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Preparation and photochromism of carboxymethyl chitin derivatives containing spirooxazine moiety

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Abstract

A novel water-soluble photochromic polymer **4** was prepared by graft copolymerization of 9′-allyloxyindolinospiro-naphthoxazine **3** onto carboxymethyl chitin (CMC) and characterized by IR, etc. The photochromism has been studied by UV–vis spectroscopy. Polymer **4** has not only shown water solubility but also usual photochromic behavior. Compared with the acetone solution spirooxazine **3**, the thermal stability of open-form of polymer **4** has been improved significantly.

Keywords: Carboxymethyl chitin; Spirooxazine; Graft copolymerization; Photochromism

1. Introduction

Photochromic polymers, i.e., polymers which contain photochromic groups in a macromolecule, are materials of significant scientific and technological interest [1–5]. Spirooxazine is an important class of photochromic compound developed on the basis of spiropyran. Owing to their excellent resistance, spirooxazine have extensive applications in image display, optical information storage and so on [6–12]. However, the colored merocyanine structure formed by the photochromic transformation is thermally unstable. It is clear that stabilizing the colored form of spirooxazine is essential to its commercial application.

At the same time, the graft copolymerization of chitin and chinosan became a frontier field of research of functional film materials, however, the properties of grafted copolymers have been improved but not so much because of their poor solubility [13–15]; this limited their applications because they cannot form films by dip-coating. Recently, researches had shown this after primary derivation followed by grafted modification. Chitin derivatives could attain much improved water solubility [15,16]. So CMC derivatives containing photochromic spirooxazine side groups probably have practical application in functional materials.

In the present paper, we report a novel polymer **4** which being prepared by graft copolymerization of spirooxazine **3** onto CMC. The studies showed that the copolymer **4** is water-soluble and it has a positive photochromism in water. Graft copolymerization leads to a significant stabilization of the photomerocyanine form and a decrease in thermal fading.

2. Experimental

2.1. Measurements

Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Infrared spectral analysis was performed on a NEXUS-670 spectrophotometer using KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer. UV–vis spectra were taken on an Agilent-8453 spectrometer. A ZF7c UV analysis apparatus (made in Kanghua Biochemical Co. Ltd. of

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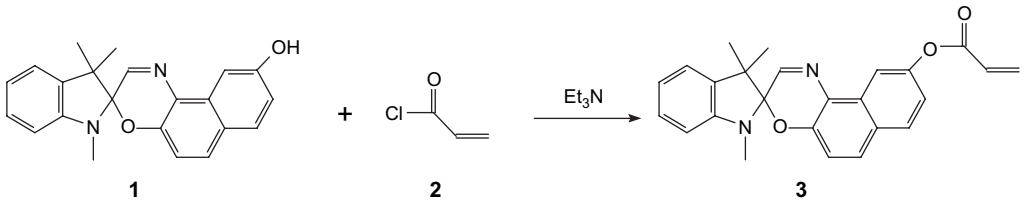


Scheme 1. Synthesis route to monomer **3**.

Shanghai, China) was used as the UV-light source, the wavelength is 365 nm.

2.2. Materials and reagents

CMC was supplied by Zhejiang Yuhuan Biochemical Co. Ltd. (China). The carboxymethylation substitution degree was 0.65 and the average molecular weight was 3.0×10^5. It was purified before use by dissolving and precipitating several times, then extracting in a Soxhlet apparatus by refluxing in acetone for 24 h, and drying at 60 °C under vacuum for 48 h. Ammonium persulfate (APS) was an analytical grade reagent and was used as an initiator. All other reagents were used as supplied by company.

2.3. Synthesis of intermediates and monomer

The synthesis of monomer **3** was carried out according to the synthetic route outlined in Scheme 1.

2.3.1. Synthesis of spirooxazie *1*

Spirooxazine **1** was synthesized from 1,3,3-trimethyl-2-methylene-indoline and 1-nitroso-2,7-hydroxy-naphthalene according the method described in Refs. [17,18]. Yield: 4.4 g (38%), m.p. 223–225 °C. IR (KBr) 3324, 1628, 1360, 1242, 835, 746.

