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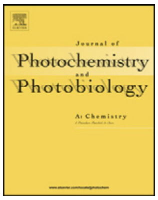

# Preparation and characterization of photochromic poly(methyl methacrylate) and ethyl cellulose nanocapsules containing a spirooxazine dye

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ABSTRACT

Poly(methyl methacrylate) and ethyl cellulose nanocapsules, containing a photochromic dye, 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-(3*H*)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 dying purposes.

## 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 ophthalmic 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[2*H*-indole-2,3′-(3*H*)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.

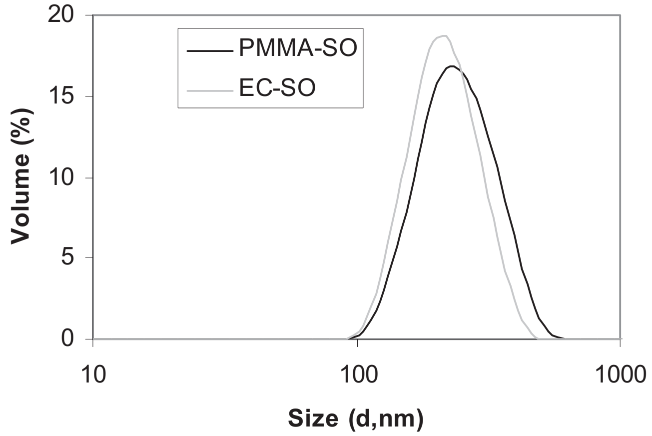

**Fig. 1.** Size distribution of poly(methyl methacrylate)–spirooxazine (PMMA–SO) and ethyl cellulose–spirooxazine (EC–SO) nanocapsules each including 30% *m*/*m* photochromic dye.

## 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[2*H*-indole-2,3′-(3*H*)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

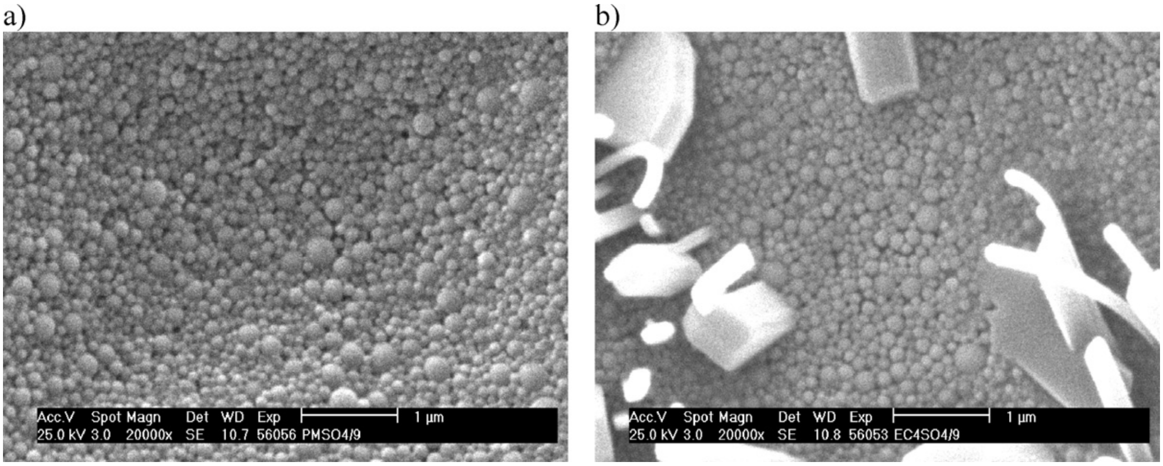

**Fig. 2.** SEM images of poly(methyl methacrylate)–spirooxazine (a) and ethyl cellulose–spirooxazine (b) nanocapsules (the large objects in b are residual dried PVA material).

(125 W) with a band filter (max. 336 nm) for UV irradiation in a right angle setup.

