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Synthesis and photochromic property of nanoparticles with spiropyran moieties via one-step miniemulsion polymerization

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Summary

Photochromic nanoparticles with spiropyran moieties were prepared by a facile one-step miniemulsion polymerization. The nanoparticle dispersion was obtained by mixing the monomers, spiropyran-containing molecules and hydrophobe, dispersing them into an aqueous solution with surfactant, subjecting the dispersion to ultrasonification and polymerizing the monomers by using a water soluble initiator. The shape and size of the nanoparticles was determined with the atomic force microscope (AFM) and dynamic light scattering (DLS), and the determined average diameter of the nanoparticles ranges from 30 nm to 60 nm. The absorption and fluorescence spectra for the nanoparticles dispersions reveal that the spiropyran molecules were successfully incorporated in the polymer nanoparticles. Moreover, the nanoparticle dispersions were found to exhibit enhanced photo-reversibility, photo-stability and relatively fast photo-responsive property compare to the same species in aqueous solution.

Introduction

In recent years, the design and synthesis of photoresponsible polymers for their potential optical applications, such as data storage, photo-optical switches, metal ions removal and regeneration and display devices have been developed [1-7]. Spiropyran, as one of the promising families of photochromic compounds, undergoes photo-reversible structural transformations in response to external inputs such as light [8-12]. The spiropyran molecules can adopt one of two stable states: the open-ring state, known as the protonated merocyanine (MC) form, and the closed-ring state, known as the spiro (SP) form. Upon the irradiation of UV light, the spiropyran molecules adopt the MC form (coloration); while with visible light, they adopt the SP form (decoloration) [9, 13]. By employing this special property of spiropyran molecules, various optically-controlled molecular switches have been constructed with photochromic spiropyran as one component of the molecules [14-16].

In general, photoresponsible devices require that either the nanostructure or the molecular structure be responsive to an external stimulus, in this case, light. However, in conventional photoresponsible molecular devices still tend to aggregate in aqueous media which usually lead to change in their optical properties; in addition, they usually lack the necessary biocompatibility for applications in the fields of biotechnology [17, 18]. Thus the development of the photoresponsible fluorescent nanoparticle is important because it opens new possibilities for developing individually addressable nanoscale devices. For biological applications, the photoreversible fluorescent nanoparticles can be used to selectively highlight cells or proteins [19, 20]. To date, there have been a few studies on photoreversible fluorescent nanoparticles [21-26]. For example, Kim [21] et al. synthesized a class of polystyrene nanocapsules containing diarylethenes and spirobenzopyran photochromophores. However, the spirobenzopyran derivative containing nanocapsule solution was unstable. Very recently, Zhu et al. incorporated a photochromic spiropyran dye into polymer nanoparticles to generate optically addressable systems, and they could use light to switch the color of the nanoparticles [22].

In most cases, the photoresponsible nanoparticles have been prepared through physical adsorption or covalent binding to incorporate the chromophore molecules into the vehicles, and the preparation procedures are complicated. In order to simplify the synthesis route, control the chromophore load in the nanoparticles, we anticipated that the miniemulsion polymerization can achieve the purpose. During the miniemulsion polymerization, aqueous dispersions of relatively stable and small oil (oilsoluble monomer) droplets can be obtained by using high shear dispersion devices such as an ultrasonicator and/or a high pressure homogenizer; moreover, droplet nucleation is predominant and monomer droplets grow to be polymer particles in miniemulsion polymerization [27, 28]. According to the mechanism of miniemulsion polymerization, once the chromophore molecules are include in the monomer droplet, they can remain inside the droplet till the completion of polymrization. Thus, the miniemulsion polymerization is suitable for encapsulation of chromophore molecules into polymer particles [29-31]. So, this particle preparation method may provide a feasible strategy to fabricate the chromophore-containing nanoparticles.

In this study, we synthesized the spiropyran-containing photochromic nanoparticles in aqueous media via a facile one-step miniemulsion polymerization. Our preliminary experimental results indicated that the stable and small (30-70 nm) photoreversible spiropyran-containing nanopartilces were successfully prepared, and the nanoparticles display high photo-stability, good photo-reversibility, and relatively fast photo-responsive property.