^{1}H NMR ($CDCl_3$) δ: 1.34 (s, 6H, 3-CH_3), 2.75 (s, 3H, NCH_3), 5.58 (s, 1H, ArO–H), 6.50–7.90 (m, 10H, ArH, 2′-H).

2.3.2. Synthesis of acrylyl chloride *2*

Acrylyl chloride **2** was prepared from benzoyl chloride and acrylic acid according the method described in Ref. [19] and used without further purification. Yield: 6.2 g (68%), b.p. 75–77 °C.

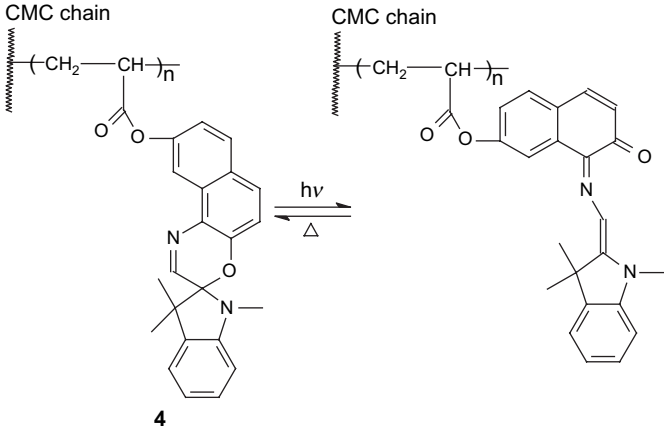
2.3.3. Synthesis of monomer *3*

To a solution of **1** (3.44 g, 0.01 mol) in triethyl amine (50 ml) was added acrylyl chloride **2** (0.91 g, 0.01 mol) dropwise at 0 °C, after which the reaction mixture was stirred for 12 h at room temperature, and the solvent was evaporated under reduced pressure. The residue was column chromatographed (silica gel) with the mixture of hexane and acetone in 20:1 (v/v) as eluent to give a light-yellow crystal of **3**. Yield: 32%, m.p. 147–149 °C. IR (KBr) ν (cm^{-1}): 1735, 1622, 1479, 1361, 1297, 1238, 1018, 969, 827, 748.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (s, 6H), 2.74 (s, 3H), 6.03 (d, 1H, $J = 10.4$ Hz), 6.37 (dd, 1H, $J = 17.2$ Hz and 10.4 Hz), 6.56 (d, 1H, $J = 7.6$ Hz), 6.64 (d, 1H, $J = 17.2$ Hz), 6.89 (t, 1H, $J = 8.0$ Hz and 7.6 Hz), 6.98 (d, 1H, $J = 9.2$ Hz), 7.07 (d, 1H, $J = 7.6$ Hz), 7.16 (t, 1H, $J = 7.6$ Hz and 8.0 Hz), 7.21 (dd, 1H, $J = 8.8$ Hz and 2.0 Hz), 7.64 (d, 1H, $J = 9.2$ Hz), 7.70 (s, 1H), 7.76 (d, 1H, $J = 8.8$ Hz), 8.28 (d, 1H, $J = 2.0$ Hz). ^{13}C NMR (aceone-d_6, 400 MHz) δ: 164.73, 151.76, 150.34, 148.16, 145.27, 136.29, 133.23, 132.83, 130.59, 129.97, 128.49, 128.38, 127.82, 122.74, 121.90, 120.28, 119.92, 116.99, 113.16, 107.64, 99.38, 52.16, 29.63, 25.29, 20.52.

2.4. Graft copolymerization

A 100 ml three-necked round-bottomed flask, filled with a stirrer in a temperature-controlled water-bath was used for the reaction. CMC was dissolved in deionized water, a desired quantity of monomer **3** was added and the suspension was mixed with constant stirring for about 3 h. After purging with N_2 for 30 min, the mixture was stirred and heated slowly to 70 °C; the required amount of APS in moderate deionized water was added into the flask. When the appropriate reaction time had elapsed, the contents of the flask was stirred for a further 15 min at room temperature and poured into alcohol. The precipitate was filtered and extracted with acetone in a Soxhlet extractor for 48 h to remove homopolymer. Some acetone got from Soxhlet extractor was added dropwise on the test-paper; after exposure to UV-light for 2 min, if the paper had not



Scheme 2. Photochromism of graft copolymer **4**.

