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Short communication

Photochromic layer-by-layer films of spiroxazine polymer

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Abstract

Photochromic films of cationic spiroxazine polymer (**SOP**) were assembled via the electrostatic layer-by-layer (LBL) method, in which SOP layers were alternated with the polyanionic polystyrenesulfonate (**PSS**). The multilayer formation was monitored via UV−vis spectroscopy by measuring the increase in absorbance at 610 nm. Photoinduced ionic conductivity response and salt effect on **SOP/PSS** multilayer have been also studied.

Keywords: Layer-by-layer (LBL); Self-assembly; Spiroxazine polymer; Photochromism; Ionic conductivity; Multilayer

Layer-by-layer (LBL) method developed by Decher et al. has proved to be a simple and effective technique for fabricating ultrathin organic multilayer films [1,2]. It is necessary to dip the substrate into two different solutions alternatively and wash off the surplus polymer solution adhering to the substrate. The overall thickness of the assembly can be controlled simply by the number of deposition cycles. This approach has been extended to various other materials, including inorganic nanoparticles [3−5] and fluorescence sensing [6,7].

Recently, photochromic materials have gained much attention, and they now constitute an active research area because of their tremendous importance in biological phenomena and in their potential application in the area of linear and nonlinear optics [8]. Structurally, spiroxazines consist of two *pi* systems linked by a tetrahedral spiro carbon. On UV irradiation the C−O bond of the colorless spiroxazine is cleaved and the colored merocyanine form is obtained. Thus, the interconversion of spiro−merocyanine system has been extensively investigated due to their potential applications in molecular devices and uses in biotechnology [9]. We have previously reported the synthesis and electrostatic layer-by-layer self-assembly of some dyes [10,11]. In this context, we have examined the synthesis of a new photochromic spiroxazine polymer in which the spiroxazines were connected by bisquaternization with *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine unit. We also report herein the LBL multilayer fabrication; characterization and photochromic properties of newly synthesized spiroxazine polymer (**SOP**) were described.

Compound **1** was prepared from 1,3,3-trimethyl-2-methyleneindoline and 1-nitroso-2,7-dihydroxynaphthalene according to the method described in Refs. [12,13]. The reaction of compound **1** with cyanuric chloride **2** gave compound **3** in 75% yield [14]. A spiroxazine polymer **SOP** was prepared by the reaction of compounds **3** and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine **4** as described in Scheme 1 [15]. The IR spectra of **SOP** show the bands at around 2915 and 2870 cm^{-1} which can be assigned to CH_2 asymmetric and symmetric stretching modes of the hydrocarbon chains in propanediamine moiety.

The glass slide (20 × 10 × 1 mm) was used as substrates for UV−vis spectroscopy. The surface of the glass is pretreated to render a net negative surface charge by placing it in 2% KOH aqueous solution under sonication for 1 h. A negatively charged glass slide was first immersed into a solution containing 0.1 g **SOP** in a mixture of 14 ml Milli-Q water

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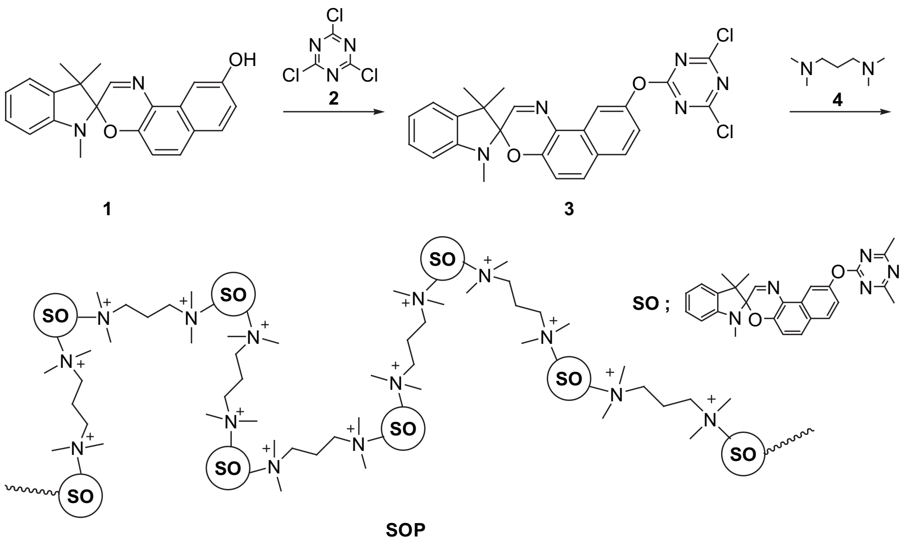

Scheme 1. Synthesis of **SOP**.

and 6 ml DMSO for 20 min. After rinsing three times in Milli-Q water, the modified substrate was dried with gentle stream of nitrogen. The layered support is then transferred into a solution containing 0.21 g **PSS** in 20 ml Milli-Q water. This process is repeated until the desired number of bilayers of **SOP/PSS** is obtained. All adsorption procedures were carried out at room temperature. A high pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm. In order to investigate the photochromic properties of the multilayer, the UV light source was switched and the multilayer was radiated.

