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Photosensitive copolymer of *N*-isopropylacrylamide and methacryloyl derivative of spyrobenzopyran

A.E. Ivanov[a,c], N.L. Eremeev[b], P.-O. Wahlund[c], I.Yu. Galaev[c], B. Mattiasson[c,*]

[a]*Shemyakin and Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, Miklukho-Maklaya 16/10, 117871 Moscow V-437, Russian Federation*
[b]*Department of Enzymology, Chemical Faculty, Moscow State University, Moscow 119899, Russian Federation*
[c]*Department of Biotechnology, Centre for Chemistry and Chemical Engineering, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden*

Abstract

The copolymer of *N*-isopropylacrylamide (NIPAM) and methacryloyl derivative of spirobenzopyran (MSBP) with a molecular weight of 21 000 g/mol and the average molar MSBP content of 1.9% was prepared by free radical polymerization. The copolymer displayed its phase transition in water in the temperature range of 30–50 °C. UV irradiation of its aqueous solution caused photoinduced transformation of MSBP units into their coloured merocyanine forms, while the cloud point of the irradiated copolymer shifted by ca. 10 °C to lower temperatures. During a long-term exposure to daylight (20 days) the copolymer gradually elapsed to its colourless spiropyran form, the process being ca. 100-times slower than that for monomeric MSBP. Due to the slow reverse isomerization of its merocyanine form and low solubility in water at room temperature the UV irradiated copolymer could be quantitatively separated from aqueous solution by centrifugation. © 2002 Published by Elsevier Science Ltd.

Keywords: Photosensitive polymers; *N*-Isopropylacrylamide; Spyrobenzopyran

1. Introduction

Copolymers and gels of *N*-isopropylacrylamide (NIPAM) undergoing phase transitions in aqueous media attract much attention because of their importance for chemical design of 'stimuli-responsive' [1] or 'smart' [2] polymeric materials. In particular, some photochromic co-monomers bearing azobenzene [1], triphenylmethane [3] or chlorophyllin moieties [4] have been used for preparation of photoresponsive NIPAM gels. Being irradiated by UV or visible light these gels display their phase transition patterns different from those of the parent samples, the phenomenon allows control of the gel swelling by its exposure to light [1,3,4]. Meanwhile, water-soluble photoresponsive copolymers of NIPAM have been less investigated: to the best of our knowledge the only described system was aqueous solution of the copolymer containing 2.7 mol% *N*-acryloyl-4-aminoazobenzene [1]. The phase transition temperature of the copolymer increased by 6.6 °C due to *trans–cis* isomerization of the pendant azobenzene moieties caused by the photoirradiation.

A strong shift of a phase transition temperature may be achieved, in our view, with a photochromic co-monomer capable of generating electric charges and, therefore, displaying a pronounced change of its polarity due to photoirradiation. Among the compounds reacting in the above manner, spirobenzopyrans seem to be most convenient as they undergo reversible isomerization between their electrically neutral spirobenzopyran and zwitterionic merocyanine forms [5–8] (Fig. 1).

The goal of the present study was synthesis of the copolymer of NIPAM and methacryloyl derivative of spirobenzopyran (MSBP) followed by investigation of its photochromic and thermoprecipitation properties. Considering that MSBP itself is not soluble in water, a study of its photochromism in the solubilized state in aqueous medium was also of interest.

2. Experimental

2.1. Materials

NIPAM was a product of Aldrich Chem. Co. (Milw. WI, USA). MSBP synthesized as described elsewhere [9] was a generous gift of Dr A.I. Gorelik (Moscow State University, Chemical Department, Moscow, Russia). ^{1}H NMR

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* Corresponding author. Tel.: +46-46-222-8264; fax: +46-46-222-4713.
E-mail address: bo.mattiasson@biotek.lu.se (B. Mattiasson).

Abbreviations: MSBP, methacryloyl derivative of spyrobenzopyran; NIPAM, *N*-isopropylacrylamide.

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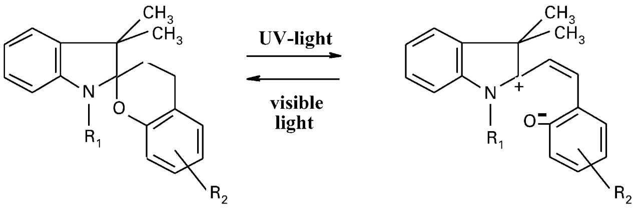

Fig. 1. Reaction scheme of MSBP photoisomerization. In the present work R_1: methacryloyloxyethyl, R_2: 6-Br.

