Scientific Research Publishing

Soft, 2017, 5, 9-19
http://www.scirp.org/journal/soft
ISSN Online: 2327-0802
ISSN Print: 2327-0799

Lyotropic Liquid Crystal Electrochemical Polymerization of Thiophene-Based Monomers: Polymerization in Cholesteric Liquid Crystal and Columnar Phase

Naoto Eguchi, Hiromasa Goto*

Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan
Email: goth@ims.tsukuba.ac.jp

How to cite this paper: Eguchi, N. and Goto, H. (2017) Lyotropic Liquid Crystal Electrochemical Polymerization of Thiophene-Based Monomers: Polymerization in Cholesteric Liquid Crystal and Columnar Phase. *Soft*, **5**, 9-19.
https://doi.org/10.4236/soft.2017.52002

Received: January 11, 2017
Accepted: June 6, 2017
Published: June 9, 2017

Abstract

Synthesis of conductive polymer poly([thiophene]-[benzo[1,2,3]thiadiazole][thiophene]) (abbreviated as P(T-Btdaz-T)) was achieved by electrochemical polymerization in hydroxypropyl cellulose (HPC)/*N*,*N*-dimethylformamide (DMF) in liquid crystal state. The polymer thus obtained shows fingerprint texture, which is derived from helical structure of the HPC in cholesteric liquid crystal state. Fourier transform infrared spectroscopy measurements revealed that the polymer film is P(T-Btdaz-T)/HPC composite. Circular dichroism optical absorption spectroscopy measurements show that the polymer has the optical activity. Next, electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) was carried out in columnar phase liquid crystal. The polymer transcribes the columnar structure and shows optical structure resembling columnar liquid crystal electrolyte solution.

Keywords

Conductive Polymer, Electrochemical Polymerization, Lyotropic Liquid Crystal, Columnar Phase

1. Introduction

Polybenzothiadiazole is one of the most studied conductive polymers as a low-bandgap polymer for applications such as photo voltaic cells, transistors [1]-[20]. An article of chiral-electroactive low bandgap polymer composite was accepted into Journal of Materials Science and Chemical Engineering [21]. In this research, hydroxypropyl cellulose (HPC, cellulose derivatives) in organic solvent is employed as an electrolyte solution for electrochemical polymeriza-

tion. HPC is dissolved in both water and organic solvents [22]-[26]. In this study, *N*,*N*-dimethylformamide (DMF) is selected as a solvent for dissolving HPC. HPC in DMF liquid crystal solution allows polymerization of organic monomers with hydrophobicity.

Electrochemical synthesis of poly(3,4-ethylelnedioxythiophene) (PEDOT) is also carried out in columnar liquid crystal electrolyte solution. Hexadecyltrimethylammonium chloride (HTAC) is used as a columnar liquid crystal. HTAC shows lyotropic liquid crystallinity. Columnar liquid crystal also acts as a template for electrochemical polymerization.

2. Experimental

2.1. Materials

Monomer [thiophene]-[Btdaz]-[thiophene] (T-Btdaz-T) was prepared by previously reported method [1]. Hydoxypropyl cellulose was purchased from Wako Pure Chemical Industries, Ltd. (Wako, Japan) and used as supplied. Tetrabutylammonium perchlorate was purchased from Tokyo Chemical Industry Co., Ltd. (TCI, Japan). *N*,*N*-Dimethylformamide was used without purification (Nacalai Tesque, Japan). 3,4-Ethylenedioxythiophene was purchased from TCI. Hexadecyltrimethylammonium chloride was purchased from TCI.

2.2. Synthesis

Electrochemical polymerization of monomer [thiophene]-[Btdaz]-[thiophene] (T-Btdaz-T) was carried out in hydroxypropyl cellulose (HPC), Figure 1. Constituents of electrolyte solution are summarized in Table 1. First, monomer and tetrabutylammonium perchlorate (TBAP) (supporting salt) were added to DMF. Next, HPC was added to the electrolyte solution and mechanically stirred by

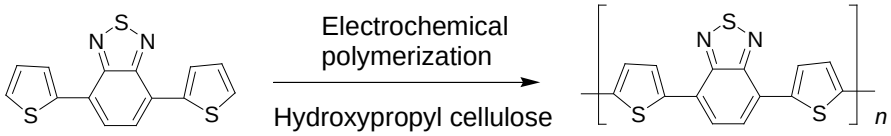
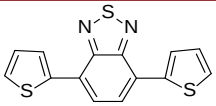


Figure 1. Scheme of electrochemical polymerization of [thiophene]-[benzo[1,2,3]thiadiazole]-[thiophene] monomer in hydroxypropyl cellulose.