A proposed structure model of a multilayer subjected to *n* dipping cycles is illustrated in Fig. 1. In step A, a substrate with a negative charged surface is immersed in the solution of the positively charged **SOP**. In step B, the substrate is dipped into the solution containing the negatively charged **PSS**.

The growth of **SOP/PSS** multilayer films formed by the sequential adsorption of **PSS** and **SOP** was examined by using UV–vis spectroscopy. In Fig. 2, the adsorption spectra upon UV irradiation in self-assembled multilayer containing **SOP** and **PSS** are shown. The films were clear and transparent in appearance. The regularity and uniformity with good optical quality of the LBL adsorption are demonstrated in the plot of the absorbance of **SOP** in its maximum at $\lambda_{max} = 610$ nm versus the number of dipping cycles applied.

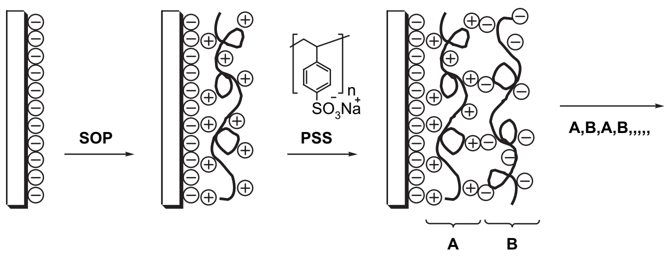

Fig. 1. Schematic representation of the adsorption process.

Upon UV irradiation a broad absorption band appeared at around 610 nm. When the sample was left in the dark at room temperature after irradiation, the absorbance at 610 nm decreased. The new band is ascribed to the generation of the open merocyanine form from the closed spiro form. **SOP** exhibited a fairly good reversibility, as can be seen in Fig. 3a, where consecutive coloration–decoloration cycles are shown. The photoinduced ionic conductivity response was analyzed at 15 °C and is shown in Fig. 3b.

For the measurement of photoinduced ionic conductivity, the device comprised of two ITO glasses (3 × 3 cm) separated by a 0.1 mm thick spacer of PET film was prepared and placed so as to face each other on the inside of the cell, and the edges

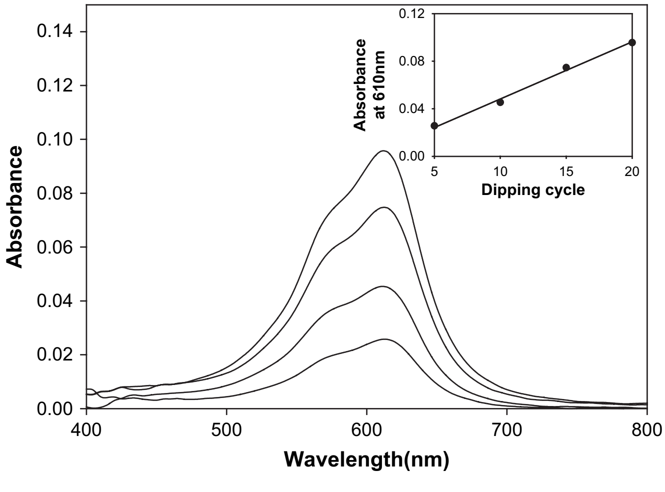

Fig. 2. UV–vis absorption spectra of **SOP/PSS** multilayer films through a consecutive LBL deposition. The inset shows the increase in absorbance at 610 nm after UV irradiation as a function of deposition cycle.

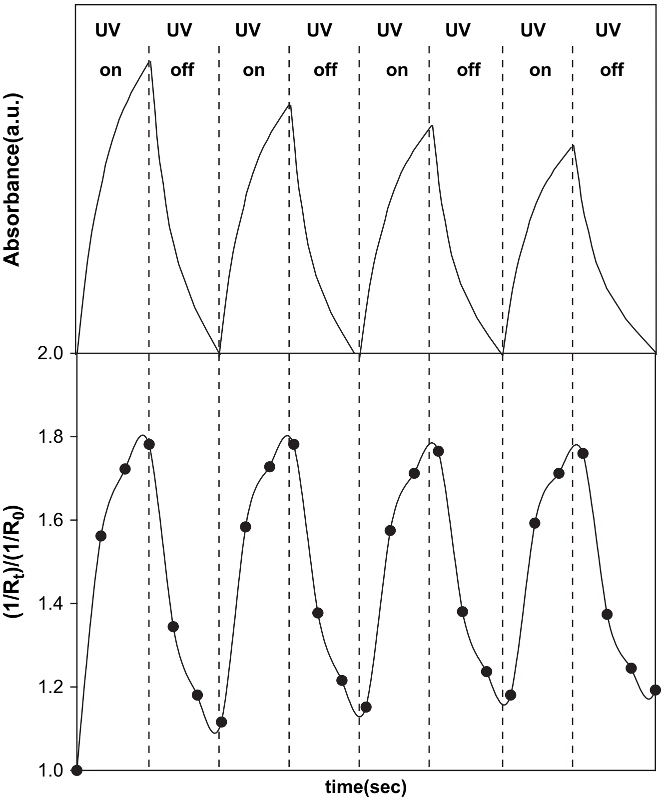

Fig. 3. Absorbance change at 610 nm (a) and photoinduced ionic conductivity response (b) following periodic UV irradiation for **SOP/PSS** multilayer.