(CD_3COCD_3): $\delta = 1.11$ and 1.25 (3H, 3H $(CH_3)_2C<$), 1.85 (3H, $C(O)C(CH_3){=}CH_2$), 3.4–3.6 (2H, $>N{-}CH_2{-}$), 4.3 (2H, $-C(O)OCH_2R$), 5.6 and 6.05 (1H, 1H, $-C(O)C(CH_3){=}CH_2$), 5.9 and 6.7 (1H, 1H, $-CH{=}CH{-}Ph$, pyran ring), 6.6 (1H, 7′H of indoline), 6.8–7.4 (7H, aromatic protons).

2,2′-Azobis(2-methylpropionitrile) (AIBN) was purchased from Acros Organics (Geel, Belgium). Diethyl ether (dried) was from Merck (Darmstadt, Germany). 1,4-Dioxane was dried over potassium hydroxide and distilled (101–102 °C).

2.2. Methods

2.2.1. Copolymerization of NIPAM and MSBP

NIPAM (330 mg, 2.925 mmol), MSBP (34 mg, 0.075 mmol) and 6 mg AIBN was dissolved in 10 ml 1,4-dioxane. The prepared solution was placed into a two-necked 100 ml round bottomed flask, equipped with reverse cooler and gas-supplement tube for nitrogen bubbling. Free radical polymerization was started by heating the reaction mixture to 70 °C under nitrogen bubbling in a water bath and carried out for 12 h. The volume of the reaction mixture was then reduced to ca. 2.5 ml by evaporation of the solvents at reduced pressure. Each of the two portions of the solution (ca. 1.2 ml) were dropped into 30 ml diethyl ether at vigorous magnetic stirring, separated from the solvent by filtration through paper, washed by ca. 50 ml ether on the filter and dried on air. The yield of the copolymer was 75%.

2.2.2. UV irradiation

UV irradiation of MSBP and MSBP–NIPAM copolymer solutions was performed by light produced with a 125 W low pressure mercury lamp of HPL-N type (Philips Ljus AB, Stockholm, Sweden), its glass casing being removed to allow irradiation in the UV-part of the spectrum. The luminous flux from HPL-N lamp was reported to be 6200 lm by the manufacturer. The sample was situated at ca. 5 cm from the arc so that the angle between the incident beam and the plane of 1 cm quartz cuvette was close to 90 °C. Absorption spectra of the irradiated samples were registered in the same cuvette quickly transported into an Ultrospec 1000 (Pharmacia Biotech, Sweden). For studies of fading kinetics the irradiated samples were kept in sealed 5 ml glass vials at daylight at room temperature (23 °C).

2.2.3. Thermal precipitation of copolymers

Thermal precipitation of MSBP–NIPAM copolymer and its irradiated forms was studied by measurements of turbidity exhibited by their thermostated aqueous solution (1 mg/ml) at 550 nm, the ambient temperature being step-wise increased.

2.2.4. Molecular weight estimation

Molecular weight of the MSBP–NIPAM copolymer was estimated by dynamic light scattering performed with a Malvern 4700c System (UK). An argon ion laser (Uniphase 2213-75 SL, 30 mW) operating at 488 nm wavelength was used as a light source. Two solutions of the copolymer in tetrahydrofuran (16 and 32 mg/ml) were studied, 10 independent measurements with each of them being performed. The intensity autocorrelation functions were registered at 90° and the data were processed by cumulant analysis using the PCS software program (version 1.35) supplied by Malvern Instruments. The scaling relationship $D = 2.49 \times 10^{-4} M^{-0.54}$ previously determined by Zhou et al. [10] was used for calculation of the molecular weight.

