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Synthesis and properties of spiroxazine polymer derived from cyclopolymerization of diallyldimethylammonium chloride and diallylamine

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Abstract

Cyclopolymerization of diallyldimethylammonium chloride and diallylamine containing photochromic spiroxazine was carried out by free radical initiation. The resulting polymer was found to be photochromic in solution and 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.

Keywords: Cyclopolymerization; Spiroxazine; Cyanuric chloride; First-order kinetics; Photoviscosity effect

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1. Introduction

A photochromic compound is characterized by its ability to undergo a reversible colour change. Interest in the photochromism of organic materials began to increase substantially around 1940. The principal studies of photochromic compounds involved acquiring an interest into mechanisms of the photoprocesses, determining the structures of the uncoloured form and the coloured form, and developing synthetic methods. The development of time-resolved or flash spectroscopy and, more recently, the use of laser photophysical means opened new approaches to study the excited states and the transient species involved in the photoreactivity of photochromic molecules. Recently, photochromic materials have gained much attention, and they now constitute an active research area because of their tremendous importance in biological phenomena and their potential applications in the areas of linear and nonlinear optics [1].

Although the photochromism of spiropyran has been extensively studied [2,3], 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

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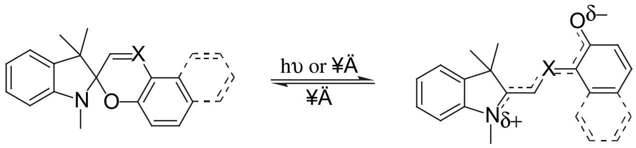
irradiation, which confers a much more commercial importance on them [4].



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

X = CH : spiropyran
X = N : spiroxazine

In 1951, Butler and Ingley reported that diallyl quaternary ammonium salts polymerized in the presence of catalytic quantities of *tert*-butylhydroperoxide to form water-soluble, noncrosslinked polymers [5]. A characteristic feature of the free-radical polymerization of allyl monomers is a cyclic intra and intermolecular polymerization mechanism [6–8]. Butler found that ammonium compounds which contained one or two allyl groups led to soluble polymers [5]. Those derivatives that possessed three or four allyl functions gave insoluble polymer. The present article reports on the synthesis of diallyldimethylammonium chloride and diallylamine and the photochromic properties of the resulting cyclopolymer.

2. Experimental

2.1. Characterization of products

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 OP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method.

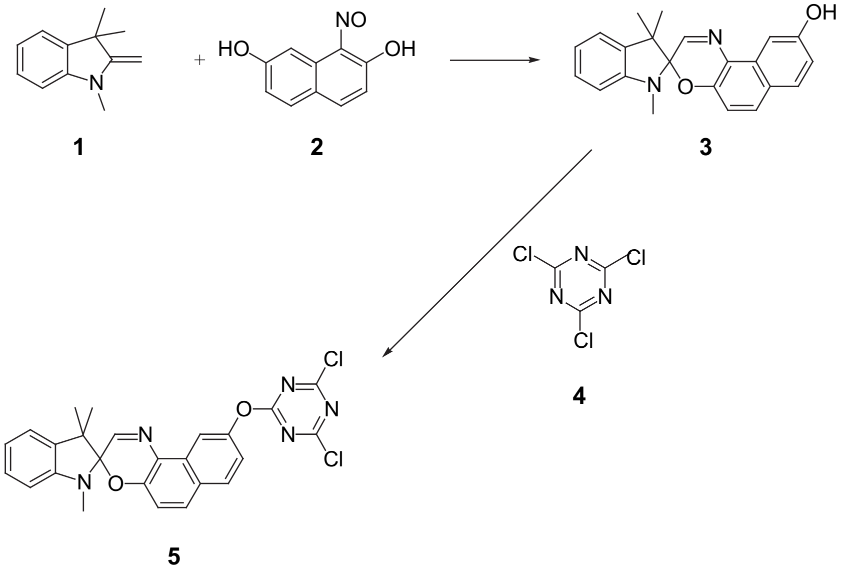
2.2. Materials

1,3,3-Trimethyl-2-methyleneindoline (Fisher's base) diallyldimethylammonium chloride (DADMAC) (65 wt% solution in water), diallylamine (DA), cyanuric chloride were purchased from Aldrich. 2,7-Dihydroxynaphthalene and ammonium peroxodisulfate were purchased from TCI. All chemicals were used without further purification. Intermediate **3** was prepared according to the literature procedures [9].