Experimental

Materials

Sodium dodecyl sulfate (SDS, Aldrich), n-hexadecane (HD, Aldrich) 2,3,3-trimethylindolenine (Aldrich), 3-iodopropanoic acid (Aldrich), *N,N'*-dicyclohexyl-carboiimide (DCC, Alfa Aesar), 4-dimethylamino-pyridine (DMAP, Alfa Aesar) and 5-nitrosalicylaldehyde (Aldrich) were used as received. Dichloromethane (DCM, A. R.) was washed with sulfuric acid and then distilled from CaH_2. 2-hydroxyethyl methacrylate (HEMA, 97%, Aldrich) was dissolved in water (25 vol%) and washed four times with an equal volume of hexane, then dried over $MgSO_4$ and distilled under vacuum prior to use. Potassium persulfate (KPS, Aldrich) was recrystallized from deionized water and dried under vacuum. The phenolic inhibitor in methyl methacrylate

(MMA, Aldrich) was removed by washing three times with 10% sodium hydroxide solution and then with deionized water until the pH of the water phase was 7, and then it was further purified by vacuum distillation. The water used in this work is the double-distilled water which was further purified with a Milli-Q system. Tetrahydrofuran (THF, A.R.) was distilled over CaH2. Petroleum ether, benzene, and other reagents were analytical reagents and used without further purification.

Characterization

^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer; UV-vis spectra were obtained on a Hitachi U-3010 UV-vis spectrophotometer at room temperature; Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The nanoparticles diameter distribution was determined by MALVERN Nano-ZS90 instrument. The nanoparticles morphology was observed with a Seiko SII atomic force microscope (AFM) in the tapping mode at room temperature.

Synthesis of the carboxyl-containing spiropyran (SPCOOH)

During the synthesis process, all the reaction vessels were wrapped with aluminum foil, so as to ensure the reaction was performed in the dark [32]. The carboxyl-containing spiropyran l-(β-carboxyethyl)-3’,3’-dimethyl-6 -nitrospiro (indoline-2’,2 [2*H*-1] benzopyran) (referred to as SPCOOH) was synthesized as follows: 2,3,3-trimethylindolenine (0.06 mol), 3-iodopropanoic acid (0.06 mol) and ethyl methyl ketone (5ml) were heated under nitrogen at 100°C for 3 h. The resulting solid material was dissolved in water, and the solution was washed with chloroform. Evaporation of water gave l-(β-carboxyethyl)-2,3,3-trimethylindolenine iodide (73% yield). The above-obtained iodide (0.04 mol), 5-nitrosalicylaldehyde (0.04 mol), and piperidine (3.8 mL, 0.04 mol) were dissolved in ethyl methyl ketone, and the red solution was refluxed for 3 h. On standing overnight, the product precipitated as a yellow crystalline powder. This was filtered and washed with methanol to give the product SPCOOH (75% yield). 1H NMR (400 MHz, DMSO-d$_6$, δ): 1.0-1.3 (s, 6H; CH_3), 2.6 (t, J = 6.8 Hz, 2H; CH_2), 3.4-3.5 (t, J = 6.4 Hz, 2H; CH_2), 5.9-6.0 (d, 2H; vinylic), 6.6-8.2 (m, 7H; aromatic), 12.0 (s, 1H; COOH).

Synthesis of SPMA from SPCOOH

SPCOOH (3.8 g, 10 mmol), HEMA (2.6 g, 20 mmol) and DMAP (0.272 g, 2 mmol) were added to a 100 ml round-bottomed flask equipped with a pressure-equalized dropping funnel, magnetic stirrer and a nitrogen inlet. Dry THF (80 ml) was added to the flask and the solution was cooled to 0°C, a red/brown solution resulted. A solution of DCC (2.06 g, 10 mmol) was prepared in dry THF (20 ml) in a small round-bottomed flask. The DCC solution was added to the SPCOOH/HEMA solution via the pressure-equalized dropping funnel over 45 minutes. The flask was maintained at 0°C for 2 hours, then was raised gradually to 25°C over 24 hours. The product was filtrated with cold (0°C) dry THF (3×50 mL) giving a red filtrate. Most of solvent was evaporated from the filtrate under vacuum, then, the product was washed by distilled water to give a red/purple precipitate. The precipitate was dissolved in benzene and filtrated again, afterwards most of the solvent was evaporated, the solution was precipitated in a large amount of petroleum ether, finally a fine red/purple precipitate of purified 2-(3-(3',3'-dimethyl-6-nitrospiro(indoline-2',2-[2*H*-1]benzopyran)-1'-yl) propanoyloxy)-ethyl methacrylate (SPMA) was obtained. The target product was dried in vacuum oven overnight at room temperature.

