

Properties of the photochromic latexes based on spiropyran by emulsion polymerization

Ting Zhang^{1,2}, Liuwa Fu¹, Zhikang Chen¹, Yanyan Cui¹, Xiaoxuan Liu^{1*}

¹Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, Department of Polymeric Materials and Engineering, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China.

²College of Chemistry and Environment, Minnan Normal University, Zhangzhou, Fujian 363000, China

*Corresponding author

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Abstract

The latexes based on 2-(3', 3'-Dimethyl-6-nitro-3'H-spiro[chromene-2,2'-indol]-1'-yl)ethanol(SPOH) were prepared via emulsion polymerization, using a macromolecular surfactant that copolymerized by methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA). The photochromism of the latexes was characterized by UV-vis spectroscopy. Through the characterization of DLS and SEM, the sizes and morphological of the latexes were studied before and after UV light irradiation. During the thermal fading process, it appeared continuous variable pattern in the emulsion, which was related to the rearrangement of the stimulated latexes to meet the dynamic balance of ionic strength, due to the reversible isomerization of spiropyran. Copyright © 2018 VBRI Press.

Keywords: Spiropyran, photochromic, latex, macromolecular surfactant, aggregates.

Introduction

In recent years, photochromic compounds[1,2] are very fascinating in fields such as molecular logic gates[3], optic/electronic devices[4], sensors[5, 6], bio-imaging[7, 8], due to their ability of reversible optical-switching and changes in physical and chemical properties. Spiropyran[9], as a typical presentation of photoresponse species, can undergo a reversible isomerization between colorless closed-ring spiroisomer SP and colored opened-ring merocyanine (MC) in visible and ultraviolet light. Besides the distinct chromic transition, facile synthesis and self-assembly abilities in certain environments has intrigued scientists and a blooming applications based on spiropyran have been found in data recording[10,11], optical and electrical switching[12-14], light-actuated nanovalves[15] and so on.

By utilization of the reversible color and other changes in physical and chemical properties, spiropyran is usually incorporated into the polymeric matrix for fabrication or commercialization of smart applications[16,17]. Emulsion or miniemulsion polymerization is a versatile method to produce smart polymeric (nano)particles[18]. However, the anionic surfactant which is used to form and stabilize the micelles in most of the emulsion systems may influence on the reversible switching, because the open form MC possesses an electric dipole in a molecule. Meanwhile, the scattering phenomenon of the emulsion affected by particle size will also dominate and suppress other photoactivities[19].

Here, the photochromic functionalized polymeric particles based on spiropyran was prepared by emulsion polymerization. After the characterization of particles, their photochromic properties were studied comprehensively.

Experimental

Provide appropriate experimental details in this section in form of subsections:

Materials

2,3,3-Trimethylindolenin, 2-bromoethanol, 2-hydroxy-5-nitrobenzaldehyde, methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), 1,6-Hexanediol diacrylate (HDDA), N-dodecyl mercaptan (NDM), triethylamine(TEA), ammonium persulfate (APS) and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purchased from Aladdin Industrial Corporation. All chemicals were used without further purification. Deionized (DI) water was used in all recipes.

Material synthesis

2-(3',3'-Dimethyl-6-nitro-3'H-spiro[chromene-2,2'-indol]-1'-yl)ethanol (SPOH) was synthesized according to the method described in the literature[20]. Particles with SPOH were prepared via emulsion polymerization. At first, the premixed solution named "MBA" was prepared by MMA, BA and AA as comonomers with a weight ratio

of 3/3/2, NDM as a chain transfer agent with 4.0 wt.% of the total monomers weight, AIBN as an initiator with 0.8 wt.% and ethyl acetate as the solvent. Then 1/3 volume of the premixture MBA was settled in a 150 mL four-necks flask with a mechanic stirring at 70 °C. The rest was added into the flask dropwise in 3 hrs. The copolymerization was kept at 80 °C for 3 hrs when the instilment was completed. While the copolymer was cooled down at room temperature, TEA with the same molar of AA was added to prepare the macromolecular surfactant. Secondly, SPOH was dissolved in the solution of MMA and HDDA ($m_{\text{MMA}}/m_{\text{HDDA}}=1000/1$) with the weight ratio of 1/50. The SPOH solution was then added into the macromolecular surfactant and dispersed in water under the agitation at 1000 rps for 30 min. At last, the photochromic particles were synthesized from the SPOH emulsion at 70 °C for 3 hrs by the initiation of APS.

