

Using Polymers To Photoswitch the Aggregation State of Gold Nanoparticles in Aqueous Solution

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Gold nanoparticles (AuNPs) coated with a water-soluble polymer displaying a photoswitchable lower critical solution temperature (LCST) were synthesized, and the photoinduced change in the aggregation state of AuNPs was investigated. The photoactivity of AuNPs was conferred by tethering on the surface a random copolymer of *N,N*-dimethylacrylamide and *N*-4-phenylazophenyl acrylamide (P(DMA-*co*-Azo)), whose LCST could be lowered upon the *trans*–*cis* photoisomerization of azobenzene groups. It was found that the dispersion of P(DMA-*co*-Azo)-coated AuNPs in aqueous solution remained stable regardless of temperature and the isomeric form of azobenzene groups. However, with the presence of free P(DMA-*co*-Azo) chains in the solution, the reversible photoinduced shift of LCST of the polymer could result in a reversible photoswitching between dispersion and aggregation of AuNPs. A stable dispersion could be obtained at $T < \text{LCST}$ of the polymer with azobenzene in the *trans* form (without irradiation), while upon UV irradiation, the lowering of LCST with *cis*-azobenzene put the solution to above the altered LCST and the insoluble polymer chains led to aggregation of AuNPs; the initial dispersion state could be recovered by visible light irradiation, bringing *cis*-azobenzene back to the *trans* form. The use of such a photoresponsive polymer to optically tune the aggregation state of AuNPs allows the surface plasmon resonance (SPR) of AuNPs to be reversibly switched by light at two wavelengths, the extent of which depends on the amount of free polymer chains in the solution.

1. Introduction

Aggregation of gold nanoparticles (AuNPs) can result in a shift of the surface plasmon resonance (SPR) as a result of closer distances between the nanoparticle surfaces.^{1,2} An ability to control the aggregation state of AuNPs by stimuli is of interest in exploring their potential for applications. For instance, Nam et al. showed that AuNPs with a hydrolysis-susceptible citraconic amide surface could aggregate in response to a pH decrease, which shifted the SPR to far-red and near-infrared (NIR) region; the absorption of longer wavelengths, which could improve light penetration through tissues, was used for photothermal cancer therapy.³ Attaching a stimuli-responsive polymer to the surface of AuNPs is an easy means to render them responsive to changes in environmental conditions and possibly induce their aggregation. The two most used stimuli to this end are pH and temperature changes.^{1,2} Generally, with a water-soluble polymer tethered to the surface of AuNPs, a stable dispersion in water can be obtained, but if the polymer chains become insoluble as a result of a temperature or a pH change, aggregation of AuNPs can occur under certain conditions. In view of the broad interest of AuNPs in many emerging applications such as sensing, delivery and cancer therapy,^{3,4} developing and understanding new stimuli-responsive

AuNPs are worth the effort. The concept of using light to control the aggregation of AuNPs is not new; there are a number of reports on photosensitive AuNPs by coating the surface mainly with small molecules bearing a photochromic moiety such as azobenzene⁵ and thymine.⁶ However, with small-molecule azobenzene derivatives or linkers, the photoreaction took place in an organic medium and the photoinduced effect was small,⁵ while using the photodimerization of thymine groups, no reversible control was demonstrated.⁶ As a matter of fact, we are unaware of any reports on exploring photoactive polymers to achieve a reversible photocontrol of the aggregation state of AuNPs in aqueous solution. Herein we present a rationally designed polymer-coated AuNP system that, by virtue of photocontrollable water solubility of polymer chains, could display phototunable aggregation state and, consequently, a reversible photoswitching of SPR.

Figure 1a shows the chemical structure of the polymer tethered to the surface of AuNPs. It is a random copolymer of *N,N*-dimethylacrylamide (DMA) and *N*-4-phenylazophenylacrylamide (Azo), referred to as P(DMA-*co*-Azo) hereafter. The reason for choosing this polymer is that it exhibits a lower critical solution temperature (LCST) in water, and upon absorption of UV light, the *trans*–*cis* photoisomerization of azobenzene side groups could shift the LCST to a lower temperature. This peculiar behavior was thought to be related to the amide group linking azobenzene and chain backbone which could favor intramolecular hydrophobic interactions of pendant groups.⁷ Making use of this feature, our

