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Multifunctional photo- and thermo-responsive copolymer nanoparticles

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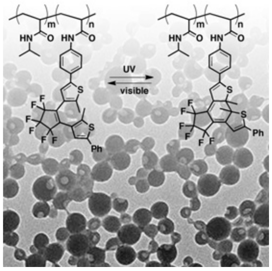
ABSTRACT

A novel amphiphilic photochromic copolymer **P1-*o*** consisting of a hydrophilic poly(*N*-isopropylacrylamide) backbone and thermally irreversible photochromic and hydrophobic 1,2-dithienylethene derivative pendants was designed, synthesized and used to fabricate self-assembled copolymer nanoparticles in an aqueous condition. The hydrodynamic diameters of the multifunctional copolymer **P1-*o*** nanoparticles reversibly switched between two stable states with two stimuli: light and temperature in an aqueous suspension.

Graphical abstract:



1. Introduction

Polymeric spherical nanostructures such as nanomicelles and nanovesicles made from fully synthetic amphiphilic copolymers are being regarded as one of the most attractive candidates for applications including encapsulation, drug delivery, nanoreactors and templates for nanostructured materials [1–8]. Although copolymeric nanostructures self-assembled in numerous aqueous conditions have structures similar to natural phospholipid micelles and liposomes, they can be optimized to possess enhanced stability and include a more varied functionality than the phospholipid nanostructures thanks to the structural and synthetic diversity available for organic materials. When the amphiphilic copolymers or the soft surfaces of the copolymer nanostructures are decorated with responsive components, they offer an additional appealing feature: their properties can be precisely controlled by external stimuli such as light, temperature, pH, and pressure [5–10]. Light is the most attractive stimulus due to the fact that its wavelength, intensity and focus can be tuned to provide both spatial and temporal control.

Photochromic molecules are among the most useful molecular elements that respond to light by undergoing reversible photoreactions generating two isomers having different molecular shapes, and optoelectronic properties such as the absorption, emission and refraction of light [11]. Among the various families of photochromic compounds, 1,2-dithienylethene derivatives (DTEs) are the most versatile because their reversible ring-closing reactions (Scheme 1) tend not to be prone to photo-fatigue and do not proceed at ambient temperatures in the dark [12]. Because DTEs not only have very high thermal barriers to isomerization in the absence of light, but also show predictable conformational shape and rigidity changes between ring-open and ring-closed photoisomers, it is expected that nanostructures made from them will also exhibit predictable changes in conformation, shape, and rigidity as a consequence of their photochromism [13–15]. Because the photoisomerization tends not to be induced thermally, the good thermal stability of both photoisomers of DTEs is a particularly attractive feature when using these photoresponsive elements in multi-component, dual-mode (more than one stimulus) systems in which light and temperature

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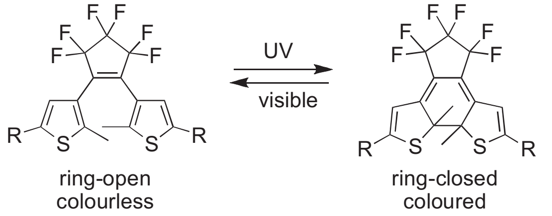


Scheme 1. Reversible photochemical reactions of dithienylethenes.

are used as independent triggers. Only with a thermally insensitive photoactive component can temperature be used to induce property changes independent of the function of the photoswitch. An illustrative example is described in this communication using a hybrid DTE-thermal polymer.

One of the best behaved temperature-responsive polymers is poly(*N*-isopropylacrylamide) (PNIPA) [16,17]. PNIPA self-assembles in aqueous solutions at temperatures higher than the lower critical solution temperature (LCST), which is typically around 33 °C. This characteristic behaviour of PNIPA can be harnessed as a 'smart' component in various thermal responsive nanostructures. Although there exist some examples of PNIPA polymers incorporating photochromic compounds such as azobenzenes and spirooxazines, they suffer from some limitations. All were investigated for their color changes by studying them in bulk hydrogels and not nanostructures [18,19]. They also contain photochromic components that spontaneously revert to their original photoisomer in the dark, preventing the demonstration of specific bistable dual-mode (light and temperature) response.