Table 1. Constituents of electrolyte solution using hydroxypropyl cellulose.

Monomer	Matrix	Solvent	Supporting salt
	HPC[b]	*N*,*N*-dimethylformamide (DMF)	$(C_4H_9)_4N^+ClO_4^-$ (TBAP[c])
 (T-Btdaz-T[a]) 8.4 mg	701.0 mg	397.3 mg	4.1 mg

a. [thiophene]-[benzo[1,2,3]thiadiazole]-[thiophene]; b. Hydroxypropyl cellulose; c. Tetrabutylammonium perchlorate.

glass rod for 1 min. Then, the electrolyte solution containing the monomer was injected to the sandwiched cell (two ITO glass electrode, ITO = indium tin oxide). The sandwich cell polymerization method thus performed was developed by our group previously. Direct current (dc) voltage of 3.0 V was applied across to the cell for 60 min. A thin polymer film was deposited on an anode side (+) of the electrode. After electrochemical polymerization, the sandwich cell was soaked into the distilled water to dissolve residual electrolyte solution and disassemble the cell. The polymer film thus deposited onto the ITO glass was washed with large volume of water, and acetone to remove residual HPC, monomer, and TBAP.

Next, electrochemical polymerization of 3,4-ehylenedoxythiophene (EDOT) was carried out in hexadecyltrimethylammonium chloride (HTAC) (Figure 2). Constituents of electrolyte solution are shown in Table 2. First, HTAC was dissolved in water. The solution exhibits columnar phase liquid crystal at appropriate concentration. Then, EDOT as a monomer was added to the solution. After injecting the electrolyte solution into the cell space of sandwiched ITO glass, dc 2.7 V was applied across to the cell for 5 min. EDOT monomer is electrochemically oxidized at an anode side and polymerized. Thin PEDOT film appeared at the anode side of the ITO glass electrode. The polymer film was washed with large volume of distilled water, and acetone to remove residual HTAC, TBAP and monomer.

2.3. Measurements

Polarizing optical microscopy measurements were carried out by using an ECLIPX LV 100 high-resolution polarizing microscope (Nikon). Fourier Transform Infrared absorption spectroscopy measurements were carried out with a

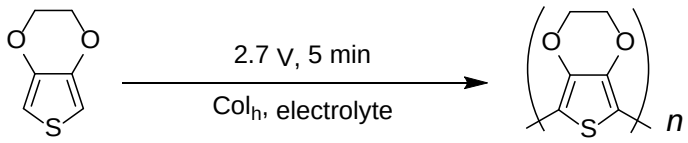
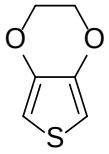
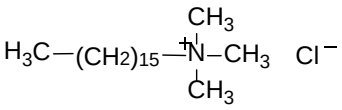


Figure 2. Electrochemical polymerization of 3,4-ethylenedioxythieophene in columnar liquid crystal.

Table 2. Constituents of columnar liquid crystal electrolyte solution using hexadecyltrimethylammnonium chloride.

Monomer	Matrix	Solvent
	HTAC[b]	Water
 (EDOT[a]) 10 μL	 60.2 mg	200.0 mg

a. 3,4-ethylenedioxy thiophene; b. Hexadecyltrimethylammonium chloride.

FT-IR 4600 (Jasco) by using the KBr method. UV-vis absorption spectroscopy measurements were carried out by using a V-630 (Jasco). Cyclic voltammetry were carried out with a μAUTOLAB TYPE III (ECO Chemie). Electrolyte solution contained 0.1 M tetrabutylammonium perchlorate in acetonitrile. Circular dichroism spectroscopy measurements were carried out with a J-720 (Jasco).

3. Results and Discussion

3.1. Polarizing Optical Microscopy

Optical texture of the polymer prepared in HPC liquid crystal was observed by polarizing optical microscopy (POM), Figure 3. POM observation revealed that the polymer surface shows fingerprint texture. Fingerprint textures commonly appear in cholesteric liquid crystal. In this case, HPC dissolved in DMF shows cholesteric liquid crystal, indicating the monomer propagated in the helical structure of the HPC during the polymerization with structural transcription mechanism to form fingerprint structure. HPC acts as a helical template in this electrochemical polymerization (liquid crystal template polymerization).