Miniemulsion polymerization of spiropyran- containing nanoparticles

A mixture containing the monomers and hydrophobe (MMA, EDMA, SPMA, HD) was added to a water solution with emulsifier (SDS) and it was then stirred (at 1000 r/min) for 20 min at 0°C, then the mixture was ultrasonicated for 15 min (420 W) to obtain a miniemulsion. Afterwards, the miniemulsion was put into a 50 mL three-necked flask equipped with a condenser and a gas inlet, which was immersed in an oil bath with a thermostat. The mixture was stirred and degassed with nitrogen for 30 min at 60°C, and the polymerization was started by adding aqueous solution of KPS and preceded at 60°C for 210 min. After the polymerization, the as-prepared spiropyran-containing nanoparticle dispersions were dialysed against distilled water for 48 h to remove water-soluble impurities from the dispersions, and finally the nanoparticles dispersion was obtained.

Results and discussion

Preparation of spiropyan-containing nanoparticles

In order to synthesize a photochromic nanoparticle via miniemulsion, we first synthesized SPCOOH according to literature [29], which is a carboxyl-containing spiropyran and referred to as SPCOOH. By esterification of SPCOOH with HEMA, we obtained a spiropyran-containing methacrylate monomer (SPMA), and ^{1}HNMR spectrum for SPMA is shown in Figure 1. The NMR result indicates that SPMA was successfully synthesized.

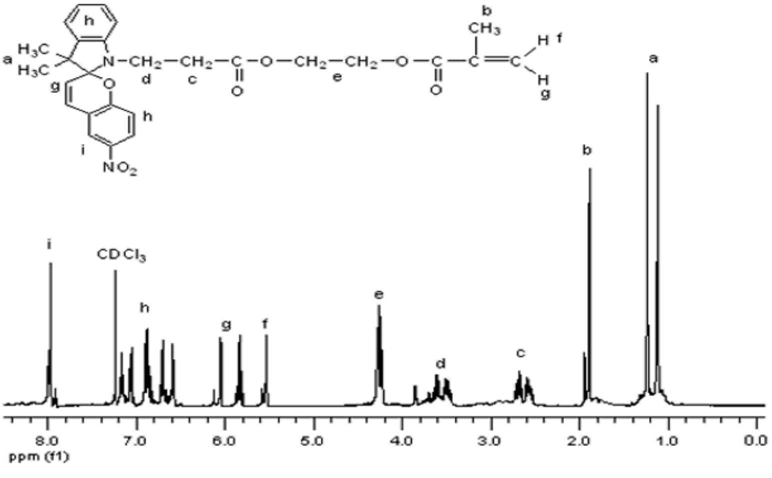

Figure 1. ^{1}H NMR spectrum of acrylate-linked spiropyran (SPMA) monomer. [^{1}H NMR (400 MHz, CDCl$_3$, δ): 1.0-1.3 (s, 6H; CH$_3$), 1.8-1.9 (s, 3H; CH$_3$), 2.6-2.7 (t, J = 6.8 Hz, 2H; CH$_2$), 3.5-3.6 (t, J = 6.4 Hz, 2H; CH$_2$), 4.2 (m, 4H; CH$_2$), 5.5-6.0 (d, 2H; vinylic), 6.1-6.5 (d, 2H; vinylic), 6.6-8.1 (m, 7H; aromatic)].