In this report, we introduce a novel amphiphilic photochromic copolymer **P1-*o*** that is composed of a hydrophilic PNIPA backbone decorated with thermally irreversible photochromic and hydrophobic DTE components. We demonstrate that in aqueous conditions, these novel, multifunctional copolymers self-assemble into nanoparticles capable of reversibly responding to two external stimuli (light and temperature). To the best of our knowledge, these copolymeric nanoparticles are the first example of multifunctional photo- and thermo-responsive (dual-mode) structures of this type.

2. Experimental

2.1. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer and a Bruker Avance 600 spectrometer. Mass spectra were measured on a Varian 4000 GC/MS by EI mode and an Agilent 6210 TOF LC/MS by ESI positive mode. Gel permeation chromatography (GPC) analysis was carried out on a Waters 510 equipped with μ-Styragel columns by using THF and polystyrenes as the solvent and the standard polymers, respectively. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC 7 under nitrogen atmosphere at a heating rate of 10 °C/min and UV–Vis absorption spectra were acquired on a Varian Cary 300 Bio spectrophotometer. The average hydrodynamic diameters and zeta potentials of **P1-*o*** nanoparticles were measured on a Nano-ZS (Malvern Instruments, Inc.) and transmission electron microscope (TEM) images were acquired on an H-8000 (200 keV, Hitachi) TEM by dropping the aqueous suspensions of **P1-*o*** nanoparticles on copper grids. A 313 nm UV hand-held lamp (5.5 mW cm^{-2}) and visible light (>500 nm) isolated from halogen white lamp (300 W) through a color filter (Newport, FS-C) were used as the excitation light sources for the photochromic ring-closing and the ring-opening reactions, respectively. Photographs of an aqueous suspension of **P1-*o*** nanoparticles undergoing the photochromic reactions were taken on a Sony Handycam (DCR-HC30) digital video camera.

2.2. Materials

All the chemicals were purchased from commercial suppliers and used as received unless otherwise specified. Tetrahydrofuran (THF) used as reaction solvent was dried over sodium metal. *N*-isopropylacrylamide (NIPA, Aldrich Chemical Co., 97%) and 1,1′-azobis(cyclohexane-1-carbonitrile) (VAZO 88, DuPont, >98%) were recrystallized from ethyl acetate/hexanes (1/4) and ethanol solutions three times, respectively. (4-Bromo-5-methylthiophen-2-yl) trimethylsilane (**2**) and 2-methyl-3-(perfluorocyclopent-1-enyl)-5-phenylthiophene (**3**) were synthesized according to the literature procedures without modification [20,21].

2.3. Synthesis of (4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)trimethylsilane (*4*)

A solution of thiophene **2** (1.05 g, 4.21 mmol) in anhydrous Et_2O (17 mL) in a flame-dried round-bottom flask was treated with *n*-BuLi (2.5 M in hexanes, 1.68 mL, 4.21 mmol) drop-wise over 10 min at −78 °C under N_2. The resulting solution was stirred for additional 30 min, at which time it was treated with a solution of **3** (1.03 g, 2.81 mmol) in Et_2O (3 mL) slowly. The resulting solution was stirred for 1 h at −78 °C, the cooling bath was removed and the reaction stirred for additional 2 h at ambient temperature. The reaction was quenched with NH_4Cl, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting dark orange oil was purified by column chromatography (SiO_2/hexanes) to yield 286 mg of a mixture of the title compound and starting material (**3**) as a colorless waxy solid (8:2, **4**:**3**) that becomes blue/purple when exposed to UV light. This product mixture was used for subsequent reactions without further purification (yield after correcting for **3** = 286 mg; 246 mg of pure product **4**, 17%). Mp = 39–42 °C. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.58–7.57 (m, 0.5H, compound **3**), 7.55–7.54 (m, 2H, compound **4**), 7.41–7.37 (m, 3H, compound **4**), 7.32–7.29 (m, 1.5H, compound **3**), 7.26 (s, 1H, compound **4**), 7.18 (s, 1H, compound **4**), 7.09 (s, 0.25H, compound **3**), 2.37 (s, 1H, compound **3**), 2.00 (s, 3H, compound **4**), 1.89 (s, 3H, compound **4**), 0.30 (s, 9H, compound **4**).