Characterizations

Dynamic light scattering (DLS) experiments were carried out on the Brookhaven spectrometer.

The morphologies of the emulsion particles were characterized with a Hitachi S-4800 Scanning Electron Microscope (SEM).

UV-vis absorption spectra were recorded with Purkinje General DSPC1810 UV-VIS spectrophotometer. The UV radiation photoreactor (Mejiro Genossen CHG-200) equipped with an Hg lamp emitting light nominally at 365 nm at the ambient temperature, was fixed left above the samples at a distance of 10 cm. The light intensity of the irradiation source was 1.2 mW/cm², which was measured by a UV radiometer (Photoelectric Instrument Factory of Beijing Normal University, China).

Dynamic studies on the stimulated emulsion during thermal fading process were carried out on an optical microscope Crystallite ST-30 with the magnification from $\times 10$ to $\times 40$.

Results and discussion

Studies on Photochromic Properties

The absorbance of the emulsion particles with photo stimulation had been demonstrated by UV-vis absorbance spectra. As shown in Fig.1, there was a very weak absorption at 500~550nm before UV light irradiation, which was the characteristic absorption band of MC form. It demonstrated that a little SP form had changed into MC form. Under UV light irradiation for a few of seconds, a notable absorption band centered at 550nm appeared, which indicated that the ratio of MC form increased. Then the sample was further placed in darkness, the absorption of MC at 550nm gradually decreased with the increase of time. It would take the stimulated SPOH emulsion a couple of hours to retrieve the initial value in darkness. The process could be accelerated by visible light for a few minutes. During the process of MC form to SP form in darkness, a slight hypochromic effect occurred in the UV-vis spectra.

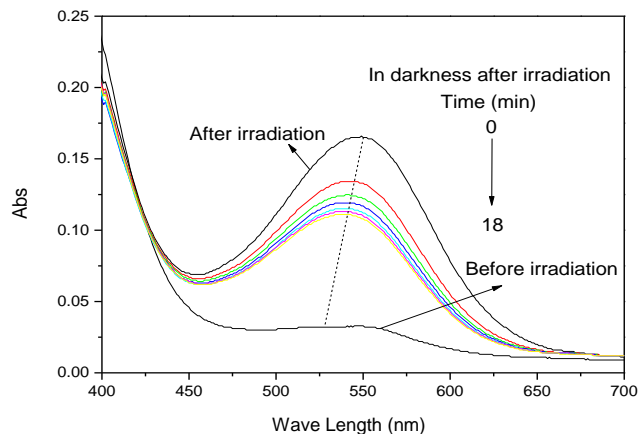


Fig. 1. UV-vis spectra of the latexes containing SPOH.

Size and Morphological Studies

The particles incorporated SPOH were prepared by the emulsion polymerization due to the polymerized surfactant. Before UV light irradiation, particles size and size distribution for the prepared samples were determined by DLS analysis and shown in Fig. 2(a). The obtained average size of the regular particles was 260 nm, and the size distribution was narrow with the polydispersity index (PI) of 0.076. The primary morphology and particle size distribution of photochromic latex particles were studied by SEM as well, the micrograph was shown in Fig. 2(b) which revealed a good agreement with DLS analysis.

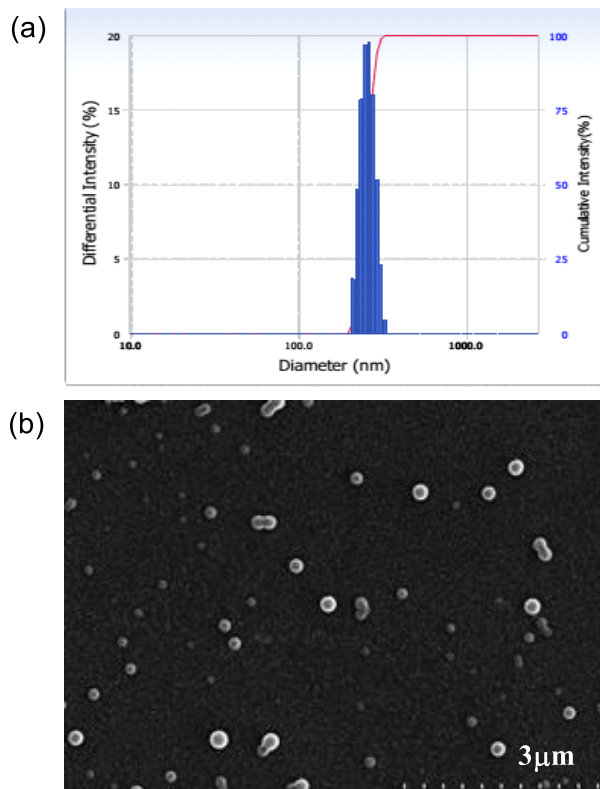


Fig. 2. (a) DLS analysis and (b) SEM image of prepared latexes containing SPOH before UV light irradiation.

