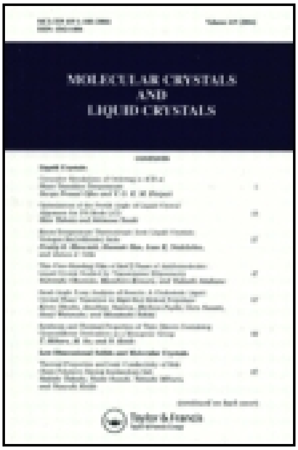
This article was downloaded by: [University of California, San Diego]
On: 09 August 2012, At: 14:18
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Self-Alignment of Liquid Crystal Molecules on Polydiacetylene Langmuir-Blodgett Films

Akira Murayama [a], Yasuhiro Niida [a], Yasuko Koshiba [a] & Yasukiyo Ueda [a]

[a] Graduate School of Science and Technology, Kobe University, Rokko, Nada, Kobe, Japan

Version of record first published: 22 Sep 2010

To cite this article: Akira Murayama, Yasuhiro Niida, Yasuko Koshiba & Yasukiyo Ueda (2007): Self-Alignment of Liquid Crystal Molecules on Polydiacetylene Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals, 464:1, 119/[701]-126/[708]

To link to this article: http://dx.doi.org/10.1080/15421400601030555

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 119/[701]–126/[708], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601030555

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

Self-Alignment of Liquid Crystal Molecules on Polydiacetylene Langmuir-Blodgett Films

Akira Murayama
Yasuhiro Niida
Yasuko Koshiba
Yasukiyo Ueda
Graduate School of Science and Technology, Kobe University,
Rokko, Nada, Kobe, Japan

Alignment structure and optical properties of Langmuir-Blodgett (LB) films of urethane-substituted polydiacetylene (poly-4BCMU) was investigated. During compression, the coil to rod transition in molecular conformation of poly-4BCMU was induced and the polymer main chains were aligned perpendicular to the compressing direction. The dichroic ratio of absorption intensity of poly-4BCMU monolayer film was about 6. LC molecules were sandwiched with two glass plates covered with the poly-4BCMU monolayer films. LC molecules aligned spontaneously along the main chain direction of poly-4BCMU in the parallel cell. On the other hand, they formed a twisted structure of 90° in the crossed cell. The monolayer film of poly-4BCMU had a high potential as rubbing-free alignment layer of LC molecules.

Keywords: liquid crystal; polydiacetylene LB film; self-alignment; two-dimensional structure

INTRODUCTION

Liquid crystal (LC) displays are expanding in application because they offer several advantages such as reduction in thickness, low power consumption and so on. Polyimides are widely used as alignment layers that play a significant role in control of alignment of liquid

This work was partially supported by a Grant-in-Aid for Scientific Research (16360040) and by the Photonics Materials Laboratory Project of the VBL of the Graduate School of Science and Technology, Kobe University.

Address correspondence to Yasukiyo Ueda, Graduate School of Science and Technology, Kobe University, 1-1 Rokkodai-cho, Nada-hu, Kobe-shi 657-8501, Japan. E-mail: yueda@kobe-u.ac.jp

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

crystal molecules. Rubbing is the most conventional method for preparation of polyimide alignment layers. However, rubbing method generate frequently irregular degree of alignment of the layers and static electricity, which degrade image quality. Therefore, an alternative to rubbing method has been strongly desired. Various methods, such as Langmuir-Blodgett (LB) technique [1–7], subsequent thermal treatment of liquid crystalline polymer [8] and photo-induced alignment technique [9–11] have been proposed as rubbing-free technique.

LB films have uniformly well-ordered structure with controlled film thickness at the monolayer level. They have been expected to be able to align LC molecules on their surfaces. Since the pioneering work of Nishikata *et al.* [1], polymer LB films have attracted considerable attention as alignment layers. Many attempts have been made to achieve alignment control of LC molecules on LB films of various polymers, such as polyimide [1–3], and polymethacrylate [4].