2.4. Synthesis of 5-bromo-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-2-methylthiophene (*5*)

A suspension of **4** (246 mg, 0.475 mmol) in MeCN (3.5 mL) in a vial was treated with NBS (84 mg, 0.475 mmol) in one portion. The reaction mixture was stirred at ambient temperature for 18 h, after which more NBS (28 mg, 0.15 mmol) was added. After stirring for an additional 4 h, the reaction mixture was concentrated onto silica and purified by column chromatography (SiO_2/hexanes) to yield 205 mg (82%) of **5** as a colorless waxy solid that turns purple upon exposure to UV light. Mp = 81–84 °C. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.55 (td, J = 8.4, 1.5 Hz, 2H), 7.39 (t, J = 8.4 Hz, 2H), 7.32–7.29 (m, 1H), 7.27 (s, 1H), 7.09 (s, 1H), 1.97 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (CD_2Cl_2, 600 MHz): δ 144.36, 143.06, 142.23, 133.76, 129.91, 129.55, 128.55, 128.38, 126.10, 126.06, 125.95, 125.91, 122.78, 110.37, 14.91, 14.80.

2.5. Synthesis of 4-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)aniline (*6*)

A solution of bromide **5** (195 mg, 0.372 mmol) in toluene (5 mL) was treated with an aqueous solution of Na_2CO_3 (2 M, 0.93 mL, 1.86 mmol), EtOH (1 mL) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (98 mg, 0.446 mmol). The reaction mixture was deoxygenated by bubbling dry nitrogen through it for 20 min. A condenser was fitted to the flask and the system was purged. Solid $Pd(PPh_3)_4$ (22 mg, 0.019 mmol) was added in one portion and the reaction was heated at reflux for 21 h. The reaction mixture was then diluted with water and EtOAc, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to a dark brown oil. Purification by column chromatography (silica gel, 1:1 hexanes:CH_2Cl_2, 1% Et_3N) yielded 168 mg (84%) of **6** as a light yellow oil that becomes blue after exposure to UV light. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.60–7.58 (m, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.38–7.36 (m, 3H), 7.32 (t, $J = 7.8$ Hz, 1H), 7.17 (s, 1H), 6.70–6.78 (m, 2H), 3.86 (s, 2H), 2.01 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (CD_2Cl_2, 600 MHz): δ 171.23, 147.29, 143.45, 142.58, 142.03, 140.10, 133.73, 129.36, 128.26, 127.29, 127.10, 126.22, 125.90, 125.85, 123.88, 122.85, 120.51, 116.74, 115.03, 113.41, 111,61, 109.82, 60.63, 21.14, 14.72. HRMS (ESI$^+$) Calculated for $C_{27}H_{20}NF_6S_2$ [M + H$^+$]: 536.0941. Found: 536.0944.

2.6. *Synthesis of N-(4-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)phenyl)acrylamide (**1-o**)*