Figure 4(a) shows POM image of electrolyte solution using HTAC. The POM image of the polymer prepared in HTAC is shown in Figure 4(b). The optical texture of the polymer resembles with columnar liquid crystal electrolyte solution. Transcription of columnar structure was also occurred in the columnar liquid crystal electrolyte solution.

3.2. Fourier Transform Infrared Absorption

Fourier transform infrared red (FT-IR) results of the HPC (LC matrix), T-Btdaz-T (monomer), and the resultant polymer are shown in Figure 5. Absorption band at around 3500 cm^{-1} is ascribed as O-H stretching vibration of pyranose unit. Absorption bands at around 3000 cm^{-1} are CH_2 and CH_3 stretching vibration. An absorption band at around 1070 cm^{-1} is due to C-O-C stretching vibration. An absorption band at 690 cm^{-1} is derived from thiophene. The polymer film prepared in HPC shows O-H stretching vibration in same region of HPC.

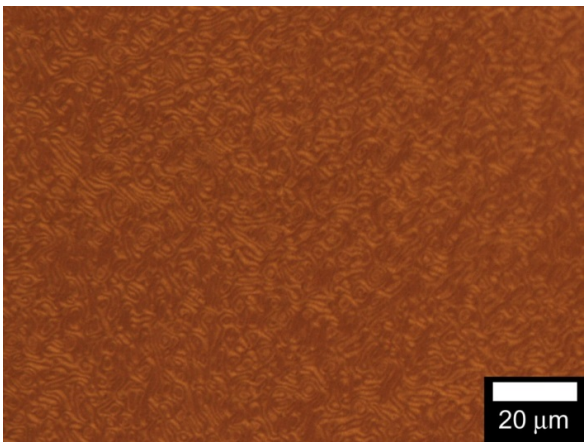


Figure 3. Polarizing optical microscopy image of obtained polymer film P(T-Btdaz-T) in hydroxypropyl cellulose (HPC).

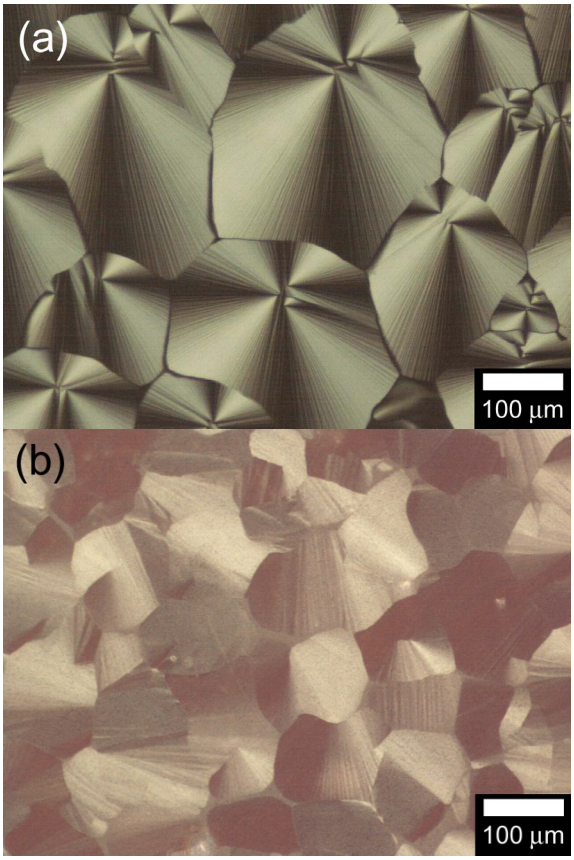


Figure 4. Polarizing optical microscopy image of columnar liquid crystal electrolyte solution (a) and polymer film (b) prepared by columnar phase.

