

Langmuir-Blodgett Films Containing Carotenoid Dye.

II. Structure and Conducting Characteristics of Ethyl β -Apo-8-Carotenoate/Cadmium Stearate LB Films

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ABSTRACT: The structure, doping, and electrical conductivity characteristics of ethyl β -apo-8-carotenoate dye (EA8C)/cadmium stearate Langmuir-Blodgett (LB) films were investigated. The EA8C/cadmium stearate mixed multilayer thin films, with the molar ratio of 1 : 4, prepared at subphase pH 6, exhibited well-defined layered structures as determined by X-ray diffraction (XRD) spectra. The mixed LB films went ready doping upon exposure to iodine vapor or dipping in sulfuric acid solution. The UV/VIS and XRD data showed that the incorporated EA8C was thermally stable up to 80°C. The best conductivity characteristics were obtained with the iodine vapor. Thus, the mixed LB films exposed to iodine vapor showed in-plane and transverse conductivities of 10^{-6} and 10^{-7} – 10^{-8} S/cm, respectively. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 619–624, 1997

Key words: Langmuir-Blodgett film; electrical conductivity; spectroscopic measurements

INTRODUCTION

We have recently been actively working on the electroconducting properties of Langmuir-Blodgett (LB) films and their interfacial behaviors¹ due to their potential technological applications as ultrathin layers and molecular information accessible in the monolayer experiments. In the preceding article,² we described the fabrication of ethyl β -apo-8-carotenoate dye (EA8C)/cadmium stearate LB films and demonstrated that the incorporation of cadmium stearate as a processing aid was critically important to the formation of highly condensed and easily transferable LB films.

In the present article, we examine structure, doping, and electrical conducting characteristics of the dye-containing LB films based upon EA8C and cadmium stearate.

EXPERIMENTAL

Preparation of the EA8C/Cadmium Stearate LB Films

Techniques for the preparation of the LB films have been described in the preceding article.²

Iodine and Sulfuric Acid Doping

The doped EA8C/cadmium stearate mixed LB films were prepared by three different methods. For the first and second methods, the mixed LB films were exposed to iodine vapor for 20 minutes at room temperature under vacuum of 160 torr or dipped into $5 \times 10^{-4}M$ sulfuric acid solution for 20 minutes at room temperature. For the third method involving doping of the spread monolayer, the doped EA8C/cadmium stearate films were prepared by spreading the mixed solution of EA8C/stearic acid/ I_2 at the molar ratio of 1 : 4 : 1 on the water subphase containing $5.0 \times 10^{-4}M$ cadmium chloride and $1.0 \times 10^{-4}M$ potassium

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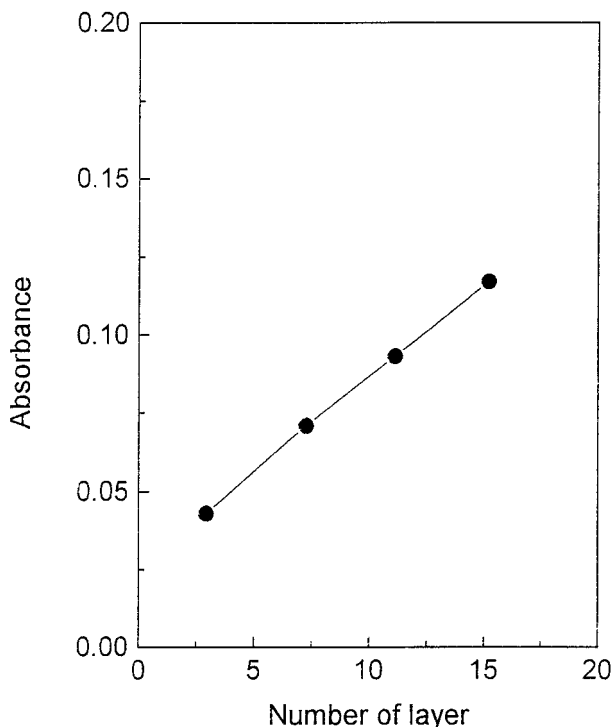


Figure 1 Intensity of UV/VIS absorption spectra at 453 nm as a function of number of layers for the EA8C/cadmium stearate mixed LB films.

bicarbonate, and, subsequently, the iodine doped mixed monolayers were deposited to the solid substrate.

