# Absolute asymmetric electrochemical polymerization

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Abstract
Electrochemical polymerization of thiophene-based achiral monomer having azobenzene as a chromophore irradiated by circular polarized light (CPL) was carried out to obtain chiroptically active polymer film on indium-tin-oxide (ITO) coated glass. Circular dichroism and optical absorption spectroscopy measurements indicate the samples show chiroptical activity. This result indicates occurrence of absolute asymmetric polymerization by laser CPL.

## 1. Introduction

Chemistry and physics of synthetic chiral polymers are among the most intriguing themes related to biochemistry. To obtain chiral polymers, introduction of chiral moieties as side chains [1], polymerization reactions using chiral catalysts [2], and polymerization in chiral liquid crystals [3,4] have been carried out. Chirality of achiral azobenzene derivatives and chirality change of the materials through photo-isomerisation [5], control of chiroptical activity by irradiation by linear polarized light for axial chiral low-molecular weight compound having azobenzene [6], and photochemical control of cholesteric liquid crystals by means of photo-isomerisation of a chiral azobenzene moiety [7,8] have been achieved.

Absolute asymmetric synthesis draws interest in chemistry, physics, and biology. This theme is related with the origin of asymmetry in living systems. Circular polarized sunlight may have triggered early formation of L- or D- form amino acids for generation of chiral biological compounds [9]. Circular polarized light (CPL) produced in star-forming regions of nebulae may contribute to the production of chiral materials via asymmetric photolysis [10]. Recently, intense CPL from the Orion massive

star-formation region was discovered and the origin of homo-chirality by irradiation of CPL in the space was proposed [11].

This result inspireed our research. We have attempted absolute polymerization under synchrotron radiation at High Energy Accelerator Research Organization in Japan (KEK, beam line-3C section, BL-3C) in 2011, based on consideration of circular polarized light from Orion massive star-formation region [12]. Further study has been carried out on origin of life [13]. In this report, absolute electrochemical polymerization under circular polarized light is carried out.

Control of both chirality of azobenzene liquid crystalline polymers with CPL and photo-induced chirality with CPL for amorphous azobenzene polymer films has been achieved [14-18]. Chirality induction for polyfluorene derivatives having no photochromic groups in thin film form upon irradiation of CPL was reported [19]. Irradiation of pulse laser CPL for polymer particle results mirror symmetry breaking [20]. In the case of chiral conjugated polymers, chiral charge carrier referred to as "chiralion" (chiral polarons and chiral bipolarons) has been reported [21-23].

In this research, electrochemical polymerization under irradiation of helical laser light to obtain chiral polymers based on consideration of absolute polymerization is performed. In these polymers, the so-called "polymer effect" for enhancement of physical properties by formation of sequential units consisting of low-molecular weight compounds and polymer collectives (aggregates) can be expected. External stimulus such as CPL can produce a bias for chirality in chemical compounds. The small bias of susceptibility from CPL may be amplified through formation of a sequence of monomer units. Therefore, polymerization under CPL can be expected to yield chiroptically active polymers from achiral monomers via the polymer effect. In this study, a thiophene derivative bearing azobenzene as a visible range chromophore is employed, and electrochemical polymerization is carried out under CPL to perform light-induced asymmetric reaction.

## 2. Experiment

2.1. Synthesis of monomer

2,5-Dibromo-benzoic acid 3-phenylazo-phenyl ester (1).

