



Preparation and characterization of photochromic poly(methyl methacrylate) and ethyl cellulose nanocapsules containing a spirooxazine dye

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ARTICLE INFO

Article history:

Received 5 April 2011

Received in revised form 6 June 2011

Accepted 15 June 2011

Available online 22 June 2011

Keywords:

Photochromic nanocapsules

Spirooxazine

Poly(methyl methacrylate)

Ethyl cellulose

ABSTRACT

Poly(methyl methacrylate) and ethyl cellulose nanocapsules, containing a photochromic dye, 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)naphth[2,1-b](1,4)oxazine], have been prepared by emulsion–solvent evaporation method. Both encapsulating polymers are suitable for the preparation of nanoparticles in a wide concentration range (0–30% *m/m* dye content). The dye concentration does not significantly influence the size of the nanocapsules, which is around 250 nm and 220 nm for poly(methyl methacrylate) and ethyl cellulose, respectively. Furthermore, the UV–Vis absorbance of the dye increases linearly with its concentration in both polymers, that is, the dye does not aggregate in the nanocapsules even in such a wide concentration range. The UV-induced coloured merocyanine form ring-closes to the colourless spirooxazine much quicker in an organic solvent than in the nanocapsules, and photochemical reactions resulting in fatigue of the coloured form are much slower in the nanocapsules as well. Consequently, a much more intense colour is achievable by UV irradiation in the nanocapsule preparations, and this intensive colour loses its intensity much slower, as compared to a solution of the same spirooxazine in an organic solvent. These circumstances are advantageous for using the preparations for dyeing purposes.

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1. Introduction

Photochromism can be defined as a reversible transformation of a chemical species induced by electromagnetic radiation between two states with visible light absorptions in spectral regions [1]. Colour changes in photochromic compounds typically are the result of the shift of optical absorption due to changes in molecular structure or conformation.

Spirooxazines are a well-established group of photochromic dyes, that in liquid or solid solution turn blue upon irradiation with UV light and rapidly fade back to colourless form when the activating radiation is removed. Spirooxazines have excellent resistance to light-induced degradation. This property, also called fatigue resistance, is considered to be due to photochemical stability of the oxazine framework. The fatigue resistance of spirooxazines has led to their successful use in various applications [1] including oph-

thalmic lenses, rewritable optical recording media, data memory, optical switches, and sensors [2,3]; transport systems, catalysis, in optoelectronics and optobioelectronics [3]; ink jet printing [4]; UV-sensor [5]; security or authentication purposes, chemical-UV-dosimeters for personal protection [6]. Furthermore, they can be incorporated into the materials used for packaging applications in the case of UV sensitive products like food [7], or could be used to produce photochromic fabrics [8].

Spirooxazine dyes open their oxazine ring upon UV irradiation, to form a merocyanine structure that has a larger conjugated system. When the irradiation is broken off, the “open-ring” isomer returns to the “spiro”, uncoloured structure, since the “spiro” isomer is the thermodynamically stable one. The colouration and decolouration of the photochromic dyes are affected by both the physical and chemical parameters of the environment [2]. In order to overcome the aggregation and improve the stability of the dyes, solid matrices are preferred. The interaction between the photochromic and polymeric entities can lead to novel photoinduced properties beyond the obvious colour changes. Polymeric materials play a crucial role in studies of photochromism, since various applications require photochromic materials in the form of films, sheets, plates, fibers, beads and so on [1]. Photochromic

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molecules have usually been incorporated into polymer matrices by binding them covalently to polymer backbones or by dissolving or suspending them in polymer solids (doping). Various types of spirooxazines have already been used in polymer matrices [9]. Most frequently, spirooxazines have been incorporated into thin solid films. The films were prepared by polymerizing the dyes with different polymers in order to synthesize novel photochromic materials [10–12], or spirooxazines have been doped into polymers, such as poly(methyl methacrylate) (PMMA) [13,14] and epoxy resin thin film [13]. Spirooxazine dyes were also often encapsulated in sol–gel matrices [15–17]. However, microencapsulation of them by organic polymers was seldom achieved, e.g. Lee et al. [8] formed photochromic PMMA/spirooxazine microspheres by in situ suspension polymerization. Rarely, other types of photochromic dyes were also embedded in organic polymer nano- or microparticles. Investigation of photochromic organic polymer nanoparticles started to get into the limelight recently, for example Su et al. [18] synthesized carboxyl containing spiropyran nanoparticles (30–60 nm) via one-step miniemulsion polymerization, while Harbron et al. [19] doped conjugated polymer nanoparticles with a photochromic spirooxazine dye. However, photochromic polymer nanoparticles might have great potential in various photonic applications and offer advantages relative to small molecule fluorophores considering their good photostability and brightness [19]. Furthermore, they could be useful for converting dyes, which are soluble only in organic solvents, to water dispersible compounds for use in numerous applications such as coatings.