A solution of amine **6** (160 mg, 0.299 mmol) in THF (2 mL) and Et_3N (46 ml, 0.329 mmol) in a vial was treated drop-wise over 10 min with a solution of acryloyl chloride (27 ml, 0.329 mmol) in THF (0.75 mL) at 0 °C. After the addition was complete, the ice bath was removed and the reaction mixture was allowed to stir at ambient temperature for 22 h. The suspension was diluted with THF and vacuum filtered, the supernatant was concentrated and purified several times by column chromatography (SiO_2/1:1 hexanes:CH_2Cl_2) to yield 70 mg (39%) of monomer **1-*o*** as a white solid that becomes blue upon exposure to UV light. Mp: 208–210 °C. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.64 (d, $J = 7.8$ Hz, 2H), 7.60 (s, 1H), 7.56 (d, $J = 7.9$ Hz, 2H), 7.53 (d, $J = 7.8$ Hz, 2H), 7.34 (t, $J = 7.8$ Hz, 2H), 7.34–7.25 (m, 3H), 6.41 (d, $J = 16.8$ Hz, 1H), 6.28 (dd, $J = 16.8$, 10.2 Hz, 1H), 5.77 (d, $J = 10.2$ Hz, 1H), 1.98 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (CD_2Cl_2, 600 MHz): δ 163.65, 142.59, 142.09, 141.98, 141.68, 138.08, 136.55, 136.39, 133.58, 131.35, 129.69, 129.30, 128.23, 128.09, 126.42, 126.03, 125.83, 125.61, 122.68, 122.25, 120.45, 118.28, 116.74, 116.58, 114.88, 111.64, 111.47, 111.30, 14.72, 14.69. HRMS (ESI$^+$) Calculated for $C_{30}H_{21}F_6NOS_2$ [M + H$^+$]: 590.0970. Found: 590.1037.

2.7. *Synthesis of photochromic copolymer **P1-o***

A solution of monomer **1-*o*** (65 mg, 0.11 mmol) and *N*-isopropylacrylamide (150 mg, 1.33 mmol) in anhydrous *N*,*N*-dimethylformamide (5 mL) in a sealable glass tube was treated with 1,1′-azobis(cyclohexane-1-carbonitrile) (VAZO 88) (17 mg, 0.07 mmol) in one portion. The resulting solution was degassed by freeze-pump-thawing and then heated to 100 °C and stirred there for 48 h. After cooling, the solvent was evaporated and the residue was dissolved in acetone. This solution was treated with distilled water at room temperature to precipitate the product (three times). The final residue was collected by filtration and re-dissolved in EtOAc. This solution was treated with excess cold hexanes to precipitate high molecular weight copolymer product (three times) until no oligomers were observed on TLC plate. **P1-*o*** was obtained as a white amorphous powder (190 mg, 82%). ^{1}H NMR (acetone-d$_6$, 400 MHz): δ 7.76–7.07 (br, 53H), 3.99 (br, 29H), 2.91–2.88 (br, 16H), 2.22 (br, 32H), 1.66 (br, 64H), 1.42 (s, 7H), 1.29 (s, 6H), 1.13 (br, 177H), 0.88–0.83 (m, 9H). ^{13}C NMR ($CDCl_3$, 600 MHz): δ 174.30, 171.98, 142.41, 142.18, 141.45, 140.90, 133.48, 129.18, 125.77, 122.54, 121.86, 120.35, 118.03, 116.35, 114.66, 42.66, 41.49, 35.76, 29.25, 27.08, 22.80, 14.74, 14.68, 11.61. $M_n = 5097$ g mol^{-1}, $M_w = 5957$ g mol^{-1} (PDI = 1.17).

2.8. *Synthesis of **P1-o** nanoparticles*

A solution of copolymer **P1-*o*** (0.5 mg) in THF (1 mL) was placed in a 50 mL round-bottom flask and irradiated with 313 nm light until the photostationary state (PSS) was reached. The dark blue solution was quickly treated with distilled water (25 mL) while the flask was continuously irradiated with 313 nm light. A portion of the mixed solvent (5–10 mL) was removed using a rotary evaporator at 50 °C in the dark. The mixture was then diluted with distilled water until a final volume of 25 mL was reached. This step was also carried out while irradiating the mixture with 313 nm light. The final aqueous suspension was stirred vigorously for 5 min with a magnetic stir bar in the dark. ^{1}H NMR spectroscopy (acetone-d$_6$, 400 MHz, 25 °C) of the final **P1-*o*** nanoparticles suspension confirmed that no residual THF remained in the aqueous suspension as no peaks corresponding to the protons of the THF solvent were observed in the spectrum. The ring-open form of the **P1-*o*** nanoparticles were fabricated using the same methods described above except that the PSS was not generated and all synthetic procedures were performed under visible light (wavelengths greater than 500 nm).