A solution of 2,4-dibromobenzene carboxylic acid (2.82 g, 0.01 mol), 4-(phenylazo)phenol (2 g, 0.01 mol), N,N'-dicyclohexylcarbodiimide (2 g, 0.01 mol), and 4-dimethylaminopyridine (4.2 g, 0.01 mol) in 20 mL of dichloromethane was stirred under argon flow at room temperature. After 24 h, the solution was filtered. After the filtrate was evaporated, the crude product was purified with silica gel column

chromatography (dichloromethane) followed by recrystalisation from acetone to give orange crystals (2.37g, Y = 51 %). $^1$H NMR ($\delta$ from TMS, ppm, 400 MHz): 7.40 (d, $J$ = 8.7 Hz, 2H, ph), 7.50 (m, 4H, ph), 7.59 (d, $J$ = 8.7 Hz, 1H, ph), 7.91 (d, $J$ = 6.4 Hz, 2H, ph), 8.00 (d, $J$ =8.7 Hz, 2H, ph), 8.15 (d, $J$ = 2.7 Hz, 1H, ph).

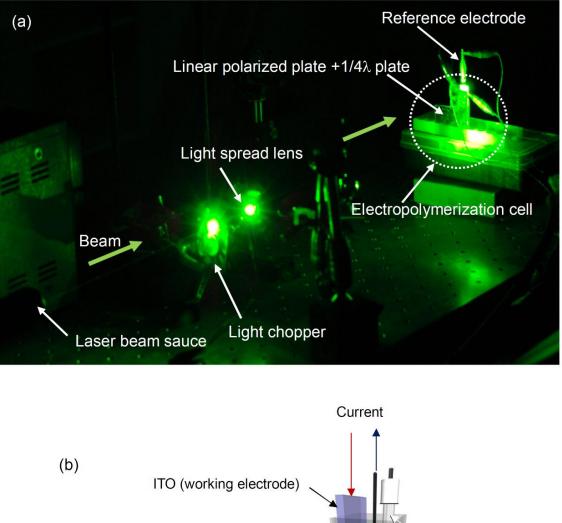2,5-Bis-[2,2']bithiophenyl-5-yl-benzoic acid 3-phenylazo-phenyl ester (2).

A solution of compound 1 (0.12 g, 2.6 x $10^{-4}$ mol), 5-(trimethylstannyl)-2,2'-bithiophene (0.17 g, 5.2 x $10^{-4}$ mol), tetrakis(triphenylphosphine)palladium (0) [Pd(PPh$_3$)$_4$] (0.58 mg, 5 x $10^{-7}$ mol)) in 1 mL of tetrahydrofuran (THF) was refluxed. After 24 h, the solvent was evaporated and the crude product was purified with silica gel column chromatography (dichloromethane) to yield orange solid (0.10 g, Y = 55%).$^1$H NMR ($\delta$ from TMS, ppm, 400 MHz): 7.04 (m, 8H, th), 7.22 (m, 2H, th), 7.37 (d, $J$ = 3.7 Hz, 2H, ph), 7.48 (m, 4H, ph), 7.59 (d, $J$ = 8.2 Hz, 1H, ph), 7.90 (d, $J$ = 5.03 Hz, 2H, ph), 7.95 (d, $J$ = 8.7 Hz, 2H, ph), 8.14 (d, $J$= 1.83 Hz, 1H, ph).

## 2.2. Polymerization

Electrolyte solution containing monomer was carried out as follows. A monomer (2) (0.01 g, 1.5 x $10^{-5}$ mol) and tetrabutyl ammonium perchlorate (TBAP, 0.17 mg) were dissolved in acetonitrile (20 mL). The monomer was partly precipitated in the acetonitrile solution because the solution was saturated.

Electrochemical polymerization under irradiation of high power pulse circular polarized laser beam was carried out. First, a pulsed laser beam (laser sauce: 800 mW, 532 nm) was produced with an optical chopper. The pulse laser was expanded to ca. 1 cm in diameter by a convex lens. The light passed through right- or left-handed circularly polarized filter (1/4 $\lambda$ wavelength retarder and linear polarizer) to produce circularly polarized light (R-CPL or L-CPL). The CPL irradiated the working electrode in the polymerization cell, as shown in Figure 1(a). Figure 1(b) displays set up of the polymerization. The polymerization cell contains Ag/Ag$^+$ reference electrode, Pt counter electrode, and an indium-tin-oxide (ITO)-coated glass working electrode. Electrochemical polymerization with application of scanning voltage (scan rate: 50 mV/s) between 0 and 1.3 V vs. Ag/Ag$^+$ reference electrode was performed under the irradiation of the pulsed R- or L-CPL. Figure 2 shows cyclic voltammetry result vs. Ag/Ag$^+$ reference electrode during the electrochemical polymerization scans under the pulse CPL in the first 10 scans. In this polymerization, total 20 scans were carried out for completion of the polymerization. Oxidation signals are observable at around 1 V.