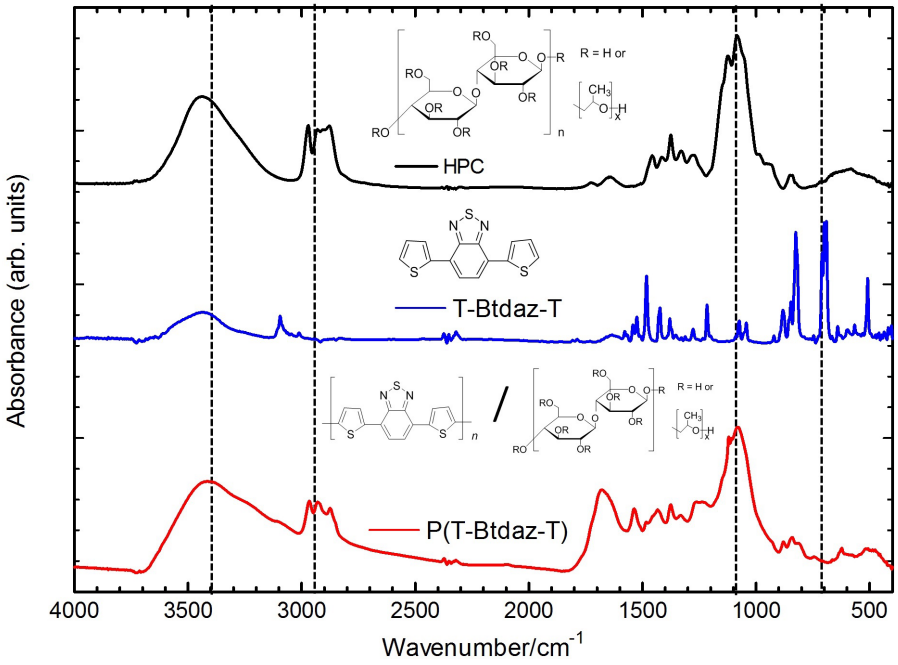


Figure 5. Fourier transform infrared (IR) spectra of hydroxypropyl cellulose (HPC) (black line), T-Btdaz-T (blue line), and resultant polymer (P(T-Btdaz-T)/HPC composite, red line).

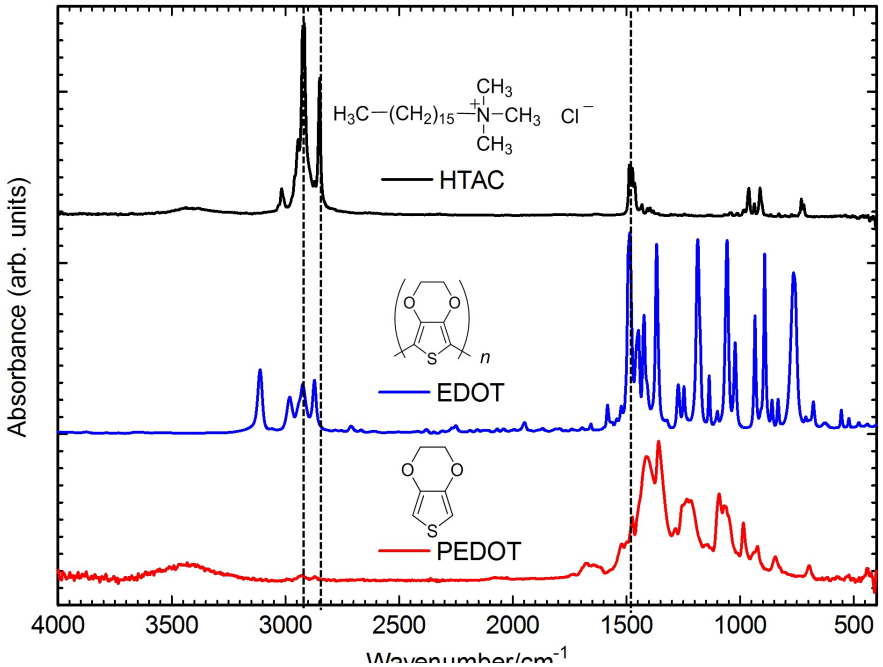


Figure 6. Fourier transform infrared spectra of hexadecyltrimethylammonium chloride (HTAC) (black line), EDOT (blue line) and PEDT (red line).

This results revealed that the polymer film prepared in HPC contains HPC, and forms P(T-Btdaz-T)/HPC composite. FT-IR spectra of PEDOT prepared in columnar liquid crystal are shown in Figure 6. Absorption band at 2913 and 2848 cm^{-1} are CH_2 and CH_3 stretching vibration of hexadecyltrimethylammonium chloride (HTAC). An absorption band at 1458 cm^{-1} is due to C=C stretching vibration of EDOT, 1358 cm^{-1} is due to $(C\text{-}C)_{ring}$ stretching vibration,1186 cm^{-1} is due to $(C=C)_{ring}$ vibration, 1057 cm^{-1} is due to $(\text{-}COCH_2CH_2OC\text{-})$ stretching vibration, 935 cm^{-1} is due to $(C\text{-}S)_{ring}$ vibration, and 763 cm^{-1} is due to CH out-of-plane vending vibration.

