

Preparation of poly(thiophene-*alt*-pyrrole) bearing chiral LC group

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ABSTRACT

Preparation of poly(thiophene-*alt*-pyrrole bearing mesogen) was carried out with Migita-Kosugi-Stille coupling type polycondensation with an aid of Pd(0) complex catalyst. The resultant polymer shows lyotropic liquid crystallinity with good film forming property. The smectic fan-shaped texture is maintained after completion of evaporation of solvent from the polymer solution. The cast film having LC (LC) order shows light emission function upon irradiation of excitation light at 460 nm. The polymer shows LC domain emission. Mechanical orientation allows to yield LC domain aligned film with band structure. Chiral mesogenic side chain induces π -conjugated main chain helicity from distance in molecular level.

Keywords: domain emission; lyotropic LC; π -conjugated copolymer; polycondensation.

Introduction

Conjugated polymers have been studied from interest in practical applications for plastic electronics such as preparation of electro luminescence devices [1], solar cells [2] and batteries [3]. Especially, polypyrrole (PPy) has been used for capacities in electronic devices as chip condensers. Performances of conjugated polymer depends on microscopic and macroscopic morphologies. In general, polymers form amorphous state and coexistence of partly crystalline region. Improvement of crystallinity is one of the important methods to give high performance for functional polymers because polymers usually consist of random coil structure. Improvement of crystallinity of polymers is somewhat difficult. In the case of polyaniline (PANI), MacDiarmid et al. proposed secondary doping as transition from compact coil to expanded coil by treatment of high boiling point organic solvent such as *m*-cresol [4]. The expanded coil prepared in that way shows high electrical conductivity compared with compact coil form of polyaniline. Introduction of liquid crystallinity for the polymers may be another option. In this case, alignment of the liquid crystal (LC) polymer is achieved by orientation with magnetic

field, electric field, and mechanical orientation. Combination of LC and π -conjugated polymer allows preparation of pseudo crystal structure [5]. Electro-magnetic anisotropy of such polymers can be controlled by external forces.

Magnetoelectric function of low molecular weight π -conjugated materials have been reported, such as magnetic properties of pyrrole and thiophene-bridged porphyrin dimers [6]. Conjugated copolymer consisting alternation of bandgap in the monomer units can decrease bandgaps. Low-bandgap conjugated polymer, containing alternating aromatic and quinonoid segments [7], and molecular super lattice based on combination of conjugated copolymer consisting pyrrole and thiophene [8] were reported. Helical polypyrrole derivatives have been synthesized [9] and evaluated optical activity and morphologies [10–12].

From these viewpoints, we develop liquid crystalline π -conjugated copolymer. The copolymer synthesized in this study is constructed by no substituted thiophene-unit and pyrrole with LC group in *N* position. Structural control problems associated with irregularly linked aromatic units (head-to-head or head-to-tail structure in β -substituted polythiophene) are avoided in this copolymer by introducing the substituents at the *N* position of pyrrole unit located center of the pyrrole ring. The copolymerization is carried out with Migita-Kosugi-Stille coupling [13]. Optical property of the polymer is confirmed

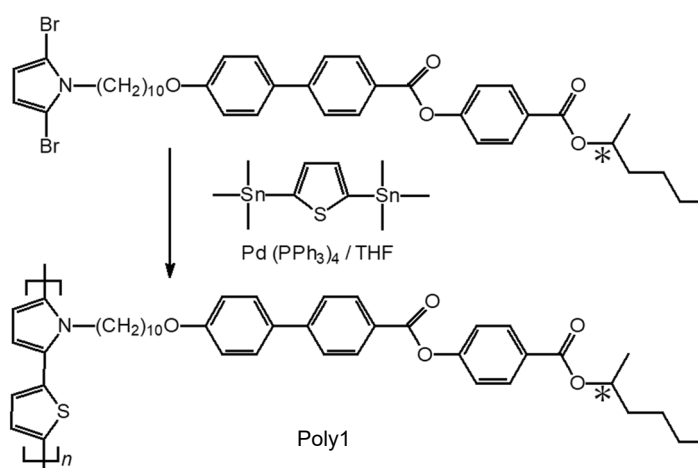
with ultraviolet-visible (UV-vis) absorption. Observation of optical texture for the present polymer with a polarizing optical microscopy (POM) reveals that the polymer shows lyotropic smectic phase with domain structure.

