

Morphology-Retaining Carbonization of Helical Aromatic Conjugated Polymers and Their Characteristic Properties

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Preface

This thesis presented the studies that the author carried out at Kyoto University, Department of Polymer Chemistry, Functional Polymer Synthesis Laboratory under the supervision of Professor Kazuo Akagi from August 2010 to March 2016.

The author would like to express her sincerest gratitude to her supervisor, Prof. Kazuo Akagi, for his kind guidance, valuable suggestions and encouragement throughout the present study. The author is also grateful to Professor Tsuyoshi Koga (Kyoto University) and Professor Yoshinobu Tsujii (Kyoto University) for their constructive and helpful suggestions and advice.

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March, 2017

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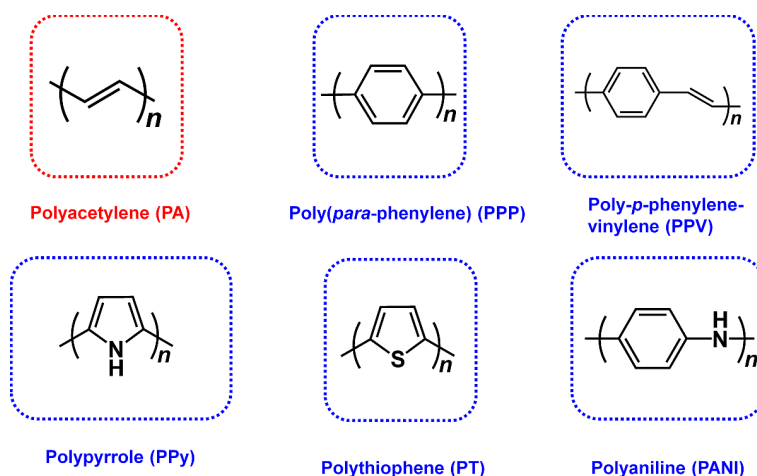
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General Introduction

1. Conjugated Polymers

Conjugated polymers have attracted much interest because of the flexibility of their unique structure of covalently bonded atoms with alternating single and multiple bonds and applications in the fields of electronics, physics, energy, biochemistry, and materials science. Various aliphatic and aromatic π -conjugated polymers have been explored because of their practical applications, all of which are based on their electrical conductivity and fluorescent property. Since vapor-phase iodine doping of a polyacetylene (PA) film resulted in a remarkable increase in electrical conductivity,¹ a huge number of conjugated polymers such as poly(*para*-phenylene) (PPP), poly(*para*-phenylenevinylene) (PPV), polythiophene (PT), polypyrrole (PPy), and polyaniline (PANI)²⁻⁴ have been investigated (Scheme 1). Following the discovery of polymer light-emitting diodes (LEDs), a variety of aromatic conjugated polymers have been designed and evaluated based on their light-emitting functions.⁵



Scheme 1. Representative conjugated polymers.

2. Whiskers

Whiskers are filamentous materials with defect-free structures and high length-to-diameter ratios. According to the theories of general filamentous composites, materials strengthened with stronger and thinner fibers are expected to achieve much higher mechanical properties. Mainly whiskers own high stiffness and strength due to their almost perfect crystal structure.⁶ It was found that whisker materials also have high thermal and chemical stabilities.^{7–10} Therefore, whiskers are considered more progressive than traditional fibers such as glass fiber and carbon fiber. Recently, diverse inorganic whiskers represented by aluminium oxide (Al_2O_3), calcium carbonate (CaCO_3), silicon carbide (SiC), and potassium titanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) were prepared and applied in the manufacturing of composites (Figure 1).

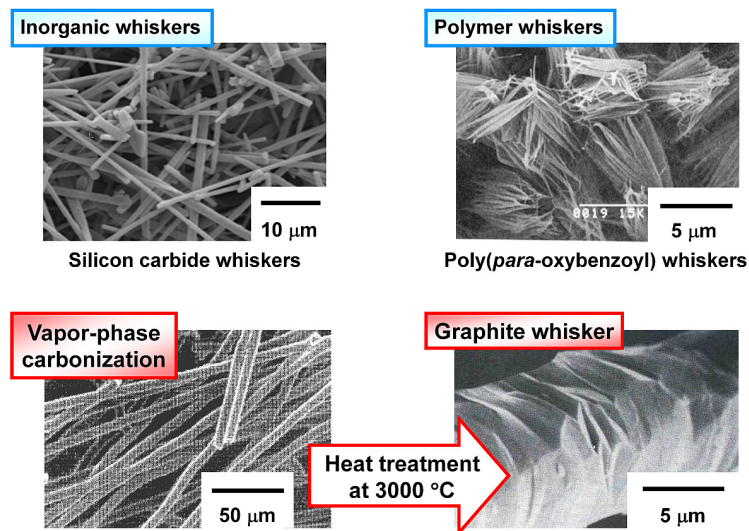


Figure 1. SEM images of various whiskers.

The use of metallic or inorganic whiskers as a reinforcement material for high performance composites and nano-composites has attracted wide interest.¹¹ Because of this interest, the development of polymer whiskers is a feasible means for fabrication of lightweight composites that shows great potential.^{12–16} Such as poly(*para*-oxybenzoyl) whiskers were synthesized via high-temperature solution polycondensation.¹⁷ On the other hand, filamentary growths of carbon or graphite have been observed to occur through a vapor-phase reaction in the presence of hydrocarbon or carbon monoxide.^{18,19}

3. N*-LC

Liquid crystals (LC) can be either thermotropic LC, where the LC phase is dependent on temperature; or lyotropic LC, where the LC phase is dependent on concentration. In the nematic LC (N-LC) phase, the individual LC molecules, which can be envisioned as inflexible rod-like structures, all align in the same direction with their positions being random. The molecules can flow freely in the direction of alignment, but not perpendicular to the direction of alignment. In the Smectic LC (Sm-LC) phase, the molecules align in the same direction are further arranged in layers, giving them an additional level of order over the N-LC phase. As molecules in a Sm-LC phase can move neither in the alignment direction nor the perpendicular direction, Sm-LCs are typically more viscous than N-LCs. The chiral nematic LC (N*-LC) phase consists of nematic layers arranged helically along an axis is prepared through adding a small amount of chiral dopant into an N-LC (Figure 2).²⁰

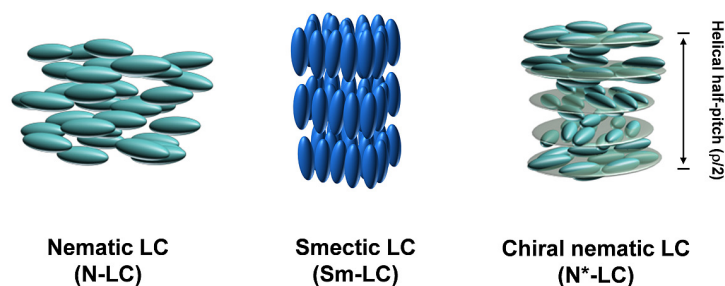


Figure 2. Schematic representation of N-LC phase, Sm-LC phase, and N*-LC phase.

The helical senses of the N*-LCs were determined through the miscibility test (contact method).^{21,22} The miscibility test is based on the observation of the mixing area between the N*-LC and the standard LC in POM. Cholesteryl oleyl carbonate is known to be a left-handed N*-LC, and therefore it is useful for the standard LC for the miscibility test. If the helical sense of the N*-LC is the same as that of the standard LC, the mixing area will be continuous. Otherwise, it will be discontinuous (shown as a Schlieren texture of the N-LC).

The helical pitches of N*-LCs were precisely evaluated by measuring the distance between Cano lines appearing on the surface of a wedge-type cell under the POM.^{23–27} This method is based on the observation of the distance between the discontinuity lines that appear when the N*-LC is inserted into a cell with a thickness gradient.

4. PEDOT

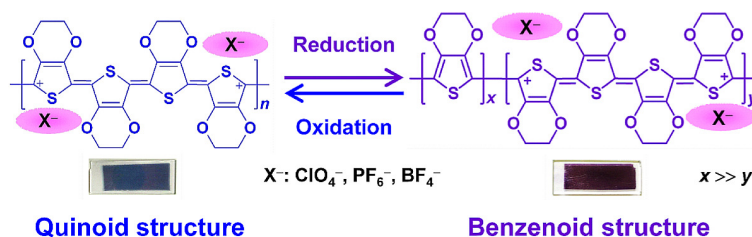
Poly(3,4-ethylenedioxythiophene) [PEDOT] was developed by Bayer company as a novel conducting polymer at the beginning of the 1990s. Owing to several distinct advantages, PEDOT rapidly acquired a prominent position among conducting polymers.

A unique combination of moderate band gap and low oxidation potential confers an exceptional stability to the oxidized charged state of PEDOT which furthermore exhibits high conductivity and good optical transparency in the visible spectral region.²⁸ EDOT easily polymerizes by way of electrochemical procedure but is relatively stable as a monomer. The corresponding polymer, PEDOT is remarkable stable and structurally homogenous due to the blocked 3 and 4 positions which preclude beta couplings. Based on promising properties many applications of PEDOT have been rapidly developed including anti-static coating, electrode material in supercapacitors or hole injection layer in OLEDs and solar cells.²⁹

5. Electrochemical Polymerization

Heterocyclic ring-based monomers such as pyrrole, furan, thiophene, and EDOT derivatives are easily polymerized through electrochemical oxidative polymerization due to their low oxidation potentials. The electrochemical polymerization is performed on an indium-tin oxide (ITO) electrode in water or in polar organic solvent with a supporting electrolyte.³⁰ The polymer product is a thin film that is formed on the electrode surface. The electrochemically produced aromatic π -conjugated polymers are usually obtained in a doped (oxidized) state (Scheme 2). Recent advances in the synthesis of H-PEDOT films through electrochemical polymerization in N*-LCs demonstrated that the use of EDOT oligomers as monomers produces H-PEDOT films with spiral morphology consisting of distinct fibril structures. This is because the use of EDOT oligomer with a rigid, rod-like molecular shape and a lower oxidation potential causes the formation of a fibril structure and the production of polymers with a high

conversion rate. In fact, the oxidation potential (E_{pa}) of EDOT dimer (0.9 V) is much lower than that of EDOT monomer (1.5 V).³¹ It is considered that the high planarity of EDOT itself also facilitates positive effects for the formation of the PEDOT fibrils.



Scheme 2. Electrochemical polymerization of PEDOT.

6. Solid-State Polymerization

Solid-state polymerization, as a polymerization method without initiators, catalysts, and solvents, was developed in the 1960s for preparing polydiacetylene single crystals.^{32,33} Late years, Wudl and co-workers reported that the highly ordered poly(3,4-ethylenedioxythiophene) [PEDOT] can be prepared from 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) crystals by only heating for several hours.^{34,35} This simple reaction interested researchers in synthesizing various highly conducting polymers such as polythiophene^{36–38} and polyselenophene^{39,40} derivatives. The close intermolecular halogen...halogen contacts in the structurally pre-organized monomer were considered to play a pivotal role in the solid-state polymerization which was investigated via the X-ray diffraction (XRD) analysis. Furthermore, PEDOT counter electrodes for dye-sensitized solar cells, which usually synthesized via chemical or

electrochemical polymerization, were also prepared using solid-state reactions.^{41,42} The merit of solid-state polymerization is not only the convenience of synthesis, but also a method for producing a highly crystalline and ordered polymer.

7. Solid-State Carbonization

There are two major types of carbonization methods: vapor-phase carbonization and solid-state carbonization. One of the advantages of the solid-state carbonization of polymeric materials is its possibility of mass production on an industrial scale. This possibility has already been demonstrated by industrially produced polyacrylonitrile (PAN)-based and pitch-based carbon fibers.⁴³ The processability of polymeric materials, such as spinnability and stretchability, plays a crucial role in the production process. In contrast, although the vapor-phase growth process can produce the previously described newly developed carbon materials, there are manufactural limitations for large-scale production because gaseous precursor molecules are currently employed for the carbonization method. Another advantage of the solid-state carbonization of polymeric materials is the potential of morphological controllability of the final carbon materials. In contrast to common polymeric materials, carbon materials are generally difficult to be precisely fabricated because they have less processability. In addition, the carbon materials prepared through vapor-phase carbonization are difficult to control morphologically.

8. Morphology-Retaining Carbonization

If the morphology of polymeric precursor materials is retained even after solid-state carbonization at a high temperature, then morphology-controlled carbon materials can be produced. These morphology-controlled carbon materials at the meso-, micro-, and nanoscales are anticipated to possess unique functional properties derived from their morphology and might introduce a pathway for next-generation carbon-based electronics. The ability to perform organic-polymeric-precursor-controlled carbonization is important to achieve unique carbon materials.⁴⁴ The key challenges for the preparation of these advanced carbon materials is the precise control of the precursor morphology, as well as the prevention of thermal decomposition and gasification of the precursor during the heat treatment, because carbonization at high temperatures causes the decomposition reaction and volatilization of hydrocarbon gases, even under an inert atmosphere, destroying the morphology of the precursor polymer. Conjugated polymers have higher thermal stability than common vinyl polymers due to their rigid conjugated molecular chain structure; thus their use as starting materials for the preparation of advanced carbon materials should be a promising approach. In addition, conjugated polymers tend to form various polymer assemblies, including those with a higher-order morphology due to their strong intra- and interchain π - π interactions during polymerization or annealing processes, as well as in a solution state.

Outline of This Thesis

In this research, various helical aromatic conjugated polymers were synthesized and used as carbonization precursors to prepare carbon films.

In *chapter 1*, carbon whiskers were prepared through hydrolysis process of PMP film and heat treatment at 800 °C. Graphite whiskers were prepared with a further heat treatment at 2600 °C. PMP films and fibers with macroscopically aligned whisker morphology were prepared by annealing the polymers on aligned substrates or drawing the polymers in fluid state. Aligned carbon and graphite whiskers were also prepared with heat treatment. The aligned carbon whiskers showed anisotropic electrical conductivity (Figure 3).

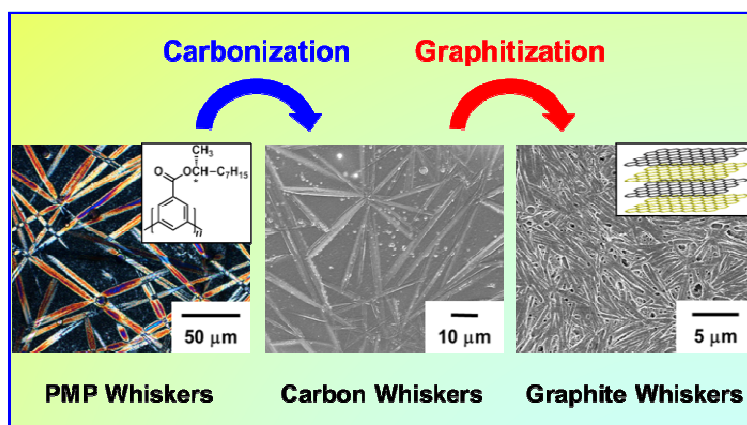


Figure 3. *chapter 1.*

In *chapter 2*, helical carbon and graphite films are prepared from helical PEDOT films with a tunable helical sense as precursors. We found that the oxidized PEDOT films consisting of closely packed polymer chains leading to the highly crystalline graphite films and the carbonization of helical aromatic π -conjugated polymer film is a

promising approach for the preparation of well-controlled helical carbon and graphite films. (Figure 4).

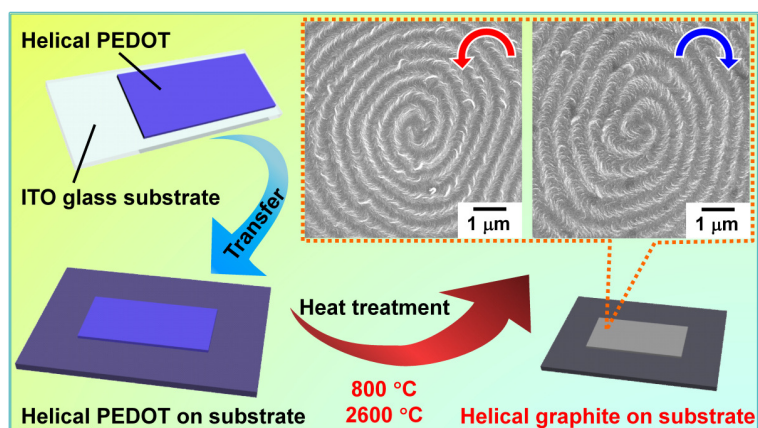


Figure 4. *chapter 2.*

In *chapter 3*, the author briefly reviews recent advances in the preparation of carbonaceous and graphitic materials through carbonization and graphitization of conjugated polymeric materials by focusing on several aliphatic and aromatic conjugated polymers, such as polyacetylenes (PAs), polythiophene derivatives, and polyphenylene derivatives, as precursors in terms of morphologically controlling the carbon materials (Figure 5).

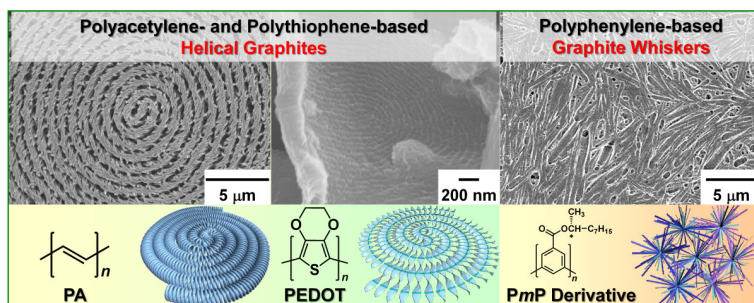


Figure 5. *chapter 3.*

In *chapter 4*, the author prepares aligned carbon and graphite fibers with high crystallinity from doped and dedoped PEDOT fibers synthesized through solid-state polymerization without any time-consuming pretreatment. X-ray diffraction and Raman scattering analysis show graphite fibers produced from the doped solid-state polymerized PEDOT (SSP-PEDOT) provide higher crystallinity than the dedoped one. The scanning electron microscope observation indicates that graphite fiber has plate and layer morphologies in the through and edge directions, respectively. Graphene layers tend to align parallel to the graphite fiber along the long axis and the surface of the aggregate of fine acicular graphite crystals with a remarkable orientation factor of 0.85. The electrical conductivity of the graphite fiber is on the order of 10^2 S/cm along the fiber axis. Furthermore, capacitance performances of carbon films prepared from SSP-PEDOTs at heat treatment at 800 °C are investigated using cyclic voltammetry and galvanostatic charge/discharge in base electrolytes (Figure 6).

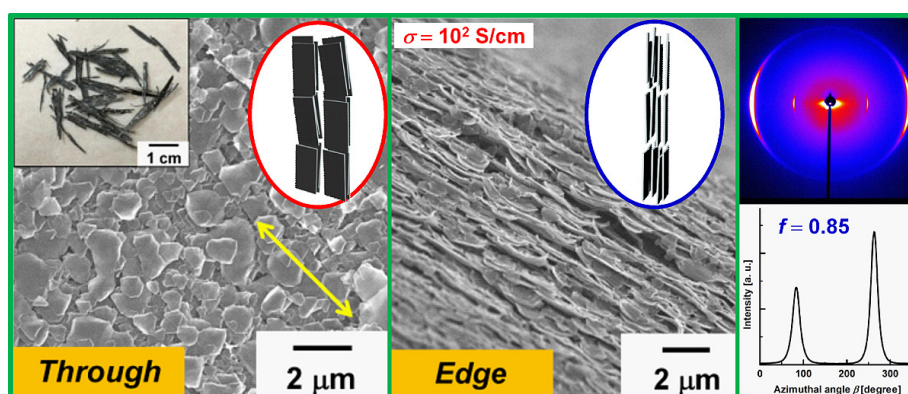


Figure 6. *chapter 4.*

In *chapter 5*, the author prepares carbon and graphite films from iodine doped amylose (ESA) with strictly controlled molecular weight as carbonization precursors. X-ray diffraction analysis shows graphite films produced from the ESA films provide high crystallinity. The scanning electron microscope observation indicates that carbon and graphite films have smooth morphologies after heat treatment at 800 and 2600°C. The carbonization yield of the ESA films can be controlled by changing the condition of iodine doping process. Furthermore, capacitance performances of graphite films prepared from ESAs at heat treatment at 2600 °C are investigated using cyclic voltammetry and galvanostatic charge/discharge in base electrolytes (Figure 7).

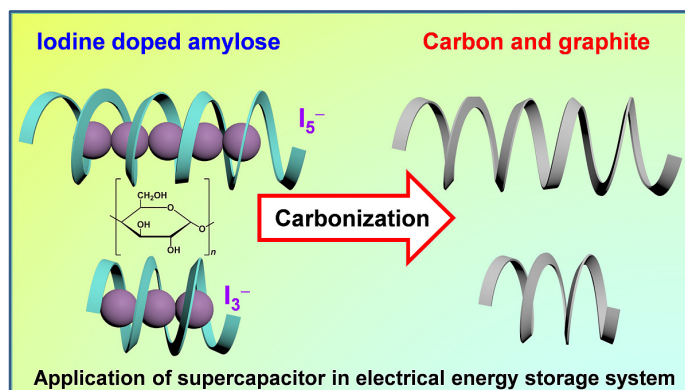


Figure 7. *chapter 5.*

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Chapter 1

Macroscopically Aligned Carbon and Graphite Whiskers Prepared from Poly(*meta*-phenylene) Derivatives with Helicene-like Helical Structures

1. Introduction

Whiskers are filamentous materials with defect-free structures and high length-to-diameter ratios. According to the theories of general filamentous composites, materials strengthened with stronger and thinner fibers are expected to achieve much higher mechanical properties. Mainly whiskers own high stiffness and strength due to their almost perfect crystal structure.¹ It was found that whisker materials also have high thermal and chemical stabilities.^{2–5} Therefore, whiskers are considered more progressive than traditional fibers such as glass fiber and carbon fiber. Recently, diverse inorganic whiskers represented by aluminium oxide (Al_2O_3), calcium carbonate (CaCO_3), silicon carbide (SiC), and potassium titanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) were prepared and applied in the manufacturing of composites.

