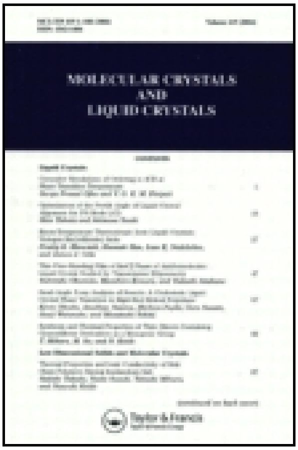

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Self-Assembly Fabrication Using Diazo Coupling Dye and Spiroxazine

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Version of record first published: 22 Sep 2010

To cite this article: Sung Hoon Kim, Young Min Park, Chang Soo Lee & Young A Son (2008): Self-Assembly Fabrication Using Diazo Coupling Dye and Spiroxazine, Molecular Crystals and Liquid Crystals, 491:1, 94-102

To link to this article: http://dx.doi.org/10.1080/15421400802329418

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 94–102, 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802329418

Self-Assembly Fabrication Using Diazo Coupling Dye and Spiroxazine

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By self-assembly layer-by-layer technique, ordered multi-layer films being composed of diazonium resin, J-acid, photochromic spiroxazine and poly-(sodium-4-styrene)sulfonate (PSS) were alternately fabricated on the glass slide, The fabrication of the multi-layer films was characterized by UV-vis spectroscopy and Atomic Force Microscopy (AFM). During the first bilayer fabrication, azo dye was simultaneously synthesized by diazo coupling reaction between diazonium resin and J-acid coupler. It is displayed from the multi-layer films that spectral chromism effect by spiroxazine moiety was determined. AFM results also show that the multi-dye layer fabrication was successfully obtained by stepwise chemical assembly and that the surface of the multi-layer was relatively uniform.

Keywords: coupling reaction; multi-layer; photochromism; spiroxazine

INTRODUCTION

Recently, much attention has been paid to multi-layer film fabrication using alternate deposition technique in which oppositely charged species based on electrostatic interaction are attracted. Because the layer-by-layer alternate adsorption is a rapid and simple method with

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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precise fabrication control of film thickness and layer composition, it has been widely used for the purpose of surface modification and functional material preparation [1–4].

A photochromic compound [5,6] is commonly characterized by its ability to undergo a reversible color change. Interests in photochromism effects with organic materials have been substantially increased due to their potential applications in many new technologies such as data recording, optical switching, displays and non-linear optics.

In this study, we described the preparation of multi-layer thin films formed by alternating deposition of diazonium resin [7,8], J-acid, photochromic spiroxazine [9,10] and poly(sodium-4-styrene) sulfonate (PSS). With fabrication process, azo dye between diazonium resins and J-acid coupler was synthesized by diazo coupling reaction. Photochromism spectral effect was also determined when the fabricated films were subjected to UV irradiation.