Experimental section

Synthesis

Dibromopyrrole with LC group (mono1) and 2,5-bis(trimethylstannyl)thiophene were prepared by previously reported method (Supplementary data). Although previous study synthesized (*S*)-4'-[4-(12-pyrrol-1-yl-dodecyloxy)-benzoyloxy]-biphenyl-4-carboxylic acid 1-methyl-heptyl ester (non dibromo group at 2,2' position of pyrrole, and carbon number of flexible group, C = 12), this study prepared (*S*)-4'-[4-(10-dibromo pyrrol-1-yl-decyloxy)-benzoyloxy]-biphenyl-4-carboxylic acid 1-methyl-heptyl ester as dibromopyrrole bearing LC group via flexible space of C = 10 (Supplementary data). Polymerization was carried out with an aid of tetrakis(triphenylphosphine) palladium (0) [Pd(PPh₃)₄] in tetrahydrofuran (THF), as shown in Scheme 1. Mono1 (311 mg, 3.7×10^{-4} mol) and 2,5-bis(trimethyltin)thiophene (151 mg, 3.7×10^{-4} mol) was added in THF (1.0 mL) in small size of Schlenk tube under N₂ gas flow. Then, Pd(PPh₃)₄ (4.3 mg, 3.7×10^{-6} mol) as a catalyst was added to the solution and stirred under reflux for ca. 12 h. The

solution was poured into a large volume of methanol and washed for several hours, and collected by filtration to yield polymer powder. The polymer thus obtained was dried under reduced pressure to obtain 88 mg of brown solid ($Y = 32\%$, calcd. from quantity/mru). Here, mru (g/mol) means to monomer repeat unit. The copolymer poly(thiophene-*alt*-pyrrole) bearing chiral LC group thus obtained is abbreviated as poly1.



Scheme 1. Synthesis of poly1. *: stereogenic center with (*S*)-configuration. $\text{Pd(PPh}_3)_4$: tetrakis(triphenylphosphine) palladium. THF: tetrahydrofuran.

Results and discussion

Characterization

Gel permeation chromatography (GPC) measurements evaluated that number-average molecular weights (M_n) and weight-average molecular weights (M_w) of poly1 are

to be 2.10×10^4 (g/mol) and 5.22×10^4 (g/mol) vs. polystyrene standard (eluent: THF), respectively. The GPC shape of poly1 is displayed in Figure 1. Dispersity (M_w/M_n) of poly1 is 2.4. Living polymerization is possible for synthesis of aromatic type conjugated polymers [14,15]. In this polymerization reaction, no living type polymerization was proceeded. However, this result demonstrated that the Migita-Kosugi-Stille type polycondensation successfully affords to yield the polymer bearing large sized LC group.

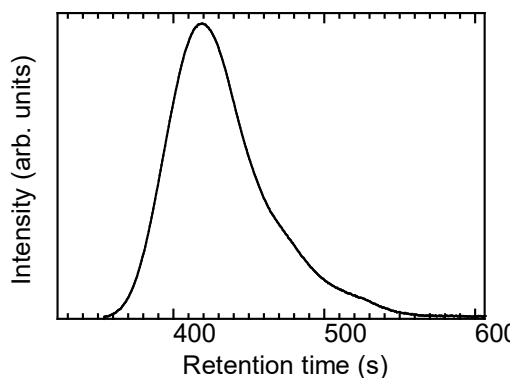


Figure 1. Gel permeation chromatography (GPC) result for the polymer.

