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SCIENCE DIRECT
Dyes and Pigments 72 (2007) 299–302
DYES and PIGMENTS
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Photochromic behaviour of poly[*N*,*N*-[(3-dimethylamino)propyl]methacrylamide] having spiroxazine pendant group

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Received 12 March 2005; received in revised form 12 June 2005; accepted 2 September 2005
Available online 24 October 2005

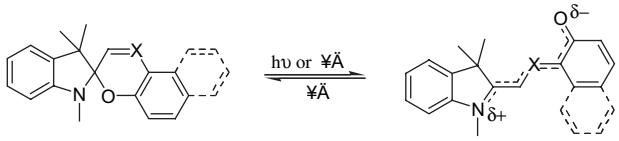
Abstract

This work describes the synthesis and photochromic properties of poly[*N*,*N*-[(3-dimethylamino)propyl]methacrylamide] bearing spiroxazines. Spiroxazine group showed reversible isomerization in this polymer upon photoirradiation. Solution viscosity of the polymer was reduced during irradiation and returns to the initial value after removing the light in DMSO. The ionic conductivity in polymer solution gradually increased upon UV irradiation and subsequently decreased in the dark.

Keywords: Spiroxazine polymer; Photochromism; Photoviscosity effect; First-order kinetics

1. Introduction

Photochromism has attracted much attention recently from the viewpoint of optical applications because of interest in refractive index or absorbance changes through optical extraction. The development of time-resolved or flash spectroscopy and, more recently, the use of laser photophysical means opened new approach to the study of the excited states and transient species involved in the photoreactivity of photochromic molecules. In recent years, photochromic and thermochromic spiropyrans and spiroxazines have been receiving considerable attention, due to their potential application in many new technologies, such as data recording and storage, optical switching, displays, and non-linear optics [1,2]. Although the photochromism of spiropyran has been extensively studied [3,4], little work has been carried out on spironaphthoxazine dyes. These two classes of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring results in spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation, which confers a much more commercial importance on them [5].



A (colorless form) **B** (colored form)

X = CH : spiropyran
X = N : spiroxazine

We have previously reported the synthesis and photoviscosity effect of spiroxazine polycation derived from cyclopolymerization of diallyldimethylammonium chloride and diallylamine [6]. The resulting polymer was found to be photochromic in solution and in thin solid film. The viscosity of a methanol solution of the polymer was reversively reduced by as much as 5% upon UV irradiation, the initial value being restored in the dark.

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doi:10.1016/j.dyepig.2005.09.003

This paper is concerned with the synthesis, photoviscosity effect and ionic conductivity of poly[*N*,*N*-[(3-dimethylamino)propyl]-methacrylamide] having spiroxazine pendant group.

2. Experimental

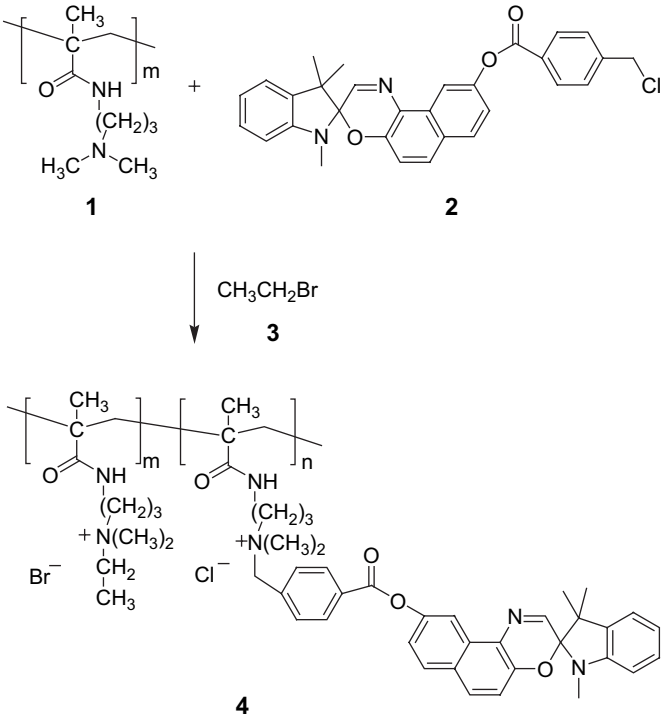
2.1. Materials and methods

Most of chemicals were purchased from Aldrich Chemical Co. Solvents were purified by normal procedures and handled under moisture free atmosphere. The other materials were commercial products and were used without further purification. Compounds **1** and **2** were prepared using previously described procedures [7,8].

Melting points were determined using an Electrothermal IA 900 and are uncorrected. A multi-channel photodiode detector (MCPD, Otsuka Electronics Co., Japan) was used to obtain visible absorption spectra and CHN analyses were carried out with a Carlo Elba model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard.

