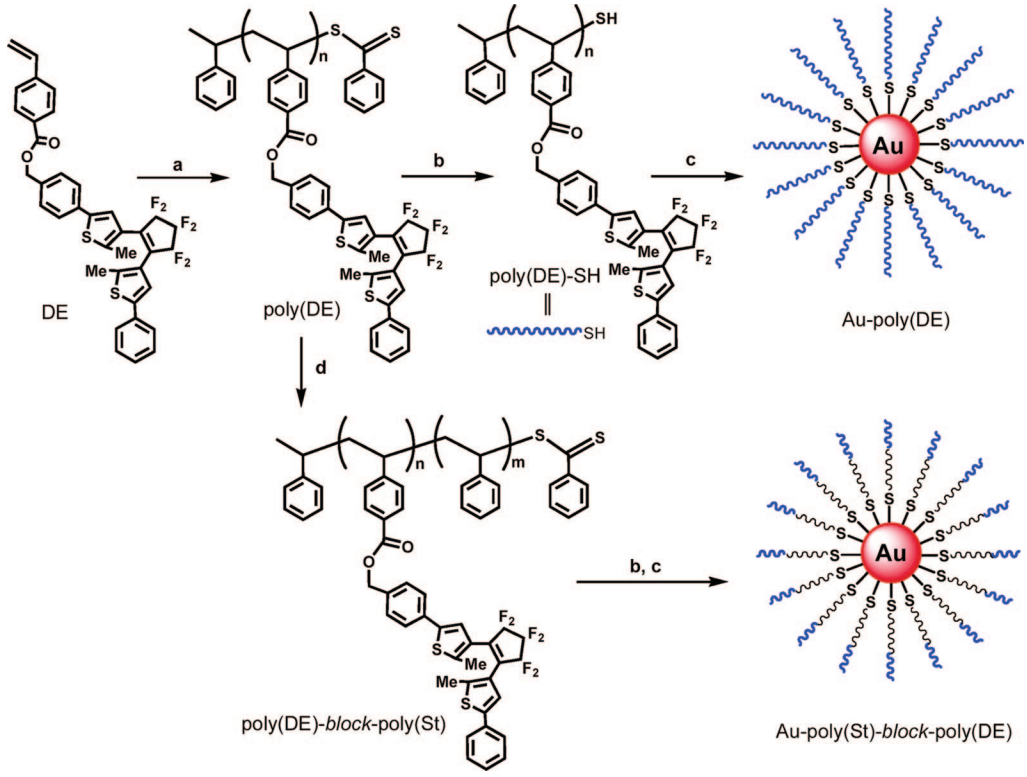
Figure 1. ^{1}H NMR spectrum of poly(DE) (n = 13).

Results and Discussion

Synthesis of Gold Nanoparticles Covered with Low-Polydispersity Diarylethene Polymers. Diarylethene polymers with various chain lengths can be prepared by adjusting the concentration of PEDB. Table 1 shows the conditions of the RAFT polymerization and characterization of the resulting polymers. Dithiobenzoate-terminated poly(DE)s with different chain lengths were obtained by changing the concentration of the RAFT agent. Figure 1 shows a typical example of the ^{1}H NMR spectrum of poly(DE). The methyl protons in the diarylethene moiety appeared at 1.9 ppm. The methylene protons between the ester and the diarylethene moiety appeared at 5.3 ppm. Furthermore, small peaks at 4.5–5.0 ppm were assigned to a methine proton bound to the dithiobenzoate end group.[50] The separation of the peaks may be due to the stereoregularity of the polymer chain at the ω-end.[50] The M_n(NMR) agrees with the theoretical value.

The synthetic route of Au−poly(DE) is shown in Scheme 1. The dithiobenzoate end group of poly(DE) was reduced to the –SH group using sodium borohydride. A stronger reduction agent such as Super–Hydride[29,32,34] is inappropriate for this

Scheme 1. Synthetic Scheme of Au−Poly(DE) and Au−Poly(St)-*block*-poly(DE)[a]



[a] Key: (a) ATMP, PEDB, toluene, 100 °C; (b) TOAB, $NaBH_4$, H_2O, toluene; (c) $HAuCl_4 \cdot 4H_2O$, TOAB, $NaBH_4$, H_2O, toluene; (d) ATMP, St, toluene, 100 °C.

reaction due to the easy cleavage of the ester O−C bond. Figure 2 shows TEM images and the core size histograms of Au−poly(DE). The diameter of a gold nanoparticle can be controlled to some extent by adjusting the reaction time, reaction temperature, and other reaction conditions (see Table S1 in the Supporting Information for the detailed reaction conditions).[53–55] The mean diameter of Au−poly(DE) and the polymerization degree of poly(DE) determined from the ^{1}H NMR are defined as d and n, respectively. It can be noted that each of the gold nanoparticles is not aggregated and is well spread out on the copper grid as seen in Figure 2. This means that particle-shaped gold nanoclusters were successfully prepared by Brust's method.