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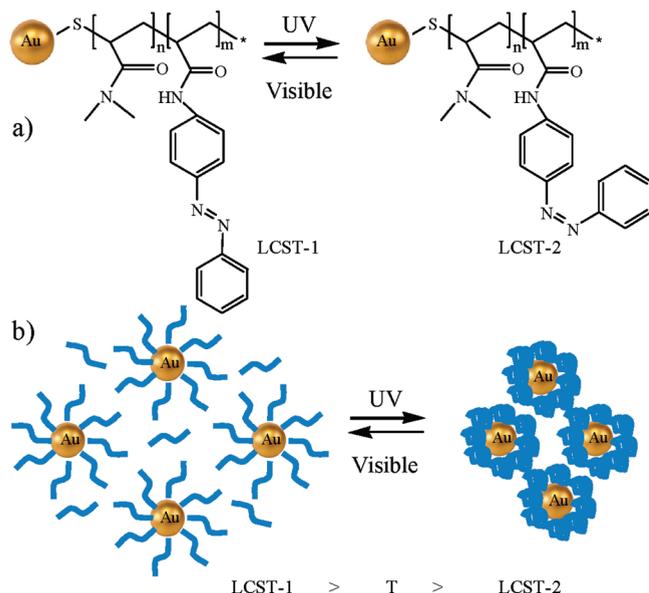


Figure 1. (a) Chemical structure of the polymer tethered to gold nanoparticles (chain end groups are omitted). (b) Schematic illustration of the reversible light-triggered aggregation and dispersion of AuNPs as a result of the photoisomerization-induced shift of LCST of the polymer.

initially expected photocontrol of the dispersion state of AuNPs is schematically illustrated in Figure 1b. At a given temperature below but close to the LCST of P(DMA-*co*-Azo) with the stable trans isomer of azobenzene (LCST-1), the dispersion of AuNPs is stable, while upon UV irradiation, the lowering of LCST with *cis*-azobenzene could reposition the solution to above the new LCST (LCST-2) and thus render the polymer chains insoluble in water and induce the aggregation of AuNPs. As will be shown below, our study found that with only polymer chains tethered to AuNPs the polymer insolubility could not lead to aggregation of AuNPs. However, with the help of free polymer chains in solution, such a reversible photocontrol of the aggregation state of AuNPs could be achieved.

2. Experimental Section

2.1. Materials. The following chemicals were purchased and used as received: hydrogen tetrachloroaurate tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) (Alfa Aesar), anhydrous anisole (Aldrich, 99.7%), Irgacure-2959 (I-2959) (Sigma-Aldrich), *N,N*-dimethylacrylamide (DMA). Literature methods were utilized to synthesize the azobenzene monomer, *N*-4-phenylazophenylacrylamide,⁶ and the chain transfer agent of 2-(2-cyanopropyl)dithiobenzoate (CPDB).⁸ 2,2'-Azobis(isobutyronitrile) (AIBN) (Polysciences) was recrystallized twice from ethanol before use.

2.2. Synthesis of P(DMA-*co*-Azo). The thermo- and photosensitive random copolymer P(DMA-*co*-Azo) tethered to AuNPs was synthesized using reversible addition-fragmentation chain transfer radical polymerization (RAFT). A one-necked round flask was filled with DMA (1.0 g, 10.09 mmol), *N*-4-phenylazophenylacrylamide (297 mg, 1.18 mmol), CPDB (30.25 mg, 0.16 mmol), AIBN (2.13 mg, 0.013 mmol), and 3 mL of anisole. The reaction mixture was degassed by freeze-pump-thaw three times and filled with nitrogen. The reaction was conducted at 110 °C for 7 h. Afterward, the solution was diluted by 5 mL of dichloromethane (DCM), precipitated in petroleum ether. The purification was repeated one more time and the collected polymer dried in vacuum. ¹H NMR (CDCl_3 , δ ppm): 7.87 (broad, 7H, m, p

ArH to $-\text{N}=\text{N}-$ and NH), 7.47 (s, 4H, o ArH to $-\text{N}=\text{N}-$), 2.89 (broad, 6H, NCH_3), 2.1–1.6 (broad, 3H, aliphatic main chain). GPC (polystyrene standards and THF eluent): $M_n = 7800 \text{ g mol}^{-1}$, PDI = 1.17. On the basis of the ¹H NMR spectrum and the M_n , the random copolymer composition was estimated to be P(DMA₅₇-*co*-Azo₆), i.e., with ~10 mol % of azobenzene comonomer units.

