Macromol. Symp. **2008**, 268, 77–80 DOI: 10.1002/masy.200850816

Optical Chirality Induced in Evaporated Poly(diacetylene) Film by Circularly Polarized Light

*Hideki Kohn, Yuki Ohshima, Takaaki Manaka, Mitsumasa Iwamoto**

Summary: 10,12-tricosadiynoic acid films were deposited on glass substrate by vacuum evaporation proceess at substrate temperatures of 273 K and 313 K, and then photopolymerized using left- and right- circularly polarized light (CPL). The resulting prepared poly(diacetylene) films changed from blue phase to red phase successfully by sample annealing at 353 K for 10 min, and the absorption spectra well reflected the red phase. Surface morphology change was not observed by anneling at 353 K. Furthermore, the CD spectra revealed that the chirality induced by CPL at 313 K was stronger that at 273 K.

Keywords: 10,12-tricosadiynoic acid; annealing; chirality; circularly polarized light; substrate temperature

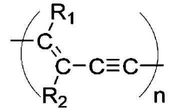
Introduction

Polymeric materials have called our attention to organic device application because of a rich functionalities, flexibility, lightweight, and so on. Among them, π-conjugated polymers are interesting, because they exhibit one-dimensional electron transport, optical anisotropy, and others. However, for utilizing these properties effectively in organic electronics devices, preparation methods that can control the geometrical structure of π-conjugated polymers are needed. Polydiacetylene (PDA) derivatives with large nonlinear optical (NLO) susceptibility and high mobility have been well studied for a long time.[1–3] It was shown that the Langmuir-Blodgett technique is one way that can prepare chiral PDA films with a helical structure which show circular-dichroism (CD). Note that precursor DA films that are deposited on substrates from a surface of water containing Cu ions must be photopolymerized.[4,5] Recently our study revealed that the PDA (Scheme 1) films prepared by the LB technique using precursor 10,12-tricosadiynoic acid (TDA) films deposited from a pure water surface also show the CD.[6–7] This successful preparation of chiral PDA films, without using Cu ions in the deposition process of TDA, motivated us to use the evaporation method for the preparation of chiral PDA, because this success suggested that chiral dopants, Cu ions, etc. are not needed in the preparation process of chiral PDA.

Interestingly, in our previous study,[6] we could show that chiral PDA films are prepared using vacuum deposited monomer TDA films that are subjected to circularly polarized light (CPL) irradiation. This result is important in that any chiral materials are not necessary during the polymerization process, though diacetylene monomer is obviously achiral. In other words, the preparation of the chiral π-conjugated polymer from symmetric materials is possible only with aid of CPL irradiation. Our experimental study also showed that the chirality of PDA films depends on the structure of starting monomer film, and it is strongly induced when films are prepared at high substrate temperature.[8] However, the UV-vis absorption of blue phase-PDA shows that high

---

Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan
Fax: (+81)-3-5734-2191;
E-mail: iwamoto.m.ac@m.titech.ac.jp



R_1:-$(CH_2)_9CH_3$
R_2:-$(CH_2)_8COOH$

1

Scheme 1.

temperature samples slightly contain red phase-PDA. To discuss deeply the effect of the substrate temperature during deposition on the induced chirality, possibility of the inclusion of red phase into blue phase should be prevented. In this paper, we compare the chirality of red phase films that were transformed from blue phase prepared with different substrate temperature during deposition.

Experimental Part

TDA was purchased from Tokyo Chemical Industry Co., Ltd, and used without further purification. The process pressure was kept less than 2.0×10^{-4} Pa during deposition, and the substrate temperature was controlled at 313 K or 273 K in each batch. Evaporation rate was controlled as $0.06\ \mathrm{nm \cdot sec^{-1}}$ during the process using quartz crystal microbalance. The film thickness of deposited TDA was approximately 100 nm. After the TDA deposition, the substrate was kept at a temperature of 293 K, and then took out from vacuum system for the succeeding polymerization. The photopolymerization of TDA films was carried out by the 314 nm UV light generated from high pressure Hg lamp (HAMAMATSU; L-8333). The intensity of left- and right-CPL was approximately $19.4\ \mathrm{mW \cdot cm^{-2}}$, and the irradiation time was 25 min. After photoirradiation, polymerized blue phase-PDA films were obtained. Finally, the resulting PDA films were changed their phase from blue into red with annealing at a temperature of 353 K for 10 min. The domains of PDA were observed using polarizing microscope, and the UV-vis absorption and CD spectra were examined using JASCO UV-vis spectrometer V-570 and CD spectrometer J-715, respectively. For the CD measurement, the spot area of incident light was 7 × 7 mm.