As for the preparation of the spiropyran-containing nanoparticles, the procedure is similar to literature report [21], except that an additional spiropyran-linked methacrylate (SPMA) monomer was used in the reaction and covalently incorporated into the nanoparticles. For this preparation, a water soluble initiator KPS was used to initiate the miniemulsion polymerization of the mixture of MMA/SPMA/HD monomer in an aqueous solution containing surfactant (SDS). The averaged particle diameter ranged from ca. 37 nm to ca. 74 nm, depending on the amount of surfactant (SDS) used. Specifically, for sample NP-SDS2, at 1:50 weight ratio of SDS to MMA, we can obtain a stable dispersion of nanoparticles with the particle diameter of ca. 45 nm, as shown in Figure 2. The average particle sizes for the samples determined by DLS are listed in Table 1. DLS measurement shows a mono-modal size distribution (Figure 2B).

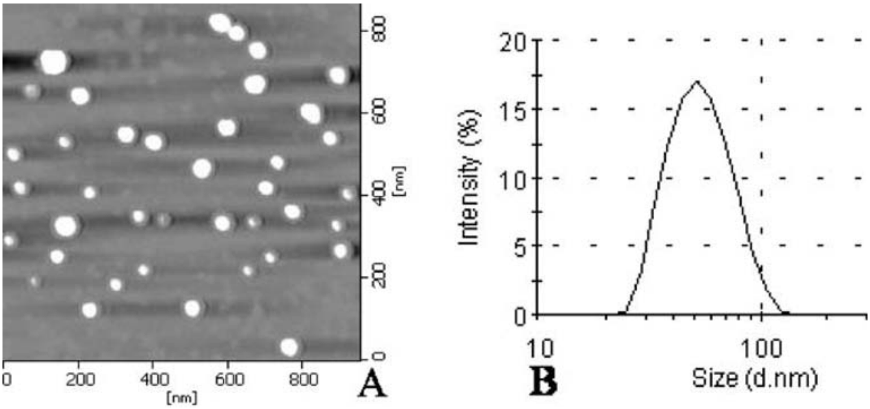

Figure 2. (A) AFM image of spiropyran-containing nanoparticles (sample NP-SDS2); (b) Size distribution for the same sample determined by light scattering.

Table 1. List of spirpopyran-containing nanoparticle samples prepared with various content of SDS in this work

Sample [a]	SDS feed (g)	Particle size [b] (diameter, nm)
NP-SDS1	0.05	73.6±15.8
NP-SDS2	0.1	54.9±8.9
NP-SDS3	0.4	41.6±6.2
NP-SDS4	0.6	40.5±8.1
NP-SDS5	1	37±6.5

a: All experiments were carried out at 60°C, using 5 g of MMA, 0.3 g of HD, 0.1 g of SPMA, 0.17 g KPS and 55 g of water; b: Determinated from DLS data

Photochromic property of nanoparticles

The absorption spectra for spiropyran-linked methacrylate monomer (SPMA) in dichloroethene and the water dispersion of spiropyran-containing nanoparticles upon UV or visible light irradiation are shown in Figure 3. It is well known that spiropyran molecules can present one of two stable states: the open-ring state, known as the protonated merocyanine (MC) form, and the closed-ring state, known as the spiro (SP) form. Upon irradiation of UV light, the spiropyran molecules adopt the MC form; while with visible light, they adopt the SP form [9]. As for the SPMA, after visible light irradiation, the spiropyran moieties assumed the SP form and exhibited no absorption band from 400 to 700 nm; while after UV irradiation, a new absorption band at 580 nm appeared due to the formation of the MC form, as shown Figure 3A. Figure 3B shows the absorption spectra for a spiropyran-containing nanoparticle dispersion under UV and visible light irradiation respectively. The absorption behavior for the dispersion is similar to that of the spiropyran-linked methacrylate monomer, except that the light scattering effect of nanoparticles makes the absorption curves exhibit a slightly declined trend from low wavelength to high wavelength. This absorption behavior of nanoparticles indicates that the spiropyran-containing nanoparticles can exhibit photochromic behavior in aqueous media.