The signal gradually shifted to lower potential range as the polymerization progressed (Scheme 1). After 20 scans, the orange-coloured polymer films deposited on the ITO were washed with hexane and methanol, and then dried. Polymers thus obtained are labeled as Poly-$R_{532}$ (polymer prepared under 532nm pulse R-CPL) and Poly-$L_{532}$ (polymer prepared under 532 nm pulse L-CPL).
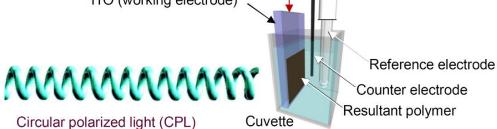


FIGURE 1 (a): Electrochemical polymerization under irradiation by circular polarized laser light. (b): Set up of electrochemical polymerization cell.
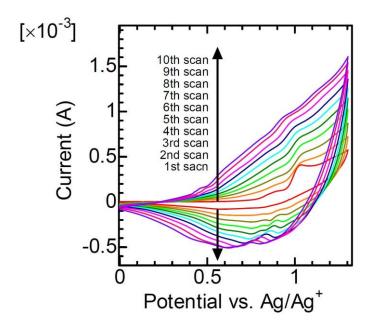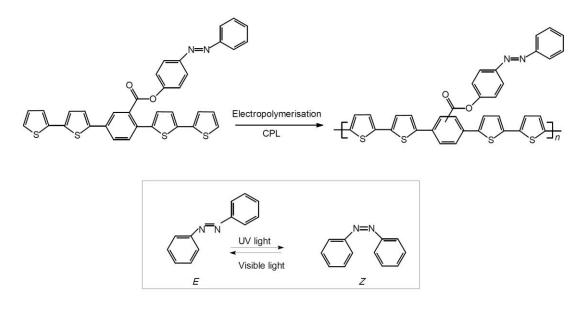
FIGURE 2 Cyclic voltammetry (CV) result in 10 scans versus Ag/Ag$^+$ reference electrode during polymerization under circularly polarized light. Polymerization under pulse L-CPL at 532 nm.



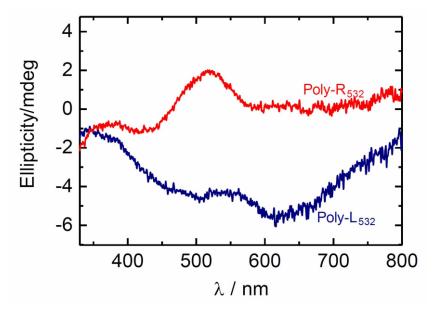SCHEME 1 Electropolymerization under L-CPL or R-CPL. CPL = circular polarized light.

## 3. Results and discussion

Circular polarized differential interference contrast optical microscopy (C-DIM) image of the Poly-R$_{532}$ showing no characteristic image such as finger print texture