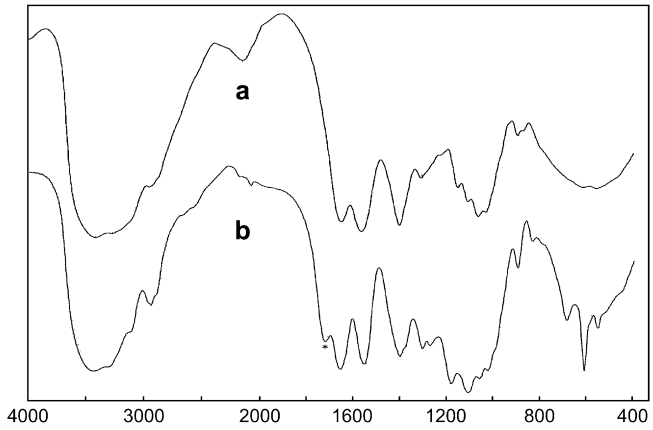


Fig. 1. IR spectra of CMC (a) and copolymer **4** (b).

become blue, it means that the homopolymer was removed completely. The graft copolymer was dried at 60 °C under vacuum to constant weight.

The percentage of grafting ($G\%$) was determined by

$$G\% = (w_1 - w_0)/w_0 \times 100\%$$

where w_0 and w_1 denote the weight of CMC and graft copolymer.

3. Results and discussion

Some graft copolymers with different $G\%$ were prepared by changing the reaction conditions. A representative condition is 0.4 g CMC, 50.0 ml water, 3 mmol monomer **3**, and 0.35 mmol APS. The $G\%$ of resulting copolymer **4**, the sample that had been characterized next, was 65%.

The structure of the graft copolymer **4** (Scheme 2) was analyzed by IR and UV–vis spectroscopies.

The IR spectra of CMC and graft copolymer **4** are shown in Fig. 1. In the IR spectrum of **4**, there is a characteristic absorption peak at 1735 of C=O cm^{-1} stretch vibration. The IR spectrum of homopolymer was similar to the spectrum of monomer **3** as shown in Fig. 2.

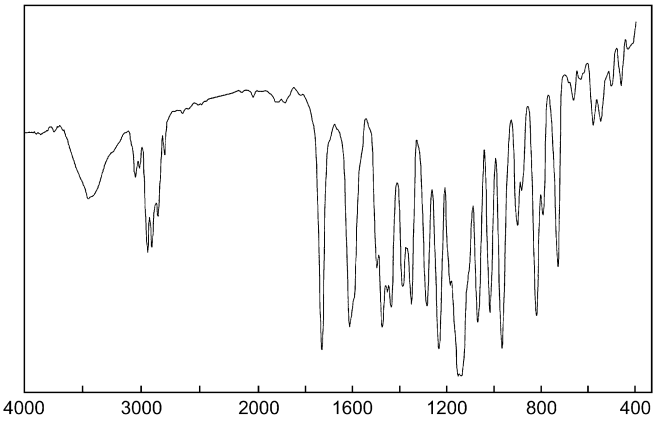


Fig. 2. IR spectra of homopolymer.

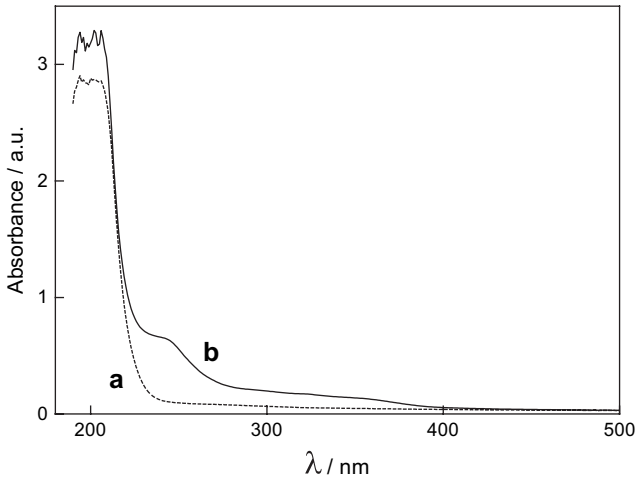


Fig. 3. The UV–vis spectra of CMC (a) and copolymer **4** (b).