3.3. UV-vis Absorption

In situ UV-vis absorption measurements were performed during cyclic voltammetry. The UV-vis absorption spectra of P(T-Btdaz-T)/HPC composite at various applied potential are shown in Figure 7. A new absorption band at 723 nm is due to polarons (radical cation) band. The absorption intensity of polaron band increases with applied potential of 0 V to 1.4 V, indicating occurrence of electrochemical oxidation (doping). Polarons change to bipolarons when heavy doping was occurred. So absorption band changes from visible region to near infrared region. Therefore, absorption band of polarons at 723 nm becomes weak with applied potentials of 1.5 V (heavy doping), and simultaneously, absorption band of bipolarons increase at long wave region. The UV-vis absorption spectrum of PEDOT film prepared in HTAC is shown in Figure 8, which confirms achievement of preparation of PEDOT film in HTAC columnar phase electrolyte solution.

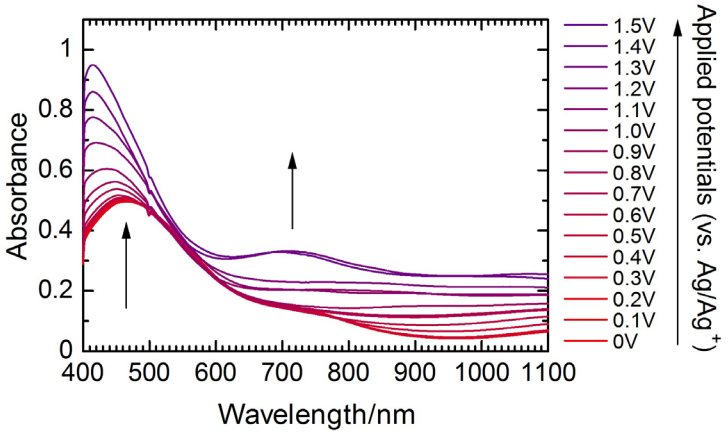


Figure 7. UV-vis absorption spectra of P(T-Btdaz-T)/HPC composite at various applied potentials (vs. Ag/Ag^{+}).

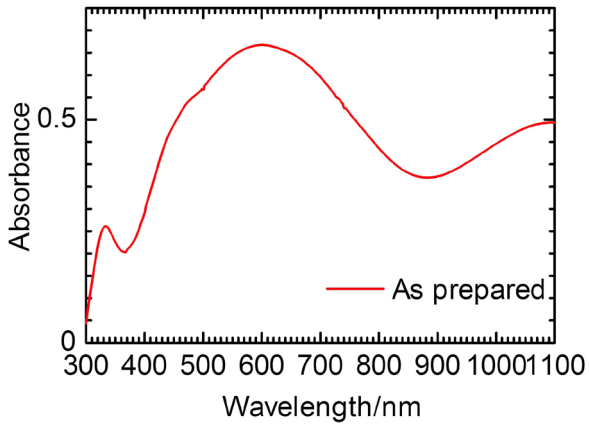


Figure 8. UV-vis absorption spectrum of PEDOT film prepared in columnar liquid crystal electrolyte solution.

3.4. Cyclic Voltammetry

Cyclic voltammetry (CV) analysis of P(T-Btdaz-T)/HPC composite was performed at various scan rates. The CV of the polymer is shown in **Figure 9**. P(T-Btdaz-T)/HPC composite film thus obtained in HPC liquid crystal shows repeatable reduction/oxidation behavior via application potential from −0.3 to 0.35 V.

The CV measurements of PEDOT prepared in HPC liquid crystal were also carried out at scan rates of 100, 200 and 500 mV/s, **Figure 10**. The polymer film shows repeatable redox behavior with application potential from −0.9 to 0.9 V.

3.5. Circular Dichroism

Circular dichroism (CD) optical absorption spectroscopy measurements was carried out for the as prepared polymer film and reduces P(T-Btdaz-T)/HPC composite film. The CD spectra are shown in **Figure 11**. Reduced sample was prepared by exposing hydrazine vapor for 30 min.