2.3. Synthesis of P(DMA-*co*-Azo)-Coated Gold Nanoparticles. AuNPs functionalized with P(DMA-*co*-Azo) chains were obtained by using a well-known method.⁹ In a typical experiment, 1 mL of an aqueous solution of 8.12 mM chlorauric acid (HAuCl_4) was added to 2 mL of an aqueous solution of P(DMA-*co*-Azo) (6.34 mg) in a reaction vessel, followed by stirring for 1 h at room temperature. Irgacure-2959 (24.36 mM) was dissolved in a mixture of distilled water and MeOH (2:1, v/v); 1 mL of this initiator solution was then added to the HAuCl_4 /polymer mixture and stirred for 1 h. The clear solution was then irradiated for 30 min in a Rayonet photoreactor using 16 75-W UV lamps at wavelength of 300 nm. As the reaction proceeded, the color of the solution turned purple, indicating the formation of AuNPs. The reaction solution was stirred at room temperature for 24 h to obtain dispersion of P(DMA-*co*-Azo)-coated AuNPs. The pH of the as-obtained colloidal solution was about 2.3. Free polymer chains were removed from P(DMA-*co*-Azo)-coated AuNP by three centrifugal precipitations followed by redispersion in water (each centrifugation at 25000 rpm for 3 h). Purified AuNPs with the polymer ligand were stored in water at room temperature, while diluted solutions (0.25 mg mL^{-1}) were used for the experiments with pH adjusted to 10 using a 0.1 M NaOH solution. TEM observations found that AuNPs formed under the used conditions had an average diameter of ~10 nm. The grafting of P(DMA-*co*-Azo) to AuNPs was easily observable from the absorption band of *trans*-azobenzene at ~350 nm. By establishing a calibration curve of absorbance at 350 nm vs concentration of P(DMA-*co*-Azo) and using 10 nm for the diameter and 19.32 g cm^{-3} for the density of AuNPs and 7800 g mol^{-1} for the molecular weight of P(DMA-*co*-Azo), the amount of polymer chains on AuNP surface was estimated to be about 3.5 chains/nm². We note that since the used M_n was a value relative to polystyrene standards, the polymer chain density is a rough estimation.

2.4. Characterizations. Gel permeation chromatography (GPC) measurements were performed at 35 °C on a Waters system equipped with a refractive index detector (RI 410), a photodiode array detector (PDA 996), and a column (Waters Styragel HR4E, 7.8 mm × 300 mm, 5 μm beads). It was calibrated with polystyrene standards, while THF was used as the eluent at an elution rate of 1.0 mL/min. ¹H NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz) using deuterated solvents and tetramethylsilane as internal standard. Variable-temperature UV-vis absorption spectra of P(DMA-*co*-Azo)-coated AuNPs, with or without free polymer chains in solution, were recorded on a Varian 50 Bio spectrophotometer with a temperature controlling sample holder, the heating rate of the solution (2–3 mL) being ~0.5 °C min⁻¹. For UV or visible light irradiation of the solution, a spot curing system (Novacure 2100) combined with interference filters for UV (354 nm, 50 mW/cm²) and visible light (440 nm, 5 mW/cm²) was used, the irradiation time being 4 min. Transmission electron microscopy (TEM) observations were made on a Hitachi H-7500 operating at 100 kV. To observe the photoinduced change in the aggregation state of AuNPs at 30 °C, the samples were prepared by casting ~5 μL of the solution before and after UV irradiation onto carbon-coated copper grids warmed to 30 °C, followed by quick drying using airflow.

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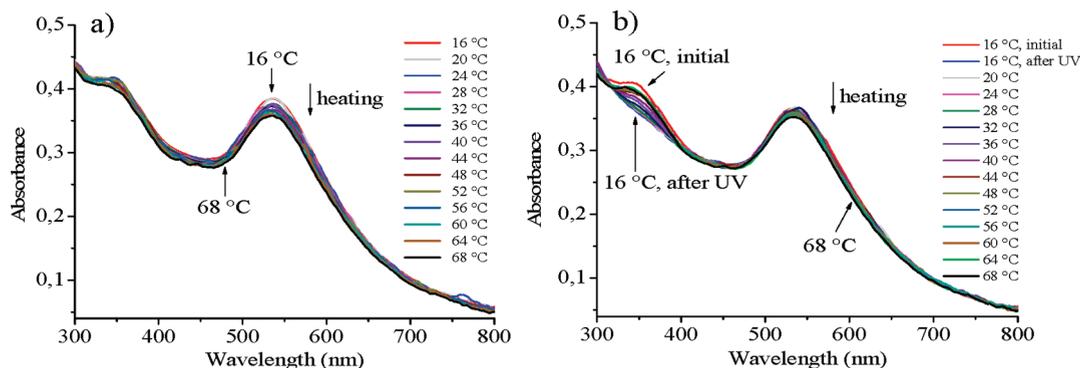