Synthesis of Au−Poly(St)-*block*-poly(DE). We synthesized a block copolymer consisting of poly(DE) and poly(St) chains by the RAFT polymerization. The resulting block copolymer had an M_n(GPC) of 12100, whereas the macro-RAFT agent (poly(DE)) had an M_n(GPC) of 9100. The increase in M_n(GPC) corresponds to the M_n of the poly(St) chain connected to the poly(DE) chain. Furthermore, the polydispersity showed little change during the block copolymerization (M_w/M_n = 1.11 to 1.16). These results indicate that the block copolymer was successfully obtained by controlling the molecular weight and the polydispersity. The block copolymer has DE units of 25 and St units of 46 as determined by the ^{1}H NMR spectroscopic analysis, and the dithiobenzoate end group was attached to the end of the poly(St) chain.

Au−poly(St)-*block*-poly(DE) was synthesized and analyzed by a method similar to the case of Au−poly(DE). The synthetic scheme of Au−poly(St)-*block*-poly(DE) is also shown in Scheme 1. The TEM image and histogram of Au−poly(St)-*block*-poly(DE) are shown in Figure 3. The particle-shaped Au−poly(St)-*block*-poly(DE) (d = 6.1 nm, m = 46, n = 25) was successfully prepared.

Photochromism of Poly(DE) and Au−Poly(DE). In our previous study, we reported that a diarylethene polymer produced by a conventional radical polymerization shows reversible photochromism upon alternate irradiation with ultraviolet (UV) and visible light.[48] Figure 4 shows the absorption spectral changes of poly(DE) (n = 80) in toluene upon irradiation with UV light. Upon exposure to UV light, a new absorption band appeared at ca. 590 nm in the visible region. The photocyclization conversion in the photostationary state reached 97% in toluene upon irradiation with 313-nm light. The absorption band in the visible region disappeared by irradiation with visible light. This indicates that poly(DE) exhibited a reversible photochromism similar to the polymer prepared by the conventional radical polymerization.

The absorption spectral changes of a toluene solution of Au−poly(DE) (d = 7.4 nm, n = 80) are shown in Figure 5. During the initial state, the red color in the solution is due to the surface plasmon band at ca. 530 nm. The absorption maximum changed to a longer wavelength upon irradiation with 313-nm light. The solution changed color from red to violet. The absorption spectrum was recovered by irradiation with visible light. The reversible color changes were observed upon alternate irradiation with UV and visible light. Figure 6 shows the time-conversion curves of Au−poly(DE) (d = 7.4 nm, n = 80) upon irradiation with 313-nm light. The conversion of the photocyclization reaction of Au−poly(DE) was determined using ^{1}H NMR and absorption spectroscopies. The photocyclization of Au−poly(DE) in toluene reached a 96% conversion in the photostationary state. This value is similar to that of Au-free poly(DE).[48] The photochromic behavior was also observed using Au−poly(DE) (d = 5.9 nm, n = 42), which has shorter polymer chains. The photochromic reaction proceeded upon irradiation with UV light. However, the photochromic conversion reached only 81% in toluene, whereas the