The use of metallic or inorganic whiskers as a reinforcement material for high performance composites and nano-composites has attracted wide interest.⁶ Because of this interest, the development of polymer whiskers is a feasible means for fabrication of lightweight composites that shows great potential.^{7–11} Such as poly(*para*-oxybenzoyl) whiskers were synthesized via high-temperature solution polycondensation.¹² However, the preparation of polymer whiskers has proven rather difficult because their

production requires a delicate combination of concomitant polymerization and crystallization, and these conditions have been successfully met in few cases. In addition, polymer whiskers have displayed limited thermal stability because they thermally decompose at elevating temperatures that are usually encountered in organic materials.

Graphite is an interesting material with high thermal and electrical conductivities as well as stability in atmospheric conditions. Carbon films and membranes have attracted considerable attention because of their versatile applicability in diverse fields, such as electrochemical energy storage¹³, fuel- and photovoltaic-cell electrodes,^{14–18} field-effect transistors,^{14–17,19,20} catalyst supports,²¹ and wear-resistant coatings.^{22,23} A great many of chemical approaches have been reported for preparing carbon films that were composed of evaporated amorphous carbons,¹³ graphene-based materials,^{14–17,24–26} randomly networked or macroscopically oriented carbon nanotubes,^{27–32} and heat treatment of polymer films.³³ On the other hand, filamentary growths of carbon or graphite have been observed to occur through a vapor-phase reaction in the presence of hydrocarbon or carbon monoxide.^{34,35} The graphite fibers prepared via heat treatment had high tensile strength, thermal stability, and low electrical resistivity. The graphite fibers prepared through vapor-phase carbonization were difficult to align macroscopically and control morphologically.

Helical conjugated polymers have attracted much interest not only because of their distinctive optical properties such as circularly polarized luminescence^{36,37} and nonlinear second harmonic generation,^{38,39} but also their unprecedented physico-chemical properties.⁴⁰ Multiple kinds of helical conjugated polymers such as helical polyacetylenes (H-PA),^{41,42} amino acid-containing monosubstituted

polyacetylene derivatives,⁴³ poly(phenylacetylene) derivatives,^{44,45} and polythiophene derivatives⁴⁶ have been reported. These helical conjugated polymers are composed by intrachain-spiral, intrachain-twisted ribbon, or interchain-helically π -stacked structures.^{47,48} However, there are a few reports^{49–55} of the conjugated polymers having a helicene-like helical structure, which is favorable for maintaining π -conjugation on the main chain despite of the intrachain helical structure. Self-assembly is one of the most auspicious ways to prepare a higher-order and even super-hierarchical structure of π -conjugated polymers. The driving forces of self-assembly are classified into π -electron overlap interactions and van der Waals interactions in the closest packing. It is well known that π -conjugated polymers with planar main chains tend to form π -stacked structures due to interchain π -electron overlap interactions. Recently, we have synthesized a series of aromatic π -conjugated polymers: poly(*meta*-phenylene) [PMP] derivatives with racemic or chiral alkyl groups in the side chains.⁵⁶ The PMP derivatives self-assembled to form polymer whiskers in which the columns consisting of hexagonal columnar packed structure were uniaxially aligned parallel to the long axis of the whisker. Particularly, the polymer whiskers from the PMP derivatives bearing a 2-nonyl group in the side chain had high aspect ratios. The formation of PMP whiskers occurred during the post-polymerization annealing process, which is in stark contrast to the before-mentioned polymer whiskers. Furthermore, macroscopic alignment of the polymer whiskers was also preliminary carried out using an oriented substrate. Macroscopically aligned materials are useful for evaluating physical, chiroptical, electrical, and electromagnetic properties.

Currently, the development of the “morphology-retaining carbonization method” has demonstrated that iodine-doped H-PA films^{57,58} and helical

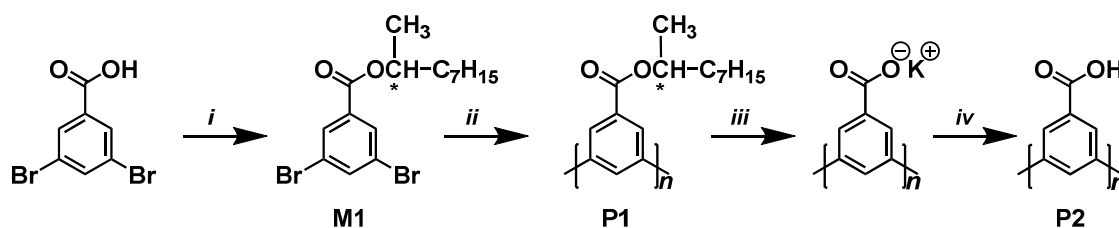
poly(3,4-ethylenedioxythiophene) films⁵⁹ synthesized through asymmetric electrochemical polymerization are promising precursors to produce helical graphite films with unique spiral morphologies. However, it is difficult to prepare carbon and graphite whiskers via carbonization of the PMP whiskers because the self-assembled hexagonal columnar packed structure will fall apart during the heat treatment due to its long aliphatic solubilizing side chains. If the whisker morphologies of the PMP derivatives are preserved even at high temperature, carbon and graphite whisker structures can be produced.

In this chapter, first the author shows (i) carbon and graphite whiskers prepared through esterolysis process of the annealed PMP film to improve its thermal stability and subsequent heat treatment at high temperature. The PMP derivatives with a 2-nonyl group in the side chain were synthesized via dehalogenation polycondensation using a nickel catalyst [Ni(cod)₂]. Next, the author shows (ii) PMP films with aligned whisker morphologies prepared using two types of oriented substrates. Finally, the author shows (iii) macroscopically aligned graphite whiskers. Here, the author presents a new aspect of aromatic π -conjugated polymers by focusing on their availability as precursors in preparing carbon and graphite whiskers.

2. Results and Discussion

2.1. Synthesis of Polymers. PMP derivatives, with side chains composed of racemic and chiral alkyl groups, were synthesized using the following steps. The esterifications of 3,5-dibromobenzoic acid with racemic or chiral (*R*)-(-)- and (*S*)-(+)-2-nonanol were carried out using dicyclohexylcarbodiimide (DCC) and *N,N*-dimethylaminopyridine (DMAP) to give the corresponding dibrominated

precursors (**M1**) as colorless oils in quantitative yields (82–84%). Polymerization of the precursors was carried out at 100 °C in *N,N*-dimethylformamide (DMF) using a nickel catalyst [Ni(cod)₂] for 24–72 h. After polymerization, the polymer was first washed in hydrochloric acid (HCl)/methanol (MeOH) (v : v = 1 : 10) for 1 h, and then washed in MeOH under constant stirring for another 24 h. Further purification of the precipitated polymer was carried out via Soxhlet extraction with THF for 24 h. The product was dried under vacuum to give the corresponding PMP derivatives, poly{5-[1-methyloctyl]-*meta*-phenylbenzoate} [**P1**], as colorless powders with yields of 60–66% (Scheme 1).^{60,61}



Scheme 1. Synthetic routes of PMP derivatives. Conditions: *i.* 2-nonanol, DCC, DMAP, CH₂Cl₂, r.t., 24 h, 82–84% *ii.* Ni(cod)₂, BPY, COD, DMF, 100 °C, 24–72 h, 60–66% *iii.* KOH, MeOH, 70 °C, 20 h *iv.* *p*-TSA, MeOH, r.t., a few minutes. Ni(cod)₂ = *bis*(1,5-cyclooctadiene)nickel(0), BPY = 2,2'-bipyridine, COD = 1,5-cyclooctadiene, DMF = *N,N*-dimethylformamide, *p*-TSA = *p*-toluenesulfonic acid.

2.2. Molecular Weights and Properties of Polymers. The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were measured using gel permeation chromatography (GPC) calibrated with polystyrene (PS) standards and using THF as an eluent. The GPC resulted in a bimodal molecular weight distribution (Figure S1 in Supporting Information). The higher molar mass part had an

M_n of 17,400–43,800 and an M_w/M_n of 1.2–1.4. The lower molar mass part was mainly composed of cyclic oligomers (Table 1).⁶²

Table 1. Results of polymerization of **P1**.

	Time (min)	M_n	M_w	M_w/M_n	D.P. ^a
(R)-P1	5.5–7.5	43,800	57,700	1.3	177
	5.5–9.1	2,600	17,300	4.7	10
(S)-P1	5.6–7.3	41,400	47,800	1.2	168
	5.6–9.1	2,900	13,900	4.7	11
(rac)-P1	5.7–7.9	17,400	24,400	1.4	70
	5.7–9.1	3,400	13,700	4.0	13

^aDegree of polymerization

All of the polymers allowed the preparation of cast films by casting the polymer solutions (dichloromethane) onto substrates. The introduction of a long aliphatic chain into the side chains led to decreased melting and clearing points of the polymers. The PMPs with chiral or racemic groups in the side chains formed whiskers when cooled from the isotropic phase (Figure 1a and b). The hexagonal columnar–isotropic phase transition temperatures of **P1** were 233 °C and 213 °C in the heating and cooling processes, respectively. From the polarizing optical microscopy (POM) and scanning electron microscopy (SEM) observations, as well as measurements of ultraviolet–visible

(UV–vis) spectra, photoluminescence (PL) spectra, circular dichroism (CD) spectra, and X-ray diffraction (XRD), the whiskers were confirmed to have a hexagonal columnar structure consisting of discotically packed helical π -conjugated polymers (Figure S2–5 in Supporting Information).⁶³

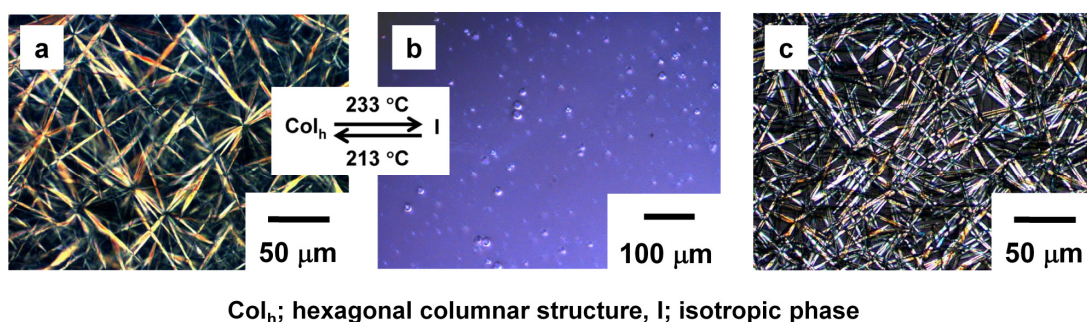


Figure 1. POM images of the **(R)-P1** film at (a) 200 °C in the cooling process and (b) 250 °C in the heating process. (c) POM image of the **P2** film with whisker morphology at 250 °C in the heating process.

Here, it is of interest to discuss differences in properties of **(R)-**, **(S)-**, and **(rac)-P1** in more detail. We examined optical properties of **P1s** in chloroform, cast film, and annealed film (Table S1 in Supporting Information). **(R)-** and **(S)-P1** showed monosignate CD bands in both chloroform and film state (Figure S3 in Supporting Information). It is worthwhile to emphasize that the positive Cotton effect of **(R)-P1** supports that **(R)-P1** is stacked within the whisker and is screwed with respect to the column axis, forming a right-handed helical structure. Similarly, **(S)-P1** with a negative Cotton effect should have a left-handed helical structure.

In addition, in the cast film of **(rac)-P1**, the fluorescence band was observed at 367

nm, which was ascribed to fluorescence of the randomly arranged zigzag main chain. However, two fluorescence bands were observed at 368–369 and 410–420 nm in the cast film of (*R*)- and (*S*)-**P1** (Figure S5 and Table S1 in Supporting Information). The band at 410–420 nm is ascribed to fluorescence of the helical main chain. These results suggest that (*rac*)-**P1** forms a randomly arranged zigzag structure but (*R*)- and (*S*)-**P1** form a partly intrachain helical π -stacked structure in cast film. The helical structure may be due to the π -stacking between spatially adjacent phenylene moieties in the folded main chain.^{64,65} It is expected that usage of (*R*)- or (*S*)-**P1** as a starting material will produce more closely packed polymer main chain in the whisker formation. Here, (*R*)-**P1** has been selected and used for all of the following measurements with an aim to develop a new approach for preparing chirality-controlled carbon materials.

2.3. Esterolysis Processes. However, the PMP whiskers were not useful for carbonization because they were easily fused at approximately 250 °C due to their long aliphatic solubilizing side chains. For this reason, a PMP derivative with carboxylic acid in the side chain (**P2**) was prepared through esterolysis of **P1**. The **P1** film with whisker morphology was prepared by annealing **P1** on a quartz plate. The **P1** film was immersed in a MeOH solution (10 mL) of potassium hydroxide (KOH) (0.60 g), and the solution was heated at 70 °C for 5 h to yield a PMP salt film. The PMP salt film was neutralized via immersion for a few minutes in a solution of MeOH (10 mL) and *p*-toluenesulfonic acid (*p*-TSA) (0.30 g) at room temperature to yield a poly{5-[(1-methyloctyl)-*meta*-phenylbenzoic acid} [**P2**] film (Scheme 1).^{66,67}

The esterolysis process was monitored by attenuated total reflectance infrared (ATR-IR) spectroscopy. The conversion from the ester-derivatized polymer **P1** to its

polycarboxylate salt was evidenced by a distinct shift of the C=O stretching band to a lower frequency (from 1714 to 1551 cm^{-1}) and broadening of the same band. In addition, the decrease in C–H stretching band intensity in the 2800–3100 cm^{-1} region upon the transition from **P1** to PMP salt indicates loss of the aliphatic solubilizing side chains. Upon protonation of the carboxylates, i.e., upon transiting from PMP salt to **P2**, the C=O stretching band shifted back to higher frequencies (1551 to 1713 cm^{-1}) (Figure S6 in Supporting Information). The POM measurements showed that the **P2** films also had whisker morphologies and were infusible at 250 °C (Figure 1c). The UV–vis and PL spectra of **P2** were examined in DMF solutions. Absorption and fluorescence bands were observed at 265 and 351 nm, respectively (Figure S7 in Supporting Information).

To examine the effect of the esterolysis processes on the thermal stability, the thermal behavior of **P1** in a heating run was compared with that of **P2** using thermogravimetry and differential thermal analysis (TG-DTA). The **P1** powder (0.10 g) was immersed in a MeOH/THF (v : v = 1 : 1) solution (50 mL) containing potassium hydroxide (KOH) (1.50 g), and the solution was heated at 70 °C for 4 days to yield a PMP salt powder. The PMP salt powder was neutralized via immersion for a few minutes in a MeOH solution (50 mL) of HCl at room temperature to yield a **P2** powder. The DTA curve showed that when the **P1** powder was heated in flowing nitrogen gas, the ester functional group in **P1** side chain thermally decomposed at approximately 316 °C (Figure 2a). The thermal decomposition accompanied a large weight loss of the **P1** powder due to volatilization of hydrocarbon gases, as shown in the TG curve of Figure 2a. In the case of **P2**, the DTA curve showed no thermal decomposition at approximately 316 °C (Figure 2b). Furthermore, the DTA curves of both **P1** and **P2**

showed thermal decomposition of the polymer main chain in the temperature range of 500 °C to 600 °C.

The infusibility of **P2** was attributed to intermolecular hydrogen bonds between side chains, by which the hexagonal columnar stacking structure of the whisker was stabilized enough to be substantially retained during the carbonization.

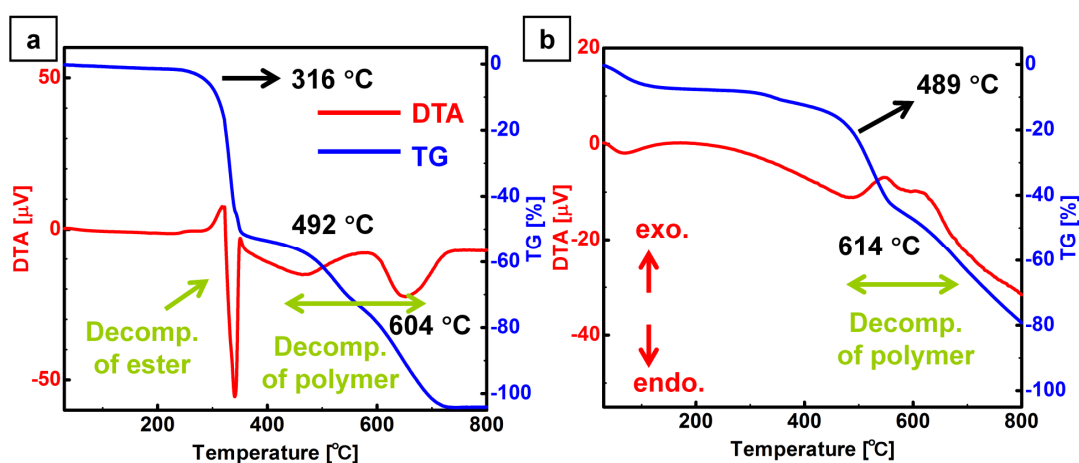


Figure 2. DTA and TG curves of (a) **P1** and (b) **P2** powders in the heating process up to 800 °C.

2.4. Carbonization of PMP Whisker Films. The **P2** film with whisker morphology was placed between carbon plates (80 × 80 × 2 mm) and was inserted into an electric furnace (KDF75, Denken). The **P2** film was then carbonized at 800 °C using the electric furnace for 1 h under flowing argon gas. The heating rate was 10 °C/min. Interestingly, the randomly aligned whisker morphology of the **P2** film remained unchanged after carbonization at 800 °C. Figure 3 shows the optical microscopy and SEM images of the carbon film prepared from the **P2** film. The electrical conductivity

of the carbon film was measured using the four-point probe method at room temperature. Although the **P1** film had an electrical conductivity lower than 10^{-5} S/cm, the carbon film with randomly aligned whisker morphology had a conductivity on the order of 1 S/cm (film thickness: 4.9 μm).

It is worthwhile to note that the preparation of carbon whiskers was possible not only from (*R*)-**P1** but also from (*rac*)- and (*S*)-**P1** as starting polymers.

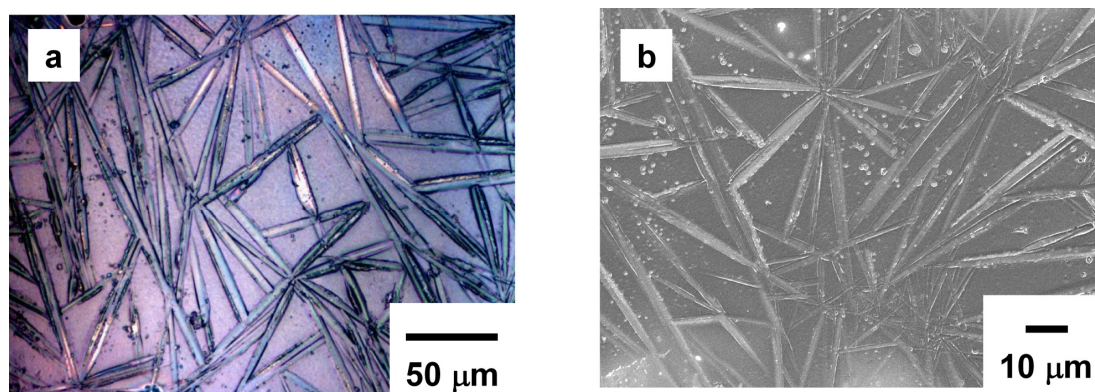


Figure 3. (a) Optical microscopy and (b) SEM images of the carbon film with whisker morphology prepared from the **P2** film through heat treatment at 800 °C.

2.5. Graphitization of PMP Whisker Films. To produce the carbon film with whisker morphology from the PMP film, a quartz plate was used because of its high heat-resistance (m.p. = ~ 1650 °C). However, the melting point of quartz is below the graphitization temperature of 2600 °C. For this reason, a freestanding PMP film with whisker morphology was prepared by annealing **P1** on a polytetrafluoroethylene (PTFE) sheet that had a smooth surface (Figure S8 in Supporting Information). A freestanding **P2** film with whisker morphology was prepared from the **P1** film through esterolysis

and subsequently heating at 800 °C. Figure 4a and b show SEM images of the freestanding **P2** and carbon films, respectively. The XRD results of the freestanding carbon film prepared from the **P2** film at 800 °C showed no crystalline reflection (Figure 5a).