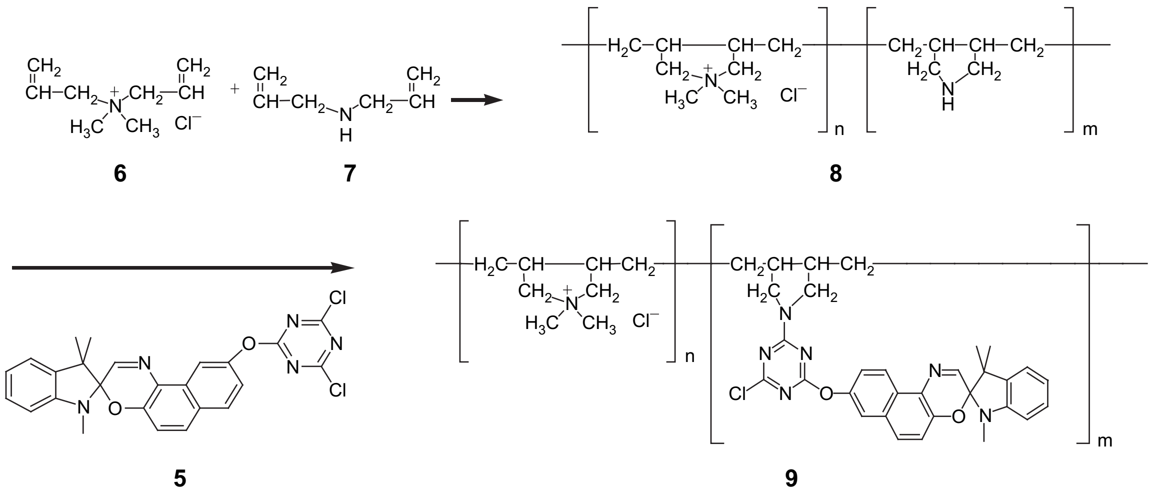
2.3. Synthesis of intermediates 5

To a solution of cyanuric chloride **4** (0.64 g, 3.46 mmol) in acetone (15 ml), compound **3** (0.5 g, 1.45 mmol) was added at 0–5 °C, and the mixture stirred for 3 h. 1 N sodium carbonate (4 ml) was added to the mixture, whereupon an intense white colour appeared, and then allowed to stir for 2 h. The mixture was poured into water and resulting product was separated and washed with water to give **5**. Yield 35%: mp 145 °C (Scheme 1).

Found: C, 60.01; H, 3.76; N, 14.13%; $C_{25}H_{19}N_5O_2C_{l2}$ requires C, 60.99; H, 3.89; N, 14.22%. Mass: 491 (M^+).



Scheme 1.



Scheme 2.

2.4. Polymerization

Diallylamine hydrochloride (DA·HCl) (3.34 g, 25 mmol) was added to 40.42 g (250 mmol) of DADMAC and 0.1 g of ammonium peroxodisulfate dissolved in 50 ml of water. The reaction mixture was allowed to react at 60 °C for 6 h. The resulting polymer solution was precipitated into excess acetone. The polymer **8** was dried under vacuum for 24 h and weighed; yield 7.44 g (17%). To solution of compound **5** (2 g, 4 mmol) in 25 ml of acetone was added to a solution of polymer **8** (5 g) in 100 ml of water. A few drops of 2 M sodium carbonate aqueous solution was added and stirred for 3 h. The solution was added to acetone to precipitate the polymer **9**. This polymer was then washed repeatedly with acetone to remove the last trace of the unreacted compound **5**. Yield 4.67 g (65%) (Scheme 2).

3. Results and discussion

The photochromic behaviour of photochromic polymers containing heterocyclic benzospiropyran group, incorporated either as side groups or as constituents of the polymer backbone, has been reported previously [10,11]. In the present paper, the photochromic behaviour of copolymer carrying side indolinonaphthoxazine group will be studied.