Ultraviolet-Visible Spectroscopic Measurements

Ultraviolet-visible (UV/VIS) Spectra of EA8C/cadmium stearate mixed LB films annealed or doped under various conditions were obtained on a Shimadzu UV-240 spectrophotometer at room temperature.

Measurements of Electrical Conductivity

A device structured with Al/Al₂O₃/mixed LB film/Al was used for the measurement of the transverse (σ_{\perp}) and the in-plane (σ_{\parallel}) conductivity values. The detailed methods for a device fabrication and conductivity measurements were described in detail in the previous work.¹

X-ray Diffraction Spectra

The X-ray diffraction (XRD) spectra of EA8C/cadmium stearate mixed LB films prepared under different conditions were obtained on a Rigaku D/

Max IIIA and Rotaflex wide-angle diffractometer with Ni-filtered CuK α radiation.

RESULTS AND DISCUSSION

UV/VIS Spectroscopic Studies

Since EA8C contains highly conjugated double bonds, UV/VIS spectroscopy should be a powerful technique for characterizing the EA8C-containing mixed LB films. EA8C gave wavelength max (λ_{max}) at 453 nm in UV/VIS spectra, which was very close to the calculated value from Fieser-Kuhn's empirical rules that work well for predicting λ_{max} for highly conjugated polyene systems.³ Figure 1 demonstrates the linear relationship between absorbance measured at λ_{max} (453 nm) and the number of layers for the EA8C/cadmium stearate mixed LB film. The good linearity suggested that the EA8C/cadmium stearate mixed LB film had well-ordered molecular structures, as others explained.⁴ Figure 2 shows the UV/VIS spectra of EA8C/cadmium stearate mixed LB films subjected to thermal treatment under various conditions. Gradual decrease in absorbance at λ_{max} was observed with increasing annealing temperatures up to 80°C due to thermal oxidation of the EA8C component.⁵ Annealing at 100°C for 30 minutes gave rise to dramatic reduction in absorbance.

X-ray Diffraction Spectroscopic Studies

Figure 3 shows XRD patterns measured on the cadmium stearate and EA8C/cadmium stearate mixed LB films. From the diffraction patterns, the unit cadmium-cadmium spacings for cadmium stearate and EA8C/cadmium stearate mixed films were determined to be 50.8 and 52.2 Å, respectively. These values are slightly smaller than two times the calculated length of a stearic acid molecule, 27 Å, which suggests that both of the films are "Y-type" and that the cadmium stearate and EA8C molecules in the films are perpendicularly oriented towards the surface of the LB films. The observed zigzag pattern in diffraction for cadmium stearate was explained by model calculations, allowing for the location of an electron-deficient layer formed by the juxtaposition of the two hydrophobic ends of the chains at the center of the cadmium-cadmium unit cell.⁶ The fact that the odd reflections are much stronger than those from the neighboring even reflections for cad-