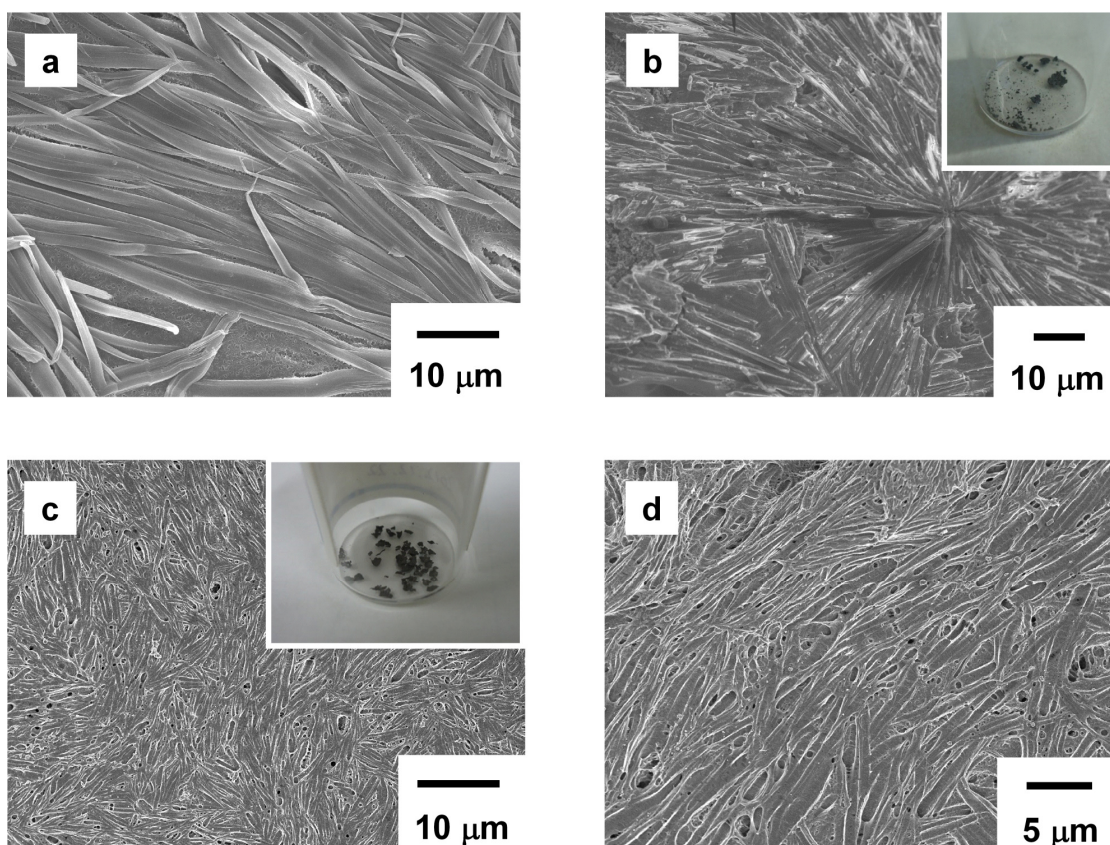


Figure 4. SEM images of the freestanding (a) **P2**, (b) carbon, and (c, d) graphite films with whisker morphologies. The insets show optical images of the (b) carbon and (c) graphite films in a sample bottle.

The carbonized film was further heated at 2600 °C for 30 min using a graphitizing apparatus (Sanriko denki) under flowing argon gas. The total yield of the graphite film

was approximately 10% of the weight of the **P1** film before the esterolysis process. The XRD peak corresponding to the (002) face of graphitic crystal at $3.6 \text{ \AA}$ indicated that the graphitic crystallization proceeded further in the carbon through the heat treatment at $2600 \text{ }^{\circ}\text{C}$ (Figure 5b). The hydrogen contents of the carbon films after carbonization and graphitization were 0.72% and 0.06% in weight, respectively. Figure 4c and d show SEM images of the graphite film prepared from the freestanding carbon film. The randomly aligned whisker morphology of the precursors remained unchanged even after the heat treatment at $2600 \text{ }^{\circ}\text{C}$.

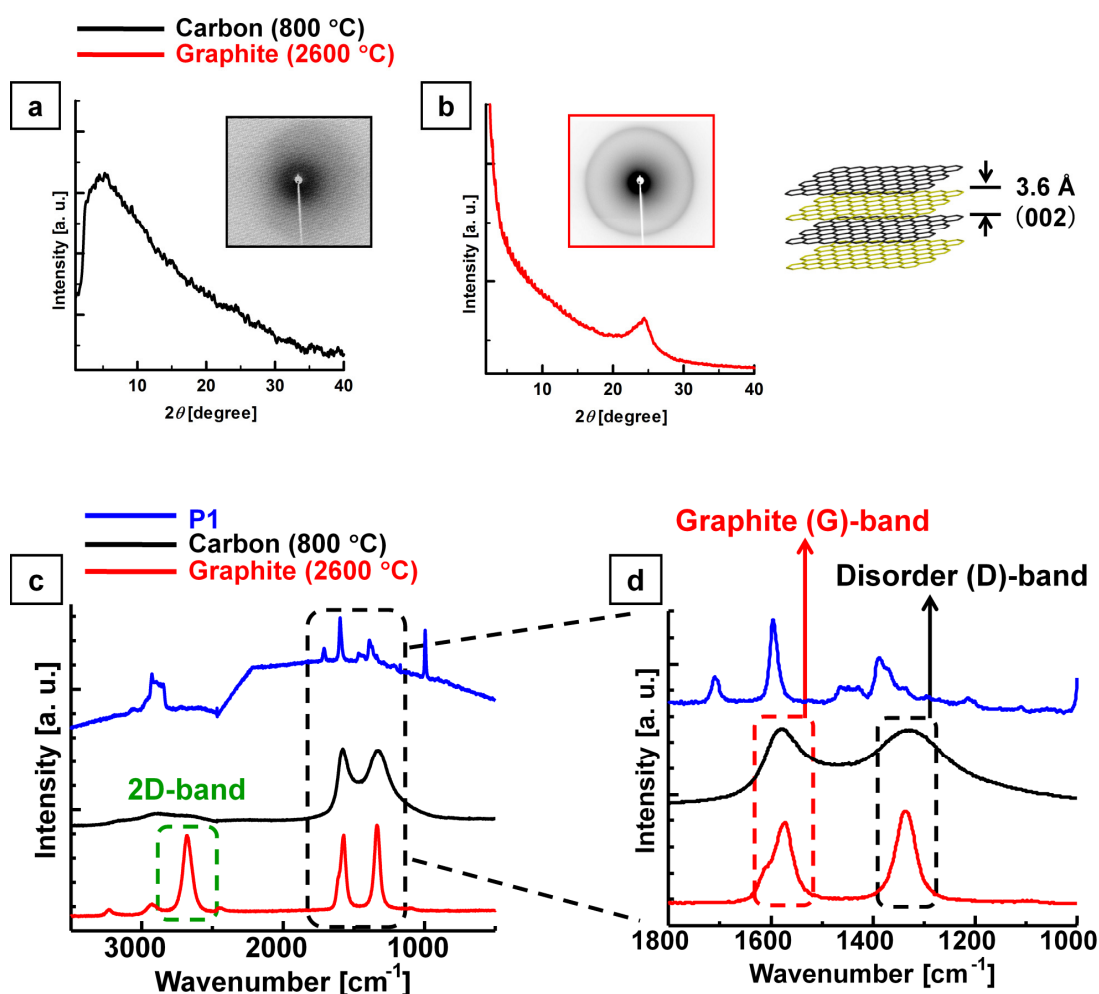


Figure 5. XRD patterns of the films (a) carbonized at 800 °C and (b) graphitized at 2600 °C. (c) Raman scattering spectra of the **P1** and carbon films heated at 800 °C and 2600 °C, respectively, and (d) their magnified spectra.

Raman scattering spectra of **P1**, carbon, and graphite films are shown in Figure 5c and d. The spectrum of the **P1** film exhibited strong bands at 996 and 1597 cm^{-1} due to aromatic ring vibrations and bands at 2848 and 2928 cm^{-1} corresponding to aliphatic groups (CH_2 and CH_3).⁶⁸ The bands at 1390, 1467, and 1711 cm^{-1} corresponded to C–O stretching vibrations, C–C stretching vibrations of the benzene ring, and C=O stretching vibrations, respectively.⁶⁹ The Raman spectrum of the carbon film showed a peak at 1329 cm^{-1} that was attributed to the disordered structure (D-band), and a peak at 1578 cm^{-1} corresponded to the structure of the sp^2 hexagonal carbon network (G-band). The resolution of the two peaks was enhanced with increased heating temperature from 800 °C to 2600 °C. This result relates to the development of crystallinity from an almost amorphous structure in the sample. The sharp Raman band observed at 2678 cm^{-1} in the graphite film was assigned to the 2D-band, which is often observed in graphite materials.⁷⁰

2.6. Macroscopic Alignment and Carbonization of PMP Whiskers. The PMP whiskers were aligned by slowly cooling (0.5 °C/min) the polymer on two types of oriented substrates from isotropic to a solid state so that the long axes of the whiskers were aligned parallel to the alignment direction of the substrate. The optical texture of the aligned polymer was well preserved even in the glassy state.

One of the oriented substrates was prepared by rubbing a PTFE rod on a glass substrate at room temperature.⁷¹ Figure S9a in the Supporting Information shows a schematic representation of the preparation of macroscopically aligned **P1** whiskers using the rubbing method. The macroscopically aligned whisker film was prepared by heating **P1** on the oriented substrate to 250 °C followed by slow cooling to room temperature. Subsequently, the aligned **P1** film (Figure 6a) was esterolyzed to obtain the aligned **P2** film (Figure S10a in Supporting Information). The aligned whisker morphology of the **P2** film was also retained after the carbonization at 800 °C (Figure 6b and Figure S10b in Supporting Information). It is worth noting that the carbon film with aligned whisker morphology showed anisotropy in electrical conductivity, where the conductivity parallel ($\sigma_{//}$) to the whisker alignment direction was higher than that perpendicular ($\sigma_{\perp}$) to it. The parallel and perpendicular conductivities were 4.0×10^{-1} and 1.4×10^{-1} S/cm, respectively, giving an anisotropic ratio (defined as $\sigma_{//}/\sigma_{\perp}$) of 2.9.

The other oriented substrate was prepared by stretching PTFE thread seal tape at room temperature. Figure S9b in the Supporting Information shows a schematic representation of the preparation of macroscopically aligned **P1** whiskers using the stretching method. Figure S11 in the Supporting Information shows an SEM image and XRD patterns of the oriented substrate. The sharp XRD reflection of 5.0 Å in the *d*-spacing was attributed to the PTFE interchain distance. The macroscopically aligned whisker film was also prepared by heating **P1** on the oriented substrate to 250 °C followed by slow cooling to room temperature (Figure 6c). Subsequently, the aligned **P1** film was esterolyzed to obtain an aligned **P2** film (Figure S10c in Supporting Information). The aligned whisker morphology of the **P2** film was also retained after the carbonization at 800 °C (Figure 6d and Figure S10d in Supporting

Information). However, the electrical conductivity of the aligned carbon whiskers prepared using the stretching method was difficult to measure due to the limited size of the sample.

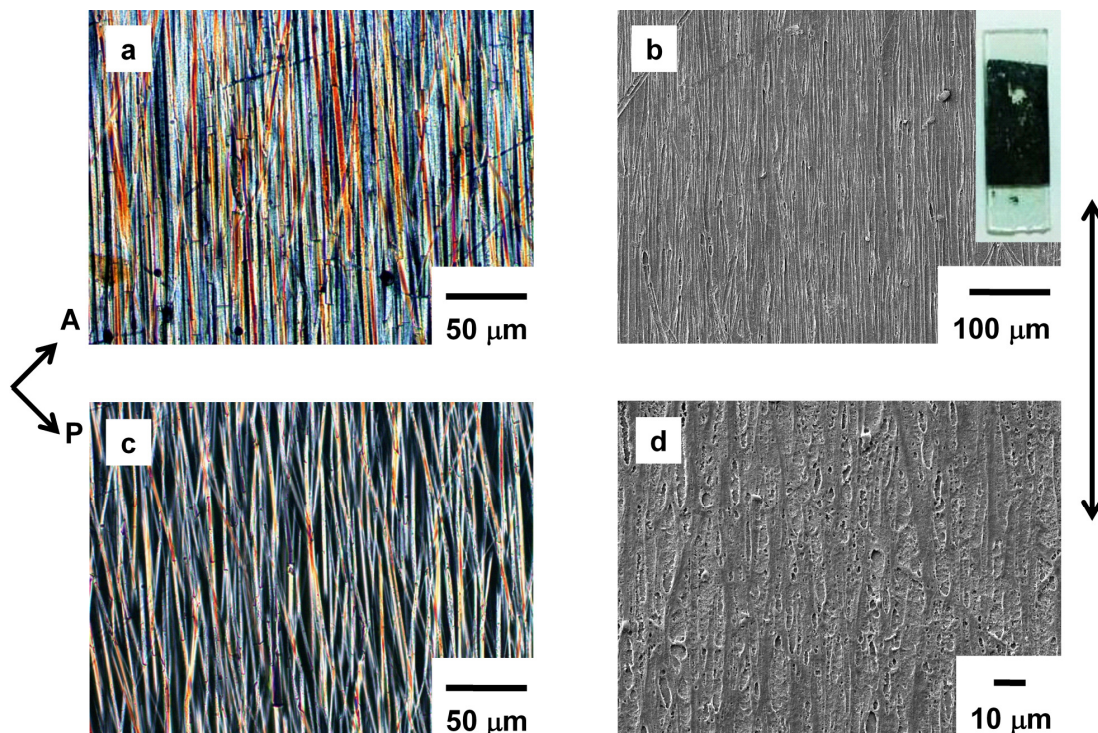


Figure 6. POM images of the **P1** films with aligned whisker morphologies prepared using the (a) rubbing method and (c) stretching method. SEM images of the carbon films with aligned whisker morphologies that were prepared from the **P1** films oriented using the (b) rubbing method and (d) stretching method through heat treatment at 800 °C. The inset shows a photograph of the carbon film (film thickness: 6.1 μm). The arrow indicates the aligned direction of the whiskers.

When the polarizer was set to an angle of 0° with respect to the long axis of the PMP whisker, the anisotropic region darkened because the optical axis of the whisker coincided with plane of polarization (Figure 7b and d). After the analyzer and

polarizer were rotated 45° from the dark position, a bright area was observed (Figure 7a and c). This result indicated that the columns of the PMP helices were uniaxially aligned parallel to the long axis of the whiskers. If the PMP whiskers are aligned macroscopically parallel to the alignment direction of the substrate, dark-field images can be produced, as shown in Figure 7b and d. However, some randomly aligned whiskers were observed as bright areas in Figure 7d. From microscopy investigations, the whiskers aligned using the rubbing method with a PTFE rod exhibited a higher degree of orientation than that of the whiskers aligned using the stretching method with a PTFE thread seal tape. Therefore, the rubbing method that produced a higher degree of orientation in PMP whiskers was hereafter used for the preparation of macroscopically aligned graphite whiskers.

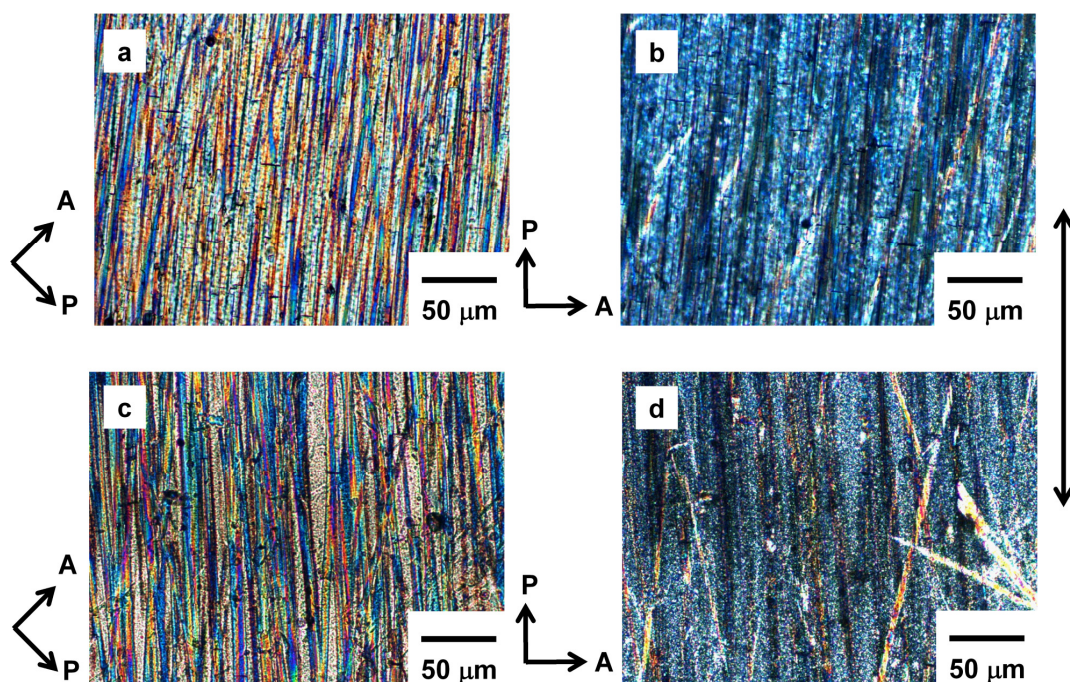


Figure 7. POM images of the **P1** films with aligned whisker morphology prepared using (a, b) the rubbing method and (c, d) the stretching method. The applied angles

between the directions of the polarizer and rubbing or stretching are (a, c) 45° and (b, d) 0° , respectively. The arrow indicates the aligned direction of the whiskers.

2.7. Graphitization of Whiskers with Macroscopically Aligned Morphology.

Macroscopically aligned graphite whiskers were prepared through esterolysis of an aligned **P1** film, heat treatment at 800°C , and further heat treatment at 2600°C (Figure 8). The whiskers were aligned by slowly cooling **P1** on the oriented substrate prepared through the rubbing method followed by covering with a carbon plate. The carbon plate was used because of its heat resistance at the graphitization temperature of 2600°C .

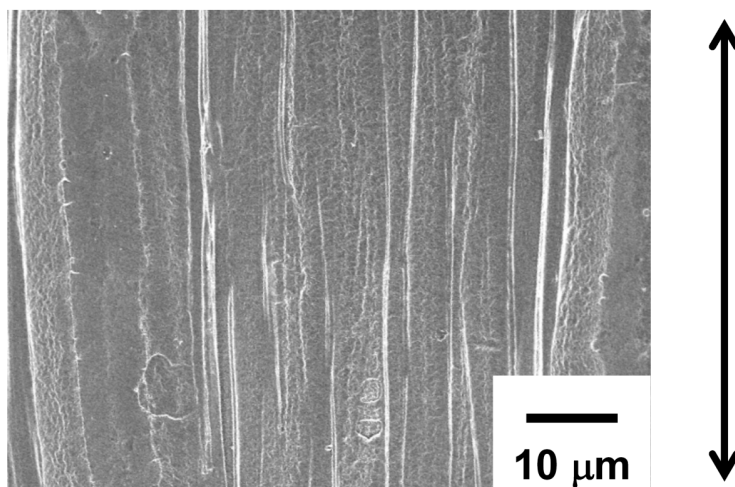


Figure 8. SEM image of the graphite film with aligned whisker morphology that was prepared from the **P1** film oriented using the rubbing method through heat treatment at 2600°C . The arrow indicates the aligned direction of the whiskers.

2.8. Structural Properties of Aligned P1, Carbon, and Graphite Fibers. It should be mentioned that because the aligned whisker films prepared using oriented substrates were too thin to measure XRD patterns, aligned whisker fibers were prepared to investigate the crystallinity and structural anisotropy. Aligned **P1** fibers were prepared by drawing **P1** in the fluid state at 210 °C in the cooling process (Figure S12 and S13 in Supporting Information). Figure 9 shows XRD patterns of the aligned **P1** fiber indicating whiskers aligned parallel to the fiber axis. Aligned carbon and graphite fibers were prepared through esterolysis followed by heat treatment (SCC-U-80/150 (2P), Kurata-giken) (Figure S14 in Supporting Information). The intensity of XRD reflection of parallel to the fiber axis was slightly higher than that of perpendicular to the fiber axis in the aligned graphite fiber (Figure 10), suggesting that the graphene layers tend to be parallel to the whisker axis. From these results, it could be mentioned that the aligned graphite fibers had a structural anisotropy, especially in the direction of graphene layers arrangement. The structural anisotropy observed in the aligned graphite fiber could be well rationalized with the POM observations that the aligned whisker films prepared using the oriented substrates have macroscopically aligned morphologies (Figure 6–8).

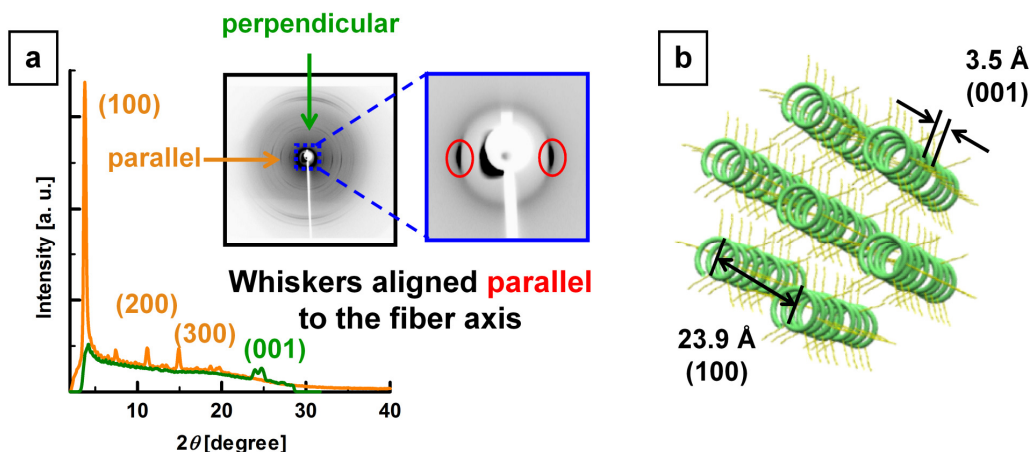


Figure 9. (a) XRD patterns of the aligned **P1** fiber. The arrows indicate the aligned directions parallel (orange) or perpendicular (green) to the **P1** fiber. (b) Schematic representation of stacking structures of the **P1**s with a hexagonal columnar structure.