2.2. Synthesis of polymer *4*

0.8 g of poly[*N*,*N*-[(3-dimethylamino)propyl]methacrylamide] **1** (4.7 mmol repeat unit) and 1.17 g of 9′-[4-chloromethylbenzoyloxy]-1,3,3-trimethyl-spiro[indoline2,3′-[3*H*]naphtha[2,1-*b*]-[1,4]oxazine] **2** (2.35 mmol) are dissolved in 10 ml of dry *N*,*N*-dimethylformamide and stirred under nitrogen atmosphere at 60 °C for 5 days. Then the solution is allowed to cool and an excess of bromoethane **3** is added, the mixture is reacted at 40 °C for another 4 days. The polymer is precipitated in ethyl acetate and then dried. Yield: 2.73 g (82%).



Scheme 1.

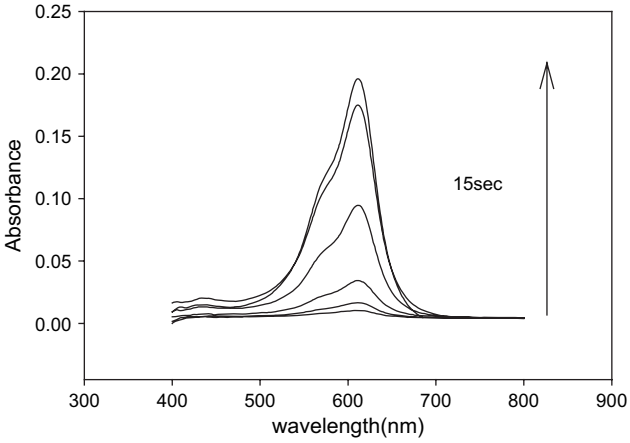


Fig. 1. Visible spectral changes of DMF solution of polymer **4** having spiroxazine units (2.64×10^{-4} mol%) upon UV irradiation.

3. Results and discussion

The synthesis of polymer **4** via the reaction of **1** and **2**, **3** at a moderate reaction condition was carried out according to the synthetic route outlined in Scheme 1. The polymer structure of **4** was characterized by elemental analysis, ^{1}H NMR spectroscopy.

^{1}H NMR (DMSO-d_6, δ ppm): 1.21 (s, 17H), 1.92 (m, 6H), 2.09(t, 2H), 2.51(t, 2H), 2.64(t, 5H), 2.89(t, 1H), 3.10(s, 16H), 4.91(t, 1H), 6.71(t, 2H), 7.20(d, 4H), 7.88(d, 6H), 8.25(s, 2H); Anal. calcd for $C_{50}H_{66}BrClN_6O_5$: C, 63.45; H, 7.03; N, 8.88%. Found: C, 54.44; H, 7.21; N, 8.9%.

The photochromic reaction is caused by the reversible heterolytic cleavage of the C(spiro)–O bond under UV irradiation, yielding the coloured form that can return to the colourless form by ring closure under visible light irradiation or in the dark. Newly synthesized polymer **4** was soluble in DMF and could afford thin solid film by dip-coating onto