Polaron band decreases at <700 nm region in reduction. On the other hands, CD absorption of π-π* transition of the main chain increases. This result de-

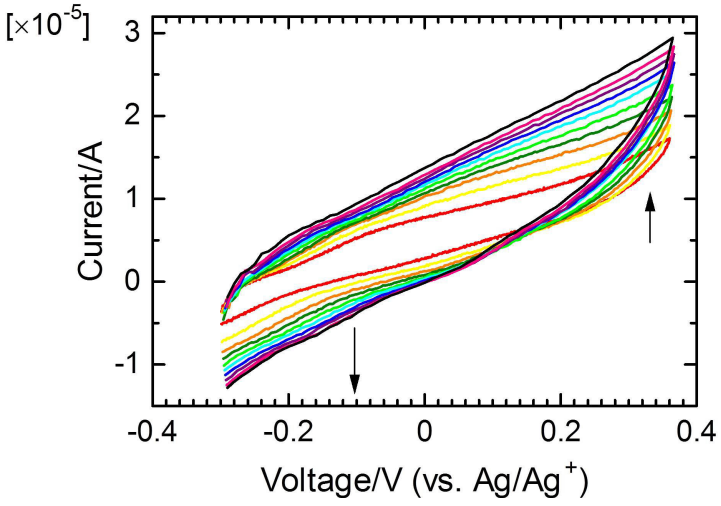


Figure 9. Cyclic voltammograms of P(T-Btdaz-T)/HPC composite at various scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV/s vs. Ag/Ag^+.

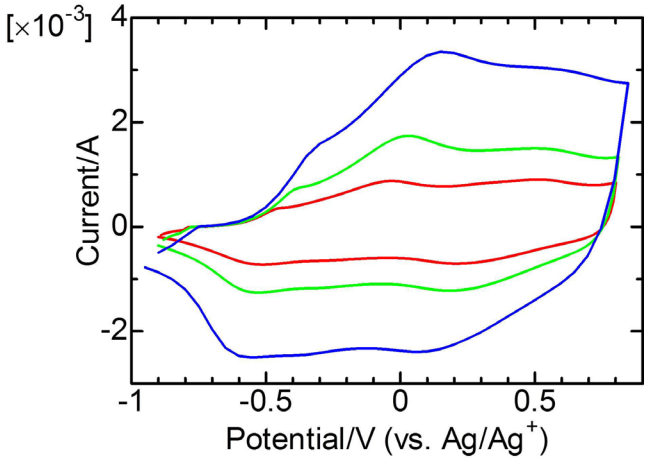


Figure 10. Cyclic voltammograms of PEDOT prepared in HPC polymer liquid crystal at various scan rates of 100, 200 and 500 mV/s vs. Ag/Ag^+.

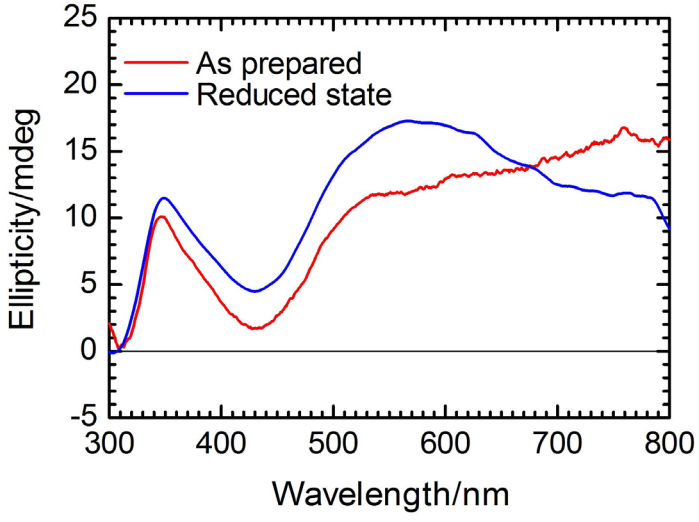


Figure 11. CD spectra of P(T-Btdaz-T)/HPC composite. (Red line): as prepared sample. (Blue line): reduced state.

monstrates that optically activity of the composite can be tuned through redox process.

4. Conclusions

We achieved preparation of P(T-Btdaz-T)/HPC composite film by electrochemical polymerization in HPC liquid crystal. The POM observation of P(T-Btdaz-T)/HPC composite reveals that the film showed fingerprint texture. The FT-IR result indicated that the polymer film is composite of P(T-Btdaz-T)/HPC. The CV measurements show that this polymer has the repeatable redox character. The polymer has optical activity derived from helical aggregation through transcription of chirality from the HPC liquid crystal matrix.