Polydiacetylenes (PDAs) are one-dimensional conjugated polymer. Among them, urethane-substituted PDAs such as poly[4,6-decadiyn-1,10-diol-bis-(n-butoxycarbonyl-methyl-urethan)] (poly-3BCMU) and poly[5,7-dodecadiyn-1,12-diol-bis-(n-butoxycarbonyl-methyl-urethan)] (poly-4BCMU) are of great interest to LB technique because they are soluble in chloroform and spreadable on water surface. Biegajski *et al.* reported that poly-4BCMU molecule exhibits coil to rod conformational transition at the air-water interface [12,13]. However, the details on alignment structure of poly-4BCMU in LB film remain unclear.

In this study, the detailed structure and anisotropic absorption property of poly-4BCMU LB film were discussed. Self-alignment behavior of LC molecules sandwiched with poly-4BCMU monolayer films was also investigated.

EXPERIMENTAL

Poly-4BCMU was prepared by solid-state polymerization of 4BCMU powder with UV-light irradiation. Unconverted monomer and oligomeric compound were extracted with acetone. A chloroform solution of poly-4BCMU with the concentration of 1.0×10^{-3} M was spread on a distilled water kept at 20°C. The molecules were compressed with a moving barrier at the speed of $2.5\,\text{Å}^2/\text{residue} \cdot \text{min}$. Layers were transferred by horizontal lifting method onto hydrophobilized glass plates treated with hexamethyldisilazane. The absorption spectra of the films were examined using a Shimadzu UV-2200 spectrometer and microscope images and electron diffraction pattern were recorded with an atomic force microscope (AFM, SPI3700, Seiko Instruments) and a transmission electron microscope (TEM, H-7100, Hitachi).

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

4-Cyano-4′-n-pentylbiphenyl (5CB) purchased from Tokyo Chemical Industries Ltd. was used as a nematic LC material. The temperature of phase transition of 5CB from nematic to isotropic is 35°C. LC cell was prepared as follows. LC molecules and glass plates covered with poly-4BCMU films were kept at 40°C. LC molecules in liquid state were sandwiched with the two glass plates to avoid any flow-induced memories of LC molecules. Then, the LC cell was cooled down to room temperature. The cell gap was controlled to be 10 μm. The LC cell was set between a polarizer and an analyzer and characterized by transmission measurement using a Nikon ECLIPSE E600 POL.

RESULTS AND DISCUSSION

The π-A isotherm for poly-4BCMU shows both an expanded and a condensed region with a well-defined transition, as shown in Figure 1. The area at the onset of the plateau (peak-like point) was 108 Å^2/residue. Extrapolation of the steep rise of the curve to zero pressure in the condensed region gave the area of 45 Å^2/residue. It is well known that poly-4BCMU have two polymorphs; yellow form taking a random-coil conformation and red form taking an extended rigid-rod one. The compression process of poly-4BCMU has been investigated in detail by Biegajski *et al.* [12,13]. According to their reports, poly-4BCMU molecule in an expanded region and in a condensed region exists in yellow form and red form, respectively. The plateau

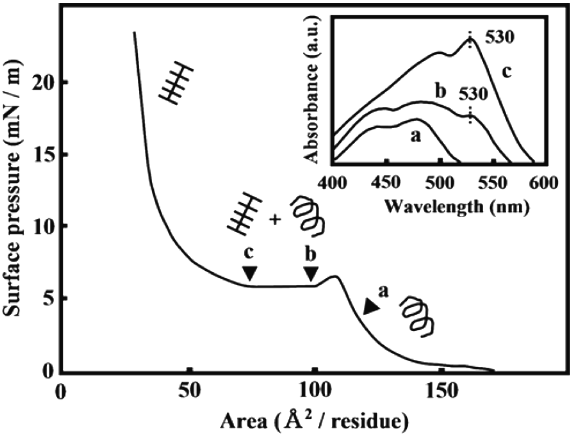


FIGURE 1 π-A isotherm for poly-4BCMU at the air–water interface. The absorption spectra of poly-4BCMU monolayer films transferred at various points of the π-A isotherm are inserted in the figure.

