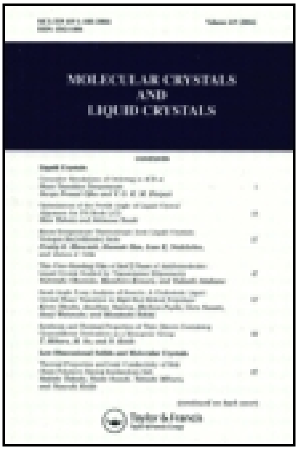


Molecular Crystals and Liquid Crystals

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

Layer-by-Layer Assembled Electrochromic Film Based on an Alkylsulfonated Polyaniline

Eunkyoung Kim [a] & Yuna Kim [a]

[a] Department of Chemical Engineering, Yonsei University, Seoul, South Korea

Version of record first published: 23 Aug 2006

To cite this article: Eunkyoung Kim & Yuna Kim (2006): Layer-by-Layer Assembled Electrochromic Film Based on an Alkylsulfonated Polyaniline, Molecular Crystals and Liquid Crystals, 447:1, 173/[491]-179/[497]

To link to this article: http://dx.doi.org/10.1080/15421400500387361

Mol. Cryst. Liq. Cryst., Vol. 447, pp. 173/[491]–179/[497], 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500387361

Layer-by-Layer Assembled Electrochromic Film Based on an Alkylsulfonated Polyaniline

Eunkyoung Kim
Yuna Kim
Department of Chemical Engineering, Yonsei University,
Seoul, South Korea

An alkylsulfonated polyaniline, poly(aniline-N-butylsulfonate)s (PANBS), was assembled by the layer-by-layer (LBL) assembling technique as an electroactive anionic polymers for the layering. The counter ions for PANBS layer were polyaniline (H^+ doped) and vinylbenzyldimethyl-n-alkylammonium salts (VBAA) as the conductive and insulating polycation, respectively. High color contrast was observed when the electrochromic (EC) film was composed alternatively of the PANBS/PAN and PANBS/VBAA layer. Interlayer insulating gap controlled by the alkyl chain length of VBAA, was an important factor to increase EC response of the window assembled by the LBL method.

Keywords: electrochromic; electron transfer; interlayer barrier energy; layer-by-layer assembly; optical response; polymer

INTRODUCTION

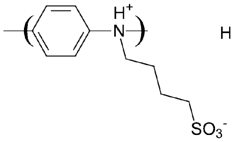
Electrochromic (EC) devices have attracted much interest due to their low power consumption as well as their memory effect [1]. Much progress has been made in developing new materials that exhibit long-term stability and various colors at different potentials, and in fabricating through nanotechnology [2]. In particular, the electrostatic layer-by-layer (LBL) assembly technique has been introduced to fabricate EC devices based on complementary coloring electrodes, using poly(3,4-ethylene dioxythiophene) (PEDOT) and polyaniline [2(b)], or a sulfonated PEDOT [2(c)], an alkylsufonated polyaniline [3], and

This work was financially supported by the Ministry of Science and Technology (MOST) of Korea and the grant from Yonsei University.

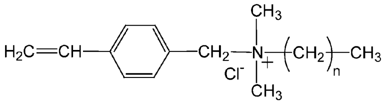
Address correspondence to Eunkyoung Kim, Department of Chemical Engineering, Yonsei University, 134, Shinchon-dong, Seodaemun-gu, Seoul, 120-749, South Korea. E-mail: eunkim@yonsei.ac.kr

inorganic electrochromic systems such as transition metal complexes [4] and poly(oxometalates) [5]. In these examples, an inert polymer such as poly(diallyl dimethylammonium chloride) (PDAC), poly(allylamine hydrochloride) (PAH), poly(acrylic acid) (PAA), poly(styrene sulfonate) (SPS), or an inert alkyl ion such as vinylbenzyldimethyl-alkylammonium chloride (VBAA) [3] is used as the counterion for the electroactive species.

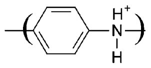
Herein we report electrochromic properties of a layer-by-layer assembled EC polymer film based on poly(aniline-*N*-butylsulfonate)s (PANBS) that offers high redox stability as well as electrochromic and self-assembling properties [6–8]. The counter ions for the PANBS layers were polyaniline (H^+-doped) and vinylbenzyldimethyl-alkyl ammonium salt (VBAA). As it is generally known that the charge transport is highly dependent on the distance between the donor and the acceptor [9], it is important to reduce the gap present between the layers, in a way to reduce interlayer barrier for charge transport. Thus we adopt vinylbenzyldimethyl-dedecyl ammonium salt (VBDA) as the counter cation. The structures are given below:



PANBS



VBDA (n=11)



PAN

EXPERIMENTAL

Polyaniline was obtained from Aldrich. VBDA was synthesized according to Ref. [10]. Aniline *N*-butanesulfonic acid was prepared as previously reported [6]. Chemical polymerization was carried out in a reaction vessel at 0°C using sodium persulfate as an oxidant [11–12].