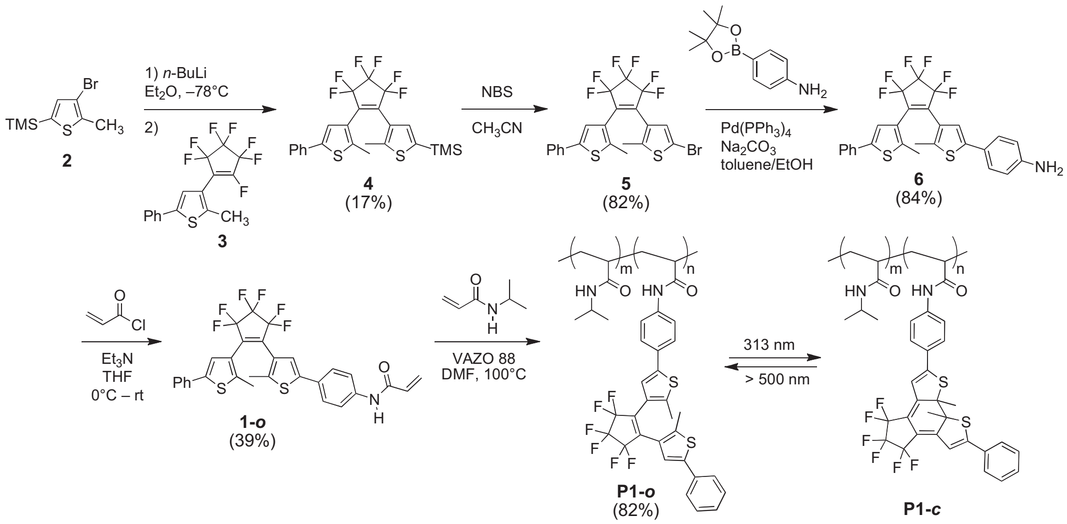
2.9. *TEM sample preparations of **P1-o** nanoparticles*

TEM samples of **P1-*o*** nanoparticles were prepared by dropping their aqueous suspensions on copper grids, followed by drying them overnight at room temperature.

3. Results and discussion

The synthetic pathway to acrylamide-functionalized photochromic monomer **1-*o*** and its multifunctional copolymer **P1-*o*** is illustrated in Scheme 2. The key intermediate is the non-symmetric dithienylethene **6**, which possesses an appropriate amine to convert it to the required acrylamide group. Compound **6** was prepared from thiophene **2** in 3 steps as shown in the scheme. The resulting monomer **1-*o*** was copolymerized with *N*-isopropylacrylamide (NIPA) using free radical methods and VAZO 88 (1,1′-azobis(cyclohexane-1-carbonitrile)) as the initiator. In the present case, the ratio of monomers was chosen to produce a random copolymer with substantially less of the photochromic component (**1-*o***) than NIPA (‘m’/‘n’ = 12) in order to ensure there is enough microscopic flexibility to allow the photo-induced cyclization of the DTE components [22]. As illustrated by the structure shown in Scheme 2, **P1-*o*** possesses an amphiphilic structure, with a hydrophilic PNIPA backbone and hydrophobic DTE pendant groups [23]. The ^{1}H NMR spectrum of an acetone-*d*$_6$ solution of the **P1-*o*** demonstrates that approximately 8 mol-% of the polymer is the photochromic component (**1-*o***) corresponding almost exactly to the co-monomer feed ratio. The polymer’s molecular weight (M_w) and glass transition temperature (T_g) were measured to be 5957 g mol^{-1} (PDI = 1.17) and 128 °C, respectively.