Figure 2. UV–vis absorption spectra of P(DMA-*co*-Azo)-coated AuNPs in aqueous solution from 16 to 68 °C: (a) after visible light irradiation (*trans*-azobenzene) and (b) after UV irradiation (*cis*-azobenzene).

3. Results and Discussion

The reversible photoswitching of LCST of free P(DMA-*co*-Azo) (not tethered to AuNPs) in pure water was first confirmed by transmittance measurements after UV and visible light irradiation. At a concentration of 1 mg mL⁻¹, the polymer exhibited a LCST at ~34 °C with *trans*-azobenzene groups and a LCST of ~20 °C with azobenzene in the *cis* form (Supporting Information). However, with the polymer tethered to AuNPs and the used low concentration (0.25 mg mL⁻¹ of polymer-coated AuNPs), the photoswitching of LCST was difficult to detect from the transmittance measurements. We found that under conditions that reduce the water solubility of P(DMA-*co*-Azo), i.e., at pH 10 and in the presence of a salt ((NaCl, 70 mM), the photoswitching of LCST of the polymer and the resulting photoswitching of the aggregation state of AuNPs became more prominent. Those conditions were used for the experiments described below. We note here that the presence of a salt is known to be able to affect the polymer solubility in water and lower the LCST.¹⁰

Figure 2 shows variable-temperature UV–vis spectra of P(DMA-*co*-Azo)-coated AuNPs recorded from 16 to 68 °C, both after visible light irradiation (with *trans*-azobenzene) and UV irradiation (with *cis*-azobenzene). No changes in SPR and transmittance were observed. This result indicates that under the used conditions the solubility change of P(DMA-*co*-Azo) chains on the surface of AuNPs could not induce aggregation of the nanoparticles. In other words, regardless of the solubility of polymer chains on surface and regardless of the isomeric form of azobenzene, AuNPs retained a good colloidal stability in aqueous solution. For the solution right after UV irradiation, the *trans*–*cis* photoisomerization can be seen from the disappeared absorption of *trans*-azobenzene at 350 nm. Upon heating of the solution, the reverse *cis*–*trans* isomerization took place due to thermal relaxation of *cis* isomers. But it can be noticed that below 40 °C, i.e., at temperatures above the LCST of P(DMA-*co*-Azo), a significant portion of *cis* isomers remained. This thermal stability of the used azobenzene moiety ensured that the effect of *cis* isomers on the LCST could be observed.

It turned out that the presence of a certain amount of free P(DMA-*co*-Azo) chains in solution was necessary for photo-induced aggregation of AuNPs. It is easy to picture that when free polymer chains become insoluble upon UV irradiation as a result of the lowering of LCST, they could interact with polymer chains tethered to AuNP surface and bring the nanoparticles together (Figure 1). The effect of the amount of free chains in solution on the photoinduced aggregation of AuNPs was investigated. Figure 3