Cyclolinear polymer **8** of DADMAC and DA was prepared by free radical initiation via an intra and intermolecular polymerization. The copolymer was, then, reacted with spiroxazine containing cyanuric chloride moiety under basic condition at 0–5 °C. The synthesis of intermediate and polymer were carried out according to the synthetic route outlined by Schemes 1 and 2. Since the polymers are polyelectrolyte, a molecular weight determination of the products was very difficult. In Table 1, the results for the polymerization are summarized.

Since the polymers are very sensitive to the moisture, it is not easy to determine the exact CHN ratio by elemental analysis. However, from the CHN ratio it was possible to determine the C/N ratio; C/N ratio of polymer **8** is 6.83 (obs.) and 6.70 (calc.), and of polymer **9** is 6.83 (obs.) and 5.89 (calc.).

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 copolymer **9** was soluble in methanol and could afford thin solid film by dip-coating onto the glass substrate. Electronic absorption spectral changes of polymer upon UV irradiation in methanol are depicted in Fig. 1.

The original pattern was reversibly recovered within 100 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 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} (615 nm) as a function of time to obtain the thermal colour fading rate (k) of the

Table 1
Elemental analysis of polymers

	Molar ratio of DADMAC/DA	Analysis (%) formal calc.			C/N ratio
		C	H	N	
Polymer **8**	100/10	44.92	9.79	7.02	6.83
		60.28	9.98	8.99	6.70
Polymer **9**	–	46.96	9.21	6.88	6.83
		61.24	8.77	10.39	5.89

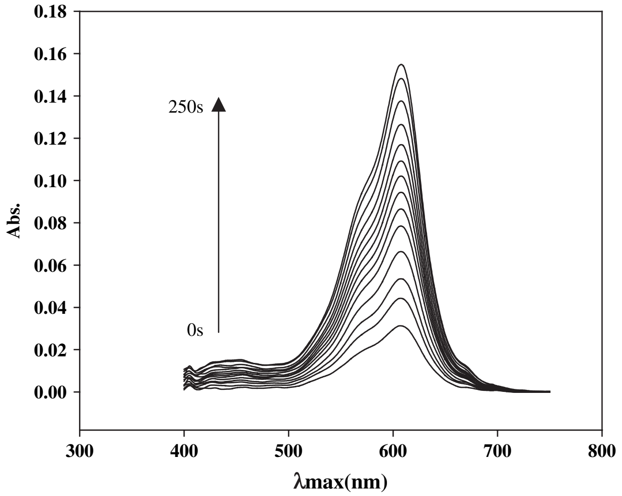


Fig. 1. Visible spectral change of polymer **9** in methanol (1% w/v, room temperature) upon UV irradiation.

transformation from the open merocyanine form to closed spiro form via first-order reaction [Eq. (1)]:

$$\ln(A_t - A_\infty)/(A_i - A_\infty) = kt \tag{1}$$

where A_i is the absorbance at 615 nm, and A_t is the absorbance at 615 nm at time t after UV irradiation. A_∞ and k refer to absorbance at 615 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 **9** are shown in Fig. 2.

