

Photopolymerization and Structural Characterization of Organized Molecular Films of Long-Chain Diynoic Acid Derivative by Using NEXAFS Spectroscopy.

Mikako Ishitsuka^a, Atsuhiro Fujimori^{a,b}, Hiroo Nakahara^{a,*}, Eisuke Ito^b, Masahiko Hara^b, Kaname Kanai^c, Yukio Ouchi^c, and Kazuhiko Seki^{c,d}

^aDepartment of Chemistry, Faculty of Science, Saitama University, Shimo-okubo 255, Saitama 338-8570, Japan. ^bLocal Spatio-Temporal Function, Frontier research system, The Institute of physical and chemical Research (RIKEN), Hirosawa 2-1, Wako, 351-0198 Japan. ^cDepartment of Chemistry, Graduate School of Science, Nagoya University. ^dResearch Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan.
Fax: +81-48-858-3700, e-mail: nakahara@chem.saitama-u.ac.jp

Photopolymerization of cadmium 10, 12-pentacosadiynoate in Langmuir-Blodgett (LB) films with the molecular packing modulated by annealing, has been investigated by polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy in addition to UV-vis spectroscopy and X-ray diffraction. Greenish films of poly(diacetylene) with $\lambda_{\text{abs}} = 701 \sim 705$ nm were newly obtained by photopolymerization of the LB films pre-annealed moderately, resulting in an extended conjugate system based on the well-ordered monomer arrangements. Thereafter, the color changed to blue and red. These facts were confirmed by the clear dependence of the incident angles for the NEXAFS spectra at the C1s- π^* transition peaks for the polymerized LB films pre-annealed.

Key words: Long-chain diynoic acid, Multilayers, Annealing effect, Greenish film, NEXAFS spectroscopy

1. INTRODUCTION

Many kinds of diacetylene derivatives $R-C\equiv C-C\equiv C-R'$ (where R and R' are the substituent groups) polymerize under UV irradiation to form blue or red colored polymers with conjugated π electron systems. This polymerization reaction proceeds in various states such as single crystals,¹ Langmuir - Blodgett (LB) film,² self-assembled monolayer³ and evaporated films.⁴ The interest in diacetylene polymers has been accelerated by a recent proposal of the use for nonlinear optical devices.⁵ Previously, Fukuda *et al* reported that the polymerization of amphiphilic monomers such as long-chain vinyl esters and long-chain diynoic acid is significantly accelerated and the structure of the resulting polymers can be controlled in the LB film.^{6, 7} And further, it was reported UV photoelectron spectroscopy (UPS) and preliminary C1s near-edge X-ray absorption fine structure (NEXAFS)^{8,9} studies through the UV photopolymerization in LB films of cadmium salts of 10, 12-tricosadiynoic acid in the form, and the results were compared with those for the evaporated films of the free acid form.¹⁰⁻¹⁴ Early, the color phase transition of polydiacetylene was ascribed to the two possible forms of acetylenic and butatrienic resonance structure. However, it was suggested that both the blue and red polymers formed acetylenic ones from the results of UPS measurement.^{11, 13} It was considered that a slight fluctuation the hydrocarbon side-chain packing induced these color phase transition with UV irradiation,

thermal treatment, or exposed organic solvents, whereas the change of detailed electronic state was not clear.

In the present paper, the effect of molecular arrangements with annealing on photopolymerization in the LB films of cadmium 10, 12-pentacosadiynoate, were investigated by UV-vis spectroscopy, X-ray diffraction (XRD), and polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. It was found that the formation of the newly greenish polymer film with the extended conjugate system and the color change could be related to the film structures, and their molecular orientation estimated by polarized NEXAFS spectroscopy.