3. Results and discussion

3.1. Photochromic properties of MSBP

Fig. 2 shows the absorption spectra of 1′-methacryloyloxyethyl-3′,3′-dimethyl-6-bromospiro[2*H*-1-benzopyran-2,2′-indoline] (MSBP) registered before and after UV irradiation (2 min). A strong absorption band with maximum at

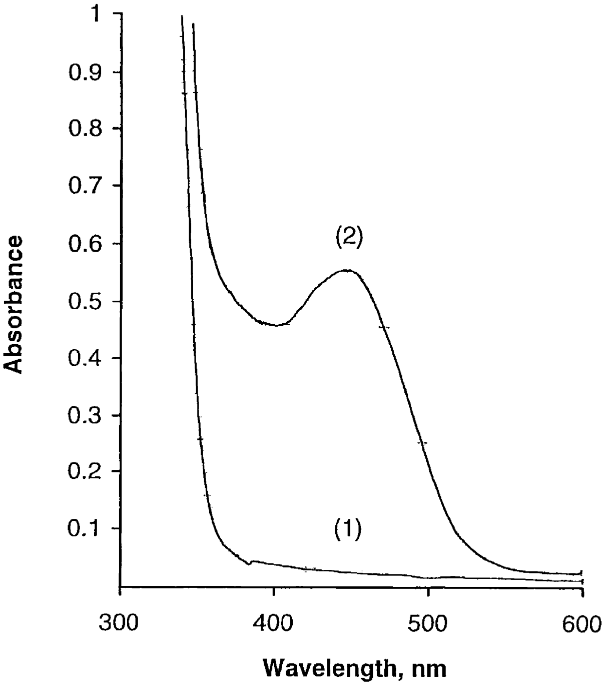

Fig. 2. Absorption spectra of MSBP in 1,4-dioxane (0.5 mg/ml), (1) before irradiation, (2) after 120 s UV irradiation.

450 nm appears in the irradiated sample indicating the formation of merocyanine form of MSBP [5–7]. On being irradiated, the substance did not change its spectrum in darkness for at least 20 min: the concentration of merocyanine form was apparently low as well as the rate of its reverse isomerization. In order to evaluate the conditions needed to approach the maximal content of merocyanine form, the apparent extinction coefficient of MSBP at 450 nm was studied as a function of irradiation time (Fig. 3(a)) and turned out to be nearly proportional to it for short irradiation times (<600 s).

The longer exposure to UV-light (>600 s) led to a sudden effect: the absorption of MSBP sharply increased and then decreased on further irradiation (960 s). That may be due to the accumulation of merocyanine form; its reverse transfer into spiropyran form could be promoted by visible light components of the mercury lamp [6,7]. Being withdrawn from the UV-light to darkness, the sample obtained by 960 s-irradiation displayed a gradually increasing absorbance (Fig. 3(b)), which, however, decreased to ε_{450} of 3700 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ after overnight in darkness at room temperature and did not change later for hours. Repeated UV irradiation of this sample carried out for 300 s caused the increase of ε_{450} to 34 200 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ in 30 min. Again, it dropped down to 3600 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ being kept overnight in darkness.

The observed behaviour of MSBP closely resembles the ‘yo-yo effect’, i.e. photobleaching of the pure merocyanine form by visible light. The resulting colourless solution rapidly recoloured in darkness by first order kinetics to an apparent equilibrium absorbance of approximately one-ninth that of the pure form [7]. A complex pattern of MSBP photochromism of this sort probably deals with the existence and different reactivity of merocyanine stereoisomers [5–7,11]. In particular, a prolonged UV irradiation was earlier reported to decrease the potential of poly(vinyl chloride)/spirobenzopyran membrane owing to interconversions of the open, charged forms of the photochromic substance [12].

Although it is difficult to clearly understand the observed absorption patterns of irradiated MSBP, one may notice that its fast adsorption changes in darkness were registered only for the samples with high content of merocyanine form. Both the direct isomerization of MSBP by short UV irradiation and the reverse isomerization of its merocyanine form led to the mixtures of the isomers characterized by the apparent extinction coefficients $\varepsilon_{450} < 4000\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ (Fig. 3), which did not markedly change in darkness. The maximal apparent extinction coefficient of MSBP registered in the present study was 34 200 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, the value comparable to those of 6-nitro-substituted spyrobenzopyrans in their charged, open forms [8]. It seems likely that MSBP was largely in its merocyanine form after 960 s-UV irradiation and during further simultaneous development of its colour (Fig. 3).