Kinetics and fatigue resistance investigation of SO dye in organic solvent (acetonitrile) and in nanocapsule suspensions were carried out at 25 °C under magnetic stirring, using a 150 W Osram XBO xenon lamp with a UG1 band filter (transmission maximum at 357 nm). The spectra were recorded with an Agilent 8453 diode array spectrometer.

The initial concentration of SO both in the organic solvent and in the nanocapsule suspensions was $10^{-4}$ M for the kinetics and fatigue resistance studies.

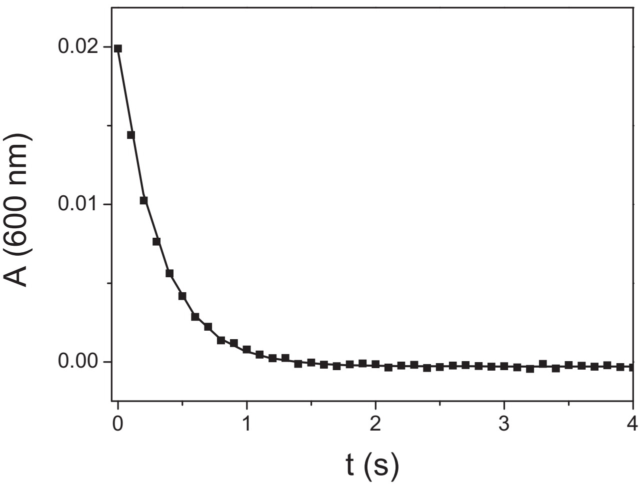

**Fig. 3.** Absorbance change at 600 nm in acetonitrile during the decolouration process at 25 °C.

**Table 1**
Volume mean diameter (nm) of poly(methyl methacrylate)–spirooxazine and ethyl cellulose–spirooxazine nanoparticles at various dye content (% *m*/*m*).

| SO content (% *m*/*m*) | Mean diameter of PMMA–SO nanocapsules (nm) ± SD | Mean diameter of EC–SO nanocapsules (nm) ± SD |
|---|---|---|
| 0 | 250 ± 5 | 228 ± 5 |
| 2.5 | 253 ± 6 | 213 ± 2 |
| 5 | 247 ± 2 | 208 ± 2 |
| 10 | 255 ± 7 | 218 ± 4 |
| 15 | 251 ± 2 | 218 ± 2 |
| 20 | 252 ± 2 | 223 ± 1 |
| 30 | 254 ± 6 | 225 ± 2 |

## 3. Results and discussion

### 3.1. Size and morphology of nanocapsules

The size of nanocapsules, synthesized by emulsion process, can be affected by numerous parameters. The most important step was to find a suitable emulsifier and adjust its concentration. In our previous study [23] PVA was found to be a very effective surfactant in a similar system for emulsifying organic droplets in an aqueous phase. According to our former experience 1% *w*/*v* PVA was applied, and upon sonication, fine nanoparticles were formulated. The increase of the polyvinyl alcohol (PVA) concentration did not affect the size of the particles significantly. We also investigated the effect of dye concentration on the size distribution of photochromic nanoparticles. Table 1 shows that the concentration of SO did not influence the mean size of either the PMMA or the EC nanoparticles. Nevertheless, the size of nanocapsules consisting of the same concentration of dye, but different polymers (EC or PMMA) had slightly different size distribution; that is to say, particles made of ethyl cellulose were mildly smaller (Fig. 1), as was also indicated by the mean diameters (Table 1).

The morphology of the PMMA–SO and EC–SO nanoparticles was monitored by scanning electron microscopy (Fig. 2) that showed spherical shape for both nanocapsule types. The particle sizes observed by SEM were in good agreement with the dynamic light scattering investigations (Fig. 1).

### 3.2. Photochromic properties of SO in acetonitrile

The photochromic behaviour of the studied dye has been investigated at first in acetonitrile solution. UV irradiation with a 150 W xenon lamp (filter max.: 357 nm) led to a small increase in the absorption intensity only in the visible region, between 450 and 650 nm with a maximum around 600 nm as a result of the generation of the photomerocyanine form.