EXPERIMENTAL

Preparation of the Diazonium Resin

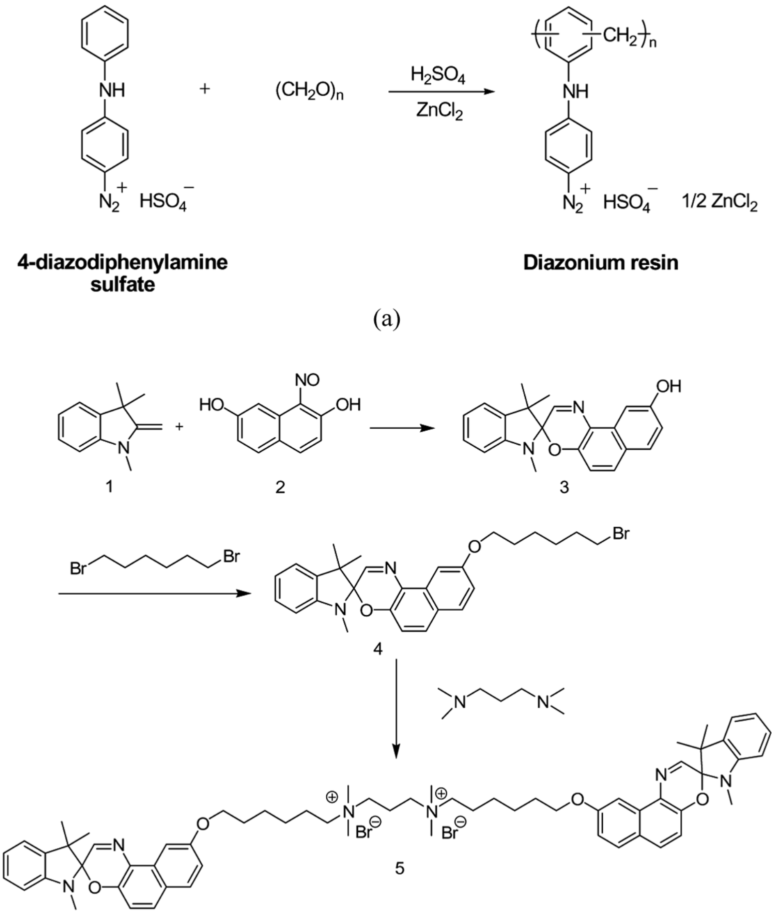
The diazonium resin compound [11–13] using the polycondensation of 4-diazodiphenylamine sulphate with paraformaldehyde was prepared. 0.017 mol (5 g) of 4-diazodiphenylamine sulphate was taken and 9 ml of 95% H_2SO_4 was added dropwise under constant stirring. Using an ice-bath, the flask was cooled and 0.02 mol (0.6 g) of paraformaldehyde was then added into batches at temperatures of 0–5°C. This reaction was continued for 3 hrs at this temperature. The reaction mixture was poured into 50 ml of ice water. 30 ml of aqueous solution containing 5 g of zinc chloride was added to precipitate the diazonium resin as a 1/2 $ZnCl_2$ complex. After filtration and drying, a yellow-green powder was obtained and kept in the dark room.

Synthesis of Spiroxazine 3, 4, 5

Spiroxazine **3** was prepared from 1,3,3-trimethyl-2-methylene-indoline **1** (9.17 g, 52.93 mmol) and 1-nitroso-2,7-hydroxy-naphthalene **2** (10.00 g, 52.91 mmol) according to the method described in references [14,15] with a yield of 50%. 1,3,3-trimethyl-6′-bromo-hexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4** was prepared by the reaction of prepared spiroxazine **3** and 1,6-dibromohexane as described in the literatures [14–16] with a yield of 63%.

Finally, the spiroxazine compound **4** (2.48 g, 4.9 mmol) and *N*,*N*,*N*′,*N*′-tertramethyl-1,3-propanediamine (0.32 g, 2.46 mmol) in 2-methoxyethanol were refluxed for 48 h. After reaction, the mixture solution was stirred in diethyl ether for 1 hr. And then, the precipitated product **5** was filtered, washed with diethyl ether and dried. Yield: 40%; m.p.: 193°C; ^{1}H NMR (DMSO-d_6) δ 7.84 (s, 2H), 7.82 (s, 2H), 7.76 (d, $J = 9.04$ Hz, 2H), 7.70 (d, $J = 9.04$ Hz, 2H), 7.15 (m, 4H), 7.05 (d, $J = 4.56$ Hz, 2H), 6.91 (d, $J = 9.04$ Hz, 2H), 6.83 (t, $J = 8.04$ Hz, 2H), 6.66 (d, $J = 7.52$ Hz, 2H), 4.14 (t, $J = 6.04$ Hz, 4H), 3.29 (m, 8H), 3.02 (s, 12H), 2.69 (s, 6H), 1.81 (m, 6H), 1.71 (m, 4H), 1.55 (m, 4H), 1.28 (s, 6H), 1.25 (s, 6H).

The general preparation schemes of diazonium resin and spiroxazine compound are shown in Fig. 1.



(a)

(b)

FIGURE 1 Synthesis of diazonium resin (a) and photochromic spiroxazine compound (b).