3.2. Photochromic properties of MSBP–NIPAM copolymers

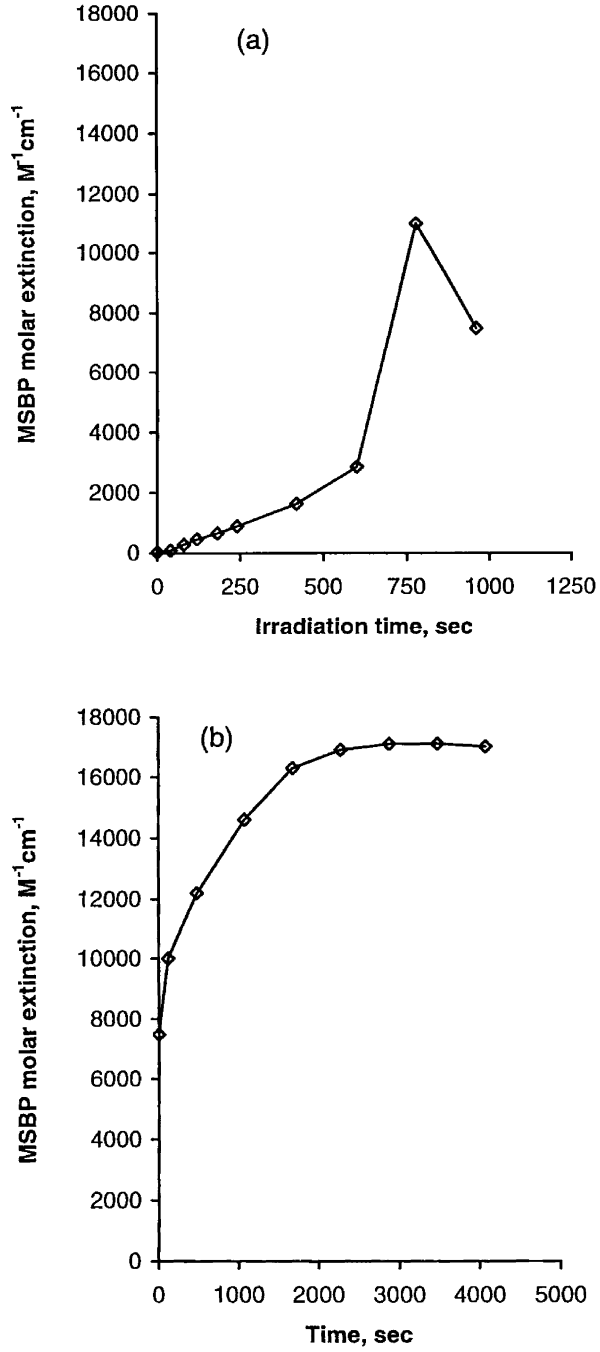

Fig. 3. (a) Dependence of the apparent extinction coefficient (ε_{450}) of MSBP (0.82 mg/ml in dioxane) on UV irradiation time. (b) Simultaneous change of the apparent extinction coefficient of MSBP previously irradiated for 960 s, as shown in (a), in darkness.

UV irradiation of aqueous solution of MSBP–NIPAM copolymer (1 mg/ml) at room temperature led to the formation of brownish flakes of the copolymer, which became largely insoluble due to the isomerization of its MSBP units. The precipitate might be, however, dissolved in water at low temperature (10 °C).

Fig. 4 shows UV spectra of the MSBP–NIPAM copolymer aqueous solution (1 mg/ml) before and after UV irradiation. The non-irradiated sample exhibits a sharp

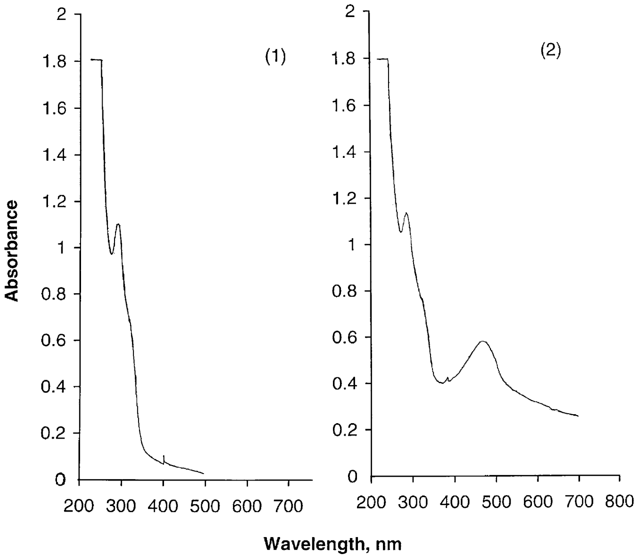

Fig. 4. UV spectra of MSBP–NIPAM copolymer aqueous solution (1 mg/ml) before (1) and after (2) UV irradiation (120 s).