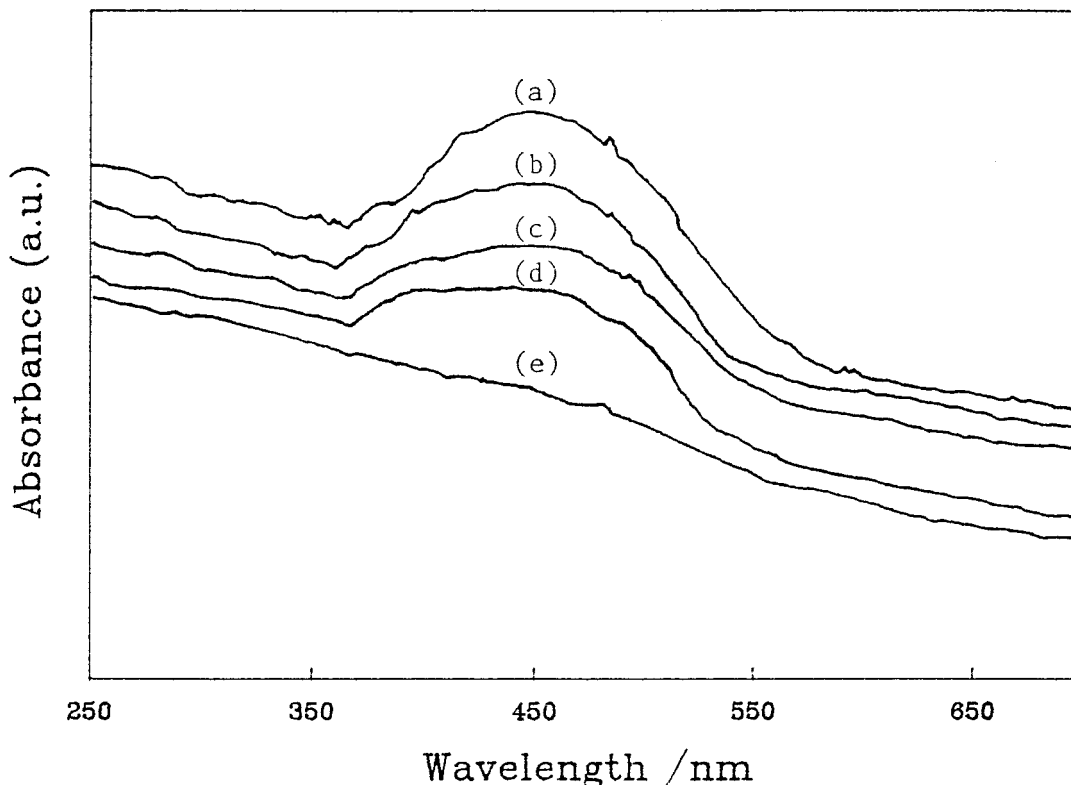


Figure 2 The effects of heat treatments on the UV/VIS spectra of EA8C/cadmium stearate mixed LB films with 15 layers: (a) before annealing, (b) after annealing at 40°C for 30 min, (c) after annealing at 60°C for 30 min, (d) after annealing at 80°C for 30 min, and (e) after annealing at 100°C for 30 min.

mium stearate [Fig. 3(b)] is completely consistent with previous observations.⁶ The effects of heat treatments on the diffraction pattern of EA8C/cadmium stearate LB films were investigated to evaluate the orientational stability of the films to thermal aging, and the results are shown in Figure 4. The samples subjected to heat treatments at 60 or 80°C for 30 minutes did not show noticeable changes in the diffraction pattern. However, at a higher aging temperature of 100°C, a dramatic decrease in diffraction intensity was observed, which suggested that molecular orientation in the film was lost due to the thermal treatment.

Doping and Electrical Conductivity Characteristics of the EA8C/Cadmium Stearate Mixed LB Films

Figure 5 shows UV/VIS spectra of doped EA8C/cadmium stearate mixed LB films. Dopants were

treated on the mixed LB film or on the monolayer spread on the water, as explained before. Thus, the mixed LB films were exposed to iodine vapor [Fig. 5(b)] or dipped into sulfuric acid solution [Fig. 5(d)]. LB film samples for Figure 5(c) was prepared from the I_2 solution doped monolayers. As shown in Figure 5(b) and (d), the mixed LB films exposed to iodine vapor or dipped into sulfuric acid solution gave rise to significant reduction in the absorbance of the $\pi-\pi$ electronic transition at about 453 nm. These results indicate that the mixed LB films underwent ready doping upon exposure to iodine vapor or dipping in the sulfuric acid solution.⁷ On the other hand, the sample for Figure 5(c) did not show dramatic loss of absorbance at around 453 nm, suggesting that the mixed monolayer spread on the water was not doped efficiently with dissolved iodine.