Fourier transform infrared (FT-IR) spectroscopy measurements was carried out with KBr method. The result of the IR is shown in Figure 2. Absorption at $2,943\text{ cm}^{-1}$ is due to $\nu_{\text{CH}_3, \text{CH}_2}$, (alkyl C-C stretching). An absorption band observed at $1,730\text{ cm}^{-1}$ is due to C=O stretching of ester group in the side chain ($\nu_{\text{C=O}}$). Ether absorption (C-O-C stretching) of poly1 is observed at $1,247\text{ cm}^{-1}$ (ν_{COC}). Vibrations due to C=C (ν_{ph}) of aromatic groups and CH out-of-plane (δ_{CH}) are observed at $1,600\text{ cm}^{-1}$ and 793 cm^{-1} ,

respectively.

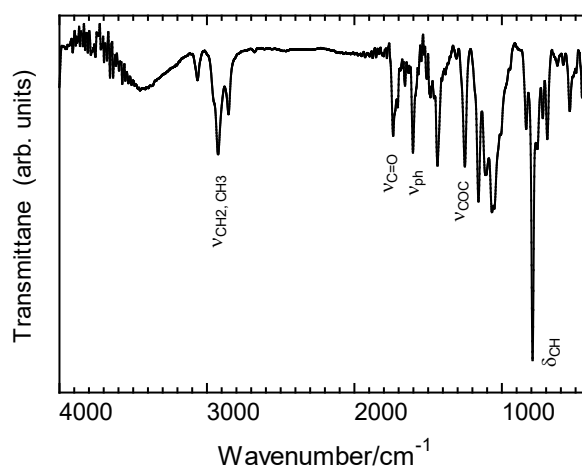


Figure 2. Fourier transform infrared (FT-IR) spectroscopy result of poly1 with KBr methods.

Liquid crystallinity

Poly1 displays no thermotropic liquid crystallinity upon heating up to 240 °C, while the polymer in toluene solution shows lyotropic liquid crystallinity. The bulky group in the substituent increases softening and melting temperature. Poly1 may have decomposition before transition to show thermotropic liquid crystallinity at high temperature in the heating process. In the case of poly1 in the solution, the polymer solution has appropriate fluidity to form self-assembly LC order with no thermal decomposition.

After completion of evaporation of toluene in the polymer solution, the poly1 forms

thin film on the glass slide with LC order. Figure 3a displays polarizing optical micrographs of poly1 in the form of cast film. The LC domain structure is observed, indicating this polymer shows lyotropic smectic phase. Poly1 performs emission upon excitation at 450 nm, as shown in Figure 3b. Furthermore, the polymer film achieves to exhibit "smectic domain emission". This experiment revealed that poly1 shows emission in the form of LC order. This sample was mechanically oriented to one direction (horizontal direction in the picture), showing band structure of LC. The method for orientation of the sample is shown in Figure 3c. Dark field observation of the POM for poly1 with reflection light was carried out, showing orientation of the LC domains (Figure 3d). The domains align perpendicular against shear direction with band structure (inset of Figure 3d).