Electrochemical polymerization of EDOT in columnar liquid crystal is successfully carried out. The POM observation for the columnar shaped PEDOT confirms occurrence of transcription of columnar structure to the polymer during the electrochemical polymerization process.

Acknowledgements

We would like to thank Tsukuba Research Center for Interdisciplinary Materials Science (TIMS).

References

[1] Karikomi, M., Kitamura, C., Tanaka, S. and Yamashita, Y. (1995) New Narrow-Bandgap Polymer Composed of Benzobis(1,2,5-Thiadiazole) and Thiophenes. *Journal of the American Chemical Society*, **117**, 6791-6792. https://doi.org/10.1021/ja00130a024

[2] Kitamura, C., Tanaka, S. and Yamashita, Y. (1996) Design of Narrow-Bandgap Polymers. Syntheses and Properties of Monomers and Polymers Containing Aromatic-Donor and o-quinoid-Acceptor Units. *Chemistry of Materials*, **8**, 570-578. https://doi.org/10.1021/cm950467m

[3] Jayakannan, M., Van Hal, P.A. and Janssen, R.A. (2002) Synthesis and Structure-Property Relationship of New Donor-Acceptor-Type Conjugated Monomers and Polymers on the Basis of Thiophene and Benzothiadiazole. *Journal of Polymer Science Part A*: *Polymer Chemistry*, **40**, 251-261. https://doi.org/10.1002/pola.10107

[4] Boas, U., Dhanabalan, A., Greve, D.R. and Meijer, E.W. (2001) Synthesis of Thiophene-Based Building Blocks via Facile α-Monoiodination. *Synlett*, **5**, 0634-0636.

[5] Van Mullekom, H.A.M., Vekemans, J.A.J.M. and Meijer, E.W. (1998) Band-Gap Engineering of Donor-Acceptor-Substituted π-Conjugated Polymers. *Chemistry A European Journal*, **4**, 1235-1243. https://doi.org/10.1002/(SICI)1521-3765(19980710)4:7<1235::AID-CHEM1235>3.0.CO;2-4

[6] Hou, Q., Xu, Y., Yang, W., Yuan, M., Peng, J. and Cao, Y. (2002) Novel Red-Emitting Fluorene-Based Copolymers. *Journal of Materials Chemistry*, **12**, 2887-2892. https://doi.org/10.1039/b203862e

[7] Yamashita, Y., Suzuki, K. and Tomura, M. (2003) Novel Electron Acceptors Containing Thiadiazole and Thiophene Units. *Synthetic Metals*, **133**, 341-343. https://doi.org/10.1016/S0379-6779(02)00332-6

[8] Svensson, M., Zhang, F., Veenstra, S.C., Verhees, W.J., Hummelen, J.C., Kroon, J.M.

and Andersson, M.R. (2003) High-Performance Polymer Solar Cells of an Alternating Polyfluorene Copolymer and a Fullerene Serivative. *Advanced Materials*, **15**, 988-991. https://doi.org/10.1002/adma.200304150

[9] Niu, Y.H., Huang, J.I.A.N. and Cao, Y.O.N.G. (2003) High-Efficiency Polymer Light-Emitting Diodes with Stable Saturated Red Emission: Use of Carbazole-Based Copolymer Blends in a Poly(*p*-Phenylenevinylene) Derivative. *Advanced Materials*, **15**, 807-811. https://doi.org/10.1002/adma.200304619

[10] Kato, S.I., Matsumoto, T., Ishi-i, T., Thiemann, T., Shigeiwa, M., Gorohmaru, H. and Mataka, S. (2004) Strongly Red-Fluorescent Novel Donor-π-Bridge-Acceptor-π-Bridge-Donor (D-π-A-π-D) Type 2,1,3-benzothiadiazoles with Enhanced Two-Photon Absorption Cross-Sections. *Chemical Communications*, **20**, 2342-2343. https://doi.org/10.1039/B410016F

[11] Zhou, Q., Hou, Q., Zheng, L., Deng, X., Yu, G. and Cao, Y. (2004) Fluorene-Based Low Band-Gap Copolymers for High Performance Photovoltaic Devices. *Applied Physics Letters*, **84**, 1653-1655. https://doi.org/10.1063/1.1667614

[12] Hou, J., Chen, H.Y., Zhang, S., Li, G. and Yang, Y. (2008) Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole. *Journal of the American Chemical Society*, **130**, 16144-16145. https://doi.org/10.1021/ja806687u