LBL self-assembly of EC film was carried as follows. PANBS was dissolved in water at a concentration of 2 mg/ml. An aqueous solution of VBDA was prepared at the same concentration. Undissolved particles were filtered using a filter paper. ITO glass was treated with *N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane to make the substrate surface hydrophilic. A multilayered film was obtained by alternatively dipping the ITO glass into a 0.2-wt.% PANBS aqueous solution and a polycation solution (PAN or VBDA, 2 mg/ml) for 10 min using a homemade dipper that controls the dipping speed. The electrochromic PANBS layer was deposited first as an anionic layer, then PAN, followed by the bilayer of PANBS and VBDA layer. Every odd-numbered layer corresponds to PANBS, and every even-numbered layer to the counter cation (either PAN or VBDA). The total number of layer in the EC film was 15. The LBL film was dried with nitrogen gas after washing with distilled water. The drying procedure between the adsorption of either cationic or anionic layers was necessary for building uniformly assembled layers. The *in-situ* spectroelectrochemical system consisted of a computer-controlled reflectance spectrophotometer using a K-Mac fiber-optic spectrometer and an electrochemical subsystem (BAS 100B). The maximum difference in absorbance between the colored and bleached states was observed at 570, 630, 800 nm for the PANBS-based electrochromic films. Layer thickness was determined by an alpha step (TENCOR INSTRUMENTS, Alpha-step IQ).

RESULTS AND DISCUSSIONS

Film Growth by LBL Assembly

Electrochromic films were fabricated using the LBL approach, which involves coating ITO glass with polycation and polyanion in an alternating manner, followed by rinsing between each deposition step [13]. The color of the EC layer become intense and absorption tail at 350 ~ 500 nm was increased in UV spectrometer, as the number of conducting polymer (PANBS and PAN) was accumulated. Figure 1

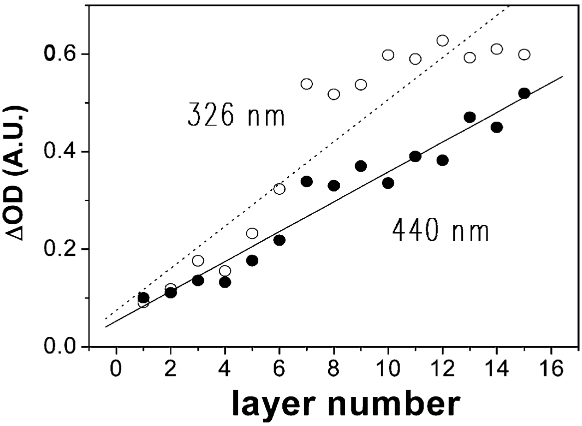


FIGURE 1 Plot of the absorbance increase (ΔOD) against the layer number of the film wavelengths (326 nm and 440 nm).

shows correlation between the layer number against absorbance increase (ΔOD) of the film at selected wavelengths (326 nm and 440 nm). A liner relationship was observed between (ΔOD) and the layer build-up with the slopes of 0.043 and 0.031 for 326 nm and 440 nm, respectively, indicating that the electrochromic layer growth in every buildup is homogeneous.

Electrochromic Property of the EC Film Prepared by the LBL Method

CV was used to identify the redox potential ranges and to elucidate the general electrochemical behavior of the electrochromic layer. PAN and PANBS have different redox potentials, and VBDA does not have a redox property in the scanning range between −1.0 V and 0.5 V *vs.* Ag/AgCl, in a supporting electrolyte of $LiClO_4$ containing $HClO_4$ in CH_3CN, with a scan rate of 50 mV/s. To assess the electrochemical accessibility of the redox polymers within the films, the redox current was determined for each film with a different composition. Figure 2 shows CV applied to the multilayer-coated ITO glass surface. The half potentials ($E_{1/2}$) were determined as 0.49 and 0.82 V from the CV, and were assigned as one-electron transfer redox process of PAN and PANBS, respectively. The half potentials of the conducting polymers were consistent with the previous results [6]. The full width at half-max (fwhm) and the peak separation are much larger than the value expected for an ideal one-electron Nernstian redox system, indicative