UV-absorption band with maximum at 300 nm typical of MSBP, which allows estimation of MSBP content in the copolymer (1.9 mol%, 7.5 wt%). The molecular weight of MSBP–NIPAM copolymer was 21 000 g/mol as determined by dynamic light scattering, $M_n/M_w = 1.23$.

UV irradiation (3 min) of its aqueous solution (1 mg/ml) resulted in the appearance of the absorption band with maximum at 450 nm similar to that observed with MSBP in dioxane (Fig. 2). It is worthwhile to note that the sample of irradiated copolymer was somewhat opalescent due to its partial thermal precipitation observed even at temperatures below 15 °C.

Apparent extinction coefficient (ε_{450}) of the UV irradiated MSBP monomer units was ca. 1300 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, i.e. it fits the range of relatively stable spectral characteristics of MSBP. In fact, the coloured forms of MSBP-copolymer did not markedly change their absorbance for about 1 h. This allowed thermal precipitation studies of the irradiated copolymer within the above time interval. Fig. 5 shows the simultaneous decrease in absorbance (450 nm) displayed by the irradiated MSBP–NIPAM copolymer and pure MSBP on their exposure to daylight.

Obviously, MSBP undergoes fading ca. 100-fold faster compared to its copolymer with NIPAM. Similar effects were earlier observed with UV irradiated spirobenzopyrans dissolved in bulk polymers like poly(methyl methacrylate) or polystyrene [11,13]. In the copolymer, there may be a steric restriction of rotation and, therefore, a hindered interconversion of the open MSBP forms. In solution, the open isomers may easily get the proper conformation for ring closure as confirmed by the observed kinetics of fading.

Covalent binding of MSBP to a water-soluble polymer offers an opportunity to solubilize the photochromic compound in water and to compare its photosensitivity to MSBP dissolved in organic solvent. The ratio of quantum yields can be evaluated if the initial rates of colouration $(\mathrm{d}A_{450}/\mathrm{d}t)_{t=0}$ and absorbances at the irradiation wavelength are known for both compounds.

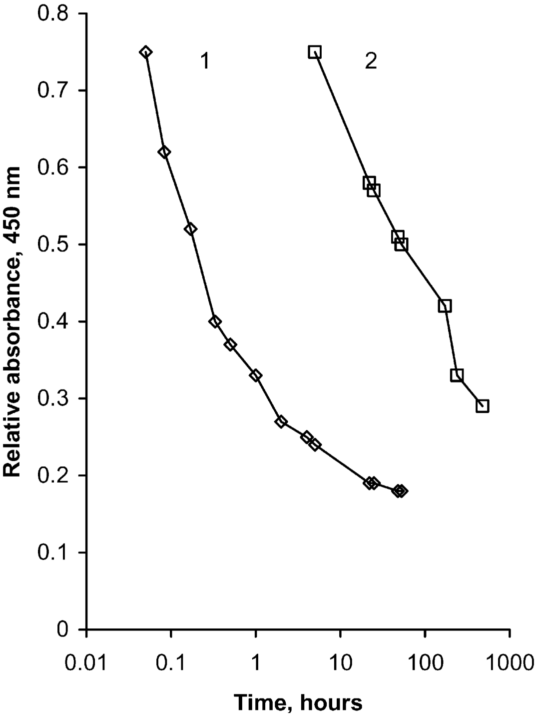

Fig. 5. Relative absorbances (A/A_0, $\lambda_{max} = 450$ nm) of the UV irradiated (180 s) photochromic samples: (1) MSBP solution in dioxane (0.5 mg/ml) and (2) MSBP–NIPAM copolymer solution in water (1 mg/ml), as functions of time. Initial absorbances A_0 were 0.52 and 0.12, respectively.