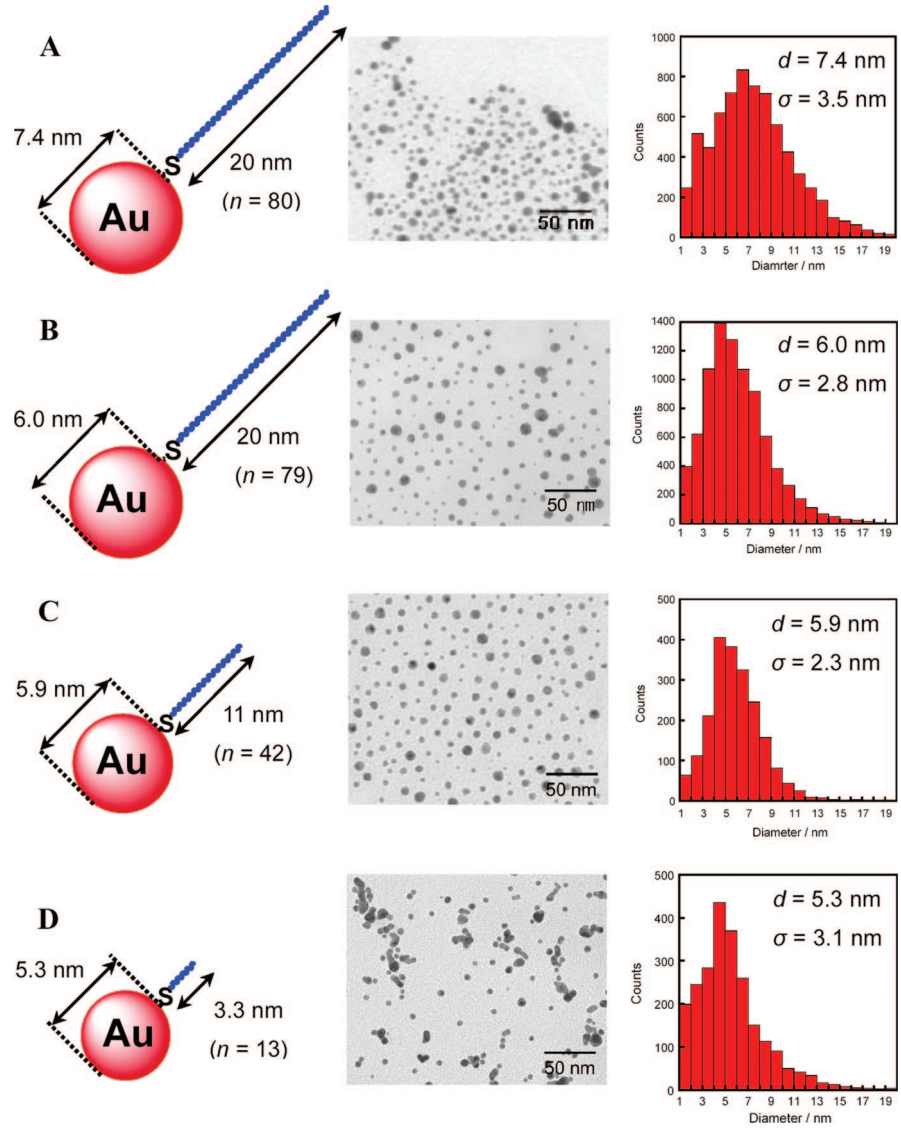


Figure 2. Schematic illustrations, TEM images, and core size histograms of (A) Au−poly(DE) (d = 7.4 nm, n = 80), (B) Au−poly(DE) (d = 6.0 nm, n = 79), (C) Au−poly(DE) (d = 5.9 nm, n = 42), and (D) Au−poly(DE) (d = 5.3 nm, n = 13). Each polymer chain length in the schematic shows the theoretical fully stretched length. The parameter σ means the standard deviation of the diameter of the gold nanoparticles.

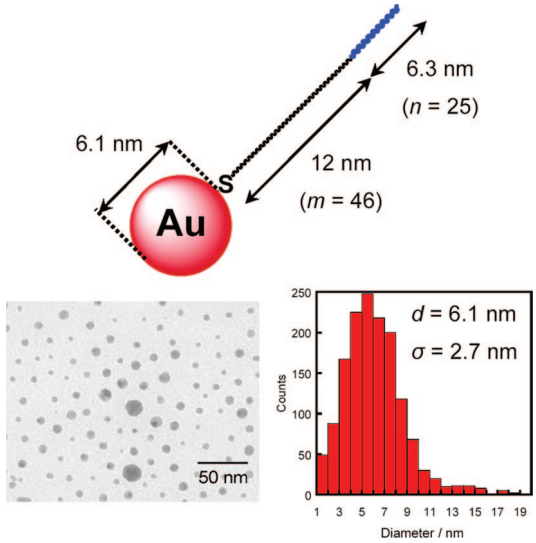


Figure 3. Schematic illustration, TEM image, and core size histogram of Au−poly(St)-*block*-poly(DE).

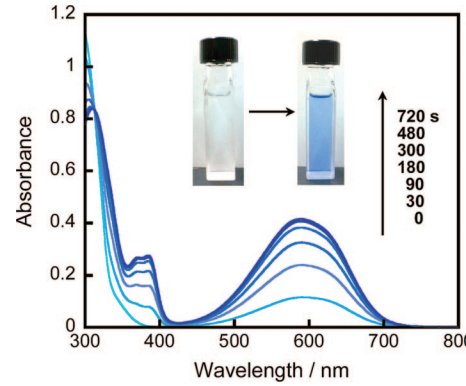


Figure 4. Absorption spectral changes of poly(DE) (n = 80) in toluene upon irradiation with 313-nm light.

photocyclization of the Au-free poly(DE) (n = 42) reached a 97% conversion in the photostationary state as shown in Figure 6. The difference in the polymer chain length of Au−poly(DE) had an influence on the photochromic conversion. The shorter chain length may be quenched into Au for a part of the diarylethene chromophores in the excited state. The quenching

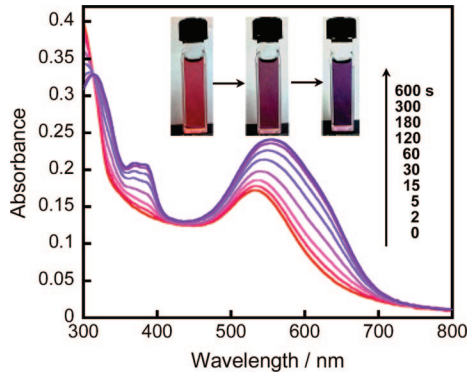


Figure 5. Absorption spectral changes of Au−poly(DE) (d = 7.4 nm, n = 80) in toluene upon irradiation with 313-nm light.