The open form generated is thermally unstable and undergoes bleaching very quickly (Fig. 3), which follows first order kinetics, reforming to the closed form, as it is expected. The coloured form has an extremely short lifetime ($\tau = 0.35$ s) which property is general in spirooxazines.

### 3.3. Photochromic properties of PMMA and EC nanocapsules containing SO

#### 3.3.1. UV–Vis absorption of SO in PMMA and EC nanocapsules

The UV–Vis spectra of PMMA–SO and EC–SO nanocapsules (Fig. 4) were measured after diluting the nanocapsule suspensions

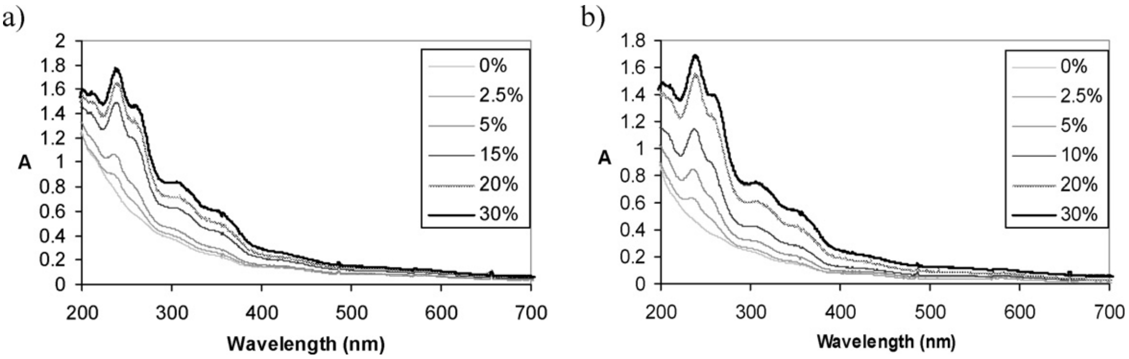

**Fig. 4.** UV–Vis absorption spectra of spirooxazine in poly(methyl methacrylate) (a) and in ethyl cellulose (b) nanocapsule suspensions without UV irradiation. Successive spectra were taken after diluting the suspensions of nanocapsules (conc.: 1% *w*/*v*) containing 0–30% *m*/*m* SO to 1:200.

containing 1% *w*/*v* nanocapsules with distilled water to 1:200 of its initial volume. The nanocapsules comprised 0–30% *m*/*m* of SO (referred to the total capsule mass). As can be seen, the blank capsules (particles without SO) also shows absorbance, mainly in the UV region. The major contribution to this absorbance can be considered as the result of light scattering by the nanoparticles, while the true absorption of the polymer plays only a minor role. It is also observable that the PMMA blank nanoparticles have substantially higher absorption in the same concentration than EC ones. As their size distribution is rather similar, this difference cannot be explained by the different scattering of PMMA and EC particles. Nevertheless, as it is well-known Plexiglas composed of PMMA is a good absorbent of UV radiation, thus, the nanocapsules formed from this polymer definitely absorb UV better than EC.

Fig. 5 displays the absorbance of SO in acetonitrile and in nanoparticles dispersions (shown in Fig. 4) recorded at 304 nm. This local maximum wavelength was chosen, because the blank absorption (caused mostly by the scattering of particles) was less substantial here than at lower wavelengths (see Fig. 4). Fig. 5 shows that the increase of dye concentration results in linear change of absorption not only in acetonitrile but also in both PMMA and EC photochromic nanocapsules in a rather wide range, i.e. 0–30% *m*/*m* (related to the total capsule mass). This means that there is no significant dye aggregation in the capsules, thus, PMMA and EC materials are appropriate for the purpose of inert photochromic capsule matrix. The slightly higher absorption coefficient measured in the nanocapsules, as compared to the acetonitrile solution might be due to the different dielectric properties of the matrices.