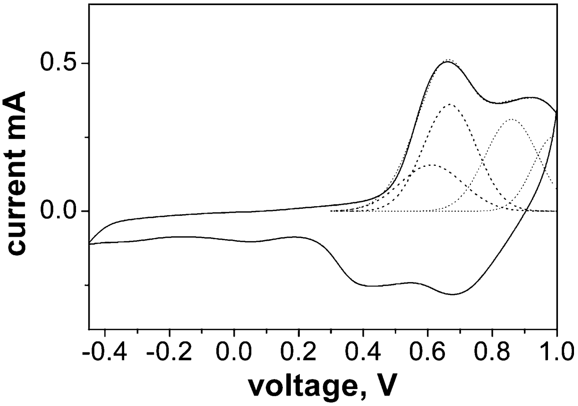


FIGURE 2 Cyclic voltammogram of EC at film in a supporting electrolyte of $LiClO_4$ containing $HClO_4$ in CH_3CN. The line indicates linear fit. Selected (scan rate: 50 mV/s).

of the repulsive interactions of the redox sites [14]. This is mainly due to the electrically resistive VBDA layer, which generate layer barrier potential as described in our previous paper [15].

When the applied potential was above 0.5 V, the color of the EC window changed to a dark-green. The color was intensified as the applied potential was raised to 0.7 V and stable even after the electricity was off. Above 0.7 V, however, the color change was not significant. On the other hand, the dark-green color faded when the potential was reversed toward negative. The bleached state was also stable when the electricity was off. Such a bistable color change was apparent in the visible spectra resulting absorbance increase >350 nm when oxidized, as shown in Figure 3.

The optical response of the EC window to a step potential of –0.1 to +0.7 V is shown in Figure 4. The optical response was much enhanced as compared to the EC film prepared with VBAA of a longer alkyl chain length (n = 17) (Fig. 4b).

Such a large increase of the optical response in the film of VBDA (n = 11) could arise from the reduced gap between the layers, judging from the general concept on the electron transfer rate that is highly dependent on the distance between the donor and the acceptor [9].

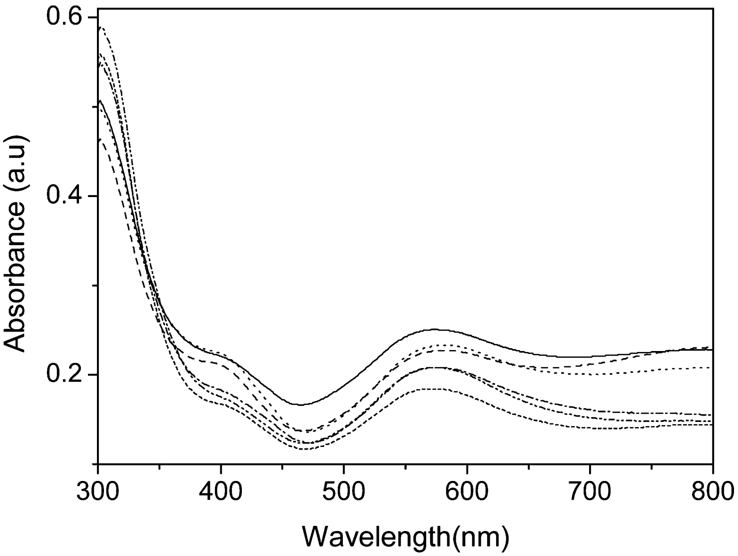


FIGURE 3 UV spectra of the EC film at different applied potentials: Top to bottom, +1, +0.7, +0.5, +0.3, +0.1, −0.1 V. In a supporting electrolyte of $LiClO_4$ containing $HClO_4$ in CH_3CN.

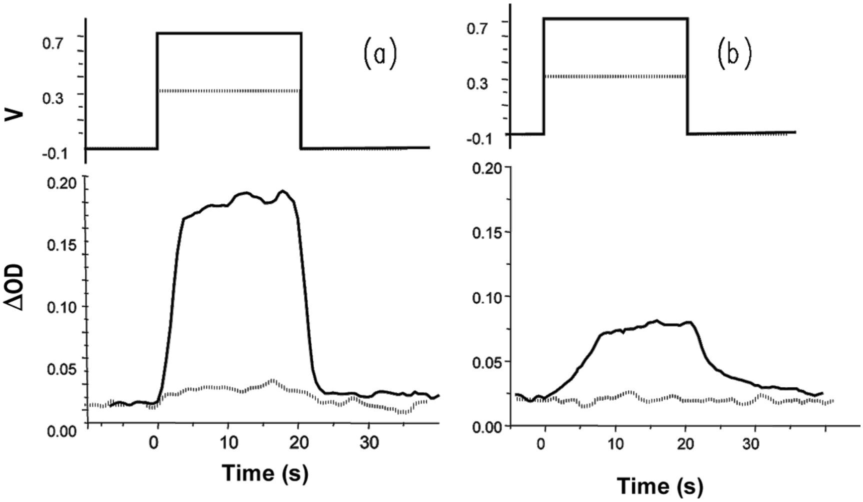


FIGURE 4 Optical response of the EC film of VBAA with n = 11 (a) and n = 17 (b) to the step potential of –0.1 to 0.7 V (solid line) and –0.1 to +0.3 V (dotted line).