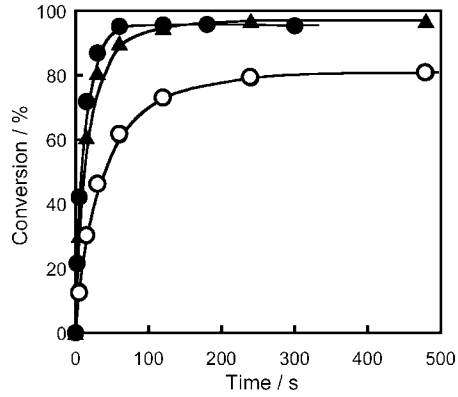


Figure 6. Time-conversion curves of poly(DE) (n = 42) (▲), Au−poly(DE) (d = 7.4 nm, n = 80) (●), and Au−poly(DE) (d = 5.9 nm, n = 42) (○) in toluene upon irradiation with 313-nm light.

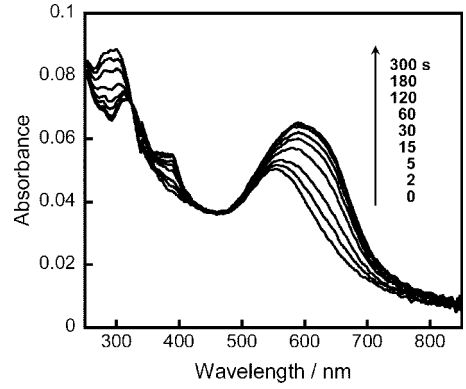


Figure 7. Absorption spectral changes of Au−poly(DE) (d = 7.4 nm, n = 80) on quartz glass upon irradiation with 313-nm light.

results in a decrease in the apparent photocyclization quantum yield and the conversion.

The photochromic behavior of Au−poly(DE) was also examined in the solid film on a quartz glass. Figure 7 shows the absorption spectral changes of the Au−poly(DE) (d = 7.4 nm, n = 80) on the quartz glass upon irradiation with 313-nm light. The sample was prepared by casting a toluene solution of Au−poly(DE). Au−poly(DE) exhibited a reversible photochromism in the solid state as well as in the toluene solution. On the quartz glass, however, the photocyclization reached only a 72% conversion as shown in Figure 8. Since the Au-free diarylethene polymer exhibits a 97% conversion on quartz glass,[48] the decrease in conversion of Au−poly(DE) indicates that the excited energy of the diarylethene chromophores near the gold surface was quenched through space.[41] The photo-

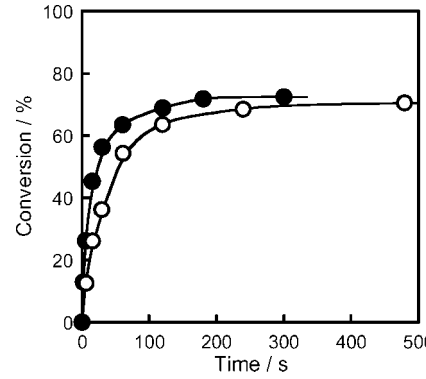


Figure 8. Time−conversion curves of Au−poly(DE) (d = 7.4 nm, n = 80) (●) and Au−poly(DE) (d = 5.9 nm, n = 42) (○) on quartz glass upon irradiation with 313-nm light.

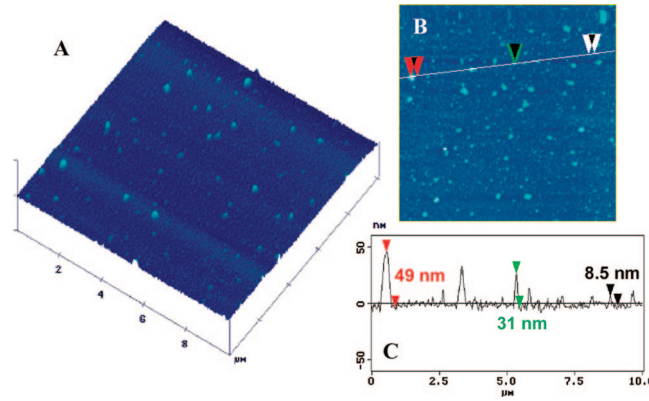


Figure 9. AFM images of Au−poly(DE) (d = 7.4 nm, n = 80) on quartz glass: (A) stereoscopic view, (B) top view, and (C) cross-sectional view.