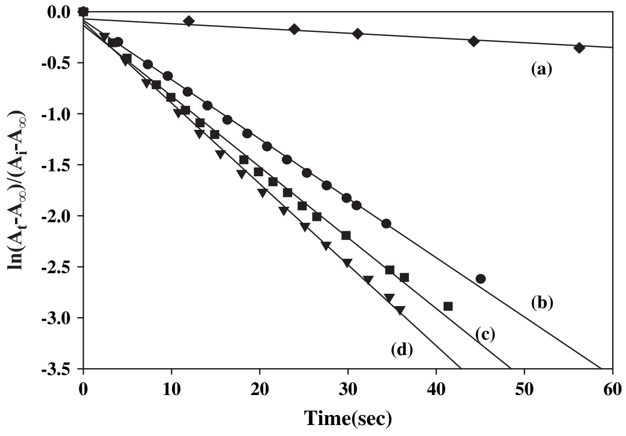


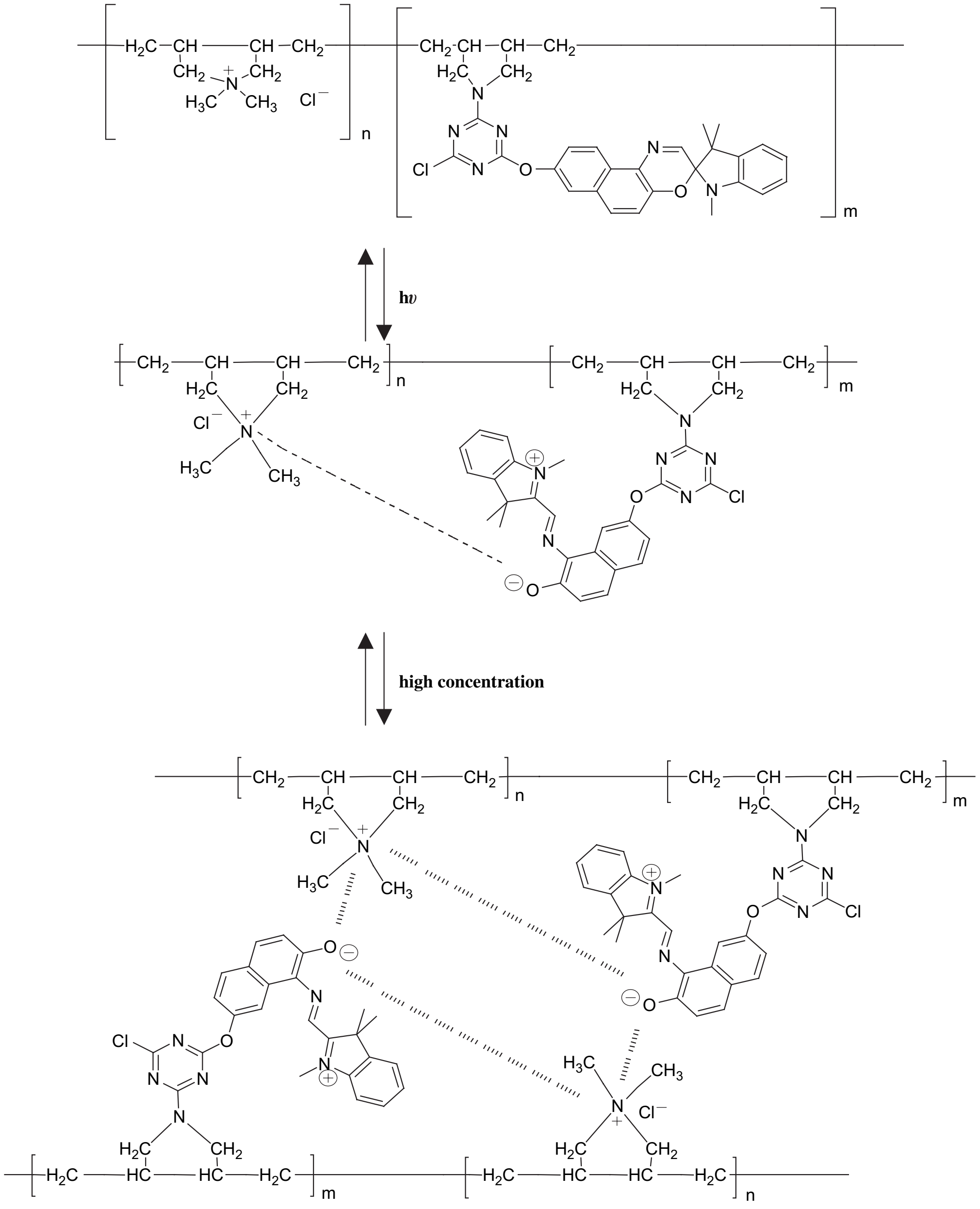
Fig. 2. First-order decolouration kinetic plot of photoisomerization (merocyanine → spiro) reaction of polymer **9**: (a) casting film, (b) 3% in MeOH (w/v), (c) 2% in MeOH (w/v), (d) 3% in MeOH (w/v), respectively.

The first-order decolouration rate constant of polymer **9** in the thin solid film was smaller than that in the solution ($k = -4.46 \times 10^{-3}$ for thin solid film, $k = -79.3 \times 10^{-3}$ for 1% polymer solution, $k = -69.4 \times 10^{-3}$ for 2% polymer solution, $k = -58.2 \times 10^{-3}$ for 3% polymer solution), which indicates that open-to-close occurs more readily in solution than in the thin solid film. The molecular structure of 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 intermolecular electrostatic interaction. Thus, the decolouration rate constant decreases with increase in the concentration of polymer. It could be said 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 intramolecular electrostatic forces (Scheme 3).