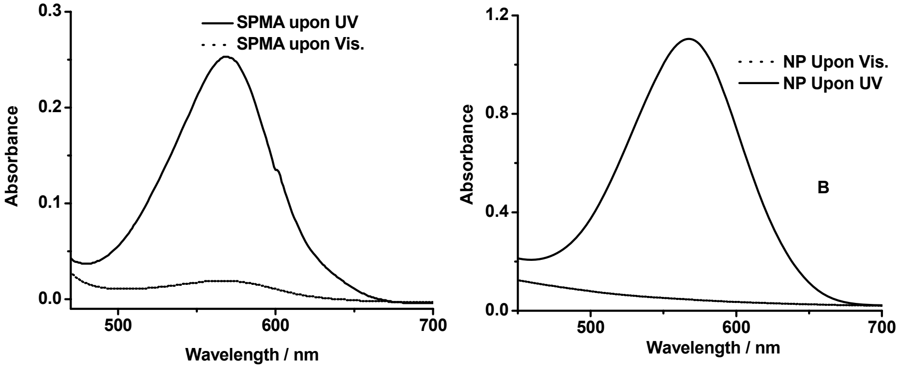

Figure 3. Absorption spectra for the SPMA monomer in dichloroethene (A), and the spiropyran containing nanoparticles (sample NP-SDS2) in water (B) upon UV or visible light irradiation.

As for the fluorescence emission, the MC form of spiropyran moieties possesse detectable fluorescence in polar organic solvents [16] and within self-assembling films [33]; while in water, the SP or MC form exhibits very weak emission. However, it was reported that that the spiropyrans displayed strong emission as they resided in hydrophobic environment [22], and the reason for that is, the spiropyran fluorophores confined within the hydrophobic cavities with protective shells are isolated from nonradiative decay pathways or electron-transfer pathways generated by collisions with solution components, thus spiropyran can exhibit stronger emission. In this study, as shown in figure 4, when the nanoparticle dispersion was irradiated by UV, the MC form of spiropyran exhibited a strong fluorescence at 650 nm, indicating the spiropyran moieties resided the hydrophobic environment. It also proves that we have successfully incorporated the SPMA moieties into the hydrophobic nanoparticles via miniemulsion polymerization.

Figure 5 shows the change in appearance of the SP containing nanoparticles upon visible light or UV irradiation. The colour of the nanoparticles solution turns into purple after UV irradiation and revert to pale yellow after visible light illumination. The purple colour corresponds to the MC form of SPMA moieties in the nanoparticles, while the pale yellow corresponds to the SP form. Thus, by forming the spiropyran containing nanoparticles, the hydrophobic spiropyran moieties can exhibit their photochoromic property in water.

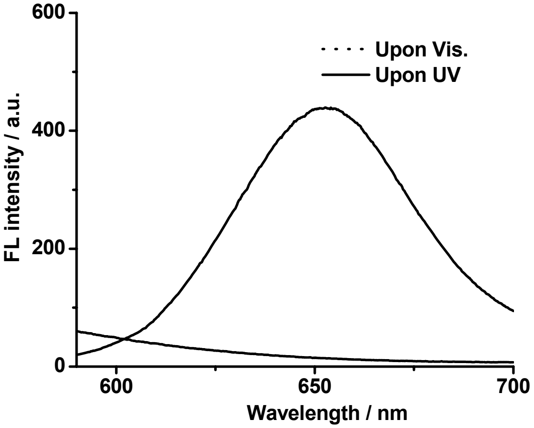

Figure 4. Fluorescence emission (excited at 490 nm, 25°C) of photo-reversible nanoparticles upon UV irradiation (300 nm) or visible light (525 nm) irradiation.

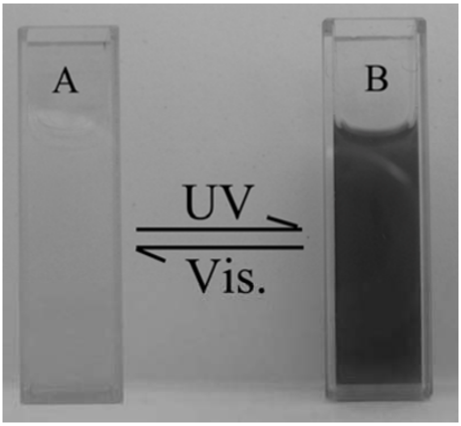

Figure 5. Photograph for the photoreversible spiropyran-containing nanoparticles in aqueous solution after visible light irradiation (A) and UV irradiation (B).