Through the selective evaporation of THF solvent from a THF/water solution of photochromic, polymeric **P1-*o***, quite uniform-sized (150 ± 50 nm, 2 × 10^{-3} wt-% in water) and highly stable (over several weeks) copolymeric nanoparticles were successfully fabricated. Fig. 1(a, b, d and e) show the transmission electron microscope (TEM) images of these **P1-*o*** nanoparticles. As shown in these figures, every polymeric nanoparticle has a hole in its soft skin. We suggest that the defect-like holes in the skins of the nanoparticles are formed as a consequence of rapid evaporation of the water captured within the nanoparticles during the high vacuum sample processing and/or imaging using TEM [24].



Scheme 2. Synthesis and photochromic reactions of copolymers **P1-*o***. The mixture of **P1-*o*** and **P1-*c*** produced with UV light is referred to as **P1-*pss*** in this manuscript.

Fig. 2(a) shows the UV–Vis absorption spectra of an aqueous suspension containing the **P1-*o*** nanoparticles, in which light scattering features are clearly observed as a result of nanoparticles formation. When the suspension of the nanoparticles in their ring-open form (**P1-*o***) was irradiated with UV light (313 nm, 5.5 mW cm^{-2}), the suspension turned blue and new absorbances in the visible region ($\lambda_{max} = 590$ nm) appeared in its UV–Vis absorption spectrum. This notable coloration clearly suggests that the dithienylethene components in the nanoparticles are undergoing photoisomerization from their ring-open form to their ring-closed form when irradiated with 313 nm light (**P1-*o*** → **P1-*c***). The 313 nm photostationary state (**P1-*pss***) was attained in 2 min, and there were no further spectral changes in the UV–Vis absorption spectrum. Moreover, the UV–Vis absorption spectrum in the 313 nm PSS is almost the same as that for the suspension of **P1-*pss*** nanoparticles containing over 98% of ring-closed DTEs (this nanoparticle suspension was prepared from a THF solution of **P1-*pss*** already in its 313 nm photostationary state, in which the photochromic conversion from ring-open to ring-closed form (**P1-*o*** → **P1-*c***) was greater than 98% as determined by ^{1}H NMR spectroscopy). Accordingly, it was estimated that the photochromic ring-closing conversion in the **P1-*o*** nanoparticles was also over 98%. This highly efficient photoisomerization of the photochromic molecules in the **P1-*o*** nanoparticles suggests that they have enough free volume and conformational flexibility to accommodate the structural changes that accompany the photoisomerization. This consideration was also supported by the fact that the molar concentration of the hydrophobic DTE component (co-monomer **1-*o***) was much lower than that of the hydrophilic acrylamide backbone components in **P1-*o*** (~8 mol-%). More interestingly, the light scattering by the ring-closed nanoparticles in the 313 nm **P1-*pss*** was higher than that observed for the ring-open form **P1-*o*** nanoparticles in near-infrared (NIR) region (750–850 nm) as shown in the Fig. 2(a). On the basis of the fact that both ring-open and ring-closed forms of the photochromic component have no absorbances in the NIR (Fig. 2(b)), these characteristic light scattering features indicated that the volumes occupied by photochromic nanoparticles are larger in the 313 nm photostationary state [25,26]. The blue-coloured 313 nm PSS suspension of the nanoparticles could