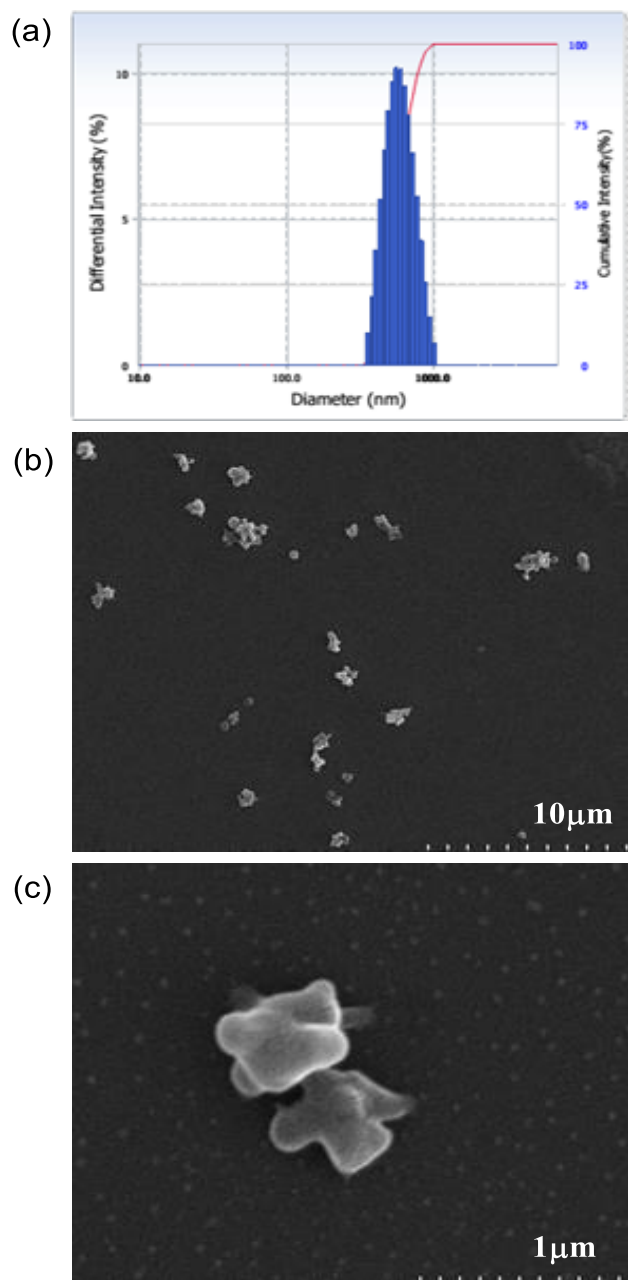


Fig. 3. (a) DLS analysis; (b) and (c) SEM images of prepared latexes containing SPOH after UV light irradiation.

Afterward, the prepared photochromic latexes were exposed to UV irradiation (365 nm), and the size and morphology were also examined (**Fig.3**). It was found that the average size of the particles enlarged to 600nm and the PI increased to 0.107. The SEM images (**Fig. 3(b)** and (c)) showed that plenty of irregularly shaped aggregates were formed. Owing to the photo-isomerization from SP to MC by UV light, the initial hydrophobic-hydrophilic[21, 22] balance of the latexes was disrupted. Because the polymerized surfactant was anionic, the hydrophilic MC form containing electric dipole would aggregate around the surfactant. Therefore, the ionic strength of the emulsion also changed from the initial and

the latexes rearranged to form aggregates to make a new balance.