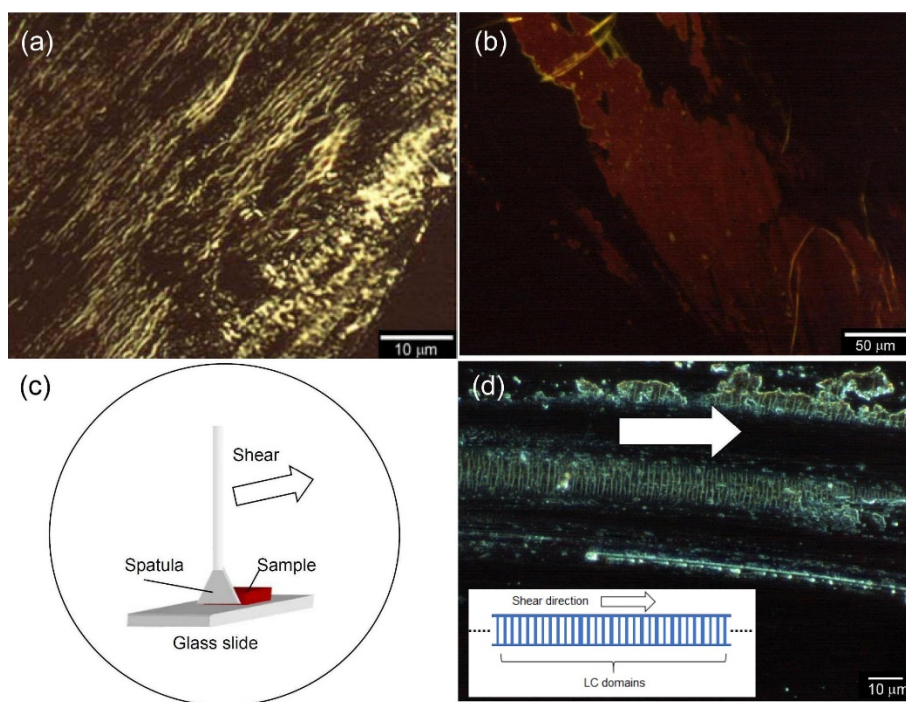


Figure 3. (a) Polarizing optical microscopy (POM) image of poly1 cast film from toluene solution. (b) Fluorescent optical microscopy image of poly1 cast film from toluene solution. (c) Mechanical orientation of the polymer. (d) Dark field observation of POM for poly1 with reflection light. Arrow indicates mechanical shear direction for orientation. Inset shows illustration of band structure of liquid crystal with mechanical orientation.

Optical property

Ultraviolet-visible (UV-vis) optical absorption spectrum of poly1 in chloroform solution is displayed in Figure 4a. The absorption band at 422 nm is due to π - π^* of the main chain.

On-set absorption of the polymer is 2.4 eV as an optical band gap (Figure 4b). E_g is

defined as,

$$E_g \text{ (eV)} = hc/\lambda_{\text{onset}} \quad (1)$$

Here, h is Plank constant, C light speed, and λ wavelength. The alternating structure of pyrrole and thiophene units can compensate increase of band gap by introduction of large size of LC group as a substituent. Photoluminescence was observed at 429 nm upon excitation light at 360 nm, as shown in Figure 4a. Inset of Figure 4a shows emission color of the polymer in vial upon irradiation of UV light exhibiting deep yellow.

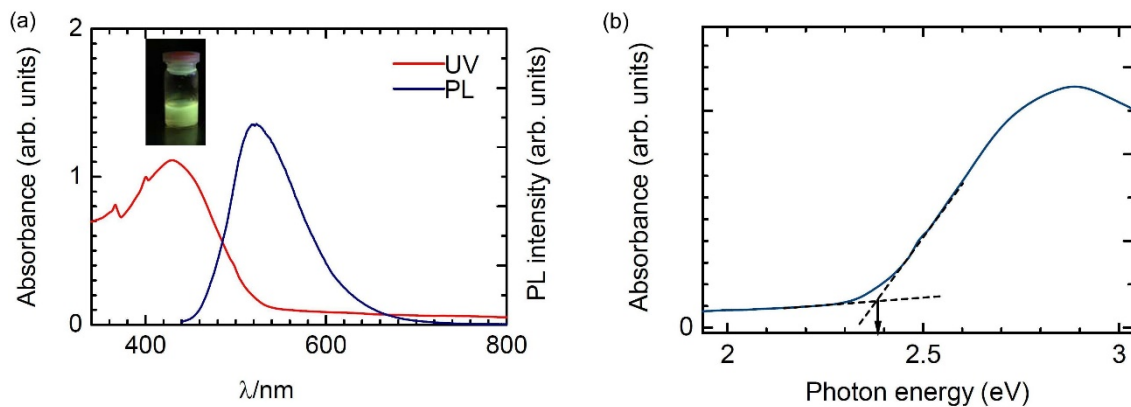


Figure 4. (a) Ultraviolet-visible (UV-vis) optical absorption and photoluminescence (PL) spectroscopy measurement results for poly1 in chloroform solution. Inset shows color of emission. (b) Estimation of optical bandgap for poly1.