2. EXPERIMENTAL

10,12-pentacosadiynoic acid [$CH_3(CH_2)_{11}-C\equiv C-C\equiv C(CH_2)_8COOH$] was purchased from Tokyo chemical industry Co. Ltd. and purified by four times recrystallization from chloroform : n-hexane =1:9 (v/v) mixed solvent. These monolayers were spread on the aqueous subphase containing 3×10^{-4} M CdCl₂ and 5×10^{-4} M KHCO₃. The multilayers were deposited at 25 mNm⁻¹ and 15 °C as cadmium salt (cadmium 10,12-pentacosadiynoate, abbreviated by PDCd), up to 20 layers by Langmuir - Blodgett (LB, vertical dipping) method. The annealing conditions of the transferred films in order to form the highly developed molecular arrangements were in the region of 45~65 (± 1.0) °C and 1~120 h in the thermostat. The optimum condition at 50 °C and 72 h was estimated by X-ray diffraction

measurements before and after annealing of the monomer LB films. Photopolymerization was carried out by exposing the films to a 500W Xe lamp at a distance of 50 mm. The dependence of the extent for polymerization on the irradiation time was followed by UV-visible absorption spectra (Hitachi, U-3210 spectrometer) of LB films on a quartz plate. Values of the long spacings for the layered structures of the deposited films were measured by an X-ray diffractometer (Rigaku, Rad-B, $\text{CuK}\alpha$ radiation, 40 kV, 30 mA) equipped with a graphite monochromator. NEXAFS spectra were measured on BL-7A soft X-ray beamlines at the Photon Factory in the National Laboratory for high-energy accelerator research organization (KEK-PF) with synchrotron radiation from a bending-magnet source. The C K-edge spectra were measured in the photon energy region 275 – 325 eV, and in the partial electron yield mode (PEY) with -200 eV retarding voltage under the vacuum of 10^{-8} Torr range, respectively. In the NEXAFS measurements, monolayers were transferred onto NESA glass coated with three layers of Cd stearate to obtain a hydrophobic surface.^{17, 18}

3. RESULTS AND DISCUSSION

Photopolymerization of PDCd molecules in multilayers prepared by LB methods (20 layers, 25 mNm^{-1} , 15 °C), together with the effect of annealing, was studied. The packing mode of monomer molecules and the size of the domain in monolayers assemblies seem to have a strong influence on the polymerization reaction and the structure of the resultant polymers. PDCd polymers were rapidly formed on irradiation with UV light. In the non-annealed usual LB film, the spectra changes readily from the blue form ($\lambda_{\text{abs}} \approx 638$ nm) to the red, whereas the annealed LB multilayers (50 °C, 72h) polymerize very rapidly and become green, having $\lambda_{\text{abs}} = 704$ nm, and then changed to blue and finally to red on the UV irradiation. It was found that the formation of this newly greenish polymer film with the extended conjugate system by annealing and UV irradiated photopolymerization were confirmed on the LB film of PDCd.

Figure 2 shows the change of the X-ray diffraction patterns of annealed and non-annealed PDCd multilayers and also those through UV photopolymerization. It was found that PDCd molecules in the LB film were developed layer structure and increased the tilt angle to the surface normal by the annealing. It was suggested this tilt angle about 33° was more comfortable to the polymerization reaction of PDCd monomers in the films than that of non-annealed film. In addition, shown as Figure 2 (c) show the appearance of the higher-order diffraction peaks at different magnification due to the extremely development of the layer structure in LB films by the annealing was confirmed.