compares the UV–vis spectra of the solution without free chains with solutions in which a varying amount of free chains was added, the spectra being recorded after UV and subsequent visible light irradiation. The weight percentage of added P(DMA-*co*-Azo) with respect to the amount of polymer chains on AuNP surface was estimated from the apparent absorbance of *trans*-azobenzene at 350 nm. As example, in 3 mL of the solution of P(DMA-*co*-Azo)-coated AuNPs, which was the volume used for the measurement, 0.22 mg of P(DMA-*co*-Azo) was added for the solution labeled with 100% of free chains. The increasing amount of azobenzene groups with increasing the amount of free chains can be noticed from change of the absorption band of *trans*-azobenzene at 350 nm (spectra after visible light irradiation), and the occurrence of *trans*–*cis* isomerization after UV irradiation is observable from the much diminished absorption band of *trans*-azobenzene and the appearance of the absorption band of *cis*-azobenzene around 440 nm. All measurements were carried out at 30 °C, which is a temperature close to the LCST of P(DMA-*co*-Azo) and at which the change in water solubility of the polymer related to its photoswitchable LCST is large (Supporting Information). It is seen from Figure 3 that without and with 25% of free chains UV and visible light irradiation of the solution resulted in no meaningful changes of the absorption spectra, indicating that AuNPs remained well dispersed. Spectral changes became significant with addition of 50% P(DMA-*co*-Azo). After UV irradiation, the maximum of SPR was shifted to longer wavelengths by about 10 nm, which was accompanied by a raised baseline due to light scattering of the solution. This result showed that when the amount of free polymer chains reached a critical level, their photoinduced solubility change was coupled with polymer chains on the surface of AuNPs, making aggregation of nanoparticles to occur. After subsequent visible light irradiation, opposite spectral changes could be seen. By increasing the amount of free polymer chains to 100%, the reversible photo-induced SPR and transmittance switching became more important, displaying a SPR shift of about 30 nm. In what follows, more results obtained with a solution of P(DMA-*co*-Azo)-coated AuNPs in presence of about 400% of free polymer are presented to better show the main features of this photoswitchable SPR of AuNPs.

The results in Figure 4, obtained with ~400% of free chains in solution, show clearly the photoswitching of LCST and the photoswitchable optical properties (SPR and transmittance). In (a), the transmittance of the solution (measured at 700 nm) is plotted as a function of temperature for the solution both before and after UV exposure. With *trans*-azobenzene (before UV), the initial LCST appeared at ~36 °C, while with *cis*-azobenzene (after UV) it was lowered to ~22 °C. In (b), the UV–vis spectra were

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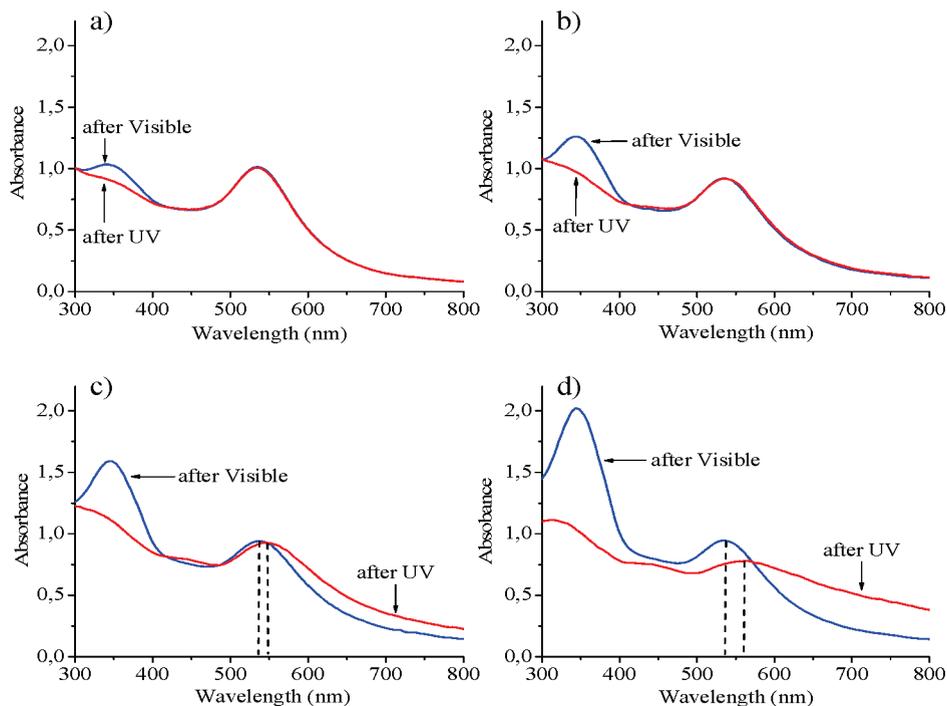


Figure 3. UV–vis spectra of aqueous solutions of P(DMA-*co*-Azo)-coated AuNPs after UV and after subsequent visible irradiation at 30 °C with 0% (a), 25% (b), 50% (c), and 100% (d) free polymer chains with respect to the amount of polymer grafted to AuNPs.