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

represents a heterogeneous two-phase region consisting of both molecules and the conformational change takes place in this region. The conformational change during compression process is reflected on absorption properties of the film transferred at each region. The absorption spectra of poly-4BCMU monolayer film transferred at various points of π-A isotherm are inserted in the figure. The absorption spectrum of the film transferred at the surface pressure of 3 mN/m in the expanded region showed the broad absorption peak around at 480 nm attributed to the π-π^* exciton of a random-coil conformation. In the spectrum of the film transferred at just after the onset of the plateau, the weak broad peak appeared at 530 nm attributed to the π-π^* exciton of an extended rigid-rod conformation in addition to initial absorption peak. The absorption intensity at 530 nm increases with the decrease of surface area in the plateau region depending on the degree of conformational transition. The absorption spectrum at the end of the plateau region has a characteristic of an extended rigid-rod conformation.

Figure 2 shows the polarized absorption spectra of poly-4BCMU monolayer film transferred at 20 mN/m in the condensed region. When the direction of polarization light is perpendicular to the compressing direction, the poly-4BCMU monolayer film shows maximum optical density at excitonic peak wavelength. In contrast, the absorption intensity is low for the light polarized parallel to the compressing

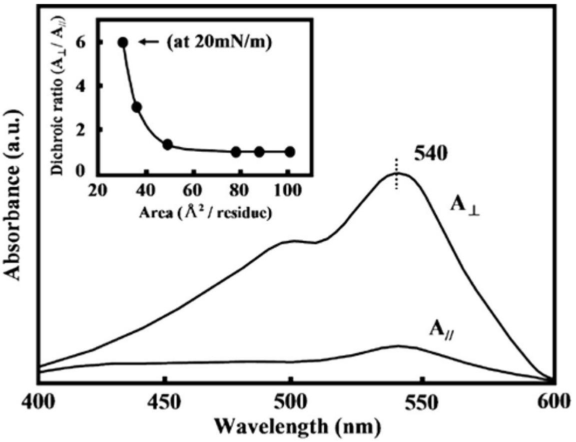


FIGURE 2 Polarized absorption spectra of poly-4BCMU monolayer films transferred at 20 mN/m in the condensed region. The relationship between the dichroic ratios of absorption intensity and surface area is inserted in the figure.

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

direction. The dichroic ratio ($A_{\perp}/A_{\parallel}$) of the poly-4BCMU monolayer film calculated directly from the ratio of the excitonic peak heights at 540 nm was about 6. The relationship between the dichroic ratios of the films and surface area is inserted in the figure. No spectral anisotropic feature is observed in the transition region. On the other hand, the dichroic ratio increases with the decrease of surface area in the condensed region, indicating that polymer main chains are gradually aligned perpendicular to the compressing direction during compression. The red-shift of the exitonic peak position is probably due to one-dimensional alignment structure of poly-4BCMU. It is obvious that the coil to rod conformational transition takes place prior to the alignment of polymer backbone.

Figure 3 shows the AFM images and electron diffraction pattern of the poly-4BCMU films transferred at 20 mN/m. The monolayer film [Fig. 3(a)] was composed of fiber-like domains aligned perpendicular to the compressing direction. 3-Layers film indicated similar texture [Fig. 3(b)]. To obtain structural information on the film, TEM observation was carried out. The electron diffraction pattern of 3-layers film shows a fiber pattern with several diffraction arcs, as shown in Figure 3(c). The interplanar spacings of arc spots on the meridian and on the

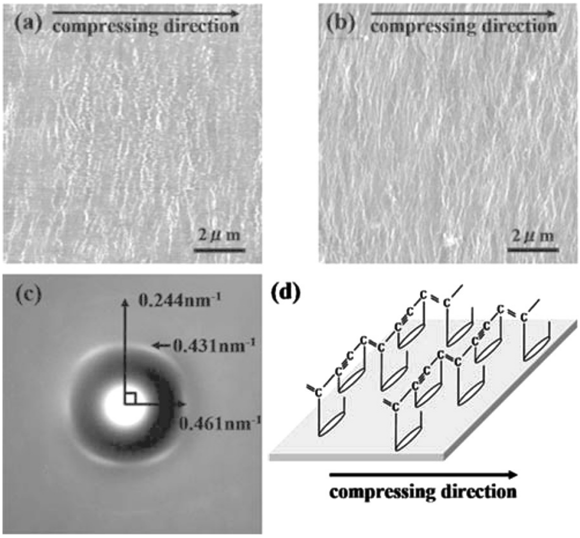


FIGURE 3 AFM images of poly-4BCMU monolayer film (a) and 3-layers film (b) transferred at 20 mN/m, electron diffraction pattern of the 3-layers film (c) and the molecular arrangement model of poly-4BCMU on the water surface (d). Arrows indicate the compressing direction.