chromic reaction of Au−poly(DE) (d = 5.9 nm, n = 42) on the quartz glass also proceeded with a 70% conversion as shown in Figure 8. This indicates that the photochromic conversion in the solid state on the quartz glass does not depend on the polymer chain lengths. Although the polymer chains of Au−poly(DE) are fully stretched in toluene (see Figure S1 in the Supporting Information), a part of the polymer chains on the quartz glass may be in a more coiled state and intertwined with the gold nanoparticle. Figure 9 shows the atomic force microscopic (AFM) image of the cast film of Au−poly(DE) (d = 7.4 nm, n = 80). The entire diameter of Au−poly(DE) (d = 7.4 nm, n = 80) is expected to be ca. 47.4 nm (average diameter of gold particle: ca. 7.4 nm, average polymer chain length: ca. 20 nm) if the polymer chain theoretically forms a planar zigzag (fully extended) conformation.[56] The sizes of the particles determined by AFM were shorter than 47.4 nm in most cases. Since the interparticle distance is shorter than that in solution, as can be seen from Figure 2, the diarylethene chromophores in the excited state may be quenched by not only the self-nanoparticle but also the adjacent nanoparticles.

Interaction between the Gold Nanoparticle and Diarylethene. To evaluate the electric field interaction between the gold nanoparticle and the diarylethene chromophores, the absorption spectra of the diarylethene closed-ring forms for poly(DE) and Au−poly(DE) were compared to each other. The difference spectrum was obtained by subtracting the spectrum before UV irradiation from that in the photostationary state. The surface plasmon resonance band can be canceled according to this subtraction process. The absorption spectrum of the diarylethene moieties can be evaluated by the difference spectrum. Figure 10A shows the spectra of poly(DE) (n = 80)

Table 2. Absorption Maximum and Bathochromic Shift between Poly(DE) and Au−Poly(DE) Having Various Chain Lengths of Poly(DE) in Various Solvents

		λ_{max}/nm: poly(DE) → Au−poly(DE)($\Delta\lambda_{max}$/nm)		
condition	n_D[a]	d = 5.3 nm, n = 13	d = 5.9 nm, n = 42	d = 6.0 nm, n = 79
in THF	1.42	590 → 602 (12)	587 → 596 (9)	589 → 596 (7)
in chloroform	1.44	588 → 602 (14)	586 → 598 (12)	588 → 596 (8)
in toluene	1.49	592 → 604 (12)	589 → 602 (13)	590 → 598 (8)
in 1-bromonaphthalene (BN)	1.66	600 → 612 (12)	597 → 611 (14)	598 → 609 (11)
on quartz glass		588 → 651 (63)	584 → 633 (49)	595 → 639 (44)

[a] Refractive index of solvent.

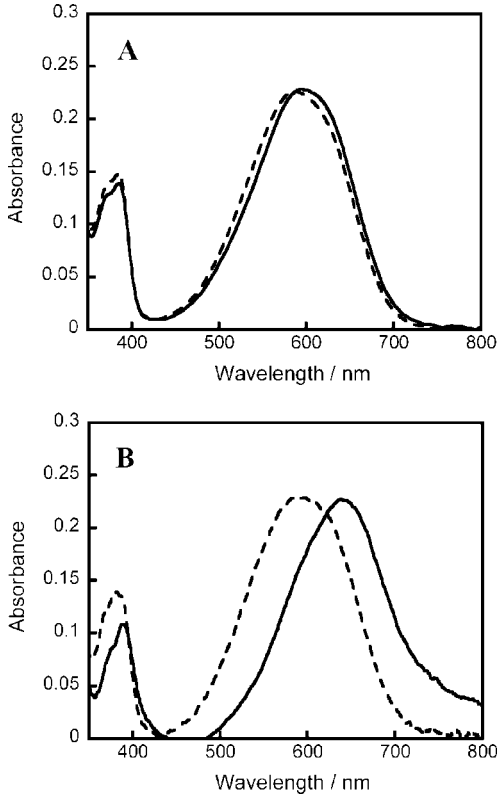


Figure 10. Difference spectra of poly(DE) (n = 80) (dashed line) and Au−poly(DE) (d = 7.4 nm, n = 80) (solid line) (A) in toluene and (B) on quartz glass. The spectra were obtained by subtracting a spectrum before UV irradiation from that at the photostationary state.