obtained in liquid crystals. Optical absorption spectra of monomer in chloroform solution, and the polymer film deposited ITO coated glass before and after irradiation of UV light for 5 min were examined. The monomer shows optical absorption maximum at 526 nm. An absorption band at 350 nm due to *E* (*trans*) form of azobenzene is overlapped $\pi-\pi*$ transition of main-chain of the monomer. The polymer (poly-L$_{530}$) shows absorption maximum at 470 nm due to $\pi-\pi*$ of the main-chain. Magnification of the UV-Vis absorption spectra shows trace change in absorption at 470 nm (isosbestic point ~ 413 nm) after irradiation of UV light, indicating *E-Z* (*trans-cis*) isomerisation affords change in the form of the main-chain (Scheme 1, bottom). However, optical absorptions due to *E* (absorption = 350 nm) and *Z* (440 nm) forms of azobenzene in the side-chain can not be observed because of overlap of the entire absorptions of the main-chain. The CD intensity of poly-R$_{532}$ was slightly increased after irradiation of UV light. As prepared polymers are *E* form because irradiation of visible range light during the polymerization maintains the polymer in stable *E* form. Figures 3 show the CD spectra of the electrochemically reduced forms. In the measurements, appropriate set position of the sample in the CD instrument is required. A certain set position of the polymerization cell for irradiation of the laser CPL during the polymerization, and the corresponding sample position for the CD measurement could allow reproducibility. Linear dichroism of the film was checked. An artifact detection/offset system (JASCO, Japan) in the CD measurement was employed. The polymers display low ellipticities in the CD. These results come from low effective induction of CPL against the polymers during the polymerization, although laser CPL exactly produces chiral polymers. Poly-R$_{530}$ show left-handed elliptically polarisation, while Poly-L$_{530}$ right-handed elliptically polarisation. The resultant samples show reproducible results in the CD measurements.

Achiral polythiophenes partly form both 3-D right-handed and left-handed helical configurations (racemisation) in the complex structures without CPL, resulting in no optical activity. Irradiation of the high-power R-CPL (right handed CPL) mainly destroys a fraction of right handed helical form of the growing polymer during the electrochemical polymerization process, resulting in the left-handed helical form grown and deposited on the substrate after the polymerization. In fact, asymmetric photolysis can be occurred during the electrochemical polymerization process. Oppositely handed helical polymers against helical direction of the incident circular polarized light remain after irradiation by circularly polarized light. Irradiation of L-CPL (left handed CPL) during the polymerization produced a polymer with right-handed elliptical polarisation.

The polymers show no repeating changes in chiroptical activities via dynamically

electrochemical redox (doping-dedoping) processes.



FIGURE 3 Circular dichroism (CD) absorption spectra of the polymers. Poly-R$_{532}$: polymer obtained under right circular polarized light (R-CPL). Poly-L$_{532}$: polymer obtained under left circular polarized light (L-CPL).

The polythiophenes with no chirality forms mixture of right and left handed helical form. Upon irradiation of the high power pulse laser CPL results photolysis of predominantly left or right handed isomers in the growing process of the polymer during the electrochemical polymerization. In general, electrochemical polymerization proceeds with generation of polarons (radical cations) and bipolarons (dications) accompanied by electrochemical doping (oxidation) in the propagation process. The polarons and bipolarons as charge carriers form gentle helical structure, which absorb circular polarized light at visible-near infrared (Vis-NIR) range [23]. So, asymmetric photolysis of the twisted charge carriers in left or right direction is occurred upon irradiation of the high power pulse laser CPL in the polymerization process. The side chain azobenzene can play a role of photosensitiser. Therefore, this asymmetric photolysis involves photosensitising effect. The residual polymer as atropisomer after photolysis can show circular dichroism.

## 4. Conclusions

Electrochemical polymerizations under irradiation of pulse laser circular polarized light were carried out. Further high-power laser beam may allow producing

optically active polymers with intense chiroptical activities. This polymerization leads to "absolute asymmetric electrochemical polymerization". In discussion of homo-chirality in origin of life, small amount of a seed of chirality is important because of high optical yield is not required in the initial stage. Asymmetric photolysis during the polymerization process might be related with origin of chirality of life.

Further research involves adjustment of appropriate laser power for the polymerization, and estimation of degree of circular polarisation of the laser CPL light is required.

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