### 3.3.2. Colouration and decolouration process of spirooxazine in PMMA and EC nanocapsules

Upon exciting the PMMA–SO and EC–SO nanocapsules with UV light, the typical absorption band of the merocyanine form appears with a maximum around 600 nm, while the spectrum in the UV does not change considerably, similarly to that observed for SO dissolved in acetonitrile. The rate of decolouration was studied by measuring the absorbance of nanocapsule suspensions at $\lambda_{max}$ (600 nm) following a 2 min irradiation by a 150 W xenon lamp equipped with an UG1 filter (max. transmission at 357 nm). The thermal decolouration processes of SO in PMMA and EC nanoparticles are illustrated in Fig. 6.

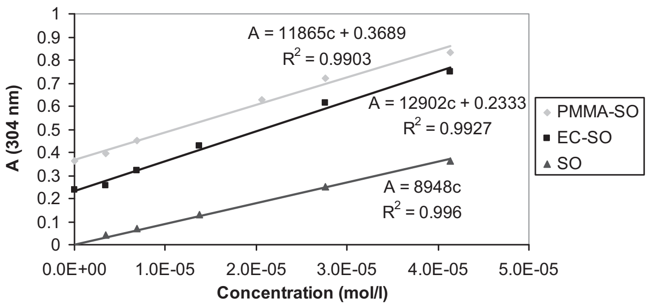

**Fig. 5.** Absorption data (measured at 304 nm) of spirooxazine in acetonitrile as well as in poly(methyl methacrylate) (PMMA–SO) and in ethyl cellulose (EC–SO) nanocapsule suspensions without UV irradiation.

The same SO concentration related to the total volume ($10^{-4}$ M) was applied in these experiments in order to enable direct comparison with the SO photochromic reactions studied in acetonitrile. It is remarkable that the greatest absorbance changes after 2 min UV irradiation in capsules ($\Delta A_{EC-SO} = 0.2$, $\Delta A_{PMMA-SO} = 0.09$) are substantially higher than in the organic solvent ($\Delta A_{SO-acetonitrile} = 0.02$). Considering the kinetics of reversible first order reaction like

$$\mathbf{S}\underset{k_d}{\overset{k_c}{\rightleftharpoons}}\mathbf{M}$$

the equilibrium concentration of merocyanine form is the following:

$$[M]_e = \frac{k_c}{k_c + k_d}[S]_0$$

where "*S*" and "*M*" mark spirooxazine and merocyanine, respectively, $[S]_0$ is the starting concentration of spirooxazine, $k_c$ is the rate constant of colouration for spirooxazine induced by UV light and $k_d$ is the rate constant of thermal decolouration for merocyanine form. However, both the colouration and the decolouration rates of the photochromic dye diminished significantly in both of the nanocapsules relative to that experienced in acetonitrile, the higher absorbance change observed in capsules is a consequence of the larger extent of decrease in the decolouration rate constant. The different absorbance change in polymers must be the result of the dissimilar variation of their colouration and decolouration rate constants. Thus, microencapsulation results in a significant shift in the equilibrium of the photomerocyanine and spirooxazine toward the merocyanine isomer.

The absorbance of merocyanine at the $\lambda_{max}$ decreased by 50% in relation to the difference of its initial and photostationary value during 105 s in PMMA matrix and 10 s in ethyl cellulose nanocapsules. Both values indicate much slower decolouration rate than in an organic solvent (<1 s). The value in our PMMA nanocapsules, is rather similar to that found by Tan et al. [14] for another spirooxazine doped into PMMA film.

The use of organic polymers moderates the common problems of dye solutions, such as low photostability, though, at the same time leads to substantial suppression of both fading and photochromic response of the dye [17]. There are two important factors which affect the photochromic conversion in the polymer matrix. The first one is the reaction rates, i.e. the