Figures 3(a), (b), (c) and (d) correspond to the NEXAFS spectra of annealed PDCd monomer film, poly-PDCd green, blue, and red films annealed PDCd monomer film. In Figure 3(a), it is found that the spectra depend significantly on the incidence angle. The peaks

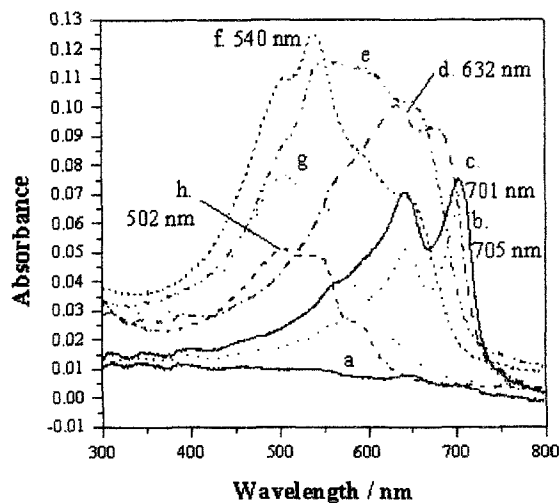


Figure 1. Change of visible absorption spectra of PDCd through photopolymerization in Langmuir-Blodgett films (pre-annealed at 50 °C for 72 hrs. UV-irradiation periods: a-0 min, b-1 min, c-2 min, d-10 min, e-20 min, f-30 min, g-1.0 h, h-1.25 h)

at 287.6 and 290.7 eV have been assigned to the transitions from the C_{1s} to the $\sigma^*(\text{C-H})$ and $\sigma^*(\text{C-C})$ orbitals, respectively. The relative intensity of the $\sigma^*(\text{C-H})$ peak, attributable to the C-H bonds of the hydrocarbon chains, with respect to the $\sigma^*(\text{C-C})$ becomes maximum at the normal incidence and weakened at grazing incidence ($\theta = 70^\circ$). These results suggest that the transition moments of the 287.6 eV band were rather parallel to the surface, indicating the nearly perpendicular orientation of the hydrocarbons. In addition, clearly difference were shown as the appearance of the incident angle dependence for the C_{1s} to the π^* transition peaks. In the spectra of annealed PDCd monomer films, the peak at 285.5 eV, attributable to the π^* orbital of functional groups, becomes maximum at the grazing incidence ($\theta = 70^\circ$) and weakened at the normal incidence. These clearly polarization dependence of C_{1s} to the π^* transition peaks indicated highly order functional groups with the inclined orientation of the π^* orbital. It was found that these incident angle dependence were kept on the spectra of green and blue polymers, which mean maintain the highly regulated molecular orientation and the difference of the molecular structure of blue films obtained from non-annealed monomer films and annealed monomer films *via* greenish film. While, in the red films, characteristic change of the NEXAFS spectra occurred. Although the polarization dependence of the C_{1s} to the $\sigma^*(\text{C-C})$ transition peaks was disappeared, that of the C_{1s} to the $\sigma^*(\text{C-H})$ transition peaks was maintained and the C_{1s} to the π^* transition peaks shifted and split from 285.5 eV to the 286.0 eV and 285.0 eV. And further, the peaks at 286.0 eV exhibited polarization dependence whereas no dependence of the peaks at 285.0 eV. In the previous study, these two peaks on the red films of polydiacetylene derivatives at higher and lower energy region correspond to the lower edge of the delocalized π^* band and the isolated π^* orbitals in the triple bond,