Circular dichroism (CD) absorption spectroscopy measurement for poly1 was carried out

(Figure 5). The polymer shows positive sign in the CD at the UV-vis absorption band, indicating the polymer is optically active derived from the side chain LC group [16]. The polymer forms main chain type helical structure because the CD signal appears at π - π^* transition of the main chain. Side chain chirality can contribute helical twist for the main chain in the solution. This indicates achievement of preparation for mesogen-side chain type helical conjugated polymer. Chirality with long distance from main chain in molecular level can induce main chain helicity. The present result can be a first report for side chain type LC polymer shows main chain helical structure through production of copolymer having appropriate distance between chiral mesogenic side-chains in the dilute solution. Further, chirality can serve good film forming to prepare LC electroactive devices using this polymer.

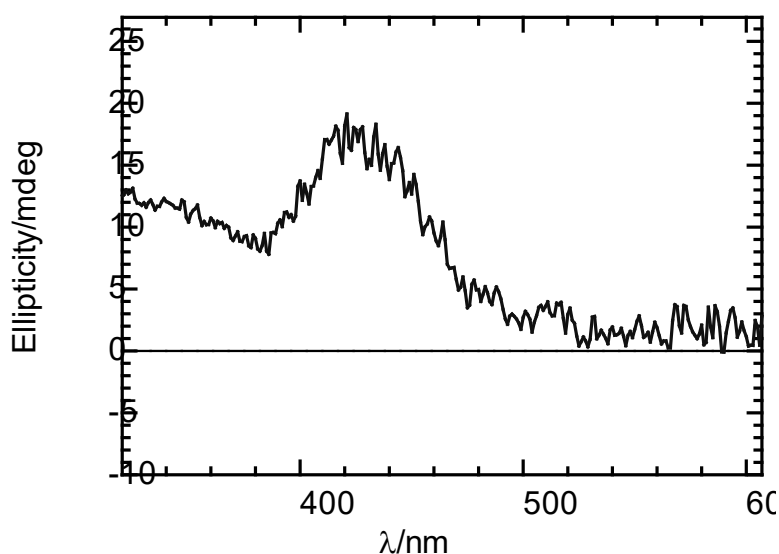


Figure 5. Circular dichroism (CD) absorption spectroscopy measurement result for poly1.

Plausible structure

Plausible helical structure of poly1 is described in Figure 6. Terminal stereogenic center induces helical position of the side chains. So, side chain helicity (Figure 6a) induces one-handed main chain helicity (Figure 6b) in the dilute solution. The main chain helicity shows optical activity. Appropriate distance between side chain mesogenic groups is formed by alternation units of the substituted pyrrole and non substituted thiophene units. In other words, the copolymer structure affords to induce main chain chirality from the distance terminal chiral group in the side chain mesogen.