Self-Assembly Multi-Layer Deposition

Figure 2 shows the schematic representation of the self-assembly fabrication using diazo coupled part and photochromic spiroxazine part. At first, the surface of the glass slide was pretreated to provide a negative charged surface by placing it in 2% KOH aqueous solution under sonication for 30 min. A negative charged glass slide was dipped into the positively charged diazonium resin aqueous solution (0.05 g/200 ml) for 10 min. After rinsing in distilled water, diazonium resin deposited on the glass slide was dried with nitrogen. Secondly, the glass slide having positively charged diazonium resin was dipped into the negatively charged J-acid aqueous solution (0.04 g/200 ml) for 10 min. At this step, azo dye coupling reaction was simultaneously occurred with layer-by-layer attraction. Thirdly, the glass slide having negatively charged J-acid was dipped into the solution containing positively charged spiroxazine compound 5 (0.05 g/200 ml) for 5 min. At last, a positively charged glass slide transferred into the negatively charged PSS aqueous solution (0.05 g/200 ml) for 5 min. The glass slide was rinsed with distilled water and dried nitrogen. This preparation process was repeated until the desired number of multi-layers was achieved. The process was also carried out in dark room to avoid decomposition of the diazonium resin.

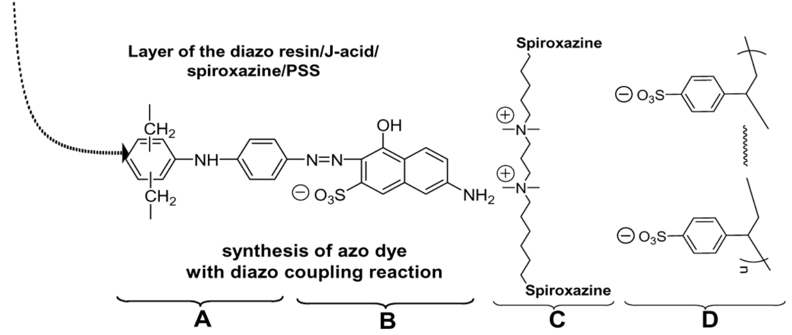


FIGURE 2 Scheme of the self-assembled fabrication multi-layer films.

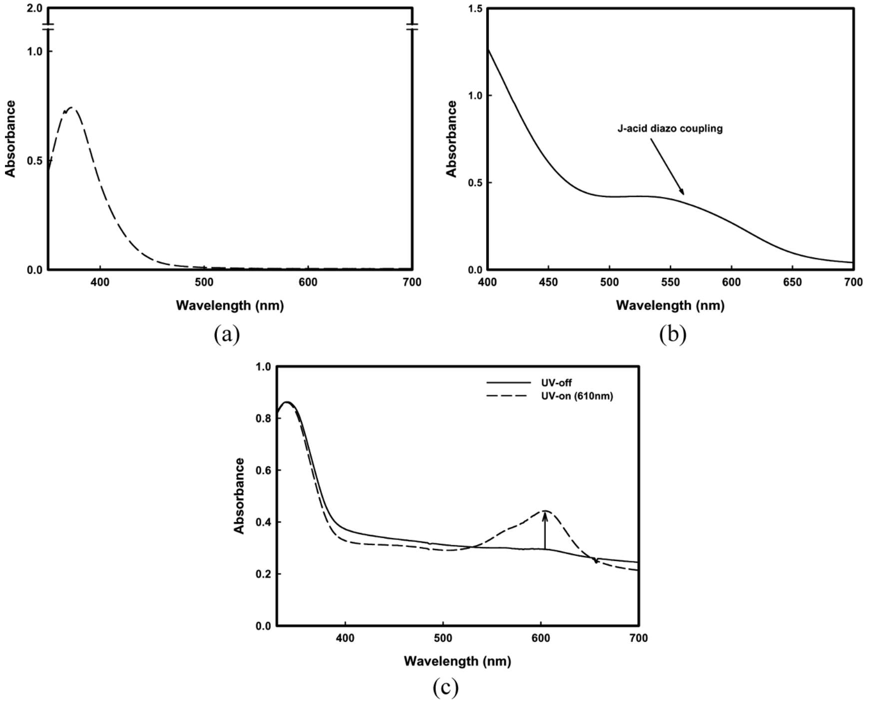
Characterization

The fabrication multi-layers showing diazo coupling reaction and reversible photochromic property were determined by UV-vis spectroscopy. The surface morphology of the multi-layer films was also recorded using Atomic Force Microscopy (AFM).