Surface Morphology

UV light irradiation to TDA monomers resulted in synthesized PDA, on keeping the crystal system of the TDA monomer (topochemical reaction),[9] where the initial structure of monomer plays an important role because of the strong interaction between side chains involved in the photopolymerization process. Due to this interaction, a lot of domains are generally observed in the microscope image of the surface. On the other hand, it is known that the substrate temperature gives directly effect on the stick shape molecular like n-paraffin in the evaporation process.[10] Thus we expect that TDA monomer structure depends on the substrate temperature. Indeed, polarized microscope images revealed the substrate temperature dependence on the domain size and shape. The size of domains in red phase is identical to that in blue phase.[8] Figure 1-(a) and -(b) show the microscope image of red phase-PDA films deposited at 313 K and then subjected to the left- or right-CPL, respectively. The microscope images of Figure 1-(a) and 1-(b) are similar, and the domains observed possess uniaxial optical anisotropy. On the other hand, the red phase-PDA deposited at 273 K is comprised of small domains (Figure 1-(c) and -(d)). As such, PDA films prepared at 313 K contains large domains in comparison with those prepared at 273 K.

UV-vis Absorption and CD Spectrum

Phase transition of PDA from blue phase to red phase by heating has attracted much attention. It is known that the phase-transition of PDA is taken place by the strain of the backbone owing to the reorientation of the side chains.[11] Therefore, we may

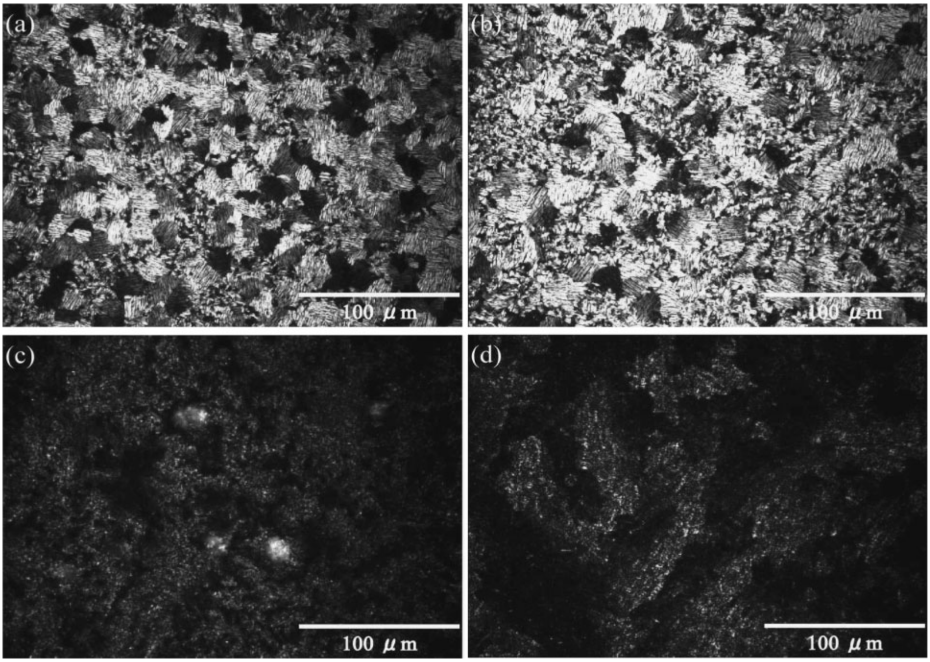


Figure 1.
Polarizing microscope images of red phase-PDA film which was deposited (a) at 313 K and polymerized with left-CPL (b) at 313 K and polymerized with right-CPL (c) at 273 K and polymerized with left-CPL (d) at 273 K and polymerized with right-CPL.

expect that the optical induced chirality we study here will also be dependent on the strain of backbone. Interestingly, our previous study showed that the thermochromic phase transition never broke the chirality of PDA induced by CPL,[6] and topochemical reaction was probable at high substrate temperature.[8] This fact indicates that we can investigate the chirality induced in red phase-PDA by using UV-vis absorption and CD spectra. Figure 2-(a) and -(b) show the UV-vis absorption and CD spectra of red phase-PDA prepared at substrate temperatures of 313 and 273 K, respectively. The absorption spectra of Figures 2-(a) and -(b) were similar and their peaks appeared at around 550 nm. Accordingly, appropriate PDA films with red phase was prepared and we can compare the induced chirality of red phase-PDA films prepared at different substrate temperetures. The CD spectra of the red phase-PDA were measured after polymerization from TDA monomer using left- or right-CPL, respectively, and annealing. The location of CD band in the region from 400 to 600 nm for 313 K sample agreed well with that of the absorption band for the red phase-PDA, as shown in Figure 2-(a). The CD spectra of the red phase-PDA polymerized using CPL indicates that the left- and right-CPL well produce the red phase-PDA film with opposite chiralities as shown in Figure 2-(a). Furthermore, the CD spectrum was independent of the rotation angle of the sample, i.e., there was no birefringence. These results indicate that the optical chirality with red phase-PDA was controllable by choosing left- and right-CPL when the substrate temperature was 313 K. On the other hand, red phase-PDA film prepared at 273 K showed no optical chirality effect as shown in Figure 2-(b), though some of the samples showed the presence of very small induced chirality by CPL at a wavelength of 500 nm as indicated by an arrow in Figure 2-(b). Taking into