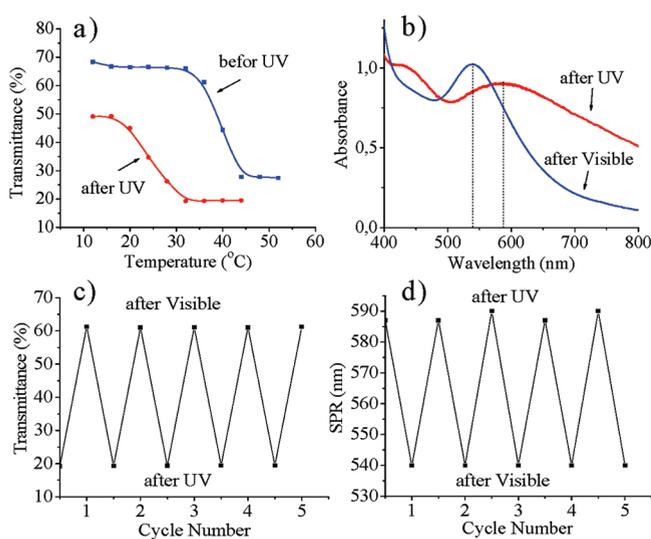


Figure 4. (a) Transmittance (at 700 nm) vs temperature for P(DMA-*co*-Azo)-coated AuNPs in aqueous solution with ~400% of free polymer chains before and after UV irradiation. (b) UV–vis spectra of the same solution thermostated at 30 °C and subjected to five consecutive cycles of alternating UV and visible light irradiation. (c) Photoswitchable transmittance of the solution and (d) photoswitchable surface plasmon resonance (SPR) of AuNPs.

recorded after five consecutive cycles of alternating UV and visible light exposure of the solution at 30 °C. The reversible photoinduced changes of the transmittance of the solution and the SPR of AuNPs are prominent. After each UV irradiation, the conversion of *trans*-azobenzene to *cis*-azobenzene was accompanied by a red shift of the SPR of more than 45 nm and a decrease in transmittance. After each visible light irradiation, the opposite spectral changes could be observed. The repeatable photoswitching of the transmittance and the SPR are shown in (c) and (d), respectively. With this solution, the reversible photoinduced large

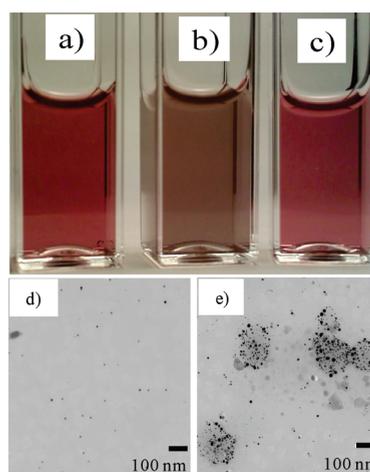


Figure 5. Pictures of a P(DMA-*co*-Azo)-coated AuNPs solution with ~400% of free polymer chains at 30 °C: (a) initial solution, (b) after UV irradiation, and (c) after visible light irradiation, along with TEM images recorded by casting the solution at 30 °C followed by drying: (d) before and (e) after UV irradiation (some larger aggregates of the salt with irregular forms can be seen).

shift of SPR of AuNPs could be observed visually from the color change of the solution as shown by the photos a–c in Figure 5. The TEM image recorded by casting the solution at 30 °C prior to UV irradiation, with water-soluble P(DMA-*co*-Azo) chains, showed well-dispersed AuNPs (photo d). By contrast, the image obtained from the solution after exposure to UV light revealed aggregates of AuNPs (photo e), further confirming that the polymer with *cis*-azobenzene became insoluble in water due to the shift of LCST to below 30 °C (Figure 4a). This phototriggered solubility change induced the aggregation of AuNPs, the consequences of which are the large red shift of SPR of AuNPs and a decreased transmittance due to light scattering. The excellent reversibility of the photoswitching can also be noted from the

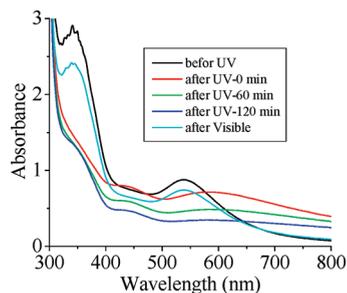


Figure 6. UV–vis spectra of P(DMA-*co*-Azo)-coated AuNPs with 400% of free chains at 30 °C: initial solution (before UV), immediately, 1 h, and 2 h after turning off UV irradiation (labeled after UV-0, 60, and 120 min, respectively) as well as after subsequent visible light irradiation (~30 min stirring). Both UV and visible light irradiations were applied for 4 min.