RESULTS AND DISCUSSION

Fabrication and Characterization of Self-Assembly Multi-Layers

Self-assembly multi-layer fabrication caused by electrostatic interaction was carried out. With fabrication process, diazo coupling reaction was simultaneously occurred to form the azo dye layer. Also the photochromic layer of spiroxazine was formed. These fabrication results on the plate were monitored by UV-vis spectroscopy. The findings are shown in Figs. 3–4. The absorption spectra of the diazonium

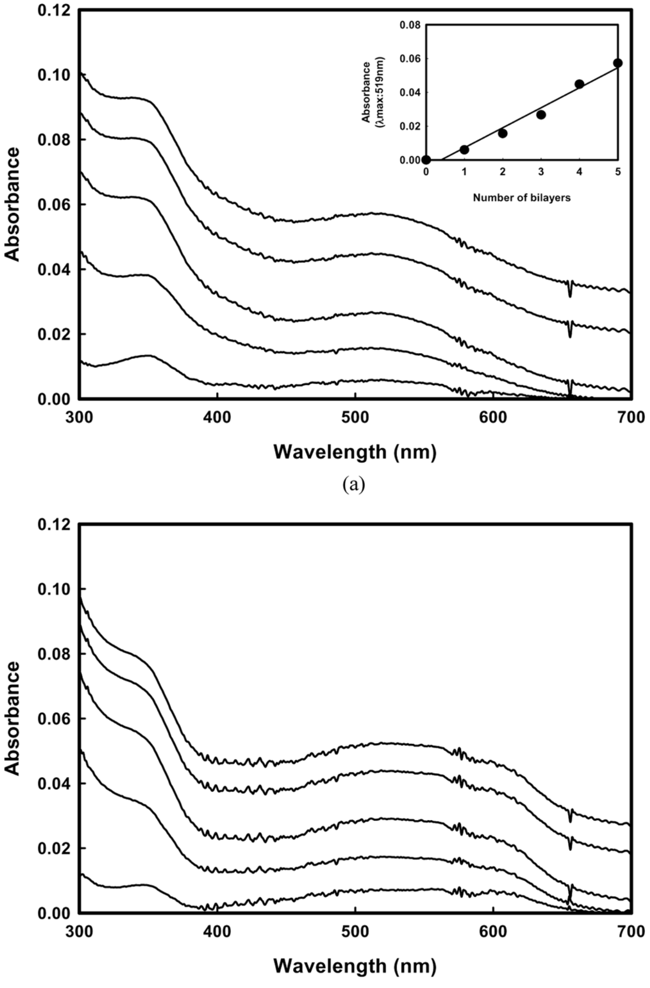


(a)

(b)

(c)

FIGURE 3 UV-vis absorption spectra of diazo resin (a), diazo coupling of diazo resin/J-acid (b) and spiroxazine compound 5 (c).



(a)

(b)

FIGURE 4 UV-vis absorption spectra of diazo resin/J-acid/spiroxazine/PSS layers (a) and UV irradiation to the multilayers (b).

resin and diazo dye solution are shown in Figure 3. While diazonium resin solution shows no absorption peak above 400 nm from Figure 3(a), new absorption peak was observed from azo dye coupling reaction between diazonium resin and J-acid in Figure 3(b). The observed new peak can be estimated as the dye synthesis by diazo coupling reaction. The absorption peak of synthesized azo dye from diazo coupling reaction was at 520 nm. Also, the photochromic absorption peak of spiroxazine **5** was determined at 610 nm. This photochromic reaction is caused by the reversible heterolytic cleavage of the C (spiro)-O bond under UV irradiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark.