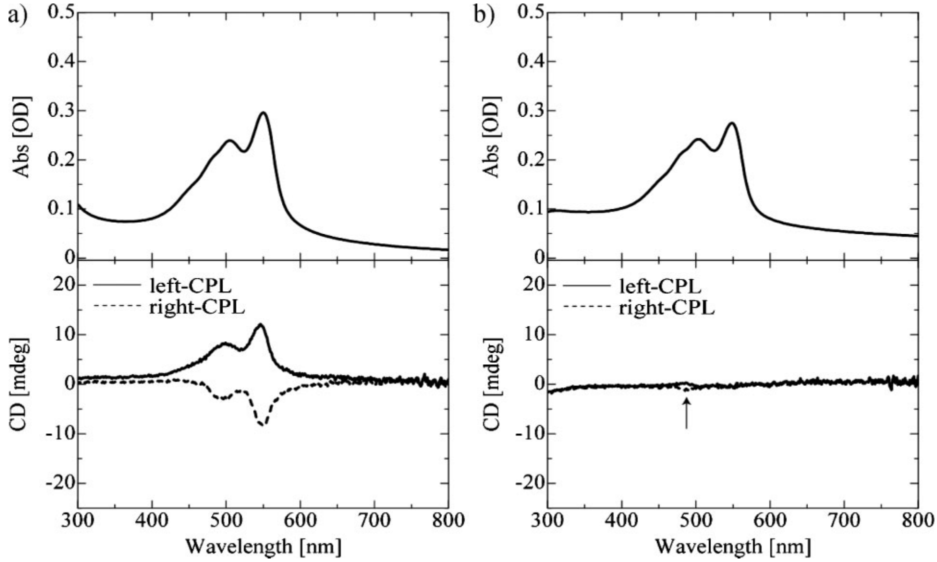


Figure 2.

UV-vis and CD spectra of PDA evaporation films. (a) Sample prepared on 313 K substrate, (b) on 273 K substrate. Solid and dashed lines represent the CD spectrum for the film polymerized with left- and right- CPL, respectively.

account these, we may conclude that the strength of chirality is effectively controlled by changing the substrate temperature during deposition. However, at the present, there is still not clear the relationship between the domain size and the chirality. Further investigation is proceeded.

Conclusion

The effect of substrate temperature on the chiral strength of PDA was investigated. TDA films were deposited at substrate temperatures of 313 K and 273 K, and they were then polymerized using left- and right-CPL to form blue phase-PDAs. Subsequently, blue phase-PDAs were transformed into red phase-PDAs with annealing process (353 K, 10 min). For both samples prepared at 313 K and 273 K, in particular at 313 K, the chirality induced in PDA was controllable by the left- and right-CPL. It was found that chiral strength strongly depended on the substrate temperature. High temperature substrate forms a film with strong chirality composed of large size domains, and the induced chirality appears reproducibly.

[1] C. Sauteret, J. P. Hermann, R. Frey, F. Pradere, J. Ducuing, R. H. Baughman, R. R. Chance, *Phys. Rev. Lett.* **1976**, *36*, 956.
[2] K. Takami, J. Mizuno, M. Akai-kasaya, A. Saito, M. Aono, Y. Kuwahara, *J. Phys. Chem. B* **2004**, *108*, 16353.
[3] K. Takami, Y. Kuwahara, T. Ishii, M. Akai-Kasaya, A. Saito, M. Aono, *Surf. Sci.* **2005**, *591*, L273.
[4] X. Huang, M. Liu, *Chem. Commun.* **2003**, *1*, 66.
[5] X. Huang, S. Jiang, M. Liu, *J. Phys. Chem. B* **2005**, *109*, 114.
[6] T. Manaka, H. Kon, Y. Ohshima, G. Zou, M. Iwamoto, *Chem. Lett.* **2006**, *35*, 1028.
[7] G. Zou, H. Kohn, Y. Ohshima, T. Manaka, M. Iwamoto, *Chem. Phys. Lett.* **2007**, *442*, 97.
[8] H. Kohn, et al., *Jpn. J. Appl. Phys.* submitted.
[9] V. Enkelmann, G. Wegner, *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 416.
[10] K. Tanaka, N. Okui, T. Sakai, *Thin Solid Films* **1991**, *196*, 137.
[11] D. C. Lee, S. K. Sahoo, A. L. Cholli, D. J. Sandman, *Macromolecules* **2002**, *35*, 4347.