Dynamic Studies on the Stimulated Emulsion

The latexes containing SPOH were photochromic due to the reversible isomerization between colorless SP and colored MC. As shown in **Fig. 4(a)**, the emulsion was white before UV light irradiation. When it was exposed to UV light, the color changed to fuchsia homogeneously (**Fig. 4(b)**). While the UV light ceased, the colored emulsion experienced a thermal fading process. However, it appeared a pattern on the surface of the emulsion during the process, which was consisted of some irregular colored “lines” in the static emulsion, as shown in **Fig. 4(c)-(e)**. The “lines” were consisted by the aggregates of the rearrangement of the stimulated latexes to meet the new balance of ionic strength. Because the MC to SP isomerization during the fading process was dynamic, the ionic strength in the emulsion would change with the increase of time. Therefore, the lines, as well as the pattern, would vary with time. The pattern disappeared after a few minutes and the emulsion kept pink, as shown in **Fig. 4(f)**. The pink color would last for a couple of days until it was exposed to the visible light. The dynamic process of during the isomerization of $SP \rightleftharpoons MC$ of the latexes containing SPOH was demonstrated in **Scheme 5**.

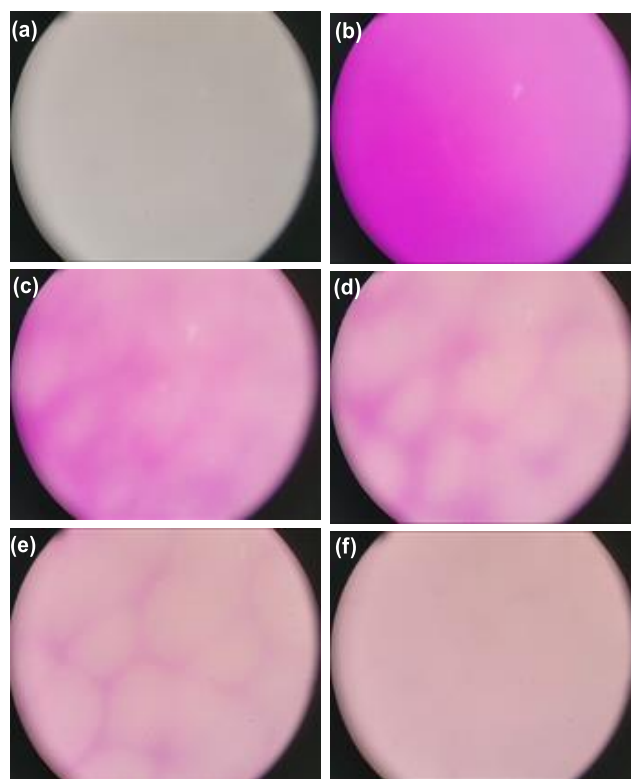
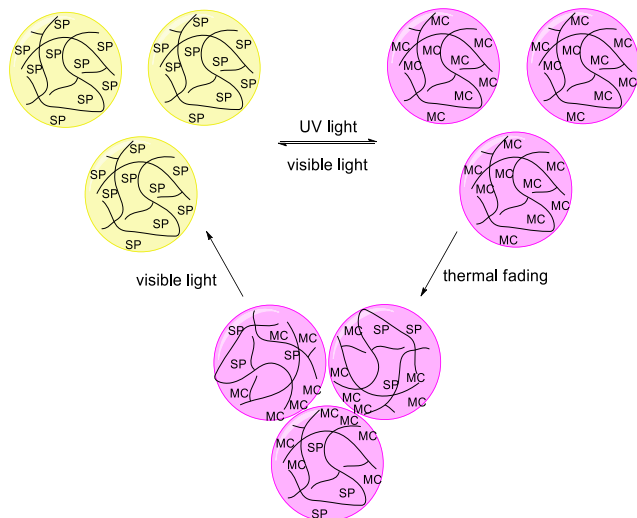


Fig.4. The microphotograph of latexes containing SPOH in photochromism and thermal fading for (a)before UV light irradiation; (b)after UV light irradiation for 10s(thermal fading at 0s); (c)-(f) thermal fading at 60 s, 120 s, 180 s and 300 s, respectively.



Scheme 5. The dynamic process of the latexes containing SPOH during the isomerization of $SP \rightleftharpoons MC$.

Conclusion

The latexes containing SPOH were prepared via emulsion polymerization, using a macromolecular surfactant that copolymerized by MMA, BA and AA. The photochromic latexes were characterized by DLS, SEM and UV-vis spectroscopy. Before UV light irradiation, the sizes of the latexes were about 260nm with narrow size dispersion. The latexes aggregated irregularly and resulting in a rising PI when exposed to UV lights. During the thermal fading process, it appeared continuous variable pattern on the surface of the emulsion. The phenomenon was related to the rearrangement of the stimulated latexes to meet the dynamic balance of ionic strength, due to the reversible isomerization of colored MC to colorless SP.

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