and Au−poly(DE) (d = 7.4 nm, n = 80) in toluene. The spectra indicate that the absorption maximum of poly(DE) was shifted to bathochromic by attachment on the gold nanoparticle. This effect suggests that there is an electric field interaction between the gold nanoparticle and the diarylethene chromophore. Moreover, on the quartz glass, the absorption maximum of Au−poly(DE) was more effectively shifted than that of poly(DE) as shown in Figure 10B. The distance between the gold surface and the diarylethene moiety on the quartz glass is closer than that in solution because the polymer chains attached on the gold nanoparticle are shrunk and intertwined with the gold nanoperticle on the quartz glass, and closely located to the adjacent particles. Thus, the bathochromic shifts are related to the distance between the diarylethene chromophore and the gold surface. Table 2 shows the bathochromic shifts in various solvents. It is found that the bathochromic shift increased with the shortening polymer chain length and the refractive index of the solvent. Since the surface plasmon resonance is sensitive to the interparticle distance and the dielectric property of the medium, these bathochromic shifts are associated with the surface plasmon resonance.

Table 3. Absorption Maximum and Bathochromic Shift between Poly(DE)-block-poly(St) and Au−Poly(St)-block-poly(DE) (d = 6.1 nm, m = 46, n = 25)

	λ_{max}/nm		
condition	poly(DE)-*block*-poly(St)	Au−poly(St)-*block*-poly(DE)	$\Delta\lambda_{max}$/nm
in toluene	588	593	5
on quartz glass	595	620	25

Photochromism and Bathochromic Shift of Au−Poly(St)-*block*-poly(DE). Au−poly(St)-*block*-poly(DE) was synthesized in order to investigate the details of the relationship between the optical properties and the distance from the surface of the gold nanoparticle to the diarylethene chromophore. Au−poly(St)-*block*-poly(DE) exhibited a reversible photochromism by photoirradiation as did Au−poly(DE). The photocyclization in toluene reached a 94% conversion. This value is similar to that of poly(DE) prepared by the conventional radical polymerization[48] and that of Au−poly(DE) (d = 7.4 nm, n = 80). Since the diarylethene chromophore in Au−poly(St)-*block*-poly(DE) is located away from the gold surface, the quenching effect is hardly observed in this system. These results indicate that the diarylethene chromophore only near the gold surface is quenched into Au in the excited state. On the quartz glass, however, the photocyclization of Au−poly(St)-*block*-poly(DE) reached only a 67% conversion. This value is also similar to that of Au−poly(DE). The decrease in conversion indicates that the polymer chains attached to the gold nanoparticles have shrunk and became intertwined with the gold nanoparticles and that the excited energy is quenched by not only the self-nanoparticle but also by adjacent nanoparticles as well as Au−poly(DE).

As shown in Table 3, the bathochromic shifts of Au−poly(St)-*block*-poly(DE) in toluene and on the quartz glass are 5 and 25 nm, respectively. These values are considerably lower than those of Au−poly(DE) as shown in Table 3. This result also suggests that the bathochromic shift caused by the gold nanoparticles is closely related to the distance between the diarylethene chromophore and the gold surface.

Origin of Bathochromic Shift. Two possibilities can be proposed as the reason for the bathochromic shift. First, as described above, the diarylethene moieties are affected by some interaction caused by the gold nanoparticles, such as a local electric field[25] attributed to the surface plasmon resonance. Second, the bathochromic shift may be derived from the change in the surface plasmon resonance band. If the surface plasmon resonance band is altered due to the refractive index change in the diarylethene moieties that are caused by the photoisomerization, the difference spectrum is apparently shifted to bathochromic by conversion. As can be seen in Figure 11, the absorption maximum of the difference spectrum of Au−poly(DE) (d = 7.4 nm, n = 80) was not changed upon irradiation with UV light. Therefore, the bathochromic shift is not due to the change in the refractive index of the diarylethene polymer.

The sensitivity of the surface plasmon resonance peak depends on the particle size of the gold nanoparticle.[18,24] When

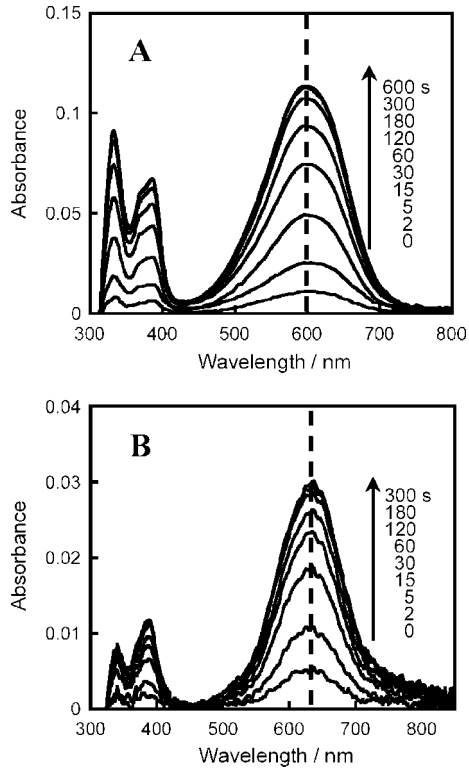


Figure 11. Differenece spectral changes of Au−poly(DE) (d = 7.4 nm, n = 80) (A) in toluene and (B) on quartz glass upon irradiation with 313-nm light. The spectra were obtained by subtracting a spectrum before UV irradiation from that at the photostationary state.