of the cell were sealed with insulating epoxide resin. The multilayer assemblies of **SOP/PSS** were deposited on the surface of only one ITO glass. Prior to the final sealing, the space between the electrodes was filled with a Milli-Q water and DMSO solution of **SOP** and tetra-*n*-butylammonium perchlorate, $[CH_3(CH_2)_3]_4NClO_4$, as electrolyte.

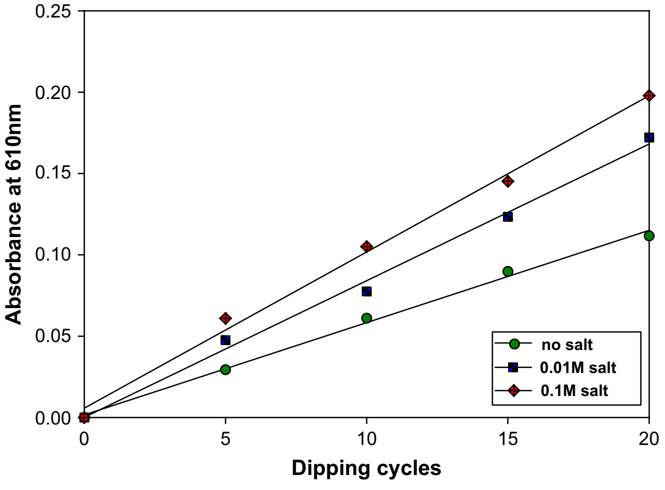

Fig. 4. Salt concentration effect on **SOP/PSS** multilayer (measured at 610 nm after UV irradiation). The solution is adjusted to three different ionic strengths by the addition of NaCl: no salt (●); 0.01 M (■); 0.05 M (◆).

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. Sufficient reversibility was found in multilayer of **SOP** and this response was completely synchronized with that in the absorbance changes.

The salt effect on the **SOP/PSS** multilayer was investigated. The dipping water/DMSO solution of **SOP** is adjusted to two different ionic strengths by addition of NaCl: 0 (no salt), 0.01 and 0.05 M. Fig. 4 shows the UV–vis absorbances of **SOP/PSS** multilayers at 610 nm as a function of number of layers deposited. The results showed that high salt concentrations tend to promote adsorption to surfaces.

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[14] All analytical data agree with the proposed structure for compound **3**: cyanuric chloride 6.61 g (35.85 mmol) **2** was dissolved in 120 ml of acetone. Temperature of the solution was maintained at 0–5 °C. Compound **1** (12.33 g, 35.85 mmol) was added to the solution, which was then stirred for 2.5 h. Forty millilitres of Na_2CO_3 (0.98 N) was added to the solution and stirred for 1.5 h. After completion of reaction, this solution was poured into 500 ml of H_2O. The resulting solid **3** was filtered and obtained. Yield: 13.3 g (75.5%); m.p. 140 °C; MS *m/z* (M^+) 492; Anal. calculated for $C_{25}H_{19}Cl_2N_5O_2$: C, 60.99; H, 3.89; N, 14.22. Found: C, 60.01; H, 3.76; N, 14.13; ^1H NMR ($CDCl_3$, δ ppm): 1.36 (s, 6H), 2.77 (s, 3H), 6.59 (d, $J = 7.52$ Hz, 1H), 6.91 (t, $J = 7.56$ Hz, 1H), 7.05 (d, $J = 8.52$ Hz, 1H), 7.09 (d, $J = 7.04$ Hz, 1H), 7.17 (d, $J = 9.04$ Hz, 1H), 7.23 (t, $J = 7.52$ Hz, 1H), 7.70 (d, $J = 8.52$ Hz, 1H), 7.72 (s, 1H), 7.83 (d, $J = 9$ Hz, 1H), 8.32 (s, 1H).
[15] Polymerization: compound **3** (0.5 g, 1 mmol) and N,N,N',N'-tetramethyl-1,3-propanediamine **4** (0.27 g, 2 mmol) were stirred at room temperature for 6 h. The resulting polymer solution was precipitated into 100 ml ether. The precipitated polymer was filtered and washed with ether and ethylacetate. The polymer **SOP** was dried to constant weight at 60 °C for 12 h. The polymer yield was 33%.