The effects of doping conditions on the electrical conductivity characteristics of EA8C/cadmium stearate LB films were investigated. As shown in Figure 6, the transverse conductiv-

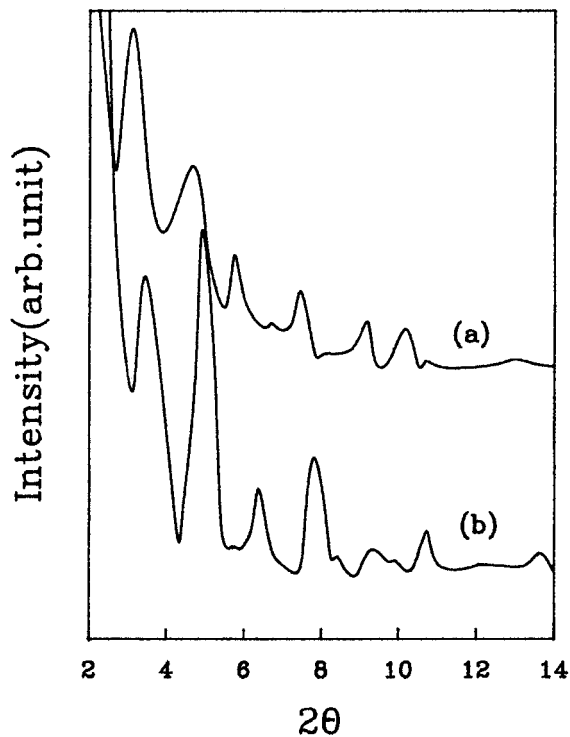


Figure 3 X-ray diffraction patterns of 15-layer LB films prepared from (a) mixtures of 1 : 4 molar ratio of EA8C/cadmium stearate and (b) cadmium stearate.

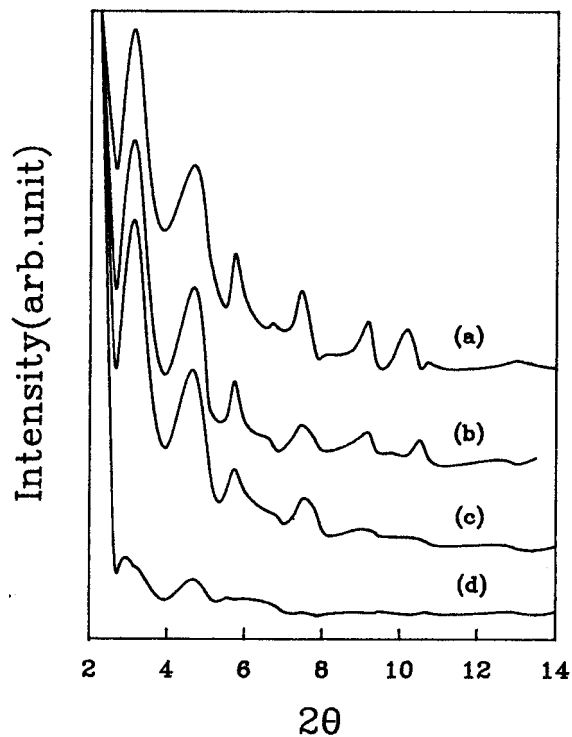


Figure 4 The effects of annealing on the XRD patterns of 15-layer LB films prepared from mixtures of 1 : 4 molar ratio of EA8C/cadmium stearate: (a) before annealing, (b) after annealing at 60°C for 30 min, and (c) after annealing at 80°C for 30 min.