the particle size is larger than ca. 10 nm, the surface plasmon resonance peak significantly influences the refractive index of the medium.[18,22] In our experiment, the particle size of the gold nanoparticle is 5–7 nm. Therefore, no change in the surface plasmon resonance peak was observed.

We can conclude that the bathochromic shift was not due to the change in the surface plasmon resonance peak, but it was due to the shift in the absorption band of the diarylethene closed-ring form caused by the local electric field on the gold nanoparticle, which is changed by the medium such as the solvent. In addition, the influence of the local electric field on the photochromic diarylethene chromophore was found to depend on the distance from the gold surface. The photochromic nanoparticle may be potentially used for application as a sensor of the medium around the particle.

Conclusion

We have developed a new type of gold nanoparticle−diarylethene complex synthesized by Brust's method using low-polydispersity and −SH terminated diarylethene polymers prepared by RAFT polymerization. These nanoparticles produced a surface plasmon resonance band and exhibited a reversible photochromism both in solution and the solid state. The cyclization reactivity of the diarylethene polymer around the nanoparticles decreased with the decreasing distance between the diarylethene chromophore and the gold surface. The difference spectrum analysis showed the presence of a local electric field interaction that is derived from the surface plasmon resonance of the gold nanoparticle to the diarylethene chromophore far from the gold surface. This mutual effect makes the absorption maximum of the diarylethene closed-ring form shift to bathochromic, and was significantly observed in the solid state. It may be due to the shorter distance between the diarylethene chromophore and the gold surface. We found and evaluated the effect of the gold nanoparticle on the photoreactivity and absorption spectrum of the diarylethene moieties.

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Supporting Information Available: Text giving details of the preparation of the gold nanoparticles and some characterization data including tables of synthetic conditions and surface plasmon reasonance peaks and a figure showing the dynamic light scattering measurments and a structural diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 2003.
(2) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
(3) Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985–996.
(4) Irie, M.; Lifka, T; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876.
(5) Miyasaka, H.; Nobuto, T.; Itaya, A.; Tamai, N.; Irie, M. *Chem. Phys. Lett.* **1997**, *269*, 281–285.
(6) Kobatake, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195–210.
(7) Kawai, T.; Fukuda, N.; Gröschl, D.; Kobatake, S.; Irie, M. *Jpn. J. Appl. Phys., Part 2* **1999**, *38*, L1194–L1196.
(8) Kim, E.; Choi, Y.; Lee, M. *Macromolecules* **1999**, *32*, 4855–4860.
(9) Nakashima, H.; Irie, M. *Macromol. Chem. Phys.* **1999**, *200*, 683–692.
(10) Irie, M. *Jpn. J. Appl. Phys.* **1989**, *28* (28–3), 215–219.
(11) Tsujioka, T.; Kume, M.; Irie, M. *Jpn. J. Appl. Phys., Part 1* **1995**, *34*, 6439–6443.
(12) Takeshita, M.; Uchida, K.; Irie, M. *Chem. Commun.* **1996**, 1807–1808.
(13) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195–7201.
(14) Matsuda, K.; Matsuo, M.; Irie, M. *J. Org. Chem.* **2001**, *66*, 8799–8803.
(15) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777–1788.
(16) Irie, M.; Kobatake, S.; Horichi, M. *Science* **2001**, *291*, 1769–1772.
(17) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778–781.
(18) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B.* **1999**, *103*, 8410–8426.
(19) Kamat, P. V. *J. Phys. Chem. B.* **2002**, *106*, 7729–7744.
(20) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346.
(21) Cheng, P. P. H.; Silvester, D.; Wang, G.; Kalyuzhny, G.; Douglas, A.; Murray, R. W. *J. Phys. Chem. B.* **2006**, *110*, 4637–4644.
(22) Miller, M. M.; Lazarides, A. A. *J. Phys. Chem. B.* **2005**, *109*, 21556–21565.
(23) Watanabe, K.; Menzel, D.; Nilius, N.; Freund, H.-J. *Chem. Rev.* **2006**, *106*, 4301–4320.
(24) Njoki, P. N.; Lim, I.-I. S.; Mott, D.; Park, H.-Y.; Khan, B.; Mishra, S.; Sujakumar, R.; Luo, J.; Zhong, C.-J. *J. Phys. Chem. C.* **2007**, *111*, 14664–14669.
(25) Campion, A.; Kambhampati, P. *Chem. Soc. Rev.* **1998**, *27*, 241–250.
(26) Imahori, H.; Arimura, M.; Hanada, T.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 335–336.
(27) Dulkeith, E.; Morteani, A. C.; Niedereichholz, T.; Klar, T. A.; Feldmann, J.; Levi, S. A.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Möller, M.; Gittins, D. I. *Phys. Rev. Lett.* **2002**, *89*, 203002–203002-4.
(28) Kuwahara, Y.; Akiyama, T.; Yamada, S. *Langmuir* **2001**, *17*, 5714–5716.
(29) Corbierre, M. K.; Cameron, N. S.; Sutton, M.; Mochrie, S. G. J.; Lurio, L. B.; Rühn, A.; Lennox, R. B. *J. Am. Chem. Soc.* **2001**, *123*, 10411–10412.
(30) Ohno, K.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2002**, *35*, 8989–8993.
(31) Lowe, A. B.; Sumerlin, B. S.; Donovan, M. S.; McCormick, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 11562–11563.
(32) Corbierre, M. K.; Cameron, N. S.; Lennox, R. B. *Langmuir* **2004**, *20*, 2867–2873.
(33) Zhu, M.-Q.; Wang, L.-Q.; Exarhos, G. J.; Li, A. D. Q. *J. Am. Chem. Soc.* **2004**, *126*, 2656–2657.
(34) Shan, J.; Nuopponen, M.; Jiang, H.; Viitala, T.; Kauppinen, E.; Kontturi, K.; Tenhu, H. *Macromolecules* **2005**, *38*, 2918–2926.
(35) Luo, S.; Xu, J.; Zhang, Y.; Liu, S. Wu, C. *J. Phys. Chem. B.* **2005**, *109*, 22159–22166.