superimposable UV–vis spectra of five cycles of UV and visible light irradiations in Figure 4b. The above results (Figures 3–5) indicate that the presence of free polymer chains is necessary for the photoswitchable aggregation of AuNPs and that the extent of aggregation is largely determined by the amount of free chains. However, we found that the occurrence of a photoinduced solubility change for the polymer chains tethered to AuNPs is also required, whose coupling and interaction with free chains leads to a change in the aggregation state. In a control experiment, AuNPs grafted with PDMA chains without photoswitchable azobenzene comonomer units were prepared; with P(DMA-*co*-Azo) added in an aqueous solution and under the same experimental conditions, no photoinduced aggregation of AuNPs was observed upon UV irradiation (Supporting Information). Conceptually, it would be possible to achieve the photoswitching without free polymer chains by increasing the number and the length of tethered azobenzene polymer chains. This requires the use of other synthetic methods such as AuNP surface-initiated polymerization.^{1d} Likewise, increasing the concentration of polymer-coated AuNPs to a certain level may also allow the photoswitching to happen without the action of free polymer chains. In the present study, we had to keep the concentration low in order to have an absorbance of AuNPs whose SPR switching could be observed. It should also be mentioned that the solution temperature could affect the extent of the photoswitchable aggregation of AuNPs. This can be understood from the effect of temperature on the photoinduced decrease of the polymer's LCST, which is the origin of the photo-triggered solubility change. A much smaller shift of SPR and decrease in transmittance was observed when the experiment described in Figure 4 was performed at 20 °C or lower temperatures (Supporting Information) because the solution after UV exposure remained essentially below the LCST of the polymer (Figure 4a). Nevertheless, the observed photoswitching at those lower temperatures still indicates some aggregation of AuNPs upon the *trans*–*cis* isomerization, which could be caused by an increased interparticle interactions from azobenzene moieties in the *cis* form.^{5c}

Finally, as mentioned above, the used azobenzene groups have a slow thermally activated *cis*–*trans* back-isomerization. Consequently, the aggregated AuNPs after UV irradiation in Figure 4 could be stable in the aggregated state for quite a long time. This can be seen from Figure 6. Even 2 h after turning off the UV irradiation, only a fraction of azobenzene groups were relaxed back to the *trans* form as revealed by the partial recovery of the absorption of *trans*-azobenzene at 350 nm and from the remaining absorption of *cis*-azobenzene at around 440 nm. However, apparently the SPR of AuNPs decreased its intensity over time. This was caused by the precipitation of the large AuNPs aggregates in the cuvette, reducing the effective concentration of AuNPs in the sampling area while recording the UV–vis spectra. The large aggregates precipitated 2 h after turning off the UV irradiation could be redispersed easily by visible light irradiation (4 min) and under stirring (~30 min) as can be seen from the spectrum labeled “after Visible”.

4. Conclusion

We synthesized AuNPs functionalized with P(DMA-*co*-Azo), a water-soluble azobenzene-containing polymer whose LCST can be photoswitched upon the reversible *trans*–*cis* photoisomerization of the chromophore. We found that a reversible photoswitching of the aggregation state of AuNPs could be achieved in aqueous solution (pH 10, 70 mM NaCl) with the presence of free polymer chains as a result of the photoswitchable LCST of the polymer. The polymer-coated AuNP dispersion is stable in the absence of UV irradiation; upon UV irradiation, aggregation of AuNPs occurs due to a decreased solubility of polymer chains both on surface of AuNPs and in solution, while a subsequent visible light irradiation can redisperse AuNPs as the polymer becomes soluble again. The photoswitchable aggregation state of AuNPs results in photoswitchable SPR of the nanoparticles and the transmittance of the solution. This general approach, which is based on using photoresponsive polymers whose solubility in water could be controlled by light, offers new possibilities of exploring stimuli-responsive AuNPs for applications. For instance, similar to the use of pH sensitivity to shift the SPR of AuNPs to longer wavelengths,³ the demonstrated ability of tuning the SPR by light may be applied to controlled photothermal therapy, with an added appealing possibility that the tuning of SPR could be temporally and spatially selective.

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Supporting Information Available: Synthesis and characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.