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

equator are 0.244 nm and 0.461 nm, respectively. The crystal structure of poly-4BCMU is orthorhombic with dimensions of a = 0.533 nm, b = 5.436 nm, and c (fiber axis) = 0.488 nm [14]. The diffraction arc on the meridian is in good agreement with the 002 reflection of the bulk crystal. This indicates that polymer backbone is parallel to the fiber direction and poly-4BCMU molecules align perpendicular to the compressing direction. On the other hand, other diffraction arcs can not be indexed with unit cell parameters of bulk crystal. However, the interplanar spacing of the diffraction arc on the equator is comparable to the 100 reflection of the bulk crystal. But it must be given attention that the 100 reflection is forbidden in the bulk crystal system [15]. It seems that poly-4BCMU in LB film crystallized into different crystal structure. Considering the extinction rule in crystallography, the two dimensional unit cell parameter in poly-4BCMU LB film are determined as a = 0.922 nm and b (fiber axis) = 0.488 nm. The molecular arrangement of poly-4BCMU on the water surface is proposed in Figure 3(d). The polar groups indicated by ellipsoids are located at the air-water interface. The polymer backbone connected hydrophilic methylene units is separated from water surface like as a water strider and aligns perpendicular to the compressing direction. This model supports firmly the anisotropic feature of the film in absorption.

The potential ability of one-dimensionally aligned poly-4BCMU monolayer film as alignment layer of LC molecules was investigated. The glass plate covered with poly-4BCMU monolayer film transferred at 20 mN/m was used as a substrate for LC cell. Two kinds of LC cells, the parallel cell and the crossed cell, were fabricated. The main chain directions of poly-4BCMU molecules on both covered glass plates were parallel in the parallel cell and perpendicular in the crossed cell, respectively. Figure 4(a) shows the experimental setup for transmission measurement of the LC cell. The LC cell was set between a polarizer and an analyzer. The main chain direction of the poly-4BCMU molecules on the substrate of incident light side is parallel to the polarization direction of the incident light. In this experiment, visible light with the wavelength of 633 nm was used as incident light and the transmission light intensity was measured as a function of the rotation angle (θ) of the analyzer. Here, θ is the angle between the polarization direction of incident light and that of analyzer. The transmission light intensity for the parallel cell is maximum at the rotation angle of 0° and is minimum at 0°, as shown in Figure 4(b). The ratio of the transmission light intensity between the brightest and darkest states is 20:1. In the case of the crossed cell, on the other hand, maximum and minimum of the transmission light intensity appear at the rotation angle of 90° and 0°, respectively as shown in

Downloaded by [University of California, San Diego] at 14:18 09 August 2012

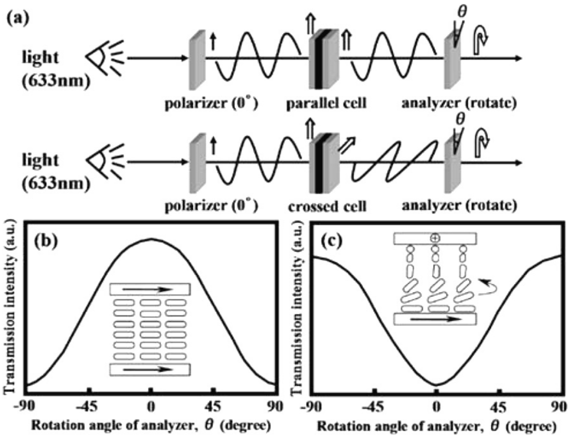


FIGURE 4 Experimental setup for transmission measurement of the LC cell (a). The changes of transmission light intensity at 633 nm as a function of rotation angle of the analyzer for the parallel cell (b) and for the crossed cell (c). Schematic diagrams of alignment structure of LC molecules in the parallel cell and in the crossed cell are inserted in the figures.