Thus this result emphasize the importance of layer gap present in the LBL assembled EC layer, which can be controlled by the alkyl chain length of VBAA.

CONCLUSION

Anodically coloring polymer, PANBS, was self-assembled by the layer-by-layer (LBL) technique using polyaniline (H^+ doped) and vinylbenzyldimethyl-*n*-alkylammonium salts (VBAA) as the counter cation. The growth of such multilayer films was characterized by the increment of absorbance through UV-visible spectroscopy. An EC window assembled with the LBL technique showed reversible electrochromic response with characteristic electrochemical behavior. Optical contrast between the oxidized and reduced state was much enhanced in the EC window assembled using VBDA (n = 11) as compared to that using VBAA (n = 17). This result could be attributed to the reduced gap between the layers of EC film, which could be deduced from the shorter alkyl chain in the EC film with VBDA.

REFERENCES

[1] (a) Platt, J. R. J. (1961). *J. Chem. Phys.*, *34*, 862.
(b) Mortimer, R. J. (1997). *Chem. Soc. Rev.*, *26*, 47.

[2] (a) Peters, A. & Branda, N. R. (2003). *J. Am. Chem. Soc.*, *125*, 3404.
  (b) DeLongchamp, D. & Hammond, P. T. (2001). *Adv. Mater.*, *13*, 1455.
  (c) Cutler, C. A., Bouguettaya, M., & Reynolds, J. R. (2002). *Adv. Mater.*, *14*, 684.
  (d) Argun, A. A., Aubert, P.-H., Thompson, B. C., Schwendeman, I., Gaupp, C. L., Hwang, J., Pinto, N. J., Tanner, D. B., MacDiarmid, A. G., & Reynolds, J. R. (2004). *Chem. Mater.*, *16*, 4401.

[3] Jung, S., Kim, H., Han, M., Kang, Y., & Kim, E. (2004). *Materials Sci. & Eng. C*, *24*, 57.

[4] Millward, R. C., Madden, C. E., Sutherland, I., Mortimer, R. J., Fletcher, S., & Marken, F. (2001). *Chem. Commun.*, *25*, 1994.

[5] Liu, S. Q., Kurth, D. G., Mohwald, H., & Volkmer, D. (2002). *Adv. Mater.*, *14*, 225.

[6] (a) Kim, E., Lee, M.-H., Moon, B. S., Lee, C., & Rhee, S. B. (1994). *J. Electrochem. Soc.*, *141*, L26.
  (b) Kim, E., Lee, K., & Rhee, S. B. (1997). *J. Electrochem. Soc.*, *144*, 227.
  (c) Kim, E., Lee, K.-Y., Lee, M.-H., Shin, J.-S., & Rhee, S. B. (1997). *Synth. Met.*, *85*, 1367.

[7] (a) Kim, E., Lee, M.-H., & Rhee, S. B. (1995). *Synth. Met.*, *69*, 101.
  (b) Jang, J. H., Kim, J., Lee, K., Lee, H., Kim, E., & Rhee, S. B. (1995). *Synthetic Metals*, *69*, 173.
  (c) Kim, E., Lee, M.-H., & Rhee, S. B. (1997). *Mol. Cryst. & Liq. Cryst.*, *295*, 77.

[8] Kang, Y., Kim, E., & Lee, C. (2001). *Mol. Cryst. Liq. Cryst.*, *371*, 87.

[9] Baldo, M. A. & Forrest, S. R. (2001). *Phys. Rev. B*, *64*, 085201.

[10] Fu, X. & Qutubuddin, S. (2001). *Polymer*, *42*, 807.

[11] MacDiarmid, A., Chiang, J., Halpern, M., Huang, W., Mu, S., Somasiri, N., Wu, W., & Yaniger, S. (1985). *Mol. Cryst. Liq. Cryst.*, *121*, 173.

[12] Krause, S. & Bohon, K. (2001). *Macromolecules*, *34*, 7179.

[13] (a) Decher, G. & Hong, J. D. (1991). *Makromol. Chem. Macromol. Symp.*, *46*, 321.
  (b) Lvov, Y., Haas, H., Decher, G., Möhwald, H., Mikhailov, A., Utchedlishvily, B., Morgunova, E., & Vainshtein, B. (1994). *Langmuir*, *10*, 4232.

[14] Bard, A. J. & Faulkner, L. R. (2001). *Electrochemical Methods. Fundamentals and Applications*, 2nd ed. Wiley: New York.

[15] Kim, E. Submitted for publication.