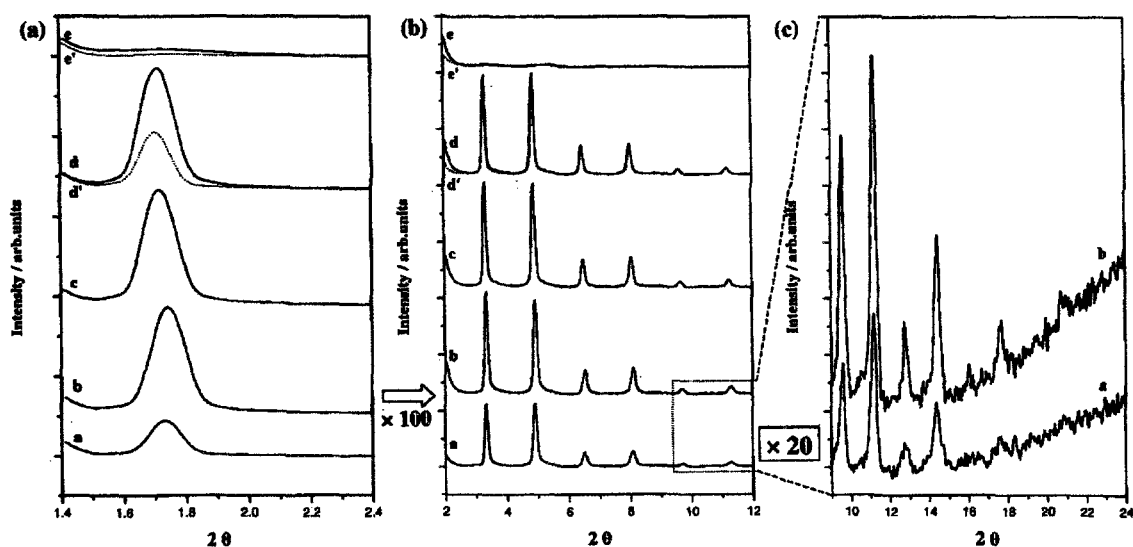


Figure 2. Change of X-ray diffractions in different extended axis-scale (a)small-angle region, (b) $2\theta=2\sim 12^\circ$, and (c)wide-angle region for PDCd LB films through the photopolymerization: a)non-annealed, b)annealed monomers at 50°C for 72 hrs, c)green poly-PDCd, d)blue poly-PDCd, and e)red poly-PDCd (dotted lines d', e'-obtained from the non-annealed PDCd monomer).