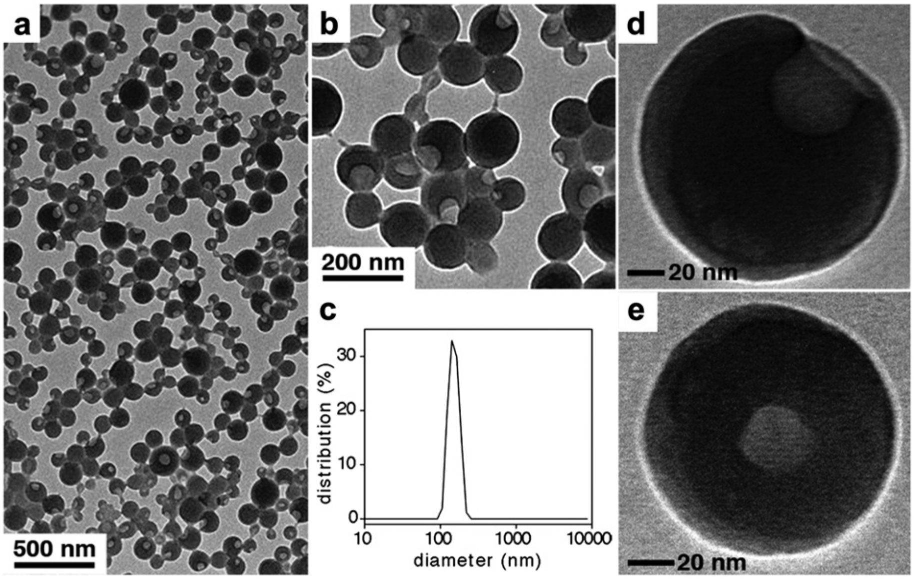


Fig. 1. Transmission electron microscope (TEM) images of the copolymeric nanoparticles **P1-*o*** with the DTE in its ring-open form. Frame (c) shows a representative particle-size-distribution spectrum of open-form **P1-*o*** nanoparticles in an aqueous suspension at room temperature.

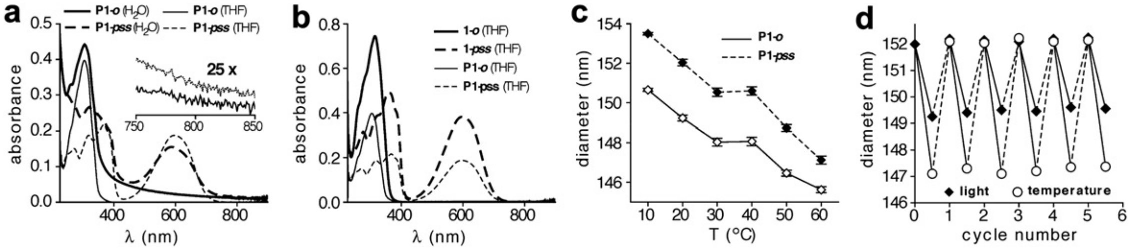


Fig. 2. (a) UV–Vis absorption spectra of a THF solution of **P1-*o*** (2.27 × 10^{-3} wt-%) and an aqueous suspension of **P1-*o*** nanoparticles (2 × 10^{-3} wt-%) at room temperature before and after irradiation with UV light. (b) UV–Vis absorption spectra of THF solutions of **1-*o*** (2 × 10^{-5} M) and **P1-*o*** (2.27 × 10^{-3} wt-%) before and after irradiation with UV light. (c) Average hydrodynamic diameter changes of **P1-*o*** and **P1-*pss*** nanoparticles at various temperatures. (d) Reversible switching of average hydrodynamic diameters of **P1-*o*** nanoparticles with alternate exposure to UV light (313 nm, 5.5 mW cm^{-2}, 2 min; dashed line) and visible light (>500 nm, 300 W, 5 min; solid line) at 20 °C and with alternating high (60 °C; solid line) and low (20 °C; dashed line) temperatures at the 313 nm photostationary state.

be bleached by irradiation with visible light (>500 nm, 300 W) to fully recover the original UV–Vis absorption profile of the suspension of ring-open **P1-*o*** nanoparticles.