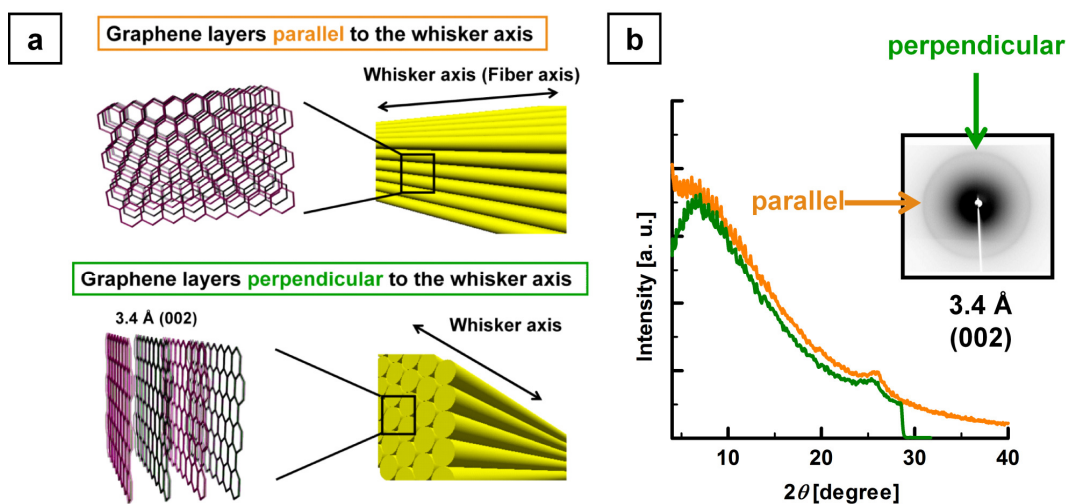


Figure 10. (a) Plausible models of arrangements of graphene layers in whiskers. The black arrows indicate the direction of whisker axis. (b) XRD patterns of the aligned graphite fiber. The arrows indicate the aligned directions parallel (orange) or perpendicular (green) to the graphite fiber.

3. Conclusions

We have prepared carbon and graphite whiskers with not only randomly but also macroscopically aligned morphologies from self-assembled PMP derivatives as carbonization precursors. The XRD profiles and Raman scattering spectra indicated that graphitic crystallization proceeded further in the carbon films though heat treatment at 2600 °C. The aligned carbon whiskers showed anisotropic electrical conductivity. It was also demonstrated that the esterolysis process is a new approach to retain the morphologies of precursors during heat treatment and could be used for other π -conjugated polymers as carbonization precursors. Thus, the prepared aligned whisker-type carbon and graphite films might be useful for anisotropic electrical materials with thermal stability and for engineering conducting wires based on microsize assemblies.

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Chapter 1 Appendix**1. Materials and Measurements****1.1. Materials****1.2. Measurements****2. Synthesis of Monomers****3. Synthesis of Polymers****4. X-ray Diffraction Analysis of P1****5. Optical Properties****6. Supporting Figures****1. Materials and Measurements**

1.1. Materials. The chemical reagents were purchased from commercially available sources and were used as received. 3,5-Dibromobenzoic acid, 2,2'-bipyridine (BPY), and *p*-toluenesulfonic acid (*p*-TSA) were purchased from Tokyo Chemical Industry Co., Ltd. *Bis*(1,5-cyclooctadiene)nickel(0) [Ni(cod)₂] was purchased from Kanto Chemical Co., Ltd. 1,5-Cyclooctadiene (COD), (*R*)-2-nonanol, (*S*)-2-nonanol, (*rac*)-2-nonanol, and calcium hydride (CaH₂) were purchased from Wako Pure Chemical Industries, Ltd. Dicyclohexylcarbodiimide (DCC), *N,N*-dimethylaminopyridine (DMAP), potassium hydroxide (KOH), hydrochloric acid (HCl), sodium (Na), sodium chloride (NaCl),

sodium sulfate (Na_2SO_4), magnesium sulfate (MgSO_4), calcium chloride (CaCl_2) were purchased from Nacalai Tesque Co. Ltd. THF and dichloromethane used in the reactions were distilled from sodium and calcium hydride or calcium chloride as drying agents under argon gas before use, respectively. *N,N*-dimethylformamide (DMF) used in the reactions were dried over magnesium sulfate and distilled prior to use. All experiments were performed under argon (>99.99% purity) atmosphere.

1.2. Measurements. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using a JEOL EX-400 and an AL-400 NMR spectrometer. Chemical shifts are represented in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed at the Center for Organic Elemental Microanalysis of Kyoto University. High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (ESI) and JEOL JMS-MS700 (EI).

The microscope observation was carried out under crossed nicols using a Carl Zeiss Axio Imager M1m polarizing microscope equipped with a Carl Zeiss AxioCam MRc5 digital camera and a temperature control system configured by a THMS600 heating and cooling stage, type 10002, connected to an LNP94/2 liquid nitrogen cooling system (Linkam). The phase transition temperatures of polymer were determined by polarizing optical microscopy (POM).

Thermal behavior of **P1** and **P2** was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with alumina pan.

X-ray diffraction (XRD) measurements were performed with a Rigaku ultra X18

diffractometer. XRD patterns were recorded with an X-ray generator with Ni filtered $\text{CuK}\alpha$ radiation (40 kV/300 mA: $\lambda = 1.54 \text{ \AA}$) and a flat-plate camera (RINT2500, Rigaku). The sample-to-film distance was 100 mm and exposure time was 1–3 h. The diffraction pattern was recorded on an imaging plate and scanned by an R-Axis DS3A imaging plate reader at 100 μm resolution. Small-angle X-ray scattering (SAXS) measurement was performed with a Rigaku Nano-Viewer using $\text{CuK}\alpha$ radiation under the operating conditions of 40 kV and 30 mA.

Raman spectra were obtained at room temperature by backscattering method, using a spectroscopy with a triple monochromator and a charge coupled device (CCD) detector cooled by Peltier device (NRS-7100, JASCO). A 100 mW argon ion laser with a wavelength of 514.5 nm was used. An exposure time was 20 sec (10 sec $\times$ 2).

The film thickness was measured using Nikon Digimicro digital length measuring system with DIGIMICRO MH-15M, DIGIMICRO STAND MS-5C, and DIGITAL READOUT UC-101.

The electrical conductivity of **P1** and carbon films was measured at room temperature using a low resistivity meter, Loresta GP with a MCP-TP06P probe (Mitsubishi Chemical Analytech).

Infrared (IR) absorption spectra of PMPs were measured in film form or in powdery solid state with a JASCO FT (Fourier transform) -IR 4200 spectrometer. When the sample is measured in powdery solid state, the measurement was performed using the KBr method. When the sample is measured in film state, the measurement was performed using ATR (Attenuated total reflection) -IR mode.

Optical absorption spectra were measured using a JASCO V-570 UV/VIS/NIR spectrophotometer, and fluorescence spectra were measured using JASCO FP-750

spectrometer with quartz cell (for solution) and quartz plate (for cast film). Absolute fluorescence quantum yield of the polymers was measured using integrating-sphere method at the JASCO FP-6500 spectrometer. Optical purity of the chiral compounds and polymers were evaluated with specific rotation measured by JASCO P2300 polarimeter. Circular dichroism (CD) spectra were measured using JASCO J-820 spectropolarimeter. Circularly polarized luminescence (CPL) was measured using JASCO CPL-200S spectrometer.

The cast films were prepared by casting the chloroform solutions of the **P1s** on the quartz glasses at room temperature. Spin coated **P1** films for optical measurement on quartz glasses were prepared using a spin coater (Opticoat MS-A150, MIKASA) at a rotational speed of 750 rpm from its dichloromethane solution (10 mg/mL) at room temperature. The cast and spin coated films were heated up to 250 °C and cooled to 180 °C at a rate of 0.5 °C/min, and then cooled further to room temperature, giving annealed films.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μ m MIXED-D (Polymer Laboratories), a JASCO MD915 UV detector and THF as an eluent at a flow rate of 1.0 mL/min during measurements, where the instrument was calibrated using polystyrene (PS) standard, and were calculated on an 807-IT integrator.

The accelerating voltage of field emission (FE) -SEM (JSM-7500F, JEOL) was 2–10 kV. The PMP and carbon films were coated with Pt or Pt-Pd alloy using an ion coater with type of JFC-1600 (JEOL) before measurements of SEM. The coating thickness was evaluated to be ca. 5 nm.

2. Synthesis of Monomers

(*R*)-(-)-1-Methyloctyl-3,5-dibromobenzoate [(*R*)-M1]

A solution of (*R*)-2-nonanol (1.08 g, 7.50 mmol), 3,5-dibromobenzoic acid (2.10 g, 7.50 mmol), DCC (1.86 g, 9.00 mmol), and DMAP (1.01 g, 9.00 mmol) in dichloromethane (100 mL) was stirred at room temperature for 24 h under an argon atmosphere. TLC indicated completion of the reaction. Then, the precipitate of DCC-urea was removed by filtration. After evaporation of the solvent, the residue was washed with water and extracted with chloroform (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography (silica gel, chloroform/hexane = 1/1 v/v as eluent) to give clear oil (yield = 84%). Anal., calcd for C₁₆H₂₂Br₂O₂: C, 47.32; H, 5.46; Br, 39.35. Found: C, 47.51; H, 5.39; Br, 39.45. MS (ESI) calcd for C₁₆H₂₂Br₂O₂ [M+Na⁺]: 426.99. Found: 426.99. ¹H NMR (CDCl₃, 400 MHz): δ 0.87 (t, *J* = 7.0 Hz, 3H, -CH₃), 1.27–1.34 (m, 13H, -CH₂, -CH₃), 1.61 (dm, 2H, -CH₂), 5.14 (sext, *J* = 12.7, 6.1 Hz, 1H, -CH), 7.83 (t, *J* = 1.8 Hz, 1H, PhH), 8.08 (d, *J* = 1.7 Hz, 2H, PhH). ¹³C NMR (CDCl₃, 100 MHz): 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 32.8, 35.9, 73.0, 123.9, 131.3, 134.2, 138.0, 163.6. [α]_D²⁶ -26.30° (c 1.02, CHCl₃).

(*S*)-(+)-1-Methyloctyl-3,5-dibromobenzoate [(*S*)-M1]

The same procedure with (*R*)-M1 was employed by using (*S*)-2-nonanol, 3,5-dibromobenzoic acid, DCC, and DMAP (yield = 82%). Anal., calcd for C₁₆H₂₂Br₂O₂: C, 47.32; H, 5.46; O, 7.88; Br, 39.35. Found: C, 47.33; H, 5.42; O, 7.70; Br, 39.15. MS (EI) calcd for C₁₆H₂₂Br₂O₂: 404.00. Found: 404.00. ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, *J* = 6.8 Hz, 3H, -CH₃), 1.27–1.34 (m, 13H, -CH₂, -CH₃),

1.61 (dm, 2H, $-CH_2$), 5.14 (sext, $J = 12.9, 7.04$ Hz, 1H, $-CH$), 7.83 (t, $J = 1.8$ Hz, 1H, PhH), 8.08 (d, $J = 2.0$ Hz, 2H, PhH). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 32.8, 35.9, 73.0, 123.9, 131.3, 134.2, 138.0, 163.6. $[\alpha]_{589}^{26} +26.62^\circ$ (c 1.02, $CHCl_3$).

(rac)-1-Methyloctyl-3,5-dibromobenzoate [(rac)-M1]

The same procedure with (*R*)-M1 was employed by using (*rac*)-2-nonanol, 3,5-dibromobenzoic acid, DCC, and DMAP (yield = 83%). Anal., calcd for $C_{16}H_{22}Br_2O_2$: C, 47.32; H, 5.46; Br, 39.35. Found: C, 47.24; H, 5.43; Br, 38.54. MS (ESI) calcd for $C_{16}H_{22}Br_2O_2$ $[M+Na^+]$: 426.99. Found: 426.99. 1H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, $J = 7.0$ Hz, 3H, $-CH_3$), 1.27–1.34 (m, 13H, $-CH_2$, $-CH_3$), 1.61 (dm, 2H, $-CH_2$), 5.14 (sext, $J = 12.9, 7.04$ Hz, 1H, $-CH$), 7.83 (t, $J = 1.8$ Hz, 1H, PhH), 8.08 (d, $J = 1.6$ Hz, 2H, PhH). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.5, 20.4, 23.0, 25.8, 29.5, 29.8, 32.1, 36.3, 73.3, 123.2, 131.5, 134.4, 138.2, 163.8.

3. Synthesis of Polymers

Poly{5-[(*R*)-(-)-1-methyloctyl]-meta-phenylbenzoate} [(*R*)-P1]

A mixture of DMF (2 mL), BPY (1.07 g, 6.87 mmol), COD (0.71 g, 6.55 mmol), and $Ni(cod)_2$ (1.89 g, 6.87 mmol) was stirred at 90 °C for 90 min under an argon atmosphere, and then (*R*)-(-)-1-methyloctyl-3,5-dibromobenzoate (0.60 g, 1.89 mmol) dissolved in 2 mL DMF was added to it. The mixture was stirred at 100 °C for 72 h. The reaction mixture was cooled to room temperature, poured into a large amount of a mixture of 12 M HCl and MeOH (1 : 9, 500 mL), and vigorously stirred for 1 h. The resulting precipitate was collected by filtration and dissolved in a minimum amount of THF.

The insoluble part was removed by filtration, and the filtrate was reprecipitated in MeOH (500 mL). After stirring for 24 h, the resulting precipitate was collected by filtration. Further purification of the precipitated polymer was carried out by Soxhlet extraction with THF for 24 h. The product was dried under vacuum to give the corresponding PMP derivatives, poly{5-[(*R*)-(-)-1-methyloctyl]-*m*-phenylbenzoate} [**P1**], as colorless powder with yield of 64%. Anal., calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00; O, 12.99. Found: C, 75.55; H, 9.05. ¹H NMR (CDCl₃, 400 MHz): δ 0.78–0.86 (m, 3H, –CH₃), 1.20–1.45 (m, 13H –CH₂, –CH₃), 1.60–1.77 (m, 2H –CH₂), 5.21–5.29 (m, 1H, –CH), 8.11 (m, 1H, PhH), 8.30–8.53 (m, 2H, PhH). ¹³C NMR (CDCl₃, 100 MHz): ¹³C NMR (CDCl₃, 100 MHz): 14.2, 20.3, 22.7, 29.5, 31.9, 36.2, 72.5, 126.0, 127.3, 130.1, 132.9, 138.1, 141.3, 165.8. [α]_D²⁶ –69.88° (c 1.00, CHCl₃).

Poly{5-[(*S*)-(+)-1-methyloctyl]-*meta*-phenylbenzoate} [(*S*)-P1**]**

The same procedure with (*R*)-**P1** was employed by using (*S*)-**M1**, BPY, COD, and Ni(cod)₂ (yield = 60%). Anal., calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C, 76.66; H, 9.09. ¹H NMR (CDCl₃, 400 MHz): δ 0.78–0.86 (m, 3H, –CH₃), 1.20–1.45 (m, 13H –CH₂, –CH₃), 1.60–1.77 (m, 2H –CH₂), 5.21–5.29 (m, 1H, –CH), 8.11 (m, 1H, PhH), 8.30–8.53 (m, 2H, PhH). ¹³C NMR (CDCl₃, 100 MHz): 14.0, 20.2, 22.6, 29.3, 31.8, 36.0, 72.6, 126.0, 127.3, 128.0, 130.7, 132.5, 140.7, 165.8. [α]_D²⁶ +69.77° (c 1.00, CHCl₃).

Poly{5-[(*rac*)-1-methyloctyl]-*meta*-phenylbenzoate} [(*rac*)-P1**]**

The same procedure with (*R*)-**P1** was employed by using (*rac*)-**M1**, BPY, COD, and Ni(cod)₂ (yield = 66%). Anal., calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C,

75.95; H, 9.09. ^1H NMR (CDCl_3 , 400 MHz): δ 0.78–0.86 (m, 3H, $-\text{CH}_3$), 1.20–1.45 (m, 13H $-\text{CH}_2$, $-\text{CH}_3$), 1.62–1.77 (m, 2H $-\text{CH}_2$), 5.21–5.22 (m, 1H, $-\text{CH}$), 8.11 (m, 1H, PhH), 8.30–8.53 (m, 2H, PhH). ^{13}C NMR (CDCl_3 , 100 MHz): 14.0, 20.1, 22.6, 29.4, 31.8, 36.0, 72.4, 126.0, 127.3, 128.0, 130.7, 132.5, 141.5, 165.8.

4. X-ray Diffraction Analysis of **P1**

Figure S2 shows the XRD profile of **P1** as annealed film. **P1** shows intense peaks at 23.9 Å and 21.5 Å correspond to the distances between polymers in hexagonal columnar structures. The diffuse peak in the wide angle region (3.5 Å) corresponds to the distance between the π -stack of phenylene cores.

5. Optical Properties

We examined the UV–vis, photoluminescence (PL), absolute fluorescence quantum yield (Φ), and specific rotation ($[\alpha]_D$) of **P1s** in chloroform, as cast film and annealed film (Table S1). **P1s** have intrachain π -stacked phenylene moiety absorption bands measuring ~259 nm and $\pi-\pi^*$ transition of main chain absorption bands measuring ~302 nm (Figure S4a).

In the chloroform solution of **P1s**, the fluorescence band was observed at 352 nm (Figure S5a). This band is ascribed to fluorescence of the randomly arranged zigzag main chain. In the cast film of (*rac*)-**P1**, the same band was also observed at 367 nm (Figure S5b). However, two fluorescence bands were observed at 368–369 and 410–420 nm in the cast films of (*R*)- and (*S*)-**P1** (Figure S5b). The band at 410–420 nm is ascribed to fluorescence of the helical main chain. In the annealed films of **P1s**, the fluorescence band at 475–484 nm increased in intensity, but the band at 386 nm was

hardly observed (Figure S5c). These results suggest that **P1s** in solution form a nonhelical zigzag structure and a partly intrachain helical π -stacked structure in the cast films and annealed films. The helical structure may be due to π -stacking between spatially adjacent phenylene moieties in the folded main chain.

Figure S3a–c depicts CD spectra of the chiral **P1s** in chloroform, cast film and annealed film. The (*R*)- and (*S*)-**P1** in chloroform showed very weak CD bands at region of 280–320 nm (Figure S3a), suggesting that the intrachain helical π -stacked structure is loosely formed in solution, as implied by the result of PL spectra (Figure S5). Meanwhile, the cast film of (*R*)- and (*S*)-**P1** showed CD bands with substantially increased intensities, compared with the cases in solution (Figure S3b). This implies that the intrachain helical π -stacking is strengthened by the self-assembly of the polymers in the cast films. In addition, the annealed films of the (*R*)- and (*S*)-**P1** showed monosignate positive and negative CD bands with remarkably increased intensities (Figure S3c). This indicates that the intrachain helical π -stacking is further strengthened by the annealing, giving rise to the highly amplified helicity in the annealed film.

We investigated the potential of CPL of the **P1s**. Figure S3d depicts the fluorescence spectra, CPL spectra, and emission dissymmetry factors (g_{em}) of the **P1s** in cast films. The g_{em} is defined as $g_{em} = (I_L - I_R) / [(I_L + I_R) / 2] = \Delta I / I$, where $|g_{em}| < 2$. The I_L and I_R are defined as the intensities of left- and right-handed polarized light, respectively. Although the polymers in chloroform showed no CPL, the cast films showed CPLs with mirror images for (*R*)- and (*S*)-**P1**. The g_{em} values of (*R*)- and (*S*)-**P1** were -1.02×10^{-2} at 428 nm and 2.06×10^{-2} at 418 nm.

6. Supporting Figures

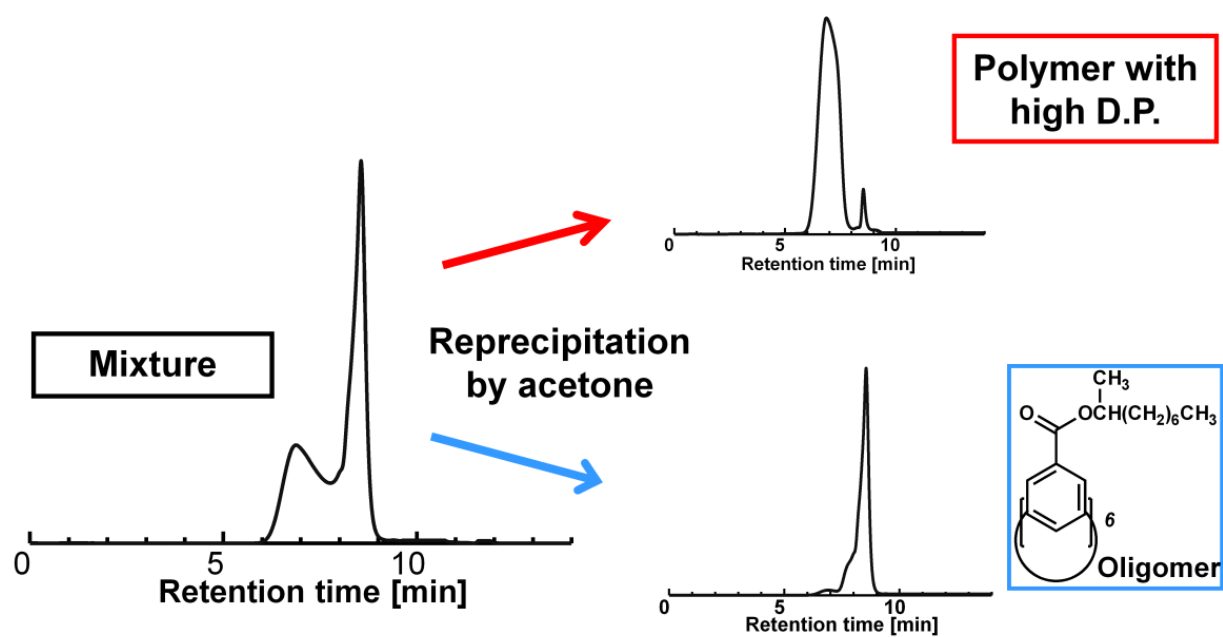


Figure S1. GPC results of the P1.