Photoreversibility of the nanoparticles

Figure 6 reflects the reversible photochromic property of the nanoparticle dispersion. With the UV irradiation, the absorbance at 570 nm gradually increased; while with the visible light irradiation, the absorbance gradually decreased. The decay of absorption of spiropyran-containing nanoparticle dispersion is due to the photoinduced conversion from MC form to SP form of spiropyran moieties. The photoresponding speed for the nanoparticle dispersion is rather fast compared to that of some water soluble spiropyran derivatives, and this process for the latter is slow because the water tends to stabilize the zwitterionic MC form. [21]. In present study, the spiropyran groups reside in the hydrophobic nanoparticles, in which the zwitterionic MC form can not be stabilized by the water, thus the reversible photochromism of spiropyran-containing nanoparticles can be much fast.

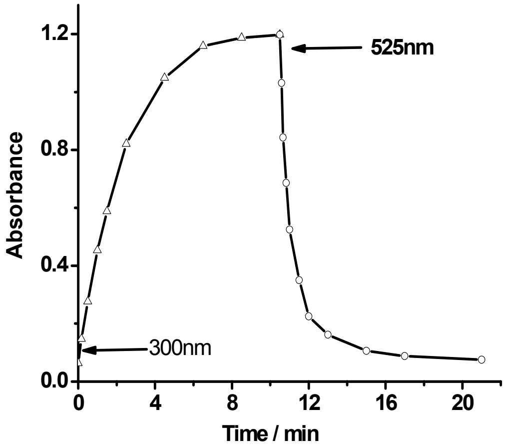

Figure 6. The absorption spectral changes of dispersed SP containing nanoparticles upon UV irradiation (300 nm, 15 W) and visible bleaching (525 nm, 15 W).

The reversible nature of the fluorescence switching for the spiropyran-containing nanoparticle dispersion upon exposure to alternating cycles of UV light (300 nm) and visible light (525 nm) illumination is illustrated in Figure 7. The visible light or UV can be applied to reversibly "turn on" and "turn off" the fluorescence of spiropyran containing nanoparticles. On the other hand, for spiropyran moieties, the "fatigue" effects caused by photodegradation of spiropyran under UV-irradiation have been commonly observed and discussed extensively elsewhere [35]. However, from Figure 7 one can see that, the incorporation of spiropyran dye into the hydrophobic environment can make the spiropyran-containing nanoparticles exhibit quite good photo-reversibility, the optical switching of fluorescence can be repeated for numerous times without any apparent "fatigue" effects or photobleaching, thus the protective nanoscale environment may impede those UV irradiation-involved photodegradation reactions.

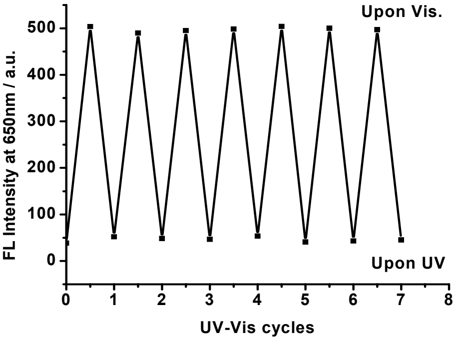

Figure 7. Fluorescence emission intensities for SP/nanoparticle complex in aqueous medium (SPMA concentration: 3.69×10^{-4} M, $\lambda_{ex} = 490$ nm, 25°C) recorded at 650 nm under 25°C upon UV illumination and visible light irradiation cycles.

Conclusions

In summary, the photoresponsible spiropyron-containing nanoparticles were successfully synthesized by a facile one-step miniemulsion polymerization. The spiropyran-containing nanoparticles displayed good photo-reversibility, photo-stability as well as relatively fast photo-responsive property in aqueous dispersion. In addition, this approach can be readily applied to other hydrophobic photochromophores, thus opening up possibilities for their fluorescence modulation in aqueous media.

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