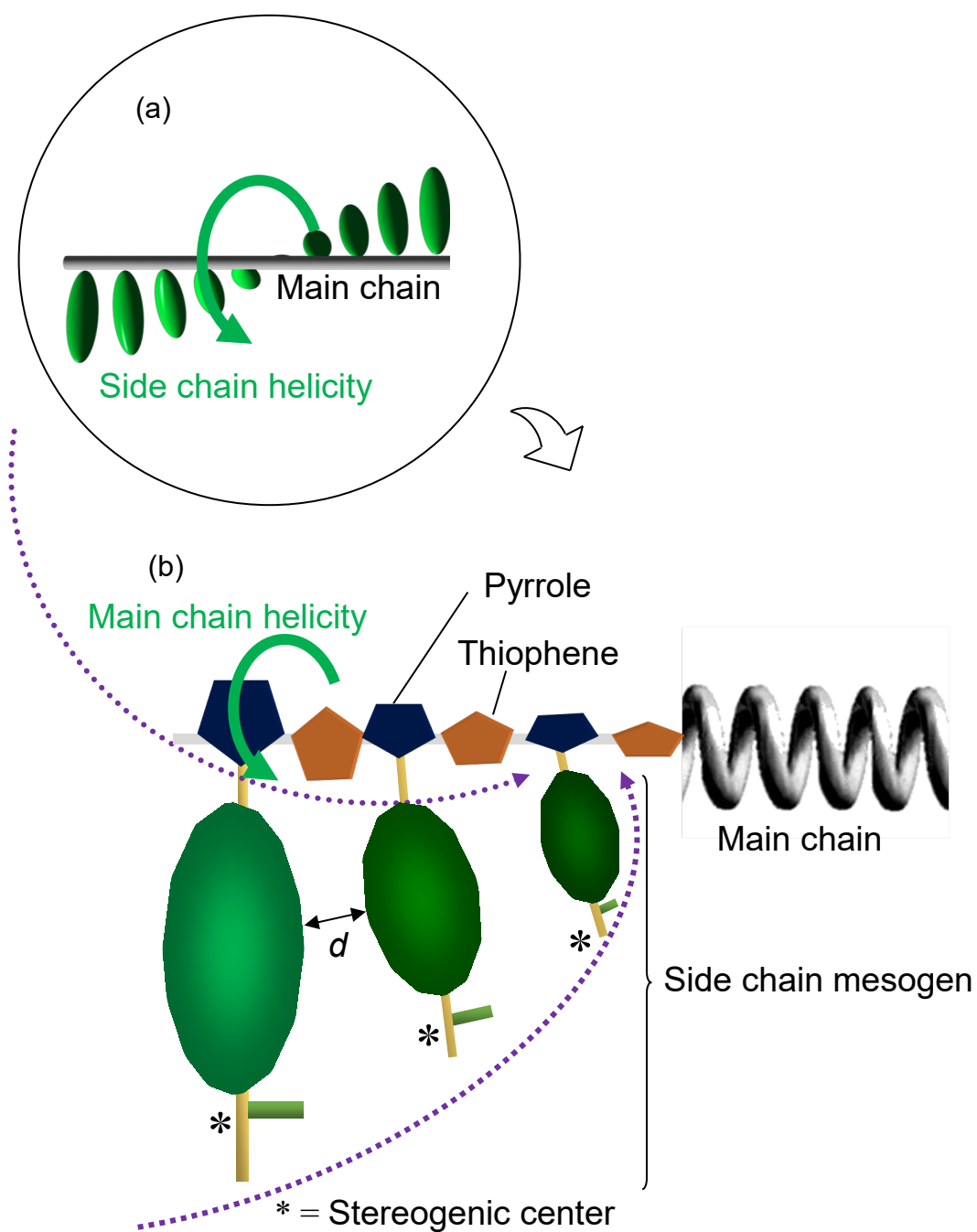


Figure 6. Plausible side chain and main chain helical structures induced by terminal stereogenic center in the mesogen. d = distance between side chains. (a): Side chain helicity. (b) Induction of main chain helicity from side chain helicity.

Conclusions

We synthesized poly(thiophene-*alt*-pyrrole bearing mesogenic group) using Migita-Kosugi-Stille coupling. The polymer shows lyotropic liquid crystallinity in toluene. Molecular weights of the polymer serve formation of polymer film with LC order. Smectic domain emission was observed in the form of the film. The CD spectrum demonstrates main chain helical structure derived from chiral mesogenic side chain. In other words, distance chirality of terminal optically active group in the mesogen induces main chain chirality. In the previous studies, main chain chirality of polymers was induced by chiral side chain located near position to the main chain, showing molecular functionalities [17–23]. The polymer prepared in this study is first founding in researches of aromatic LC conjugated polymers that the optically active group in the terminal induces main chain chirality from distance in molecular level.

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Instruments

Molecular weights of the polymers were determined by GPC against polystyrene standards using THF as an eluent with a 5 μm -MIXED-D column (Polymer Laboratories, Church Stretton), a PU-980 HPLC pump (JASCO, Tokyo), and an MD-915 multiwavelength detector (JASCO, Tokyo). ^1H NMR spectrum was recorded on JNM-ECS-400 NMR Spectrometer (JEOL, Tokyo). All signals were reported in ppm with the internal TMS (tetramethylsilane) at 0.00 ppm. FT-IR absorption spectrum was obtained with an FT/IR-4600 (JASCO) using the KBr method. All spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} . POM observation was conducted with an Eclipse LV100 high resolution polarizing microscope (Nikon, Tokyo). UV-Vis absorption spectra were recorded on a V-630 UV-Vis spectrophotometer (JASCO, Tokyo). CD spectroscopy measurement was conducted with a J-720 spectropolarimeter (JASCO, Tokyo).

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