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

A polymer having photoisomerizable unsaturated linkage in the backbone is suspected to change its conformation under photoirradiation. This idea was realized using polyamide having azobenzene residues in the backbone [12]. The polymer having azobenzene pendant group would also be expected to show a conformational using photoviscosity effect [13]. The change of intramolecular interactions in polymer systems induces a conformational change in the polymer chain and can be detected by viscosity measurement.

A viscosity change by photoirradiation of spiropyran system was observed for the first time for poly(methylmethacrylate) with spiropyran pendant groups by Irie et al. [14]. A change in dipole moment due to isomerization from photochromic spiroxazine to the merocyanine form would be expected to alter intramolecular interaction of polymer chain when the spiroxazines are incorporated into the polymer pendant groups or backbone groups. 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 methanol the relative viscosity after UV irradiation is 5% 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 (Fig. 5).



Scheme 3.

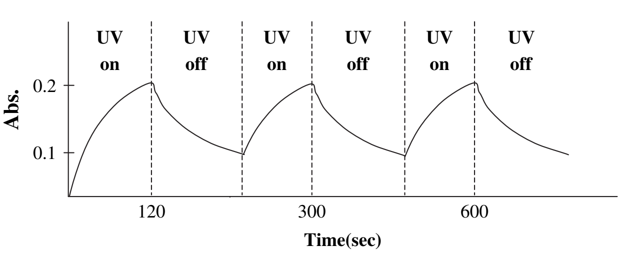


Fig. 3. Absorbance change at 615 nm of polymer **9** in MeOH (1% w/v) following periodic UV irradiation.

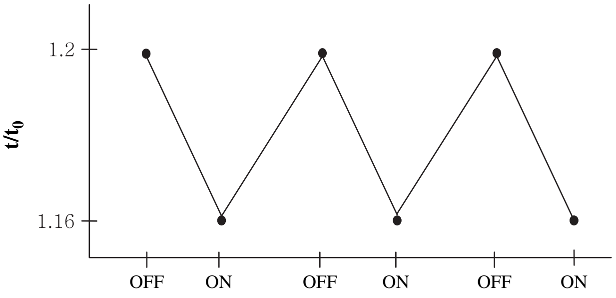


Fig. 4. Change of the viscosity of a methanol solution of polymer **9** having spiroxazine pendant group on UV irradiation at −5 °C. Concentration of the polymer is 2% w/v.

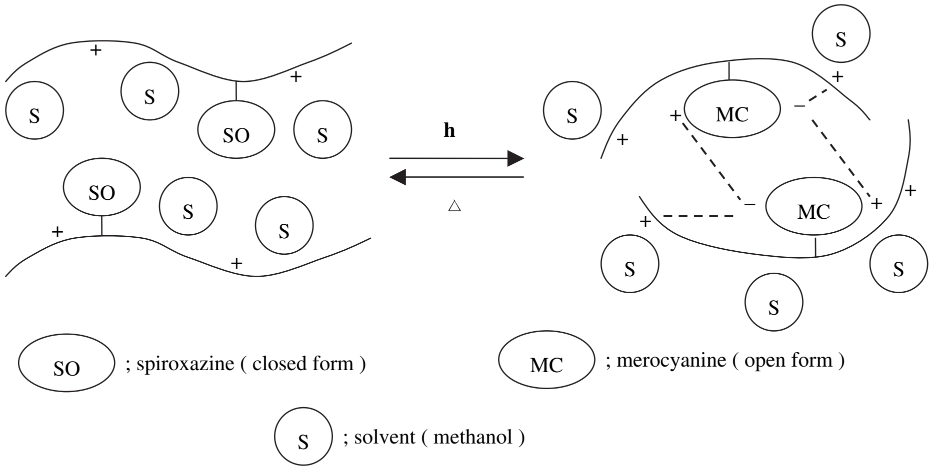


Fig. 5. Schematic illustration of photostimulated conformation change of polymer chain on UV irradiation.

Acknowledgements

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