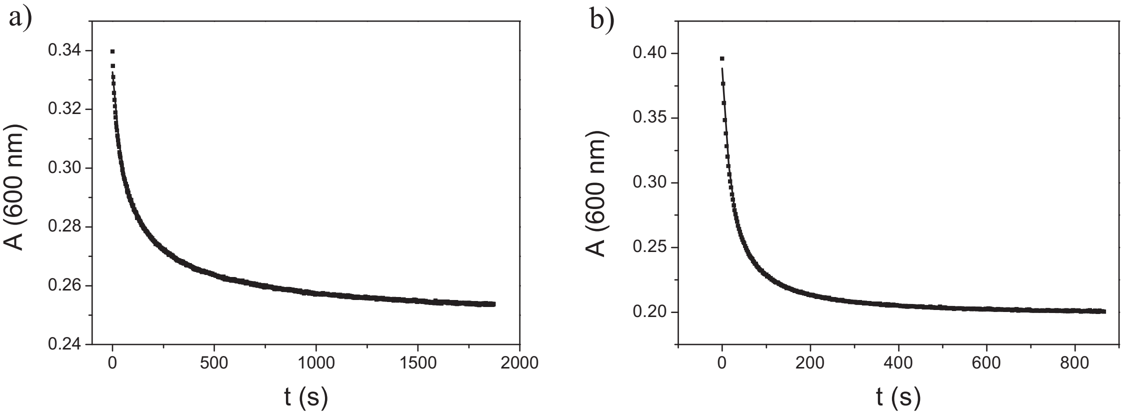

**Fig. 6.** The absorbance change at the $\lambda_{max}$ (600 nm) of spirooxazine in poly(methyl methacrylate) (a) and in ethyl cellulose nanocapsule dispersions (b), respectively, during the decolouration process.

decolouration rate in rigid matrices is slower than in more flexible systems. The second factor that can have influence on photochromic behaviour is the free volume of the matrix [24]. The photochromic molecules need some free volume in the matrix to transform. In solid matrices there is free volume generally in such amount that can be enough for the conversion of some photomolecules, otherwise, if it is insufficient, it can decelerate or inhibit the structure change [19]. Since the Young's modulus of PMMA [25] is higher by almost an order of magnitude than that of EC [26], this means that the ethyl cellulose polymer is a more flexible matrix in the nanocapsules formed by the emulsion–solvent evaporation method. This correlates well with the faster decolouration measured in EC as compared to that in PMMA. Even though we do not have data about the free volume of the PMMA and EC nanocapsules, considering the similar density of the polymers and the close size distribution of the nanoparticles, it is very likely that the influence of this property on the photochromic conversion is not too pronounced.

SO in organic solvent had first order decolouration kinetics, hence, the decolouration curve can be characterized with a single lifetime; on the contrary, the bleaching curves of dye in nanocapsules can be fitted properly only by using at least two exponential decay equation (in certain case three exponential decay results in a considerably better fit), as it is general in photochromic dyes in polymer matrices [7]. However, Harbron et al. [19] found that a spirooxazine included in poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] nanoparticles indicated monoexponential decay and similar decolouration rate as in organic solution, while the polymer films made of the same polymer or polystyrene showed bi-exponential decolouration kinetics. It is noteworthy that the mean diameter of these nanoparticles [19] was smaller than 25 nm, which is around the tenth of the mean size of our particles.

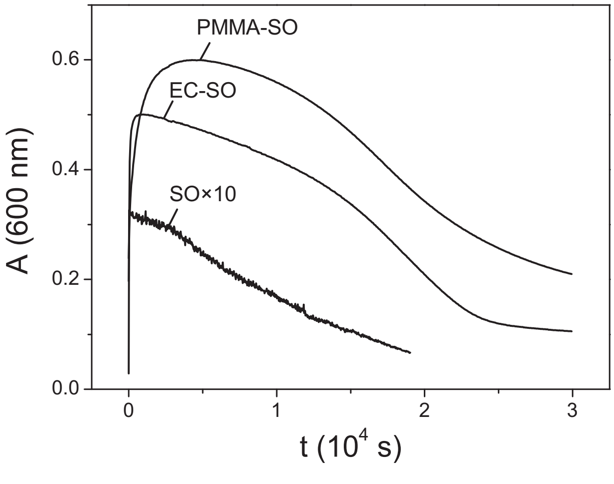

**Fig. 7.** Fatigue of SO in acetonitrile solution ($10^{-4}$ M, the measured absorbance data were multiplied by 10 which results were drawn and marked with SO × 10) as well as of PMMA–SO and EC–SO nanocapsules (SO concentration was $10^{-4}$ M in each type of nanoparticles, related to the total volume of each dispersion) upon continuous UV irradiation.