(36) Okubo, K.; Shimada, T.; Shimizu, T.; Uehara, N. *Anal. Sci.* **2007**, *23*, 85–90.
(37) Rosi, N. L.; Mirkin, C. A. *Chem. Rev.* **2005**, *105*, 1547–1562.
(38) Jennings, T. L.; Singh, M. P.; Strouse, G. F. *J. Am. Chem. Soc.* **2006**, *128*, 5462–5467.
(39) Manna, A.; Chen, P.-L.; Akiyama, H.; Wei, T.-X.; Tamada, K.; Knoll, W. *Chem. Mater.* **2003**, *15*, 20–28.
(40) Matsuda, K.; Ikeda, M.; Irie, M. *Chem. Lett.* **2004**, *33*, 456–457.
(41) Yamaguchi, H.; Ikeda, M.; Matsuda, K.; Irie, M. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1413–1419.
(42) Kudernac, T.; van der Molen, S. J.; van Wees, B. J.; Feringa, B. L. *Chem. Commun.* **2006**, 3597–3599.
(43) Sidhaye, D. S.; Kashyap, S.; Sastry, M.; Hotha, S.; Prasad, B. L. V. *Langmuir* **2005**, *21*, 7979–7984.
(44) Ipe, B. I.; Mahima, S.; Thomas, K. G. *J. Am. Chem. Soc.* **2003**, *125*, 7174–7175.
(45) Ikeda, M.; Tanifuji, N.; Yamaguchi, H.; Irie, M.; Matsuda, K. *Chem. Commun.* **2007**, *13*, 1355–1357.
(46) Feringa, B. L. *J. Org. Chem.* **2007**, *72*, 6635–6652.
(47) Perrier, S.; Maurel, F.; Aubard, J. *J. Phys. Chem. A* **2007**, *111*, 9688–9698.
(48) Kobatake, S.; Kuratani, H. *Chem. Lett.* **2006**, *35*, 628–629.
(49) Perrier, A.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2002**, *35*, 8300–8306.
(50) Feng, X.-S.; Pan, C.-Y. *Macromolecules* **2002**, *35*, 4888–4893.
(51) Hong, C.-Y.; You, Y.-Z.; Pan, C.-Y. *Chem. Mater.* **2005**, *17*, 2247–2254.
(52) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802.
(53) Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036–7041.
(54) Yonezawa, T.; Yasui, K.; Kimizuka, N. *Langmuir* **2001**, *17*, 271–273.
(55) Van Hyning, D. L.; Zukoski, C. F. *Langmuir* **1998**, *14*, 7034–7046.
(56) Cameron, N. S.; Eisenberg, A.; Brown, G. R. *Biomacromolecules* **2002**, *3*, 124–132.

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