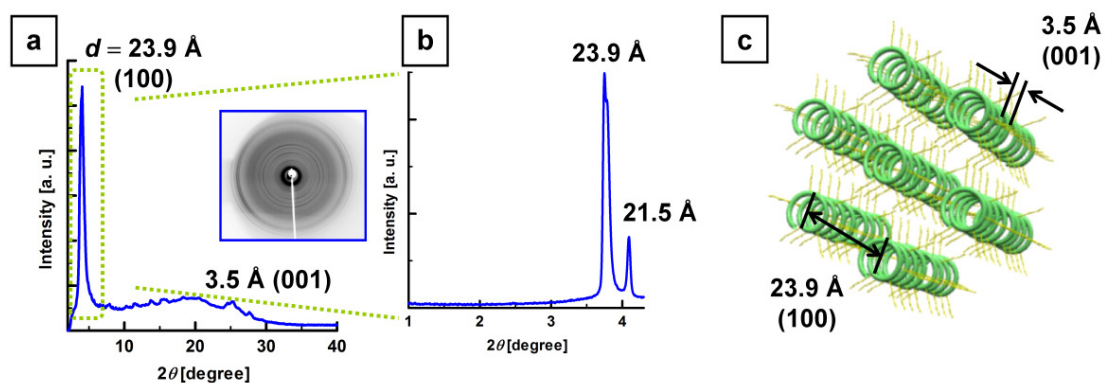


Figure S2. XRD patterns of (a) WAXS and (b) SAXS of the **P1** in annealed film. (c) Schematic representation of stacking structures of the **P1**s with a hexagonal columnar structure.

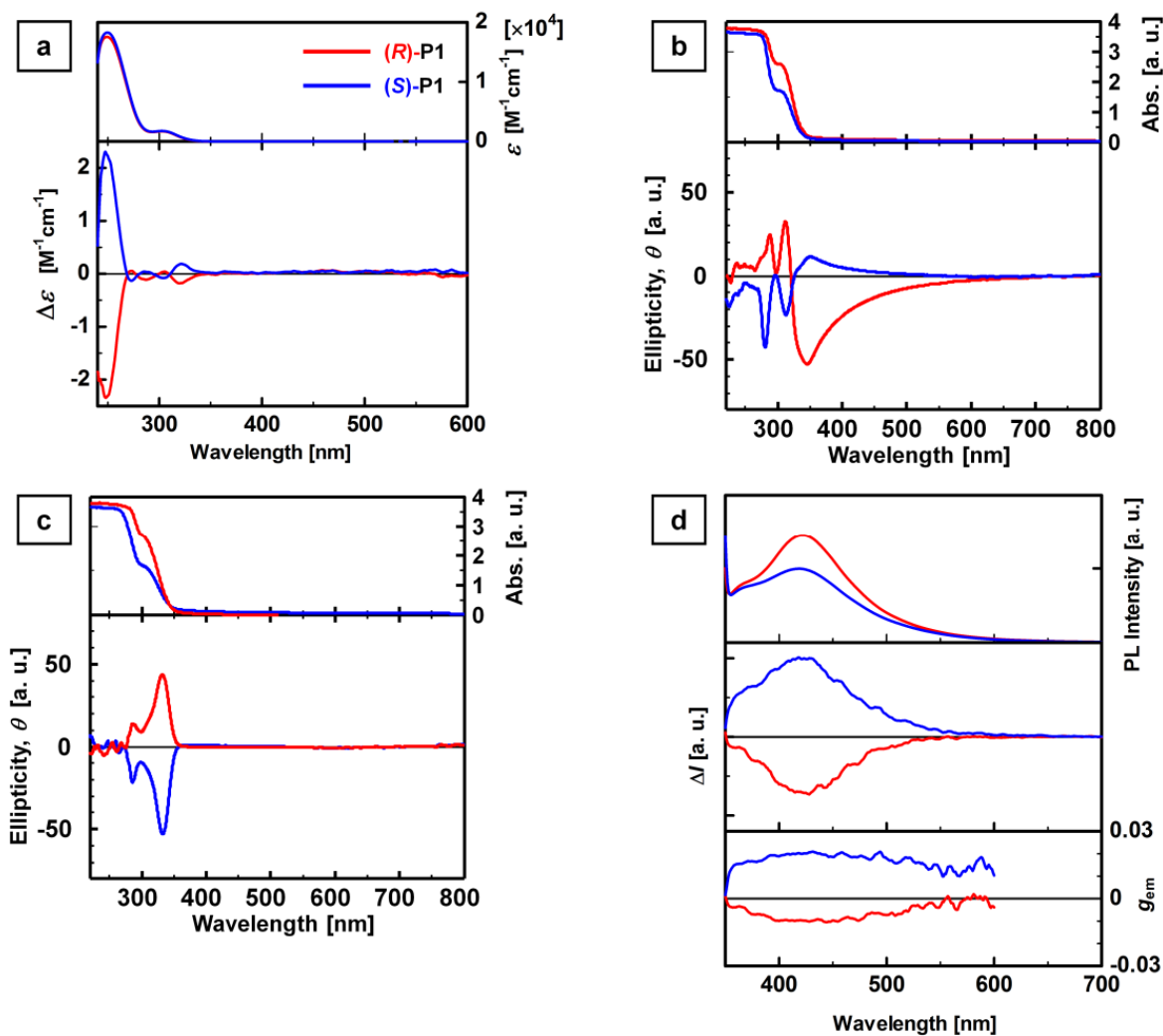


Figure S3. UV-vis (upper) and CD spectra (lower) of the (*R*)- and (*S*)-**P1** in (a) CHCl_3 (1.2×10^{-4} M), (b) cast film, and (c) annealed film. (d) PL (upper), CPL (middle), and g_{em} (lower) spectra of the (*R*)- and (*S*)-**P1** in cast film (Ex = 300 nm).

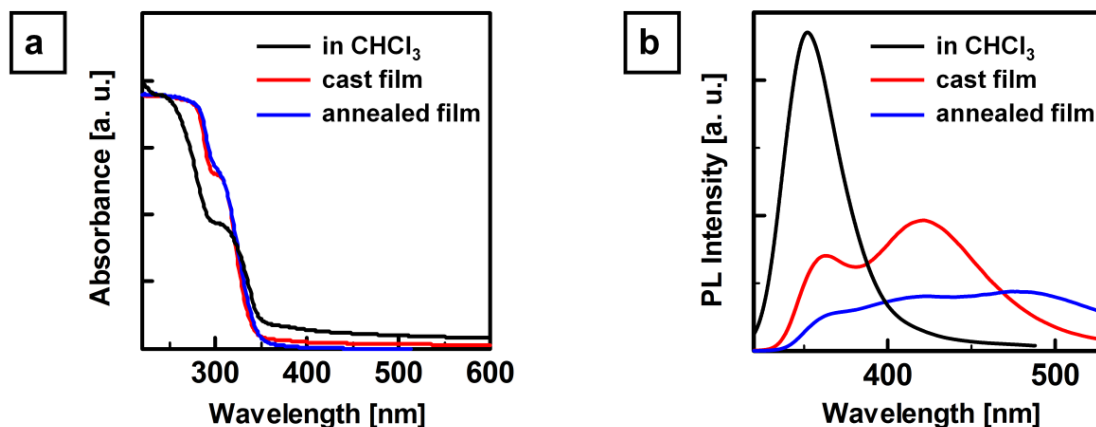


Figure S4. (a) UV-vis and (b) PL spectra of the **P1** in CHCl_3 (1.2×10^{-4} M), cast film, and annealed film.

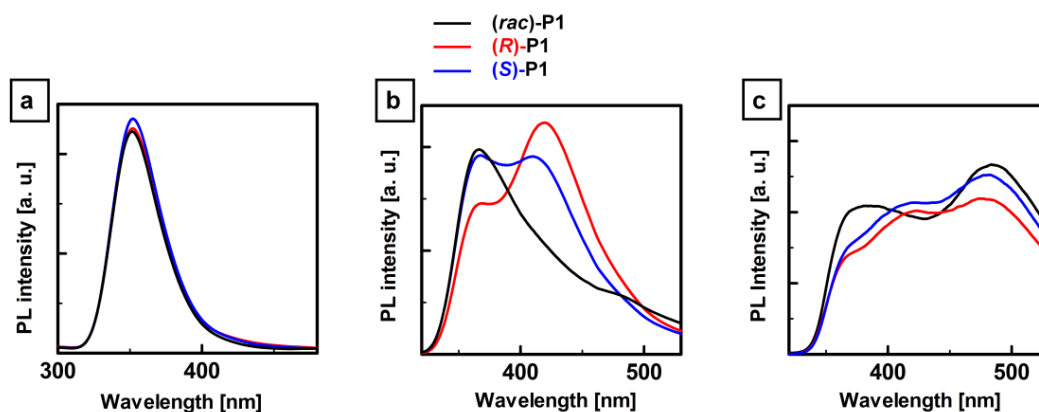


Figure S5. PL spectra of the (*rac*)-, (*R*)-, and (*S*)-**P1** in (a) CHCl_3 , (b) cast film, and (c) annealed film.

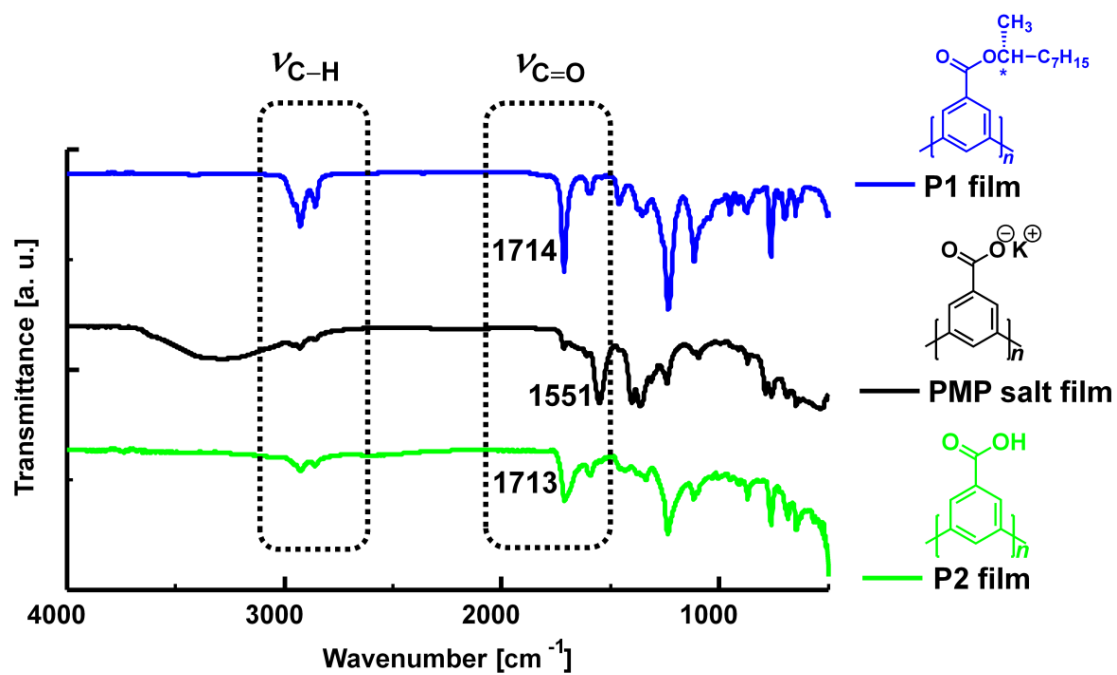
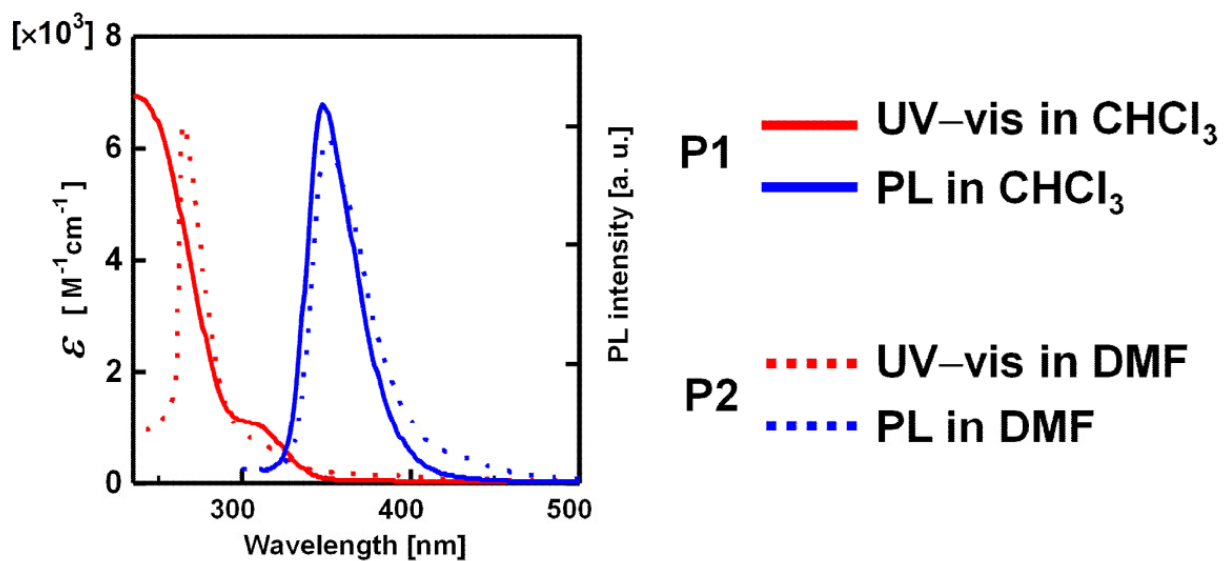


Figure S6. ATR-IR spectra of the **P1**, PMP salt, and **P2** films.



	λ_{max} (nm)	Em_{max} (nm)	Ex_{max} (nm)
P1	250, 302	348	302
P2	265	351	276

Figure S7. UV-vis and PL spectra of the **P1** in $CHCl_3$ and the **P2** in DMF (1.2×10^{-4} M).

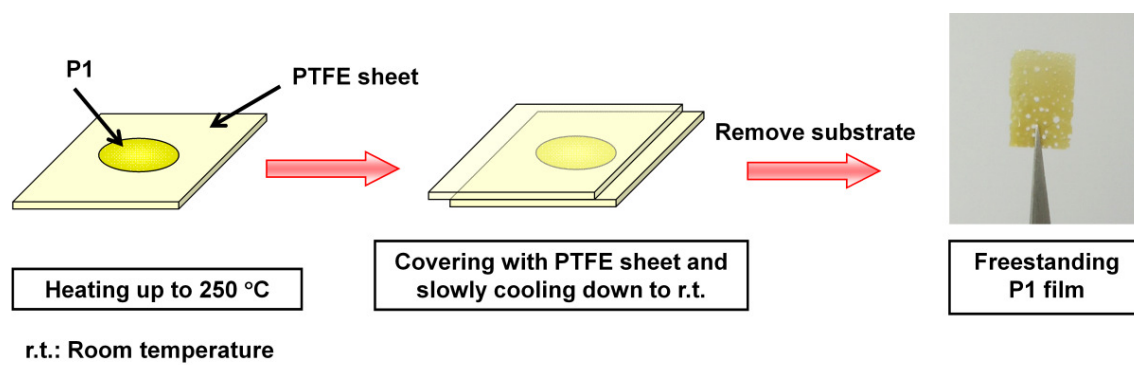


Figure S8. Preparation of the freestanding **P1** film.

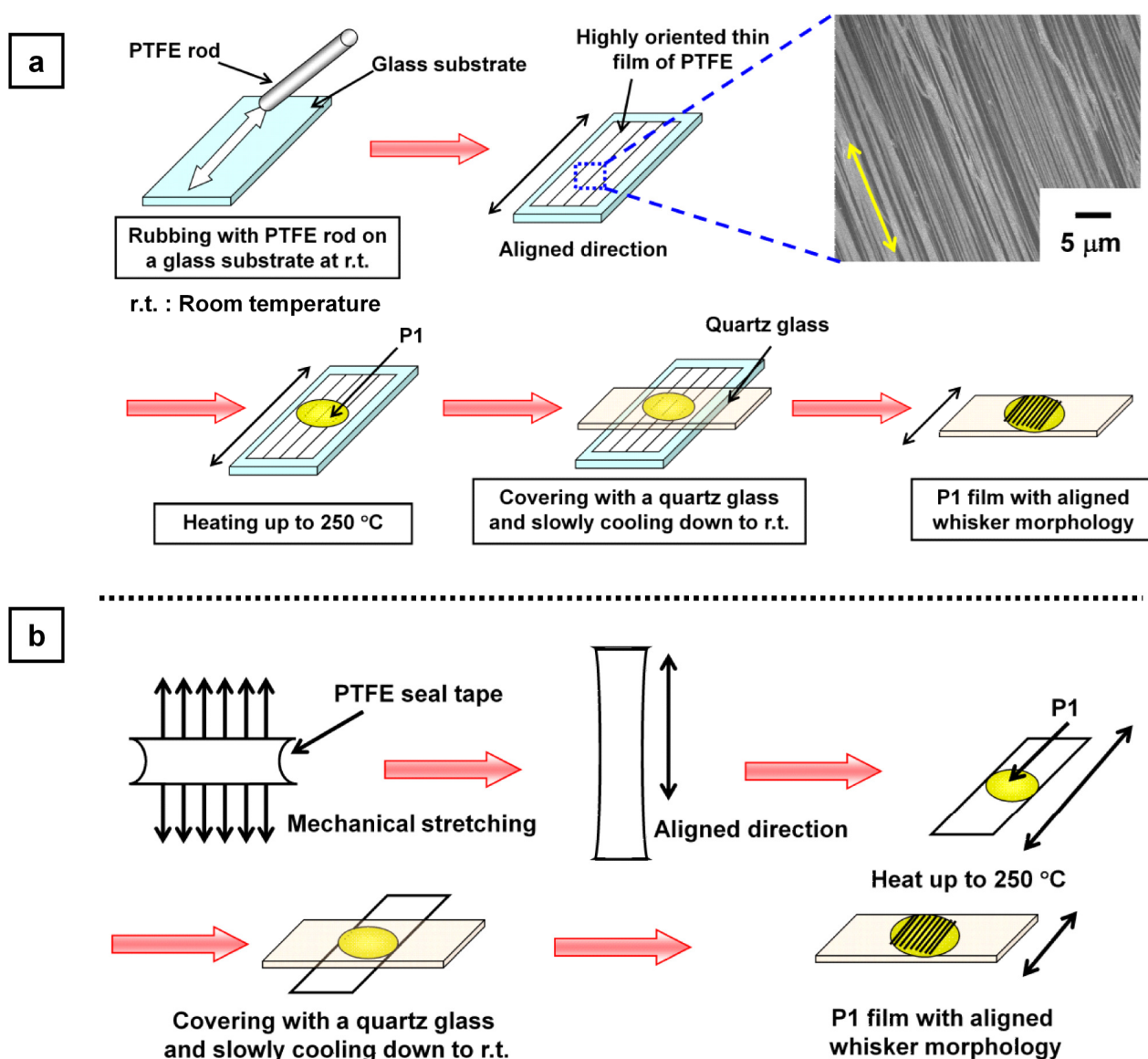


Figure S9. (a) Macroscopic alignment of **P1** whiskers using the rubbing method. The inset shows an SEM image of the oriented substrate. (b) Macroscopic alignment of the **P1** whiskers using the stretching method.