Growth of the spiroxazine multi-layers with UV irradiation and the azo dye layers was measured by the UV-vis spectroscopy. The absorption spectra of the self-assembled multi-layer and photochromism are shown in Fig. 4. Figure 4(a) shows that new absorption shoulder peak caused by diazo coupling reaction at 520 nm. And the absorption intensity increases with increasing bilayer numbers, which indicates the successful fabrication procedures. The plots (inset in Fig. 4(a)) were linearly increased between absorbance and bilayer numbers. This result also represents uniform build-up fabrication. In Figure 4(b), the absorption spectra upon UV irradiation to the self-assembled multi-layers containing spiroxazine moiety **5** are shown. From the Figure 4(b), visible spectral absorption change of the multi-layers due to spiroxazine moiety was observed. The spectral change appeared at 610 nm to be like Figure 3(c). The reason for absorption spectral change is owing to the reversible heterolytic cleavage of the C (spiro)-O bond under UV irradiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark. From these results, it can be proposed that the fabrication of azo dye coupling and spiroxazine compound **5** was successfully achieved.

Image of Atomic Force Microscopy (AFM)

Information concerning the surface morphology of the multi-layer films was obtained by Atomic Force Microscopy (AFM). Figure 5 shows the surface of diazonium resin/J-acid/spiroxazine/PSS multi-layer films with 1, 3 and 5 repeating cycles assembled on glass substrate. From the Figure 5, it is considered that the multi-dye layers are relatively uniform and smoothly fabricated. The surface of Figures 5(a–c) is uniformly covered with diazonium resin/J-acid/spiroxazine/PSS layer. The RMS roughness of 1, 3, 5 bilayers was determined to be 2.4 nm, 2.9 nm and 5.2 nm in an area of $1.0 \times 1.0\,\mu m^2$, respectively.

CONCLUSIONS

In this paper, the multi-layer films of diazonium resin/J-acid/spiroxazine/PSS have fabricated on the glass slide by electrostatic layer-by-layer self-assembly method. The formation of multi-layer

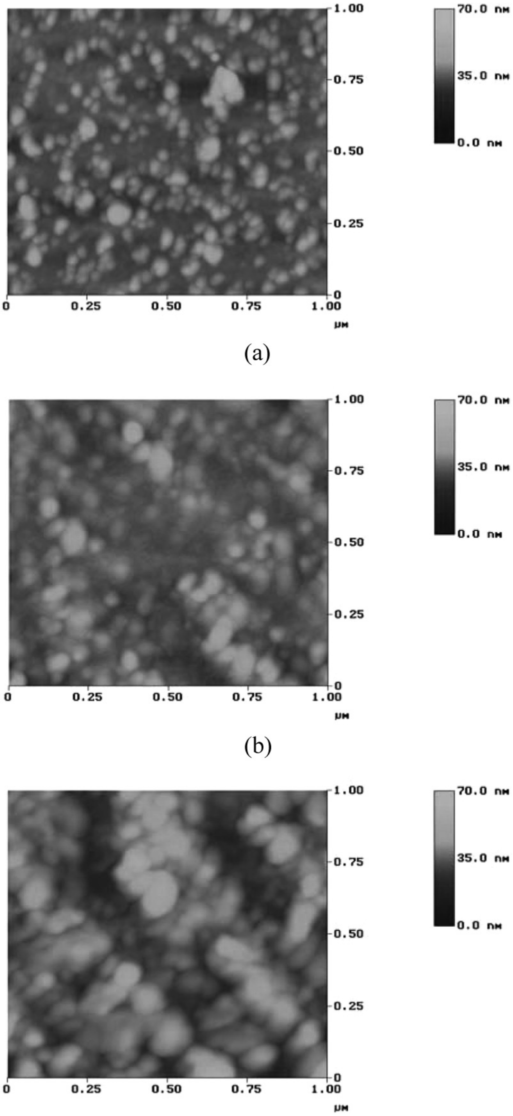


FIGURE 5 AFM images of diazo resin/J-acid/spiroxazine/PSS; 1-layer (a), 30-layers (b), 5-layers (c).

was confirmed by the measurement of UV-vis spectroscopy and AFM. The absorption spectra of the fabricated layer showed gradual increasing behavior with film thickness. In the case of a layer using diazonium resin/J-acid, the new absorption peak was observed by diazo coupling reaction between diazonium resin and J-acid. In the case of layer using spiroxazine moiety, the absorption spectra upon UV irradiation showed that photochromic spectral change was generated by the open merocyanine form from the closed spiro form. The result of AFM images showed that the deposition process is progressive and relatively uniform.

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