Both the colourization and the decolourization were found to be significantly slower in our polymer nanocapsules than in an organic solvent, however, the kinetics was quantified only in the case of decolourization. The time constants of bi-exponential decay of the coloured form of SO in our PMMA nanoparticles show a much slower conversion of merocyanine ($\tau_1 = 50$ s; $\tau_2 = 430$ s) than in EC capsules ($\tau_1 = 20$ s; $\tau_2 = 130$ s). This is to be compared with the single exponential decay of the merocyanine form in acetonitrile ($\tau = 0.35$ s). In a solution SO molecules experience identical environment, resulting in a single exponential decay for the decolouration. On the contrary, in the nanocapsules SO molecules are surrounded by a range of slightly different environment leading to a range of decolouration rate constants. Unfortunately, the number of data point taken does not support the determination of a distribution of rate constants, but the existence of more than a single decolouration rate constant is clearly indicated.

### *3.4. Fatigue resistance of SO in acetonitrile and in PMMA- or EC nanocapsules*

The loss of photochromic properties upon prolonged exposure to UV light, called fatigue, limits the use of photochromic molecules in outdoor applications [27]. One of the commonly used techniques to study the fatigue of photochromic systems is continuous irradiation. This technique monitors fatigue on long time scales, extending from tens of minutes, to many hours. The sample is irradiated continuously, while the absorbance at a particular wavelength is monitored.

SO dissolved in acetonitrile as well as PMMA–SO and EC–SO nanocapsules in water dispersions were irradiated with a 150 W xenon lamp (with a band-pass filter at max. transmission at 357 nm). The absorbance changes of the three systems were recorded with a spectrophotometer at 600 nm till their absorbances fell to their minima. The fatigue curves are shown in Fig. 7.

SO in acetonitrile loses its steady-state absorption in the visible quicker than in nanocapsules (Fig. 7). The parameter $t_{\Delta A_0/2}$ is defined as the time required for the decrease of the maximal absorbance ($\Delta A_0$) at the $\lambda_{\max}$ of the merocyanine form to its half value ($\Delta A_0/2$). This parameter is 170 min for SO dissolved in acetonitrile. However, the fatigue resistance is prolonged significantly in the polymers applied (Fig. 7). SO in poly(methyl methacrylate) shows the slowest fatigue; its $t_{\Delta A_0/2}$ is found to be 300 min; while that of SO in EC nanoparticles was 290 min. These values are significantly higher than that was found by Tan et al. [14] for PMMA films (170 min) containing novel heterocycle-containing spirooxazines improved for longer fatigue resistance.

The semi-rigid environment of PMMA or EC does not only slows down the ring-closure to the spiro form, but also significantly hinders the side degradative reactions causing fatique. The photodegradation of spirooxazine was investigated in several studies [1,28] that proposed a number of mechanisms for the oxidative degradation processes, which occurred through free radical or singlet oxygen formation. Hence, the incorporation of photochromes in a matrix with low oxygen permeability decreases the rate of degradation [29]. The higher fatigue resistance of PMMA indicates that the more rigid environment is less permeable to the oxygen.

## 4. Conclusions

Both PMMA and EC have been found to be appropriate polymers for encapsulating 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-(3*H*)naphth[2,1-*b*](1,4)oxazine]. Both types of prepared nanocapsules are characterized by spherical shape and similar size distribution. Aggregation of the dye was not observed in a wide concentration range in the nanoparticles. Both polymers slow down the photochemical reactions of the dye, by providing a rigid environment which results in a considerably higher visible absorption under UV irradiation as well as slower fatigue, as compared to the dye dissolved in acetonitrile. However, in EC matrix the SO decolourized much faster than in PMMA, in good correlation with the higher Young's modulus of the latter polymer.

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