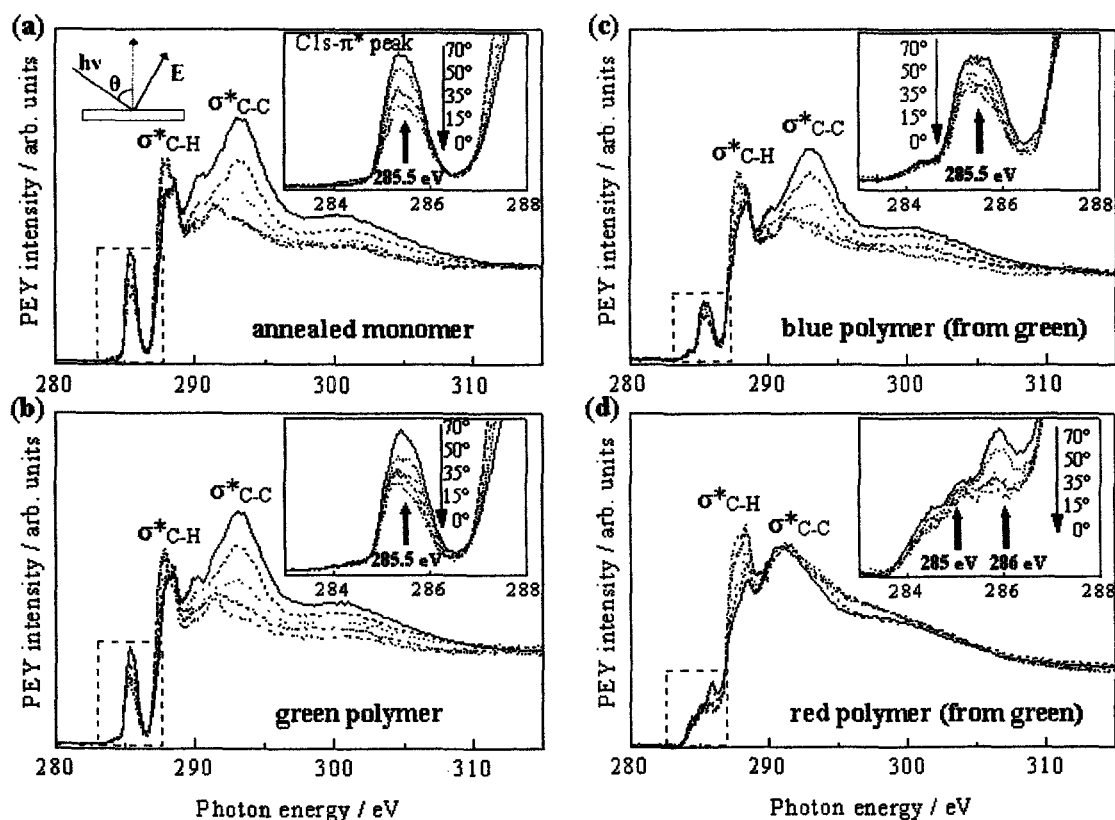


Figure 3. Dependence of the incident angle on the C K-edge NEXAFS spectra of the LB films: (a)annealed monomer PDCd, (b)green poly-PDCd, (c)blue poly-PDCd, (d)red poly-PDCd, together with those of the C1s- π^* bands at 283-288 eV in the inserted

respectively. However, this splitting of these peaks were not confirmed on the previous studies of diacetylene LB film because polymerization does not proceed regularly. Which is probably due to disordering of molecular arrangements. It was considered that formation of highly order molecular orientation was

indicated by clearly polarization dependence and this packing mode of the molecules was not favorable to the polymerization, in facts. Whereas the annealed PDCd films exhibited no dependence of the incident angle on the transition peaks from the C1s to the $\pi^*(\text{C}\equiv\text{C})$.

Figure 4 shows the plots of the normalized

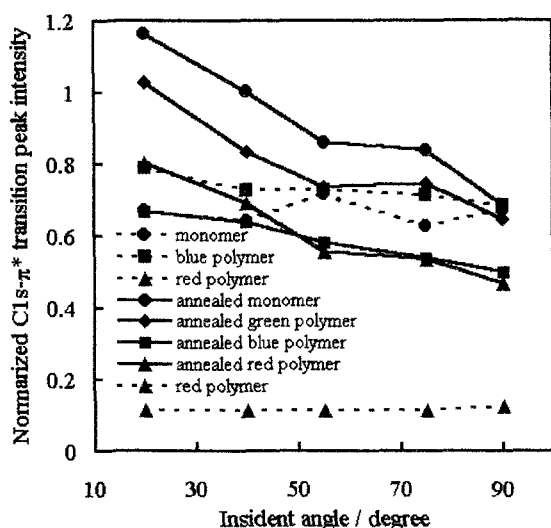


Figure 4. Plots of the normalized intensities of the C1s- π^* transition NEXAFS spectra v.s. the incident angles.

285.5 eV peak intensity vs. the incident angle on the NEXAFS spectra. The comparison of the uniformity of alignments for the functional groups at the several diacetylene and poly-diacetylene films carried out from the normalization of the C1s to the π^* transition peaks by the edge-jump and plot of these values. From these results, although uniformity of alignment of the functional groups slightly reformed by UV irradiated photopolymerization on the non-annealed system, in the annealed system, regularity of functional group arrangements formed by annealing declined with the polymerization reaction. It was noted that the split the C1s to the π^* transition peaks at 286.0 eV on red films from annealed monomer film via green and blue films, increased normalized intensity compared to the blue film due to the reorientation together with the color phase transition whereas incident angle dependence of 285.0 eV peaks disappeared both red films. According to the previous interpretation, these experimental facts indicates the ordering delocalized π^* orbital and the disordering isolated π^* orbital on the color phase transition.