Fig. 2(c) shows the characteristic average hydrodynamic diameters of **P1-*o*** nanoparticles in an aqueous suspension as determined by particle-size analysis (PSA) at various temperatures [27]. The average hydrodynamic diameters shown in Fig. 2(c) were measured over 30 times at each data point to reduce the experimental error and a representative particle-size-distribution spectrum of an aqueous suspension containing ring-open **P1-*o*** nanoparticles at room temperature is illustrated in the inset in Fig. 1(c). As presented in Fig. 2(c), the average hydrodynamic diameters of ring-open **P1-*o*** nanoparticles decreased continuously with increasing temperatures, with a change in the temperature dependence near the lower critical solution temperature (LCST) of PNIPA (∼33 °C), and the diameters were highly reproducible when the temperature was varied either by heating or cooling. These characteristic changes of the hydrodynamic diameter of the ring-open **P1-*o*** nanoparticles depending on the temperature likely results from the reversible degree of swelling of water molecules into the **P1-*o*** nanoparticles [27]. Intramolecular hydrogen bonding within each PNIPA chain is more favorable than the intermolecular interaction between the PNIPA chains and the water molecules at higher temperatures [16,17,28,29], thus the number of water molecules swelled in the **P1-*o*** nanoparticles decreases with increasing temperatures, which results in the smaller average hydrodynamic diameters of the **P1-*o*** nanoparticles at higher temperatures. In addition, the zeta potential (ζ) values of the ring-open **P1-*o*** nanoparticles followed these characteristic changes precisely. The ζ values of the ring-open **P1-*o*** nanoparticles were −37 mV at 20 °C, −35 mV at 40 °C, and −27 mV at 60 °C, and these values were also temperature-dependent and highly reproducible in the same way as the average hydrodynamic diameters of the ring-open **P1-*o*** nanoparticles. The higher degree of swelling of water molecules into the ring-open **P1-*o*** nanoparticles at lower temperatures is the likely cause of the higher negative ζ values (or the higher stabilities) of the **P1-*o*** nanoparticles. On the other hand, the average hydrodynamic diameters of the **P1-*o*** nanoparticles increased by several nanometers upon switching to the 313 nm PSS as shown in Fig. 2(c). Given that the photochromic conversion from ring-open form to the ring-closed form of the DTE photoisomers in the nanoparticles was over 98% at the 313 nm PSS, and that the ring-closed photoisomers of DTE derivatives generally have more rigid structures [12–15], the larger diameters of the **P1-*pss*** nanoparticles in the 313 nm PSS can be attributed to the change in the shape and rigidity of the pendant DTE groups within the **P1-*o*** nanoparticles. This conversion into the larger diameters was also consistent with the higher light scattering features at the NIR regions in their UV–Vis absorption spectra at the 313 nm photostationary state (Fig. 2(a)). In addition, the ζ values of **P1-*pss*** nanoparticles at the 313 nm photostationary state were all higher than those of the ring-open **P1-*o*** nanoparticles at all investigated temperatures (−44 mV at 20 °C, −39 mV at 40 °C, and −30 mV at 60 °C at the 313 nm PSS). Moreover, the average hydrodynamic diameters of **P1-*pss*** nanoparticles in the 313 nm photostationary state recovered to those for the ring-open **P1-*o*** nanoparticles at each temperature, within experimental error, after irradiation with visible light (>500 nm, 300 W), and the ζ values as well as the light scattering features at the NIR regions precisely corresponded to these reversible changes in hydrodynamic diameters. Taken as a whole, these results suggest that the change in the shape and rigidity of the DTE molecules in **P1-*o*** nanoparticles followed by photochemical ring-closure should expand the diameters of the **P1-*o*** nanoparticles mechanically or that the ring-closed form of the DTE components in the 313 nm photostationary state could enhance the degree of swelling of water molecules into the amphiphilic nanoparticles [12–15]. On the basis of these results, the average hydrodynamic diameters of **P1-*o*** nanoparticles could be switched reversibly between two bistable states not only with alternate UV and visible light irradiation at 20 °C but also with alternate high (60 °C) and low (20 °C) temperatures in the 313 nm photostationary state as shown in Fig. 2(d).

4. Conclusion

A novel kind of amphiphilic photochromic copolymer **P1-*o*** consisting of a hydrophilic PNIPA backbone and hydrophobic DTE pendants was designed, synthesized and used to fabricate self-assembled copolymer nanoparticles in an aqueous condition. The hydrodynamic diameters (or volumes) of these multifunctional **P1-*o*** nanoparticles reversibly switched between two bistable states with the dual stimuli of light and temperature in an aqueous suspension.

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