In the UV–vis spectra (Fig. 3), CMC only has stronger absorption below 215 nm, compared with the water solution of graft copolymer **4**, for which the absorption from 190 nm to 380 nm was found.

Spirooxazine **3** and homopolymer were soluble and photochromic in organic solvent but insoluble in water, the color of the acetone solution of **3** and homopolymer changed from colorless to blue upon UV irradiation, but the color faded immediately at room temperature. The reaction was too fast to measure the visible absorption spectrum of the colored form with the ordinary method [20].

CMC and copolymer **4** was soluble in water but insoluble in acetone, etc. When the water solution of copolymer **4** was irradiated by UV (365 nm), it significantly becomes blue. The change of visible absorption spectra of irradiated **4** in water during the thermal color decay at 298 K was recorded and

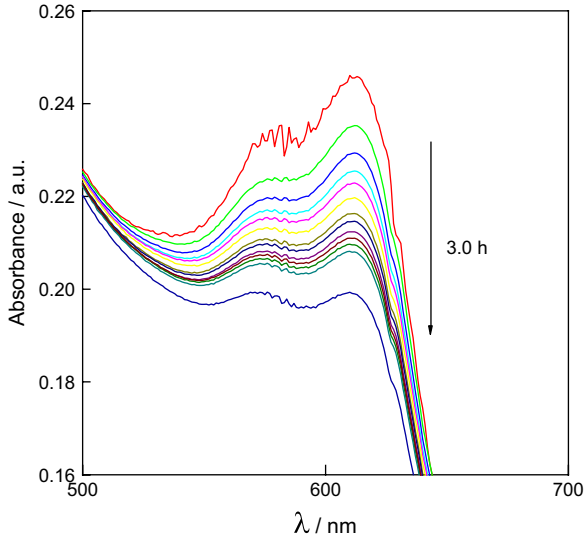


Fig. 4. Change of visible spectrum of copolymer **4** in water after irradiation with UV. The time between the first spectrum and last spectrum was 3 h.

is shown in Fig. 4. The change was small perhaps because of our poor test facilities and instruments. In testing, we founded that the absorbance of open-form of **4** was reduced very fast in the beginning time after irradiated. So, the time in this testing was very important. In fact, we wasted about 3–5 s in moving the irradiated sample to the UV–vis spectrometer.

In Refs. [20–22], in order to recorde the change of UV–vis spectra of open-form of spirooxazine derivative, it was measured at lower temperature. Using our method at room temperature, the change of UV–vis absorbance spectra of colored monomer **3** in acetone solution with the concentration of 8×10^{-5} mol/l cannot be recorded because the reaction was too fast, but the change of color can be seen with eyes. Compared with this, it was enough to prove that the thermal stability of the open-form of copolymer **4** has been improved. The enhanced stability may be attributable to a limited free volume in the polymer surrounding the spirooxazine groups [23].

The visible absorption has maximum at 611 nm and a shoulder around 580 nm. The shape of the spectra remains uncharged during the thermal color decay of the irradiated water solution. With the time went by, the absorption in visible range decreased slowly, that was to say, the close-form of copolymer **4** is more stable in the water solution than the open-form. Perhaps it meant the open merocyanine form has a predominant quinoid character. Research shows that spiropyran compounds supported by polyethylene glycol in water solution have a negative photochromic property [24]; these were different from our results. The spirooxazine derivatives in water solution have a positive photochromism.

4. Conclusions

In the present work, the CMC derivative with spirooxazine side group was synthesized firstly and it showed not only water solubility but also usual photochromic behavior; the graft copolymerization leads to a significant stabilization of the photomerocyanine form and a decrease in thermal fading.

Acknowledgment

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