4. CONCLUSION

The effects of molecular arrangements with the annealing on photopolymerization in the transferred films of cadmium diynoate, were investigated. It was found that the formation of the newly greenish polymer film with the extended conjugate system could be related to the film structures. The angular dependence of the incident X-ray on the NEXAFS spectra for the organized molecular films of long-chain diynoic acid derivatives on solids gives very effective information on the orientation of the functional groups with annealing and photopolymerization. Clearly incident angle dependence of the C1s- π^*

transition peaks on the annealed transferred film with the extended conjugate system were confirmed by C K-edge polarized NEXAFS spectroscopy whereas these dependency was not observed on the non-annealed multilayer film.

ACKNOWLEDGMENTS

The authors thank Dr. Kenta Amemiya, Tokyo Univ. for his help of NEXAFS measurement and helpful discussion. One of the authors (A. F.) thanks the Japan Society for Promotion of Science for the postdoctoral fellowship. This work was partially performed under approval of the Photon Factory Program Advisory Committee (proposal No. 2002G288).

REFERENCES

- [1] G. Z. Wegner, *Naturforsch.*, **24b**, 824 (1969); Wegner, G. *Molecular Metals* (ed. Hatfeld, W. E., Plenum, New York), pp.209 (1979).
- [2] B. Tieke, G. Wegner, D. Naegel, H. Ringsdorf, *Angew. Chem. Int. Ed.*, **15**, 764 (1976).
- [3] D. N. Batchelder, S. D. Evans, T. L. Freeman, L. Häussling, H. Ringsdorf, H. Worf, *J. Am. Chem. Soc.*, **116**, 1050 (1994).
- [4] T. Kanetake, Y. Tokura, T. Koba, *Solid State Commun.*, **56**, 803 (1985).
- [5] C. Sauert, J. P. Herman, R. Fer, F. Predieere, J. Ducing, R. H. Baughman, R. R. Chance, *Phys. Rev. Lett.*, **36**, 956 (1976).
- [6] K. Fukuda, Y. Shibasaki, H. Nakahara, *Thin Solid Films*, **99**, 87 (1983).
- [7] K. Fukuda, Y. Shibasaki, H. Nakahara, *Thin Solid Films*, **133**, 39 (1985).
- [8] J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin), (1992).
- [9] D. A. Outka, J. Stöhr, J. P. Rabe, J. Swalen, *J. Chem. Phys.*, **88**, 4076 (1988).
- [10] H. Nakahara, K. Fukuda, K. Seki, S. Asada, H. Inokuchi, *Chem. Phys.* **188**, 123 (1987).
- [11] K. Fukuda, Y. Shibasaki, H. Nakahara, *Thin Solid Films*, **160**, 43 (1988).
- [12] K. Seki, I. Morisada, K. Tanaka, M. Edamatsu, M. Yosiki, Y. Tanaka, T. Yokoyama, T. Ohta, S. Asada, H. Inokuchi, H. Nakahara, K. Fukuda, *Thin Solid Films*, **179**, 15 (1989).
- [13] K. Seki, I. Morisada, K. Edamatsu, H. Tanaka, H. Yanagi, T. Yokoyama, T. Ohta, *Phys. Scripta*, **41**(1), 173 (1990).
- [14] K. Seki, T. Yokoyama, T. Ohta, H. Nakahara, K. Fukuda, *Mol. Cryst. Liq. Cryst.*, **218**, 609 (1992).
- [15] Y. Tokura, T. Kanetake, K. Ishikawa, T. Koba, *Synth. Met.*, **17**, 407 (1987) and references therein.
- [16] D. S. Eckhardt, D. S. Boudreaux, R. R. Chance, *J. Phys. Chem.*, **85**, 4116 (1986).
- [17] A. Fujimori, T. Araki, H. Nakahara, E. Ito, M. Hara, H. Ishii, Y. Ouchi, K. Seki, *Langmuir*, **18**, 1437 (2002).
- [18] A. Fujimori, T. Araki, H. Nakahara, E. Ito, M. Hara, H. Ishii, Y. Ouchi, K. Seki, *Chem. Phys. Lett.*, **349**, 6 (2001).

(Received December 20, 2002; Accepted January 31, 2003)