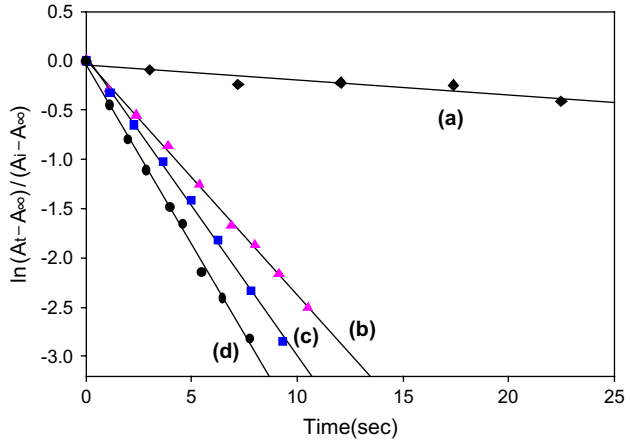
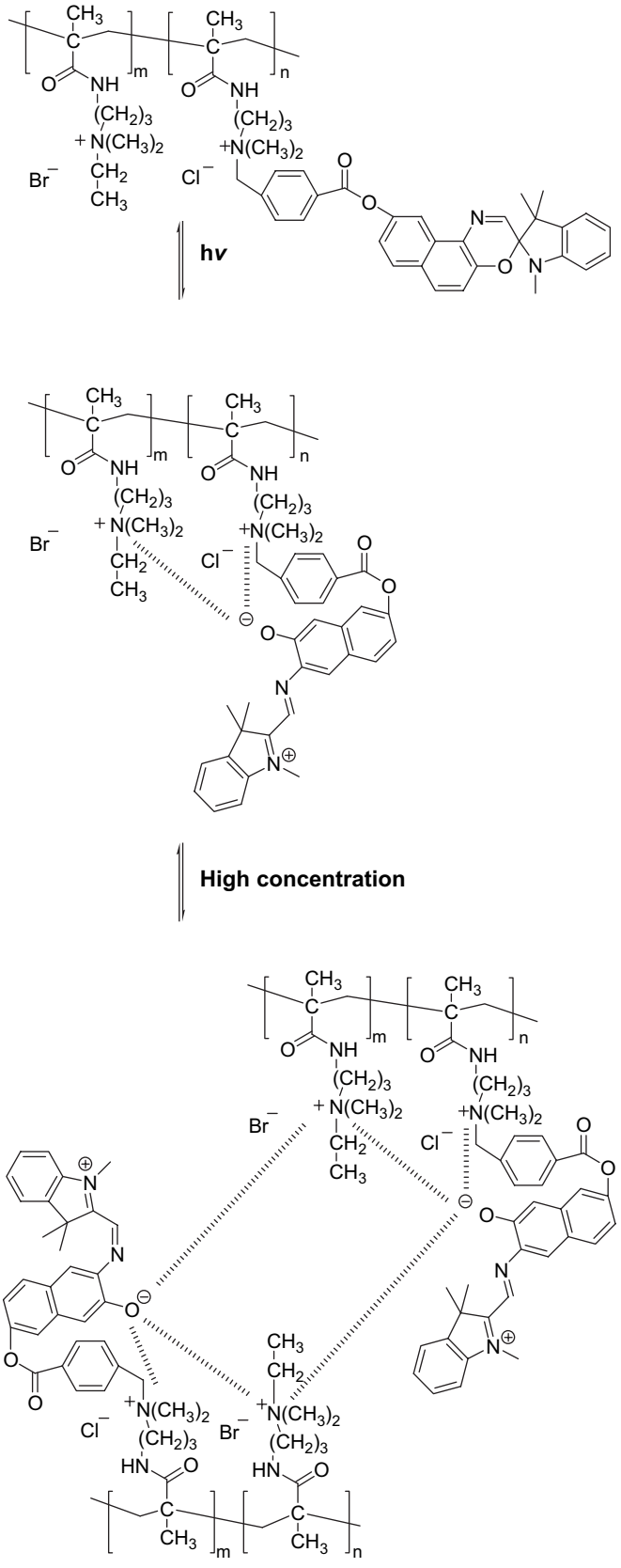


Fig. 2. First-order decolouration kinetic plot of photoisomerization (merocyanine → spiro) reaction of polymer **4**: (a) casting film, (b) 5.28×10^{-4} mol% in DMF, (c) 2.64×10^{-4} mol% in DMF, and (d) 1.32×10^{-4}% in DMF.



Scheme 2.

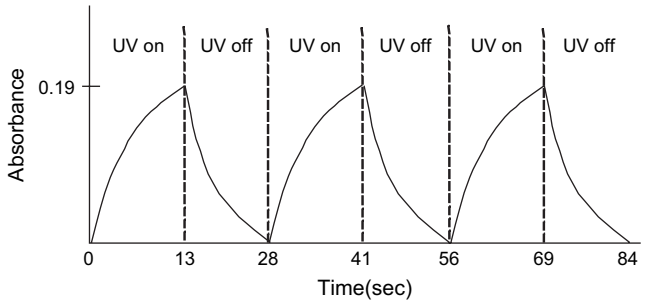


Fig. 3. Absorbance-change at 605 nm of polymer **4** in DMSO following periodic UV irradiation.

the glass substrate. Electronic absorption spectral changes of polymer upon UV irradiation in DMF are depicted in Fig. 1.

The original spectral pattern is reversibly recovered within 15 s. The new band is ascribed to the generation of the open merocyanine form from the closed spiro form. Spectra measured after UV irradiation are at any time proportional to each other in the visible region, indicating that only one species is formed. This allowed the absorption to be monitored at λ_{max}(605 nm) as a function of time to obtain thermal colour fading rate (k). Tomioka has examined the thermal decolouration rate for photochromic spiropyran derivatives using first-order kinetics [9]. The kinetic equation approach to the open merocyanine to closed spiro form via first-order reaction in the present case, is given by

$$\ln(A_t - A_\infty)/(A_i - A_\infty) = kt \quad (1)$$

where A_i is the absorbance at 605 nm, and A_t is the absorbance at 605 nm at time t after UV irradiation. A_∞ and k refer to absorbance at 605 nm after 1 h and first-order colour changing rate constant, respectively. In the thermal colour changing process, the kinetic analysis predicts the logarithm of the difference between A_∞ and A_t at time t to be linear with time, the slope giving the decolouration rate constant, k. First-order plots according to Eq. (1) for polymer **4** are shown in Fig. 2.