[13] Zhou, H., Yang, L., Stuart, A.C., Price, S.C., Liu, S. and You, W. (2011) Development of Fluorinated Benzothiadiazole as a Structural Unit for a Polymer Solar Cell of 7% Efficiency. *Angewandte Chemie*, **123**, 3051-3054. https://doi.org/10.1002/ange.201005451

[14] Bundgaard, E. and Krebs, F.C. (2006) Low-Band-Gap Conjugated Polymers Based on Thiophene, Benzothiadiazole, and Benzobis (Thiadiazole). *Macromolecules*, **39**, 2823-2831. https://doi.org/10.1021/ma052683e

[15] Sonar, P., Singh, S.P., Li, Y., Soh, M.S. and Dodabalapur, A. (2010) A Low-Bandgap Diketopyrrolopyrrole-Benzothiadiazole-Based Copolymer for High-Mobility Ambipolar Organic Thin-Film Transistors. *Advanced Materials*, **22**, 5409-5413. https://doi.org/10.1002/adma.201002973

[16] Herguth, P., Jiang, X., Liu, M.S. and Jen, A.K.Y. (2002) Highly Efficient Fluorene- and Benzothiadiazole-Based Conjugated Copolymers for Polymer Light-Emitting Diodes. *Macromolecules*, **35**, 6094-6100. https://doi.org/10.1021/ma020405z

[17] Peng, Q., Liu, X., Su, D., Fu, G., Xu, J. and Dai, L. (2011) Novel Benzo[1,2-b:4,5-b']-Dithiophene-Benzothiadiazole Derivatives with Variable Side Chains for High-Performance Solar Cells. *Advanced Materials*, **23**, 4554-4558. https://doi.org/10.1002/adma.201101933

[18] Tamilavan, V., Kim, S., Agneeswari, R., Lee, D.Y., Cho, S., Jin, Y. and Hyun, M.H. (2016) Benzodithiophene Based Ternary Copolymer Containing Covalently Bonded Pyrrolo[3,4-*c*]Pyrrole-1,3-Dione and Benzothiadiazole for Efficient Polymer Solar Cells Utilizing High Energy Sunlight. *Organic Electronics*, **38**, 283-291. https://doi.org/10.1016/j.orgel.2016.08.028

[19] Deng, C. and Ling, J. (2016) Amphiphilic Copolymers of Polyfluorene Methacrylates Exhibiting Tunable Emissions for Ink-Jet Printing. *Macromolecular Rapid Communications*, **37**, 1352-1356. https://doi.org/10.1002/marc.201600188

[20] Doyranlı, C., Çolak, B., Lacinel, G., Can, M., Koyuncu, F.B. and Koyuncu, S. (2016) Effect of the Planar Center Moiety for a Donor-Acceptor Polymeric Electrochrome. *Polymer*, **108**, 423-431. https://doi.org/10.1016/j.polymer.2016.12.016

[21] Naoto, E. and Hiromasa, G. (2017) Chiral-Electroactive Low-Bandgap Polymer

Composite. *Journal of Materials Science and Chemical Engineering*, **5**, 1-10.

[22] Werbowyj, R.S. and Gray, D.G. (1976) Liquid Crystalline Structure in Aqueous Hydroxypropyl Cellulose Solutions. *Molecular Crystals and Liquid Crystals*, **34**, 97-103. https://doi.org/10.1080/15421407608083894

[23] Chang, S.A. and Gray, D.G. (1978) The Surface Tension of Aqueous Hydroxypropyl Cellulose Solutions. *Journal of Colloid and Interface Science*, **67**, 255-265. https://doi.org/10.1016/0021-9797(78)90010-3

[24] Werbowyj, R.S. and Gray, D.G. (1984) Optical Properties of Hydroxypropyl Cellulose Liquid Crystals. I. Cholesteric Pitch and Polymer Concentration. *Macromolecules*, **17**, 1512-1520. https://doi.org/10.1021/ma00138a016

[25] Fortin, S. and Charlet, G. (1989) Phase Diagram of Aqueous Solutions of (Hydroxypropyl)Cellulose. *Macromolecules*, **22**, 2286-2292. https://doi.org/10.1021/ma00195a050

[26] Guido, S. (1995) Phase Behavior of Aqueous Solutions of Hydroxypropyl Cellulose. *Macromolecules*, **28**, 4530-4539. https://doi.org/10.1021/ma00117a023