Figure 4(c). The intensity ratio of the transmission light is 15:1. For both parallel and crossed cells, the transmission light intensity changes periodically with a period of 90° of rotation angle.

These results indicate as follows:

(1) LC molecules in the parallel cell aligned spontaneously along the main chain direction of poly-4BCMU molecules, as inserted in Figure 4(b).
(2) LC molecules formed a twisted structure of 90° in the crossed cell, as inserted in Figure 4(c).
(3) Poly-4BCMU monolayer film transferred at condensed area of isotherm has a high potential as rubbing-free alignment layer of LC molecules.

CONCLUSION

Alignment behavior of poly-4BCMU at the air/water interface was investigated. The coil to rod conformational transition of poly-4BCMU took place in the plateau region. After the transition, the polymer main chains aligned perpendicular to the compressing direction. The dichroic ratio of absorption intensity of poly-4BCMU monolayer film was about 6. Two kinds of LC cells were fabricated by sandwiching with poly-4BCMU monolayer films. LC molecules in the parallel cell spontaneously aligned along the main chain direction of poly-4BCMU molecules. They formed a twisted structure of 90° in the crossed cell. The transmission light intensity of LC cells changed periodically depending on the rotation angle of analyzer.

REFERENCES

[1] Nishikata, Y., Takiguchi, Y., Kakamoto, A., Suzuki, M., & Kakimoto, M. (1987). *Nippon Kagaku Kaishi*, *1987*, 2174.
[2] Lu, R., Xu, K., Gu, J., & Lu, Z. (1999). *Phys. Lett. A*, *260*, 417.
[3] Kim, H.-W., Lee, H.-S., & Kim, J.-D. (2002). *Liq. Cryst.*, *29*, 413.
[4] Lu, R., Xu, K., Zhang, Y., Gu, J., Wu, H., & Lu, Z. (1997). *Phys. Lett. A*, *231*, 449.
[5] Aoki, N. & Ueda, Y. (2004). *Mol. Cryst. Liq. Cryst.*, *425*, 159.
[6] Manaka, T., Taguchi, D., Nakamura, D., Higa, H., & Iwamoto, M. (2005). *Colloids and surfaces A; Physicochem. Eng. Aspects*, *257*, 319.
[7] Sakuhara, T., Tomita, E., Nakahara, H., & Fukuda, K. (1992). *Thin Solid Films*, *209*, 269.
[8] Misaki, M., Ueda, Y., Nagamatsu, S., Yoshida, Y., Tanigaki, N., & Yase, K. (2004). *Macromolecules*, *37*, 6926.
[9] Umanskii, B. A., Novoseletskii, N. V., Torgova, S. I., & Dorozhkina, G. N. (2004). *Mol. Cryst. Liq. Cryst.*, *412*, 313.
[10] Advincula, R., Park, M.-K., Baba, A., & Kaneko, F. (2003). *Langmuir.*, *19*, 654.
[11] Chigrinov, V., Prudnikova, E., Kozenkov, V., Kwok, H., Akiyama, H., Kawara, T., Takada, H., & Takatsu, H. (2002). *Liq. Cryst.*, *29*, 1321.
[12] Biegajski, J. E., Burzynski, R., Cadenhead, D. A., & Prasad, P. N. (1986). *Macromolecules*, *19*, 2459.
[13] Biegajski, J. E., Burzynski, R., Cadenhead, D. A., & Prasad, P. N. (1990). *Macromolecules*, *23*, 816.
[14] Ohnuma, H., Inoue, K., Se, K., & Kotaka, T. (1984). *Macomolecules*, *17*, 1285.
[15] Ueda, Y., Kuriyama, T., Hari, T., & Ashida, M. (1994). *J. Electron Microscope.*, *43*, 99.

Downloaded by [University of California, San Diego] at 14:18 09 August 2012