The first-order decolouration rate constant of polymer **4** in the thin solid film was smaller than that of in the solution ($k = -1.52 \times 10^{-3}$ for thin solid film, $k = -36.4 \times 10^{-3}$ for 1.32×10^{-4} mol% polymer solution, $k = -30.3 \times 10^{-3}$ for 2.64×10^{-4} mol% polymer solution, $k = -23.7 \times 10^{-3}$ for 5.28×10^{-4} mol% polymer solution); which indicates that open-to-close occurs more readily in solution than in the

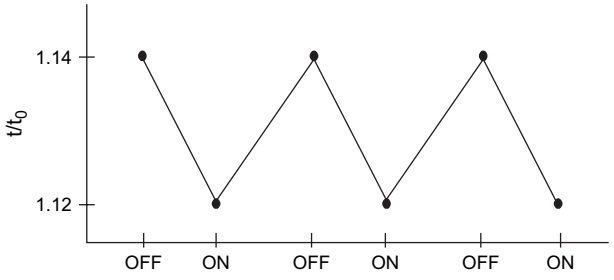


Fig. 4. Change of the viscosity of a DMSO solution of polymer **4** having spiroxazine on UV irradiation at −5 °C.

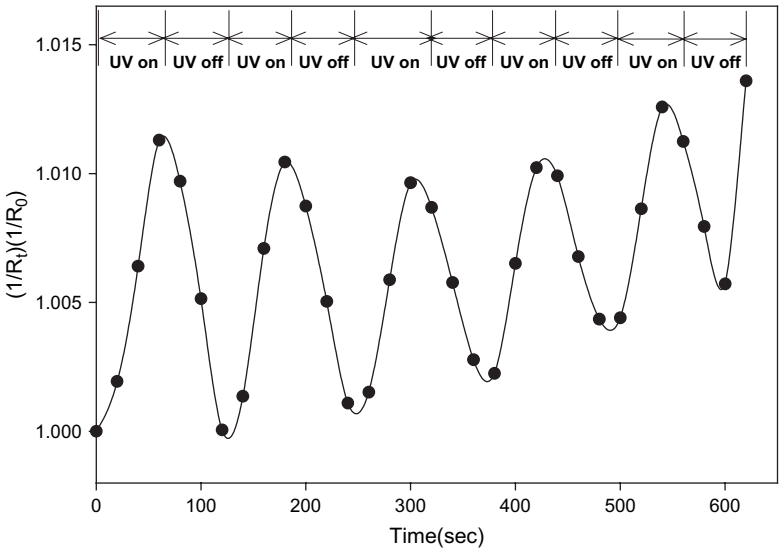


Fig. 5. Photoinduced ionic conductivity response for polymer **4** at 15 °C.

thin solid film. The molecular structure of the open form spiroxazine provides two binding sites such as indolenine cation and oxazinic O^-. The betainic nature of merocyanine gives rise to simultaneous binding of the oppositely charged moiety via an intra-and inter-molecular electrostatic interaction. Thus, the decolouration rate constant decreases with increase in the concentration of polymer. It could be inferred that the decolouration reaction in the polymer film after UV irradiation is much retarded by reducing the distance between polymer chains and increasing inter- and intra-molecular electrostatic forces (Scheme 2).

The photochrome also exhibited a fairly good reversibility, as can be seen in Fig. 3, where consecutive colouration–decolouration cycles are shown.

Fig. 4 shows the viscosity changes of the polymer having spiroxazine as side group in methanol before and after UV irradiation. The viscosity during UV irradiation returns to the initial value in less than 5 min at −5 °C after the light is removed. In DMSO the relative viscosity after UV irradiation is 2% lower than the viscosity in dark. The recovery cycles of the viscosity can be repeated many times without any noticeable fatigue. Electrostatic attractive forces between the zwitterions and the charges on positive ammonium residues of the polymer chain tend to contract the polymer chain. In dark, the attractive force considerably decreases because of the disappearance of the zwitterions structures of spiroxazine.

The photoinduced ionic conductivity response was analyzed at 15 °C and is shown in Fig. 5. The photoinduced ionic conductivity can be estimated from the expression $(1/R_t)/(1/R_0)$ where R_0 and R_t are the resistance before and after UV irradiation. The ionic conductivity increased upon UV irradiation, which brought about the generation of zwitterion form, and subsequently decreased in dark, which in turn brought about the generation of closed spiro form. Sufficient reversibility was found in this polymer and this response was completely synchronized with that in the absorbance changes.

Acknowledgements

This research was supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

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