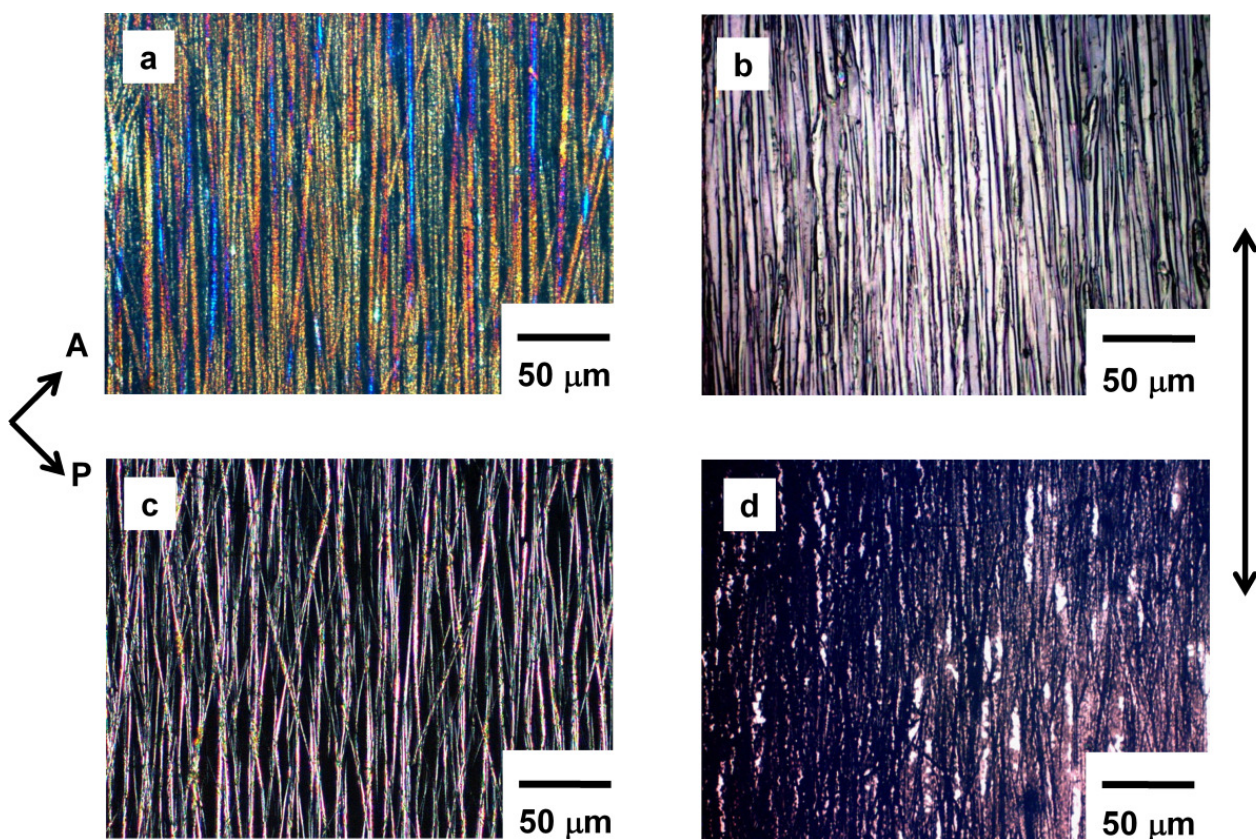


Figure S10. POM images of the **P2** films with aligned whisker morphologies prepared using the (a) rubbing method and (c) stretching method. Optical microscopy images of the carbon films with aligned whisker morphologies that were prepared from the **P1** films oriented using the (b) rubbing method and (d) stretching method through heat treatment at 800 °C. The arrow indicates the aligned direction of the whiskers.

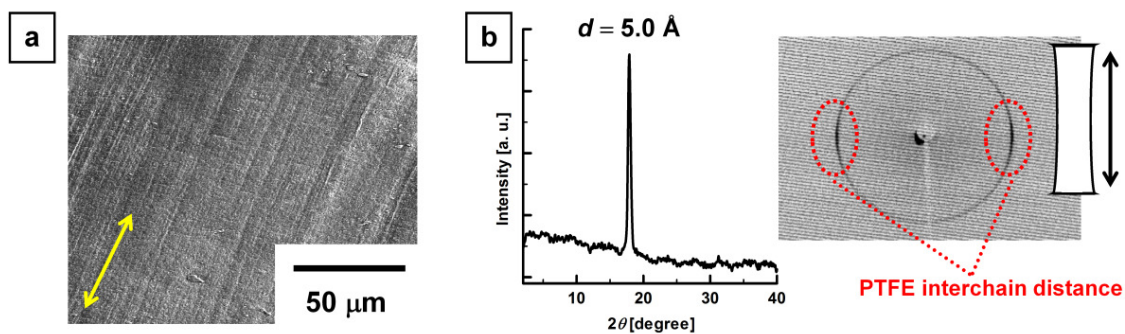


Figure S11. (a) SEM image and (b) XRD profile of the oriented substrate prepared using the stretching method.

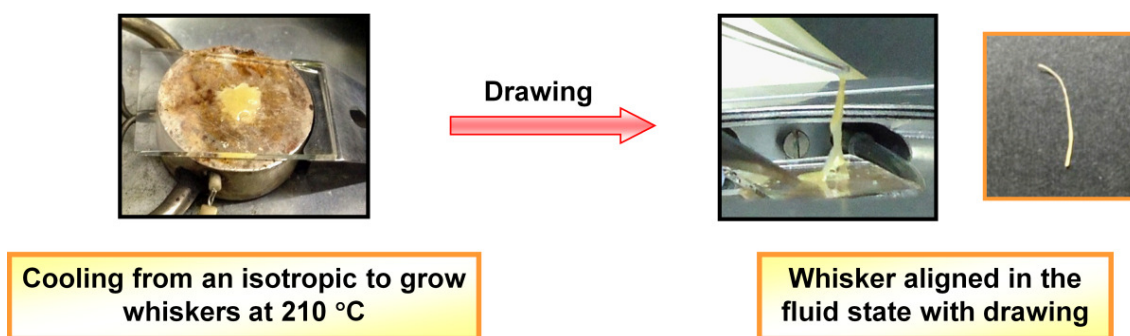


Figure S12. An approach to prepare the aligned **P1** whiskers.

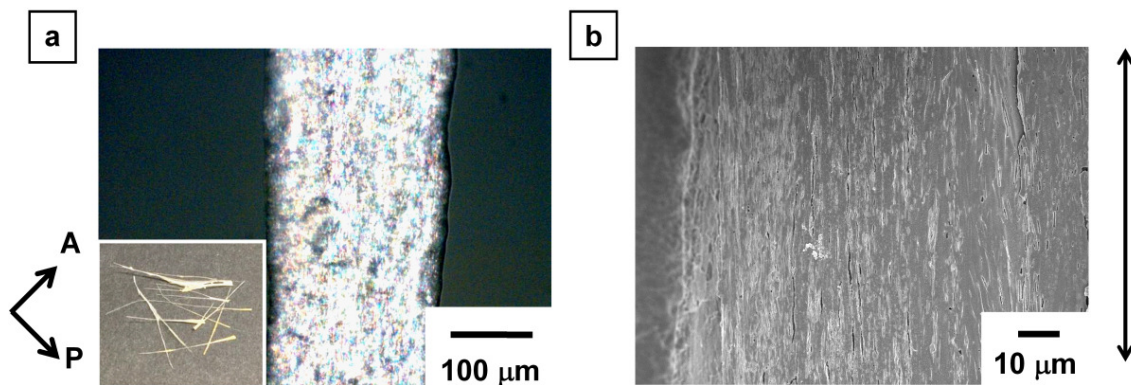


Figure S13. (a) POM and (b) SEM images of aligned **P1** fiber. The inset shows an optical image of the aligned **P1** fiber. The arrow indicates the aligned direction of the **P1** whiskers.

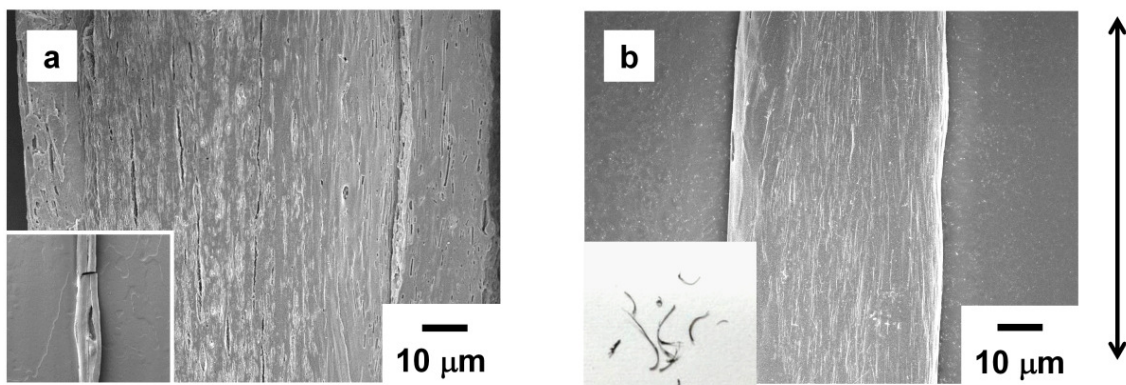


Figure S14. SEM images of the aligned (a) carbon and (b) graphite fibers. The arrow indicates the aligned direction of the whiskers. The insets show an SEM image of the aligned carbon fiber and an optical image of the aligned graphite fibers.

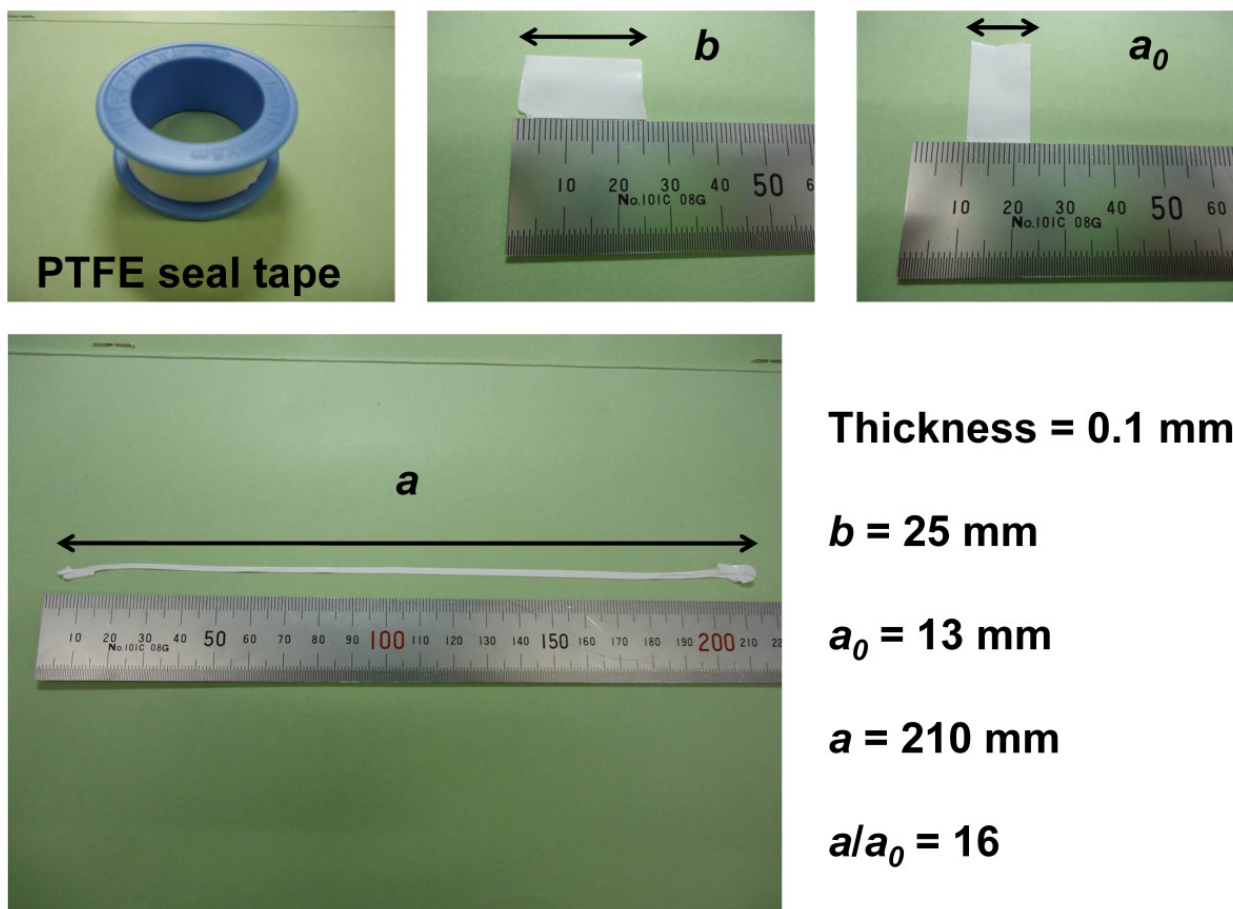


Figure S15. Optical images of the oriented substrate prepared using stretching method.

The inset shows the draw ratio (a/a_0) of the PTFE seal tape used as oriented substrate.

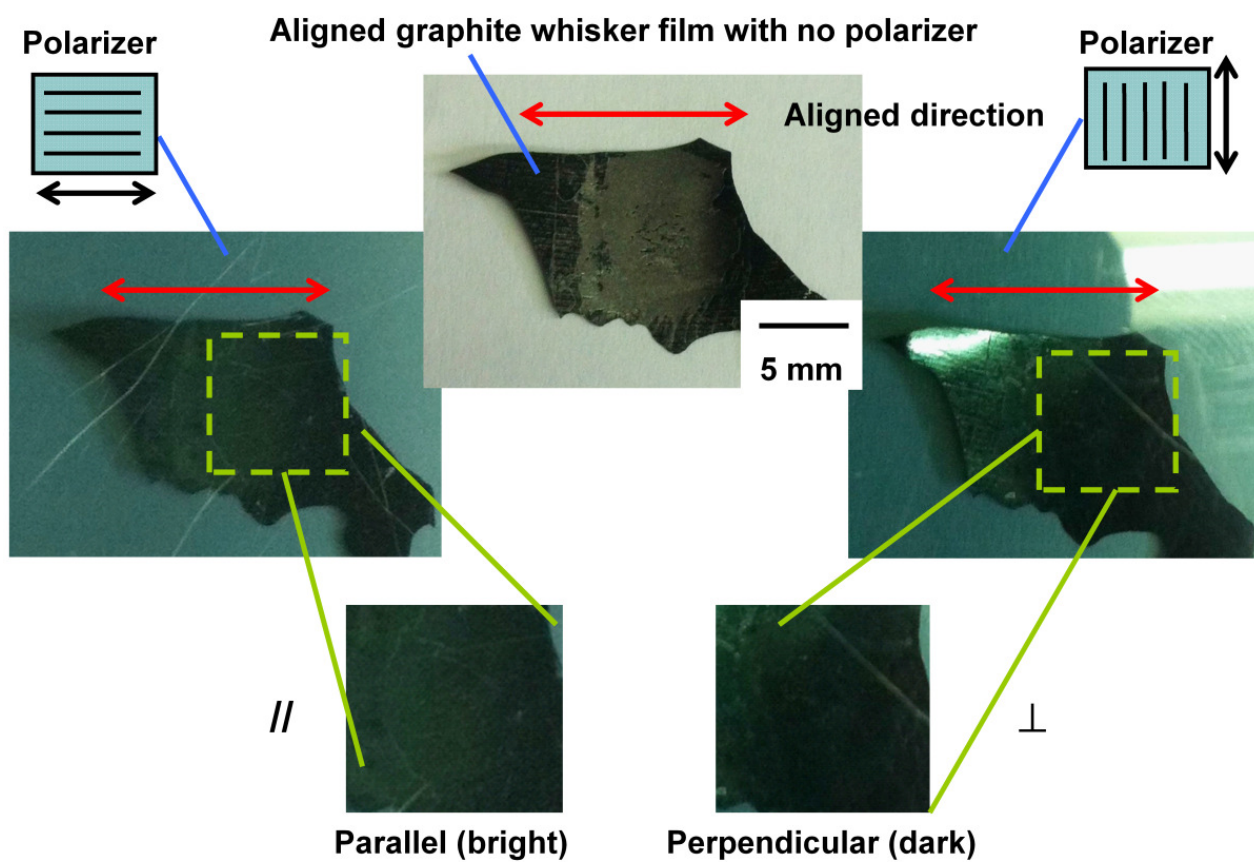
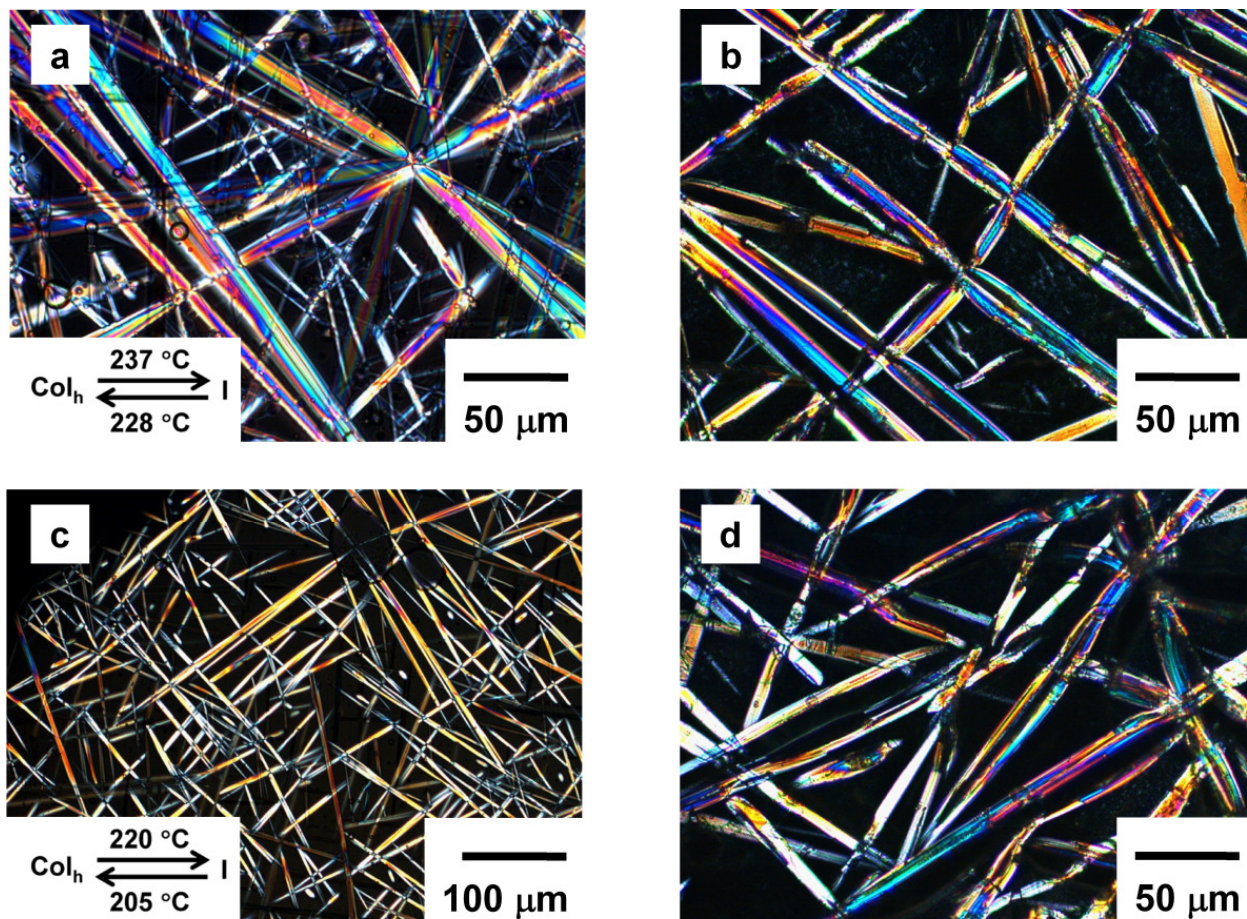


Figure S16. Optical images of the aligned graphite whisker film on a carbon plate where polarizer is arranged parallel (bright) and perpendicular (dark) to the aligned direction of the graphite whisker.



Col_h ; hexagonal columnar structure, I; isotropic phase

Figure S17. POM images of (a) the (S)-P1, (b) (S)-P2, (c) (rac)-P1, and (d) (rac)-P2 at room temperature.

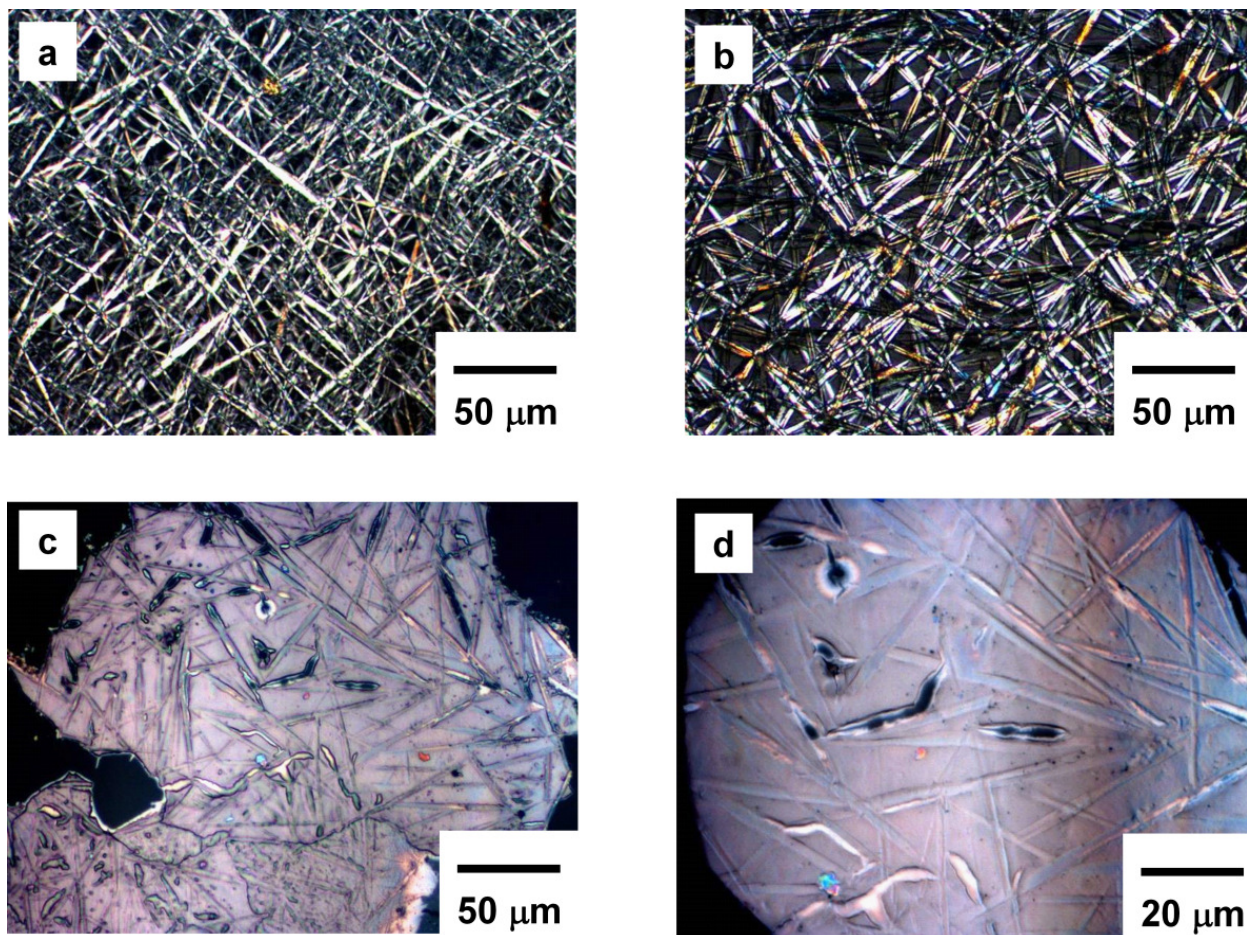


Figure S18. POM images of the oligomer (a) **P1** and (b) **P2**, and (c, d) optical microscopy images of the carbon whiskers prepared from the oligomer **P2** through heat treatment at 800 °C.