Poly(methyl methacrylate) is an important polymeric material with outstanding water-clear colour, stability even under severe conditions, high surface resistivity, and resistance to weathering and moisture. Due to these superior characteristics, PMMA has been widely used as sizer, additive, coating and polishing agent, binder, sealer, optical fibre, high voltage insulator, and outdoor electrical applications [8], as well as host material in photochromic polymeric systems shown above. It was generally applied as film or capsule forming material in various compositions, although, according to our knowledge, so far it has not been used as wall material in photochromic nanocapsules. It is noted that in the pertaining literature the term ‘micro- or nanocapsule’ is not only used for core-shell type micro- and nanoparticles but also for the synonym of micro- and nanoparticle.

The use of natural polymers receives considerable attention, especially from the point of view of their environmentally friendly character. Ethyl cellulose (EC) is a frequently used hydrophobic polymeric coating material for extended drug release applications [20] and other sustained delivery schemes, e.g. for controlled herbicide release [21]; quite recently, it has also been used as encapsulating material of fragrances [22,23]. To our knowledge, nobody has utilized this polymer to formulating photochromic capsules yet, although transparent particles might be produced from it.

The aim of this study was to synthesize photochromic polymeric nanocapsules that are capable of increasing the fatigue resistance and the extent of colouration of the applied photochromic dye. Commercially available spirooxazine dye (5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)naphth[2,1-b](1,4)oxazine]) (SO) was incorporated by PMMA and EC wall materials, respectively. Both PMMA and EC nanocapsules were prepared by an oil-in-water emulsion, solvent evaporation method. Regarding the scientific literature, this method can be considered as a simple and novel method for synthesizing photochromic nanoparticles. The size and morphology of the nanoparticles were measured. The UV–Vis absorption, photochromic kinetics and fatigue resistance of the spirooxazine in organic solvent and polymer nanoparticles were compared.

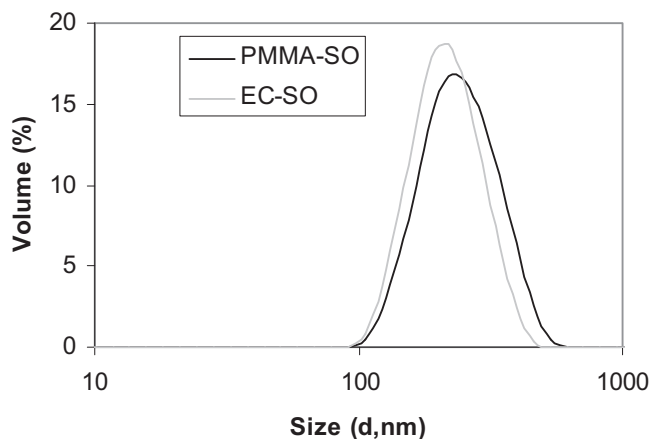


Fig. 1. Size distribution of poly(methyl methacrylate)–spirooxazine (PMMA–SO) and ethyl cellulose–spirooxazine (EC–SO) nanocapsules each including 30% *m/m* photochromic dye.

2. Materials and methods

2.1. Materials

Dichloromethane, acetonitrile, polyvinyl alcohol ($M_w = 30,000$ – $70,000$, 87–90% hydrolysed), poly(methyl methacrylate) ($M_w \sim 15,000$), ethyl cellulose (viscosity: 4 MPa s, 5 wt% in 80:20 toluene/ethyl alcohol, 25 °C) and 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)naphth[2,1-b](1,4)oxazine] were obtained from Sigma Aldrich.

2.2. Preparation of photochromic nanocapsules

The photochromic nanocapsules were synthesized by an oil-in-water emulsion, solvent evaporation method. Briefly, 70–100 mg PMMA or EC and 0–30 mg SO (total weight of the polymer + dye was kept constant), were dissolved in 4 ml dichloromethane (DCM) using magnetic stirring. The oil-in-water emulsion was formulated by adding the organic phase into 10 ml distilled water containing 1% polyvinyl alcohol, then, sonicating the two phases with a probe sonicator, Model W-220 (Heat Systems-Ultrasonics Inc.) at 70 W, for 60 s in an ice bath. The dichloromethane was removed from the droplets by evaporation during magnetic stirring for 2 h under atmospheric pressure at room temperature.

Nanoparticles were centrifuged by a Beckman L8-55 ultracentrifuge with 15,000 rpm for 25 min, and redispersed in distilled water for the scanning electron microscope measurements.

2.3. Investigation of nanocapsules

The size of photochromic nanoparticles was measured by dynamic light scattering using a Zetasizer 3600 (Malvern Instruments, Malvern, UK). The average particle size was expressed in volume mean diameter.

The morphology of nanocapsules was monitored after centrifuging and redispersing them in distilled water, dropping onto grid, and drying under room temperature. Then they were vacuum-coated for 3 min with a mixture of gold and palladium and examined with Philips XL-30 environmental scanning electron microscope (ESEM) at 25 kV.

The UV–Vis absorption of the spirooxazine dye in acetonitrile and in suspension of polymeric nanocapsules was monitored with a SPECORD S-600 diode array spectrophotometer under continuous magnetic stirring at 25 °C, using a medium-pressure mercury lamp

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