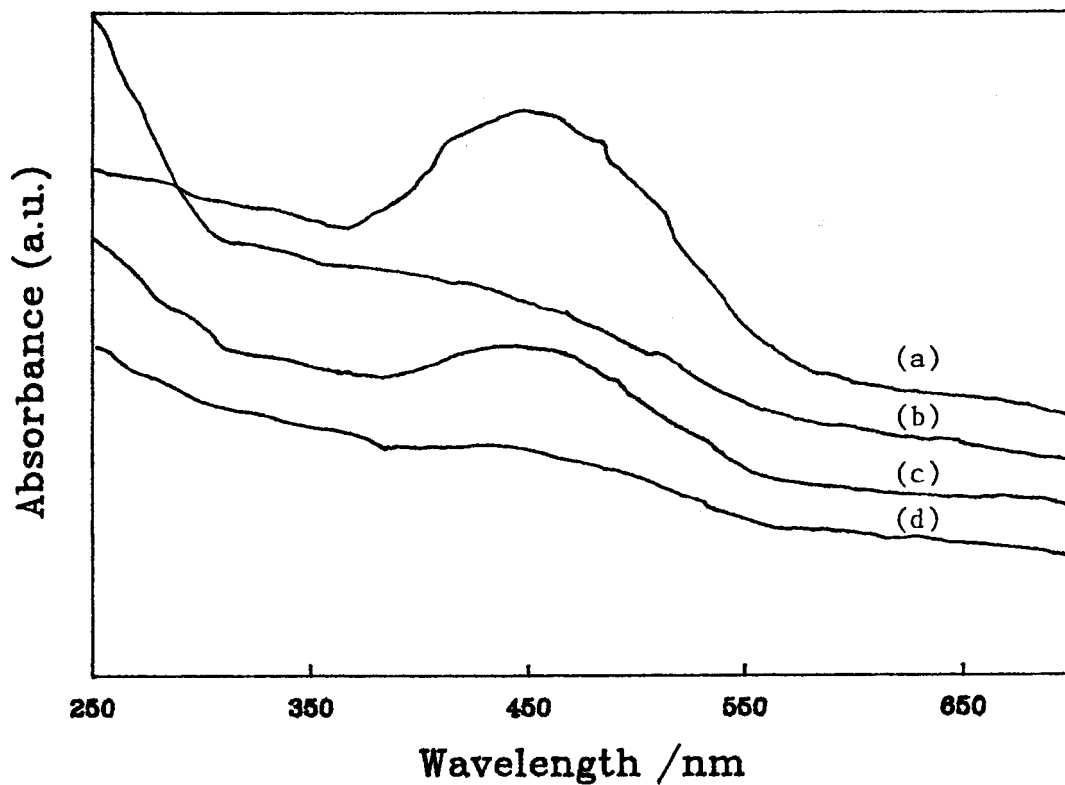


Figure 5 UV/VIS absorption spectra of the EA8C/cadmium stearate mixed LB films (15 layers) doped under different conditions: (a) undoped, (b) I_2 vapor doped, (c) I_2 solution doped, and (d) H_2SO_4 solution doped.

ity of the LB films was observed to be fairly constant for a given system irrespective of the number of LB film layers. As expected, the LB films treated with iodine vapor or sulfuric acid solution were observed to have higher conductivity values than those of the untreated LB films. The samples exposed to iodine vapor generated best results, showing the conductivities ranging from 10^{-7} to 10^{-8} S/cm; but good results were not obtained for the samples doped with iodine solution. These observations are consistent with the UV/VIS spectroscopic data that were already discussed. In-plane (σ_{\parallel}) conductivity measurements were performed on the iodine vapor doped and undoped LB films, and their results are shown in Figure 7. The in-plane conductivity of the iodine vapor doped samples was 10^{-6} S/cm, yielding conductivity anisotropy of about $10-10^2$. This conductivity anisotropy implies an anisotropic organization in the film; that is, along the direction perpendicular to the film surface, iodine molecule layers are expected to be interposed by randomly dispersed EA8C/cadmium stearate layers.

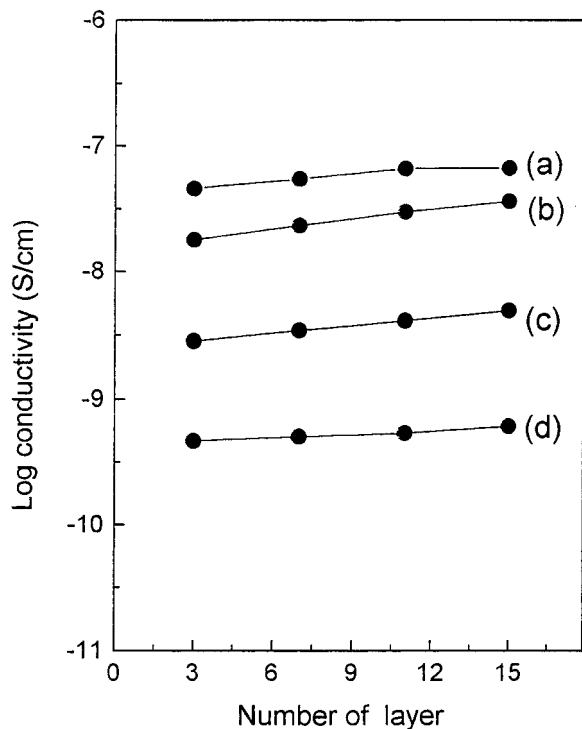


Figure 6 Log σ_{\perp} of the EA8C/cadmium stearate mixed LB films versus the layer number of the films doped under different conditions: (a) I_2 vapor doped, (b) H_2SO_4 solution doped, (c) I_2 solution doped, and (d) undoped.