Absorbances (A) of MSBP and MSBP–NIPAM solutions in dioxane and water, respectively, were very high at 254 nm (the main irradiation wavelength of a low pressure mercury lamp) at the used concentrations of the substances and the fractions of adsorbed light $I_a = I_0(1 - 10^{-A_{254}})$ were above 0.98 for both compounds. On the other hand, the rates of thermal colouration $k_c(c_0 - c)$ and decolouration $k_d c$ were insignificant at low irradiation times. The quantum yields Φ for MSBP and MSBP–NIPAM can be expressed as follows [7]:

$$\Phi = [(\mathrm{d}A_{450}/\mathrm{d}t)_{t=0} - k_c(c_0 - c) + k_d c]/I_0(1 - 10^{-A_{254}})$$

Under the conditions mentioned earlier they should relate as the initial rates of colouration, whose ratio was found to be close to 7. MSBP is, therefore, more photosensitive in dioxane than in the solubilized state in water. Lower quantum yields of spyropyrans in polar solvents compared to nonpolar ones were earlier reported in the literature [7].

3.3. Thermal and UV-induced precipitation of MSBP–NIPAM copolymers

Thermal precipitation curves registered for the parent and irradiated copolymers dissolved in distilled water (1 mg/ml) are presented in Fig. 6. Unlike poly(NIPAM) undergoing its

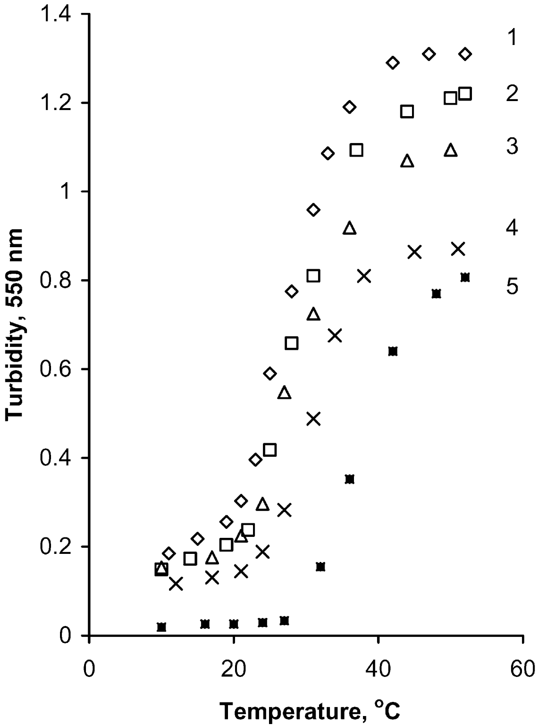

Fig. 6. Temperature dependencies of turbidity of UV irradiated (180 s) MSBP–NIPAM aqueous solution (1 mg/ml) undergoing the reverse isomerization at times: (1) 0 h, (2) 22 h, (3) 53 h, (4) 240 h. Curve (5): MSBP–NIPAM (1 mg/ml) before UV irradiation.

phase transition at 32 °C [14], MSBP–NIPAM copolymer did not exhibit a sharp transition but a gradual decrease of its solubility on raising the temperature from 30 to 50 °C. This may be attributed to a superposition of thermal precipitation curves displayed by the copolymer fractions with different MSBP content. On the other hand, the increased temperature of phase transition may be explained by protonation of MSBP tertiary aminogroup resulted in a better solubility of the copolymer.

UV irradiation exerts a dramatic effect on thermal precipitation of the copolymer. Its precipitation range shifts to lower temperatures at least by 10 °C. The observed shift of the phase transition temperature resembles one reported for spirobenzopyran derivative of elastin-like polypeptides recently suggested as a molecular machine to convert sunlight into mechanical work [15]. As time progresses and merocyanine form of MSBP isomerizes to its spiropyran form (Fig. 5), the shape and position of thermal precipitation curves get closer to that of non-irradiated copolymer as shown in Fig. 6. However, the absorbance band of merocyanine form could still be found in the copolymer spectrum even after 20 days of the copolymer exposure to daylight.

As mentioned earlier, the MSBP–NIPAM copolymer forms a flaky precipitate on UV irradiation. Such precipitate obtained after 180 s-irradiation of the copolymer solution (1 mg/ml) could be effectively separated by centrifuging (13 100g rpm, 10 min) from the aqueous phase and the copolymer bearing no MSBP monomer units. Judging by its absorption at 230 and 250 nm in the supernatant, the latter was only 7% from that of the parent sample. The precipitated photoreactive copolymer was coloured in dark orange and formed rather stable deposits, which dissolve at room temperature (23 °C) in not earlier than 20–30 min. Provided the copolymer carried some biospecific ligands, its photoinduced precipitation may be used for facile separation of proteins or cells as was earlier done with several thermosensitive copolymers of NIPAM [2].

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