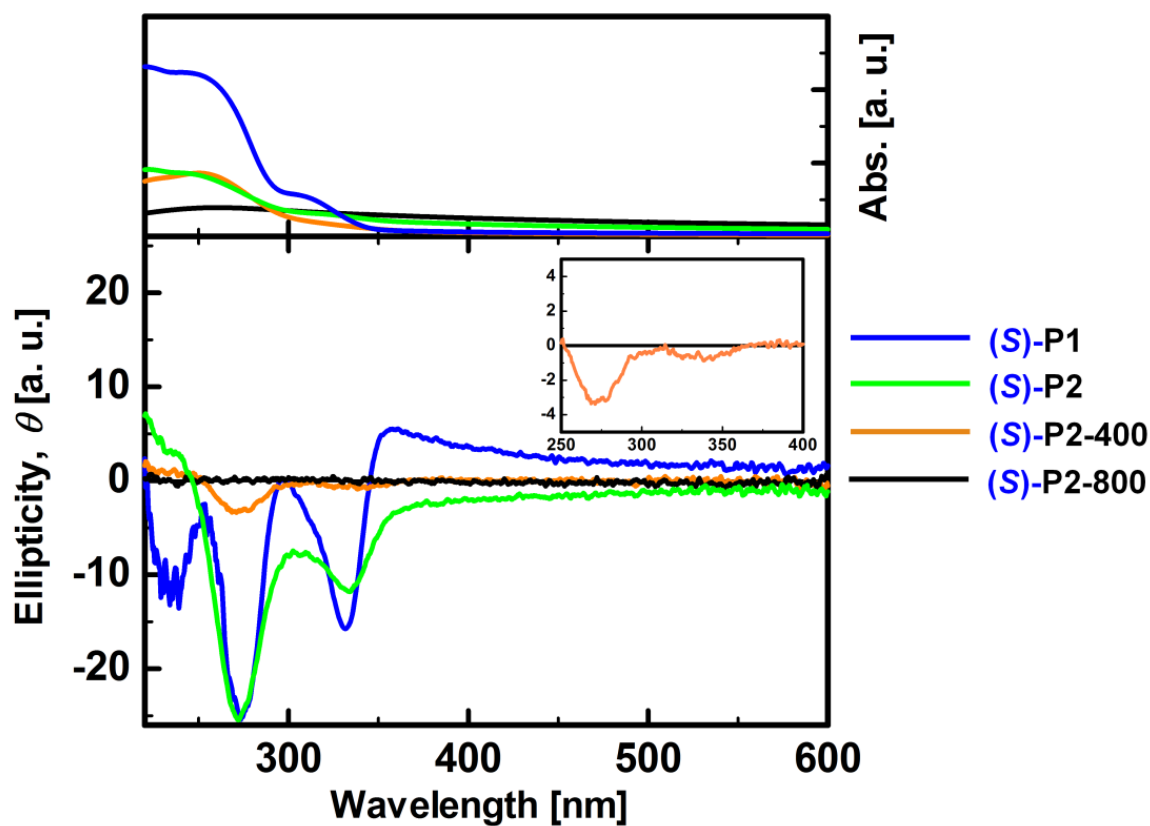


Figure S19. UV-vis (upper) and CD spectra (lower) of the (*S*)-**P1** in annealed film, (*S*)-**P2**, and (*S*)-**P2** through heat treatment at 400 °C and 800 °C. The annealed film was prepared from spin coated (*S*)-**P1** film.

Table S1. Maximum absorbance (λ_{max}), emission (Em_{max}), excitation (Ex_{max}), quantum yield (Φ), and specific rotation ($[\alpha]_{\text{D}}$) of **P1**.

	λ_{max} (nm)			Em_{max} (nm)			Ex_{max} (nm)			Φ (%)			$[\alpha]_{\text{D}}^{\text{a}}$ (°)
	CHCl_3	cast film	annealed film	CHCl_3	cast film	annealed film	CHCl_3	cast film	annealed film	CHCl_3	cast film	annealed film	CHCl_3
(R)-P1	249, 302	245, 305	245, 305	352	369, 420	475	257	280	280	10	7	3	−69.88
(S)-P1	249, 302	244, 307	244, 307	352	368, 410	481	257	285	280	11	8	4	+69.77
(rac)-P1	249, 302	244, 305	244, 305	352	367	386, 484	257	280	280	11	6	3	N/A

Chapter 2

An Advanced Method for Preparation of Helical Carbon and Graphitic Films Using a Carbonization Substrate

1. Introduction

Graphite is widely used due to the high thermal and electrical conductivity and stability in atmospheric conditions. Lump, crystalline flake, and amorphous graphite are three types of natural graphite distinguished by their physical characteristics. In contrast, pyrolytic carbon is a man-made material and normally not found in nature. Pyrolytic carbon exhibits unusual anisotropic properties owe to the graphene layers are crystallized in a complanate structure. Pyrolytic carbon is one of the best planar thermal conductors, which shows a larger thermally conductive along the cleavage plane than graphite. In addition, pyrolytic carbon can be magnetically levitated from a permanent magnet. Recently, a report of pyrolytic graphite showed a possibility of responding to laser light or natural sunlight in the direction of the field gradient, which could lead to the construction of a new solar energy conversion system.¹

There are kinds of approaches invented for producing carbon films such as evaporated amorphous carbon,² graphene-based materials,³⁻⁹ and carbon nanotubes.¹⁰⁻¹⁵ Nevertheless, preparing a graphite film via the carbonization of a polymer film in a desirable form is generally considered to be difficult. Conjugated polymers were considered to have higher thermal stability than universal vinyl polymers owe to their

rigid conjugated structure. For this reason, the use of conjugated polymers as carbonization precursors for the production of superior carbon materials is a feasible method.^{16–17} Recently, numerous carbonaceous materials with various morphologies, such as nanoparticles,¹⁸ nanotubes,¹⁹ nanofibers,^{20–22} anisotropic structures,²³ whiskers,²⁴ and even helical structures, prepared via heat treatment of multifarious conjugated polymers have been reported.²⁵ An approach named “morphology-retaining carbonization method” was developed by using iodine-doped helical polyacetylene (PA) films which synthesized in an asymmetric reaction field as carbonization precursors for preparing helical graphite films with spiral morphologies.^{26–30} The polymerization method using LC is a fascinating approach to synthesize anisotropic structured conjugated polymers during the process of polymerization directly. However, further improvements of the technique for the preparation of helical graphite are desired. Electrochemical polymerization under ambient conditions for the synthesis of the carbonization precursor was considered as a possible approach to improve the carbonization method, and it is simpler and less dangerous than the acetylene polymerization. On the other hand, helical, aromatic, π -conjugated polymers could also be considered as steady precursors than those helical, aliphatic ones with poor stability. Carbon films with an N* structure can be produced via approaches by using cellulose and biomimetic materials as precursors.^{31–32} New carbon materials with attractive hierarchically controlled helical structures are getting the attention because of their distinctive properties based on helicity and conductivity in the field of electrical and electromagnetic applications. This is why carbon materials with helical carbon structures and morphologies could be important and relevant.

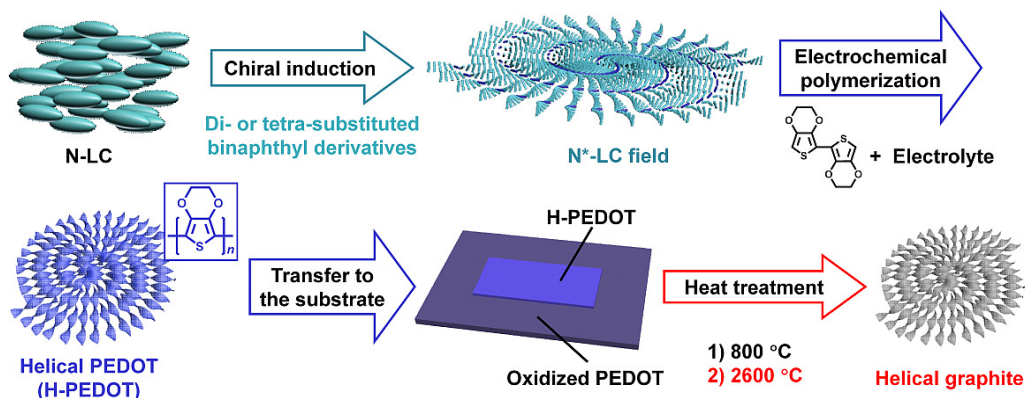
Recently, we have reported the production of helical graphite films by using

perchlorate ion (ClO_4^-) doped helical PEDOT (H-PEDOT) films as carbonization precursors that were prepared via an electrochemical polymerization in an N*-LC solution.³³ The N*-LC was provided by mixing a spot of di-substituted axially chiral binaphthyl compound with N-LC as the chiral dopant. A tetra-substituted chiral dopant was also used to provide a highly twisted N*-LC. The idea of using oxidized (doped) PEDOT can be explained as follows. From the results of XRD and Raman measurements of the graphite films produced from carbonization at 800 °C and subsequent heat treatment at 2600 °C, the graphite films prepared from the oxidized PEDOT film had a higher crystallinity than that prepared from the neutral (undoped) one. This difference was based on the dissimilarity of crystallinity between the oxidized and neutral precursor PEDOTs, i.e., the former has a more ordered structure than the latter. Doped ClO_4^- ions in the oxidized PEDOT make the polymer chains packed closely, leading to the ordered structure. The closely packed polymer chains could cross-link during the carbonization easily. As a consequence, the graphite film with high crystallinity is prepared from the oxidized PEDOT film. The highly crystalline graphite film is expected to perform high electrical conductivity. This is rationale of choosing oxidized PEDOT as a carbonization precursor.

To prepare the helical carbon, a quartz plate was used as the carbonization substrate due to its high heat resistance (m.p. = ~1650 °C). In the subsequent graphitization at 2600 °C, a carbon plate was used as a substrate to produce helical graphite. The carbon plate with a smooth surface was prepared via the heat treatment of a dialysis membrane (cellulose derivative) as a carbonization precursor. Although, scanning electron microscope (SEM) observations confirmed that the unique spiral morphologies of the original H-PEDOT films were partly preserved after carbonization at 800 °C and

graphitization at 2600 °C, a critical problem remained unresolved in this process, i.e., the difference in the thermal shrinkage between the substrate (carbon plate) and H-PEDOT film during the graphitization process at high temperatures. The thermal shrinkage deformation of the graphite film made the domain size of the spiral morphologies too small to be observed. For the same reason, it is also difficult to discriminate the screw directions of the spiral morphologies. Consequently, only the oxidized H-PEDOT film synthesized in the highly twisted N*-LC solution with the tetra-substituted chiral dopant was chosen as the graphitization precursor.

In view of the above-mentioned problems, the author employed novel strategies to innovate the polymerization and carbonization processes. First, a new type of chiral dopant bearing the cyanobiphenyl (CB) moiety that is the same mesogenic core as that of the parent LC [4-cyano-4'-pentylbiphenyl (5CB)] was used to prepare the N*-LC polymerization systems. This chiral dopant provided high miscibility and strong helical twisting powers (HTPs) to the N*-LC systems. Second, instead of carbon plate, oxidized PEDOT films were used as the advanced carbonization substrates to reduce the thermal shrinkage deformation of the H-PEDOT films during heat treatment. Helical graphite films with clearly discriminated left- and right-handed multi-domain spiral morphologies were prepared using these strategies (Scheme 1).



Scheme 1. Schematic representation of the process of preparing a helical graphite film.

2. Results and Discussion

2.1. Polymerization of mono- and bis-EDOT in an Isotropic Solvent. The dimer of 2,2'-bis(3,4-ethylenedioxythiophene), (abbreviated as bis-EDOT), was synthesized via a copper-catalyzed Ullmann coupling³⁴ of 2-lithio-3,4-ethylenedioxythiophene with CuCl_2 . Synthesis details for bis-EDOT are given in the Supporting Information (Scheme S1).

The electrochemical polymerizations of mono- and bis-EDOT were performed by using acetonitrile (ACN) as an isotropic solvent. The polymerizations of the corresponding monomers were performed on ITO glass (5×5 cm) (anode) by using platinum (Pt) mesh as the counter electrode (cathode) at normal atmospheric temperature with stirring. The concentration of the monomer and supporting electrolyte (tetra-*n*-butylammonium perchlorate; TBAP) was 0.05 M. The polymerization was taken proceed on the voltage of 4 V for 30 min. The PEDOT films were washed with methanol, hexane, and ACN at room temperature then dried for

6 h at 90 °C. The as-grown PEDOT film after polymerization, containing the ClO_4^- dopant, is named the “oxidized PEDOT film”. The amount of doped ClO_4^- in the oxidized PEDOT film was determined using elemental analysis. The oxidized PEDOT film synthesized using mono-EDOT yielded the following elemental analysis: C, 40.48; H, 2.56; and Cl, 5.47. The molecular ratio of the doped ClO_4^- to the EDOT unit in the oxidized PEDOT film ($\text{ClO}_4^-/\text{EDOT}$) was calculated to be $[\text{EDOT}(\text{ClO}_4^-)_{0.26}]_n$ from the elemental analysis.

2.2. Morphologies of the PEDOT Films. The PEDOTs prepared in ACN were obtained as freestanding films (Figure S1a in the Supporting Information). SEM observations showed that the PEDOT film prepared using bis-EDOT had a fibril-like morphology (Figure S2b in the Supporting Information). In contrast, the PEDOT film prepared from mono-EDOT had a globular morphology (Figure S2a in the Supporting Information). This is because the rigid, rod-like molecular shape of the bis-EDOT is favorable for directional polymer growth, which results in a fibril structure.

2.3. De-doping of the PEDOT Films. A “neutral” PEDOT film can be prepared by reducing the oxidized PEDOT film via an incompletely electrochemical de-doping process. The electrochemical de-doping was carried out at 4 V to the oxidized PEDOT films on ITO glasses (cathode) in an ACN solution of TBAP (0.05 M) using Pt mesh (anode) at room temperature with stirring (Figure S1b in the Supporting Information). The PEDOT film prepared using mono-EDOT yielded the following elemental analysis after de-doping process for 20 min: C, 51.42; H, 2.88; O, 22.83; and S, 22.87. The PEDOT film after the de-doping process still contained a trace amount of residual

chlorine derived from the dopant species. The molecular ratio of the doped ClO_4^- to EDOT in the PEDOT film ($\text{ClO}_4^-/\text{EDOT}$) was calculated to be $[\text{EDOT}(\text{ClO}_4^-)_x]_n$ ($x < 0.01$) from the elemental analysis. The theoretical elemental composition of PEDOT was calculated for $[\text{EDOT}]_n$: C, 40.74; H, 2.66; Cl, 5.41. This confirmed that almost all of the ClO_4^- ions are released from the oxidized PEDOT, $[\text{EDOT}(\text{ClO}_4^-)_{0.26}]_n$, after the electrochemical de-doping process. Thus, the de-doped PEDOT will be called “neutral PEDOT”, but the present de-doping process does not yield a completely neutralized PEDOT.³⁵

2.4. TG-DTA Curves of the PEDOT Films. The thermogravimetric analysis (TGA) curves showed that the PEDOT films were stable up to 200–220 °C. Major decomposition occurred in the region between 360 and 600 °C (Figure S3 in the Supporting Information).^{36–37}

2.5. Carbonization and Graphitization of the PEDOT Films. The PEDOT film was sandwiched between two pieces of carbon plates and put into an electric furnace. The PEDOT film was heated at 800 °C with argon gas flow at the rate of 10 °C/min for 1 h. The carbonization yields for the neutral and oxidized PEDOT films were 32–37 and 21–34%, respectively. The carbon film carbonized from the neutral PEDOT film (abbreviated as Carbon-*N* film) had a lower weight loss compared to the black char obtained from the undoped PA film (<30%) at 800 °C.^{26–27} The Carbon-*N* film prepared from the neutral PEDOT film, $[\text{EDOT}(\text{ClO}_4^-)_x]_n$ ($x < 0.01$), which was synthesized using mono-EDOT after de-doping for 20 min yielded the following elemental analysis result: C, 82.27; H, 2.25; S, 13.66; and Cl, 0.0 (total, 98.18%). No residual chlorine was remained in the carbon film. On the other hand, the carbon film

prepared from the oxidized PEDOT film, $[\text{EDOT}(\text{ClO}_4^-)_{0.26}]_n$, (abbreviated as Carbon-*O* film) yielded the following elemental analysis result: C, 81.80; H, 1.98; S, 13.74; and Cl, <0.10 (total, 97.52%). The carbonized film was graphitized at 2600 °C with graphitization equipment for 30 min with argon flow. The graphitization yields of the Carbon-*N* and -*O* films were 73% and 69%, respectively. The graphite films produced from the neutral and oxidized PEDOTs (abbreviated as Graphite-*N* and -*O* films, respectively) yielded the following elemental analysis result: C, 99.89 and H, 0.0 (total, 99.89%) and C, 99.97 and H, 0.0 (total, 99.97%), respectively. The carbon and graphite films were prepared from the PEDOT films via carbonization at 800 °C and subsequent graphitization at 2600 °C, irrespective of whether the PEDOT films were oxidized or neutral (Figure S4 in the Supporting Information). These results owe to the thermal stability at high temperature of the aromatic π -conjugated polymers with rigid backbones.

2.6. Crystallinity and Diamagnetic Levitation of the Carbon and Graphite Films.

A number of experiments, such as XRD and Raman scattering measurements, have been performed in previous reports to check the crystallinity of PEDOT, carbon, and graphite films.³³ In this research, the phenomenon of diamagnetic levitation was used to measure the crystallinity of the carbon and graphite films. The orbital motion of free electrons in a material makes current loops controlled by the Lorentz force. These current loops produce the opposite magnetic moment when a magnetic field applied to the material. This effect is named diamagnetism. All materials have diamagnetic properties but almost of those effects are very weak. Since the benzene rings in the graphite structures are highly oriented in the planar direction, graphite is one of the strongest diamagnetic materials and can be levitated stably on NdFeB magnets at

normal atmospheric temperature.³⁸ If the carbon and graphite films prepared from PEDOT films have graphitic structures, the phenomenon of diamagnetic levitation can be expected. Figure 1 showed the Carbon-*O* film (1.1 mg) and Graphite-*O* film (1.2 mg) on the magnetic levitation stage which consists of twelve 360 mT NdFeB magnets ($15 \times 10 \times 5$ mm) arranged so that they face in alternate directions. Figure 1a showed that the Carbon-*O* film did not perform a diamagnetic levitation. This result exhibited that Carbon-*O* film exists in an amorphous state. Surprisingly, the Graphite-*O* film can achieve a levitation height of approximately 1 mm, which implies that a Graphite-*O* film with an oriented graphitic structure and high crystallinity was prepared via heat treatment at 2600 °C.