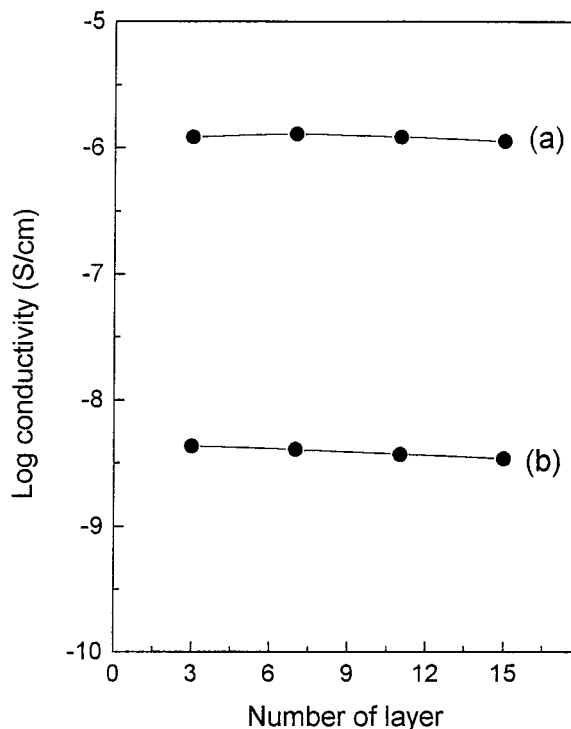


Figure 7 Log σ_{\parallel} of EA8C/cadmium stearate mixed LB films versus the layer number of the films: (a) I_2 vapor doped; (b) undoped LB.

CONCLUSIONS

Electroconductive EA8C/cadmium stearate mixed LB films were prepared by doping the EA8C/cadmium stearate mixed LB films with iodine or sulfuric acid. XRD spectroscopic studies provided an evidence that the EA8C/cadmium stearate mixed LB films are "Y-type" and have well-defined layered structures. XRD patterns further suggested that the cadmium stearate and EA8C molecules in the mixed films are perpendicularly oriented towards the film surface. As evidenced by UV/VIS and XRD data, the incorporated EA8C was thermally stable up to $80^{\circ}C$. Doping characteristics of the EA8C/cadmium stearate mixed LB films under different conditions, and their electrical conductivity were studied. The films exposed to iodine vapor generated the best results. They showed in-plane and transverse conductivity values of 10^{-6} and $10^{-7}-10^{-8}$ S/cm, respectively, yielding the conductivity anisotropy of about $10-10^2$.

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REFERENCES

1. Y. H. Park, S. Y. Park, S. W. Nam, C. R. Park, and Y. J. Kim, *J. Appl. Polym. Sci.*, **60**, 865 (1996).
2. Y. H. Park, B. I. Kim, and Y. J. Kim, *J. Appl. Polym. Sci.*, **63**, 779 (1997).
3. D. L. Pavia, G. M. Lampman, and G. S. Kriz Jr., *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*, W. A. Saunders Co., Philadelphia, 1979, p. 200.
4. M. M. Choi, W. J. Lee, and D. Y. Kang, *First Conference on Molecular Electronic Devices*, 1991, p. 37.
5. M. Tadahihiro, M. Tokuji, and M. Miniru, *Macromolecules*, **22**, 2706 (1989).
6. A. Matsuda, M. Sugi, T. Fukui, S. Iizima, M. Miyahara, and Y. Otsubo, *J. Appl. Phys.*, **48**, 771 (1977).
7. M. Rikukawa and M. F. Rubner, *Thin Solid Films*, **210**, 274 (1992).