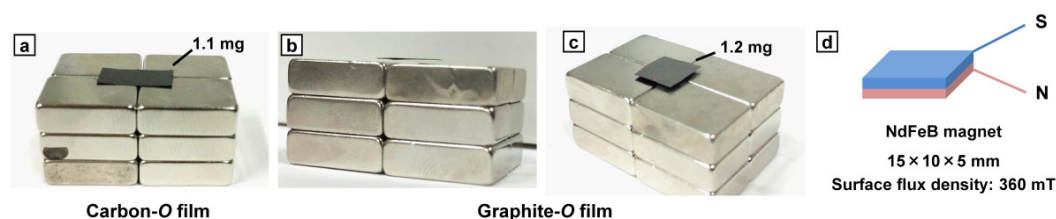
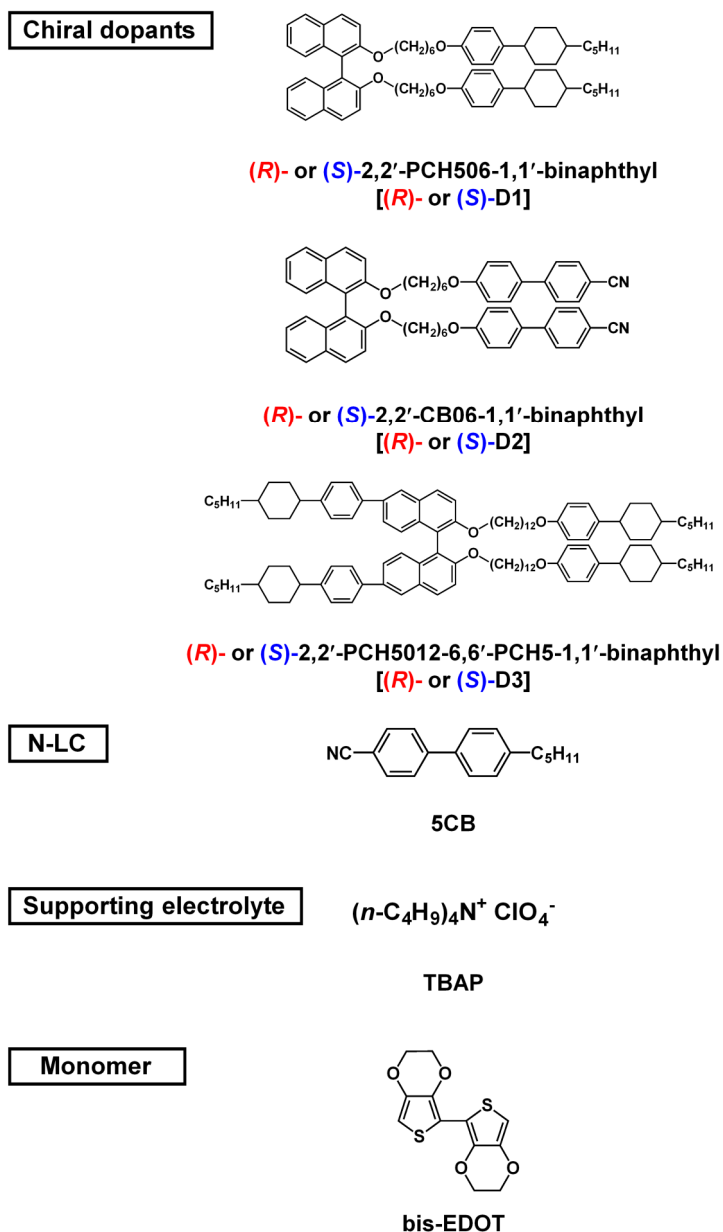


Figure 1. Photographs of diamagnetic levitation of (a) Carbon-*O* film (1.1 mg) and (b,c) Graphite-*O* film (1.2 mg). The magnetic levitation stage consists of twelve (d) 360 mT NdFeB magnets ($15 \times 10 \times 5$ mm) arranged so that they face in alternate directions.

2.7. Electrical Conductivities of the Carbon and Graphite Films Prepared from PEDOT Films. Four-point probe method was used to measure the electrical conductivities of the PEDOT, carbon, and graphite films. The neutral and oxidized PEDOT films have electrical conductivities approximately 10^{-4} and 46 S/cm,

respectively.³⁹ The electrical conductivity of the neutral PEDOT film is several orders of magnitude larger than the theoretically expected value because of the residual dopant.⁴⁰ In contrast, the conductivities of Carbon-*O* and Graphite-*O* films are approximately 10^{-1} and 10^1 S/cm, respectively.

2.8. Preparation of the N*-LCs. The chemical formula of the chiral dopants, the N-LC, the supporting electrolyte (TBAP), and the monomer were shown in Scheme 2. Synthesis details of di- and tetra-substituted axially chiral binaphthyl compounds were reported in the past work.^{41–42} The chiral dopants also used in previous are (*R*)- or (*S*)-2,2'-PCH506-1,1'-binaphthyl [abbreviated as (*R*)- or (*S*)-D1] and (*R*)- or (*S*)-2,2'-PCH5012-6,6'-PCH5-1,1'-binaphthyl [abbreviated as (*R*)- or (*S*)-D3]. In addition, a new type of chiral dopant with a cyanobiphenyl (CB) mesogenic core, (*R*)- or (*S*)-2,2'-CB06-1,1'-binaphthyl [abbreviated as (*R*)- or (*S*)-D2], was used in this research. The synthesis details for (*R*)- and (*S*)-D2 are given in the Supporting Information (Scheme S1).



Scheme 2. Composition of the N*-LC system.

HTPs (β_M) of the chiral dopants, concentration ratios, and helical pitches of the N*-LCs were summarized in Table 1. The N*-LCs of systems 1 and 2 were provided by mixing 1 mol % of the di-substituted chiral dopant, D1 or D2, with the 5CB. The

N*-LCs of system 3 were provided by mixing 1 mol % of the tetra-substituted chiral dopant D3 with the 5CB.

Table 1. The HTPs of the chiral dopants, the concentration ratios, and the helical pitches of the N*-LCs.

chiral dopants			N*-LCs			
		helical twisting power, β_M (μm^{-1})	system	mole ratios between components of N*-LCs	helical pitch (μm)	helical sense
di-substituted	D1	<i>R</i> : 32	1	5CB : (<i>R</i>)- or (<i>S</i>)-D1 = 100 : 1	<i>R</i> : 3.1	right
		<i>S</i> : 32			<i>S</i> : 3.1	left
	D2	<i>R</i> : 56	2	5CB : (<i>R</i>)- or (<i>S</i>)-D2 = 100 : 1	<i>R</i> : 1.8	right
		<i>S</i> : 59			<i>S</i> : 1.7	left
tetra-substituted	D3	<i>R</i> : 293	3	5CB : (<i>R</i>)- or (<i>S</i>)-D3 = 100 : 1	<i>R</i> : 0.34	right
		<i>S</i> : 294			<i>S</i> : 0.34	left

2.9. Characterization of the N*-LCs. The polarizing optical microscope (POM) images of systems 1 and 2 showed typical fingerprint textures. In contrast, the POM images of system 3 showed fan-shaped focal conic textures (Figure S5 in the Supporting Information). In the case of system 3, the distances between the striae are too short to be observed under the POM. (*R*)- or (*S*)-N*-LCs showed enantiotropically thermotropic LC behavior. The miscibility tests (contact methods)^{43–44} were performed to determine the helical senses of the N*-LCs with fingerprint textures. (*R*)- and (*S*)-chiral dopants have right- and left-handed screw structures proved by the miscibility tests method, respectively. The helical sense of chiral dopants was summarized in Table 1.

Cano's wedge method was used to evaluate the helical pitches of N*-LC systems 1 and 2.^{45–48} The helical pitch of the (*R*)- and (*S*)-N*-LCs (system 1) was 3.1 μm and the HTP of D1 in the system was 32 μm^{-1} . The helical pitch of the (*R*)- and

(*S*)-N*-LCs (system 2) was 1.7–1.8 μm and the HTP of D2 in the system was 56–59 μm^{-1} . Both D1 and D2 are di-substituted chiral dopants with different mesogenic cores. The HTP of D2 in system 2 is stronger than that of D1 in system 1, which implies that the introduction of the same CB moieties as substituents increased the miscibility of the binaphthyl compounds towards the parent LC 5CB and also afforded strong enough HTP to induce chiral nematic phases.

On the other hand, selective light-reflection method was used to evaluate the helical pitches of system 3.^{49–50} The helical pitches of system 3 were 341 nm and the HTPs of D3 in system 3 were 293–294 μm^{-1} (Table 1). The same amount of tetra-substituted chiral dopant (*R*)- or (*S*)-D3 mixed with an N-LC allowed us to make a highly twisted N*-LC system.

2.10. Preparation of H-PEDOT films using bis-EDOT in N*-LC and De-doping of the H-PEDOTs. The electrochemical polymerizations were carried out in N*-LCs in the preparation of H-PEDOTs. The N*-LCs were provided by mixing 1 mol % of D1, D2, or D3, 3 mol % of bis-EDOT, and 0.5 mol % of TBAP with the 5CB. Figure 2 showed the POM images of N*-LC solutions, including bis-EDOT and TBAP, before the electrochemical polymerizations. The H-PEDOTs used in the ultraviolet–visible (UV–vis) and circular dichroism (CD) measurements were prepared in the N*-LCs with 1 mol % of D1, D2, or D3, 2 mol % of bis-EDOT, and 0.2 mol % of TBAP in 5CB. The polymerization conditions of the H-PEDOT films for carbonization and optical measurements were optimized by changing the aging time and cooling rate of the N*-LC systems.

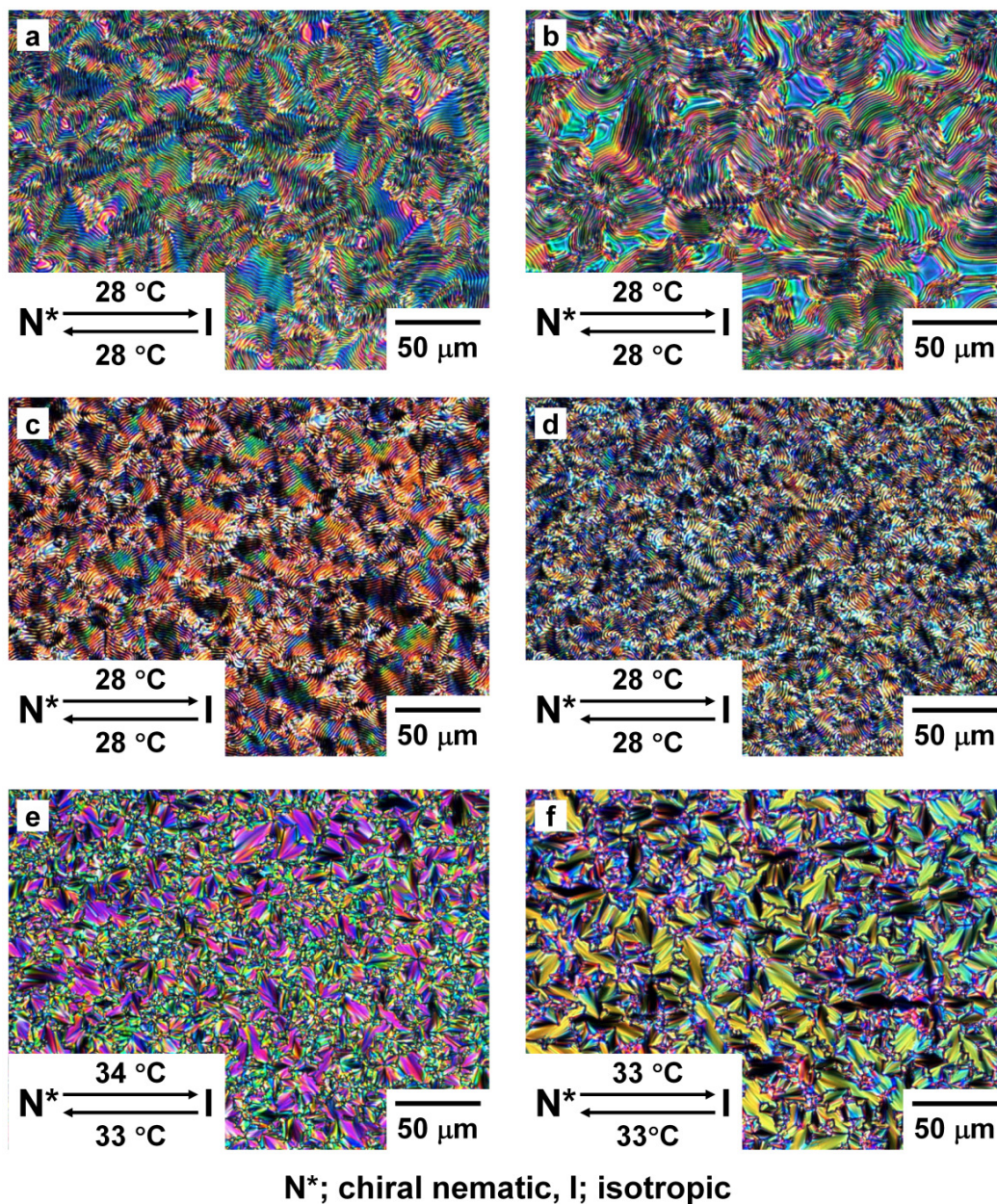


Figure 2. POM images of N*-LC solutions at 20 °C during the cooling process prepared using (a) (R)- and (b) (S)-D1 (system 1) (c) (R)- and (d) (S)-D2 (system 2) and (e) (R)- and (f) (S)-D3 (system 3).

The de-doping process of the H-PEDOT films was under 4 V in an ACN solution of TBAP (0.05 M) for 5 min at normal atmospheric temperature. The H-PEDOT film

prepared in N*-LC was too thin to obtain an enough quantity for elemental analysis. Although it was difficult to estimate the dopant species (ClO_4^-) contained in the H-PEDOT film, the amount of the dopant species in the H-PEDOT film was close to that in the PEDOT film synthesized in ACN.

2.11. UV-vis, CD, and g_{abs} Measurements of the H-PEDOT Films. Figures 3 and 4 show the optical spectra in UV-vis, CD, and g_{abs} measurements of the H-PEDOT films in both oxidized and neutral states on ITO glass prepared by using D1, D2, and D3 as the chiral dopants. The λ_{max} of the H-PEDOTs in neutral state is 504–510 nm. This is assigned to the π - π^* transition of the conjugated polymer main chain. The absorption band observed in the neutral H-PEDOT film showed a red shift in the oxidized H-PEDOT film owe to the changing of structure in the PEDOT main chain from a benzenoid to a quinoid form. The neutral and oxidized states are reversibly generated via the electrochemical de-doping and doping procedures. The bisignate Cotton effects from the CD measurements showed that the neutral H-PEDOT has an interchain helically π -stacked structure.⁵¹ The optimization of the aging time and cooling rate of the N*-LC systems before polymerization resulted in the Cotton effects exhibiting near mirror images in sign. On the basis of the exciton coupling theory,⁵² the (*R*)- PEDOT film has a right-handed helical senses (*P*-helicity) and the (*S*)- PEDOT film has a left-handed one (*M*-helicity). The dissymmetry factor (g_{abs}) was used to evaluate the degree and intensity of circular polarization [$g_{\text{abs}} = 2(\epsilon_{\text{L}} - \epsilon_{\text{R}})/(\epsilon_{\text{L}} + \epsilon_{\text{R}}) = \Delta\epsilon/\epsilon$]. Both neutral and oxidized H-PEDOTs showed g_{abs} 10^{-3} – 10^{-2} in the absorption region. The g_{abs} of the H-PEDOT in neutral state prepared in a highly twisted N*-LC (system 3, including D3) was larger than that of the H-PEDOT prepared using systems

1 and 2 (Table 2). Based on these measurement results, the H-PEDOT films could be considered as chiral carbonization precursors with an interchain helically π -stacked structure.

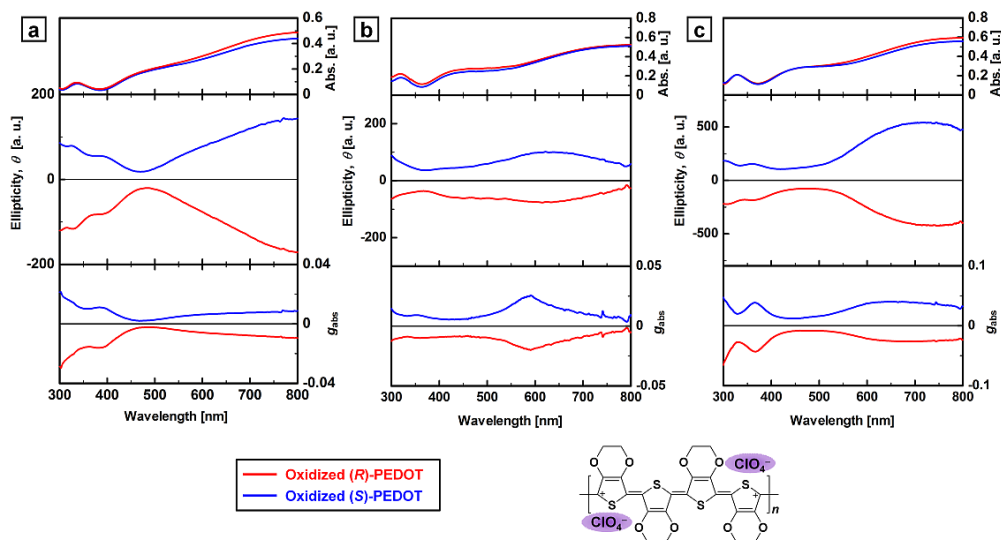


Figure 3. UV-vis, CD, and g_{abs} spectra of the oxidized H-PEDOT films prepared in N*-LCs using (*R*)- and (*S*)- (a) D1, (b) D2, and (c) D3. [polymerization; 5CB : D1, D2, or D3 : bis-EDOT : TBAP = 100 : 1 : 2 : 0.2, ITO glass (anode), ITO glass (cathode), 4 V, 5 min, 20 °C].

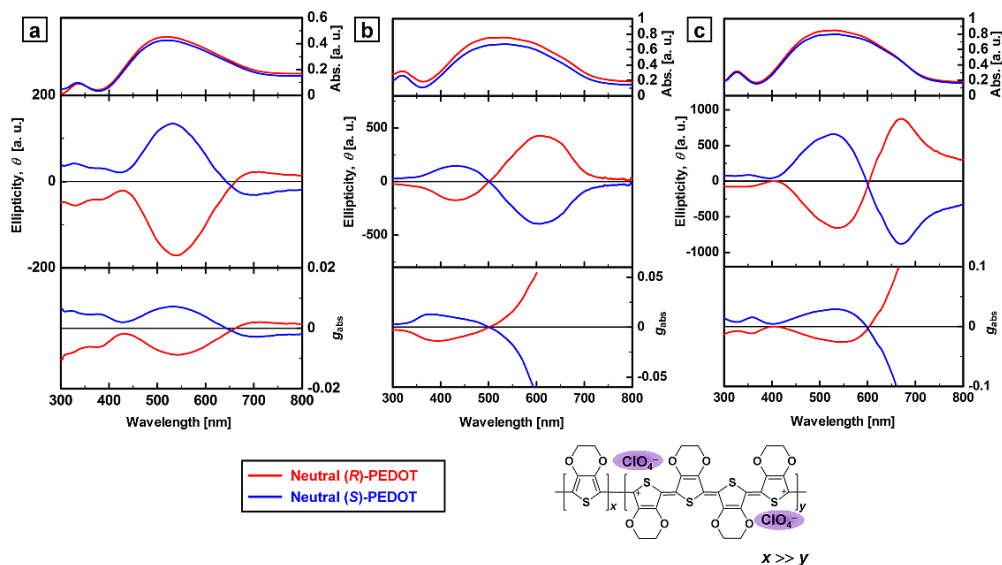


Figure 4. UV-vis, CD, and g_{abs} spectra of the neutral H-PEDOT films synthesized in N*-LCs using (R)- and (S)- (a) D1, (b) D2, and (c) D3 [polymerization; 5CB : chiral dopant : bis-EDOT : TBAP = 100 : 1 : 2 : 0.2, ITO glass (anode), ITO glass (cathode), 4 V, 5 min, 20 °C] [de-doping; TBAP: 0.05 M, in ACN, Pt wire (anode), ITO glass (cathode), 4 V, 5 min, room temperature].

Table 2. The g_{abs} evaluated values from the CD spectra of the H-PEDOT films.

N*-LCs				g_{abs} (wavelength/nm) ^a	
chiral dopants	system			oxidized H-PEDOT	neutral H-PEDOT
di-substituted	D1	1	R	-9.3×10^{-3} (780)	-8.8×10^{-3} (540), $+2.1 \times 10^{-3}$ (710)
			S	$+8.6 \times 10^{-3}$ (780)	$+7.2 \times 10^{-3}$ (530), -2.9×10^{-3} (710)
	D2	2	R	-2.0×10^{-2} (591)	-1.4×10^{-2} (394), $+5.4 \times 10^{-2}$ (601)
			S	$+2.6 \times 10^{-2}$ (591)	$+1.3 \times 10^{-2}$ (383), -6.0×10^{-2} (594)
tetra-substituted	D3	3	R	-2.6×10^{-2} (669)	-2.6×10^{-2} (548), $+9.9 \times 10^{-2}$ (665)
			S	$+4.0 \times 10^{-2}$ (657)	$+2.9 \times 10^{-2}$ (532), -9.9×10^{-2} (660)

^a Wavelength at which g_{abs} was evaluated. Although the oxidized H-PEDOT films show absorption bands and Cotton effects in the visible to near-infrared region, the g_{abs} values were evaluated in the visible region because of the limitation of CD measurements.

2.12. Morphologies of H-PEDOT Films. The H-PEDOT film exhibited a multidomain morphology, which resembled the texture of the N*-LC reaction field from POM observation. Figure 5 showed the POM and SEM images of the H-PEDOTs prepared in the N*-LC systems. SEM observation indicates the morphology of a large spiral morphology domain that consisted of a fibrous structure (Figure S6 in the Supporting Information). The fibril morphology was not found in the case of preparing H-PEDOT when mono-EDOT used as a monomer.⁵³ This result correlates with the polymerization of mono-EDOT in ACN (Figure S2a in the Supporting Information). The fibrous morphology was also found in the PEDOT film prepared by using the N-LC with bis-EDOT as a monomer (Figure S7 in the Supporting Information). The distances between the fibril bundles (system 1: 1.5–1.6 μm ; system 2: 0.9–1.0 μm ; system 3: 150 nm) are practically the half-helical pitch of the N*-LC systems (system 1: 1.6 μm ; system 2: 0.9 μm ; system 3: 170 nm).⁵⁴ The screw direction of the spiral morphology is shown in the Table S1 in the Supporting Information).⁵⁵

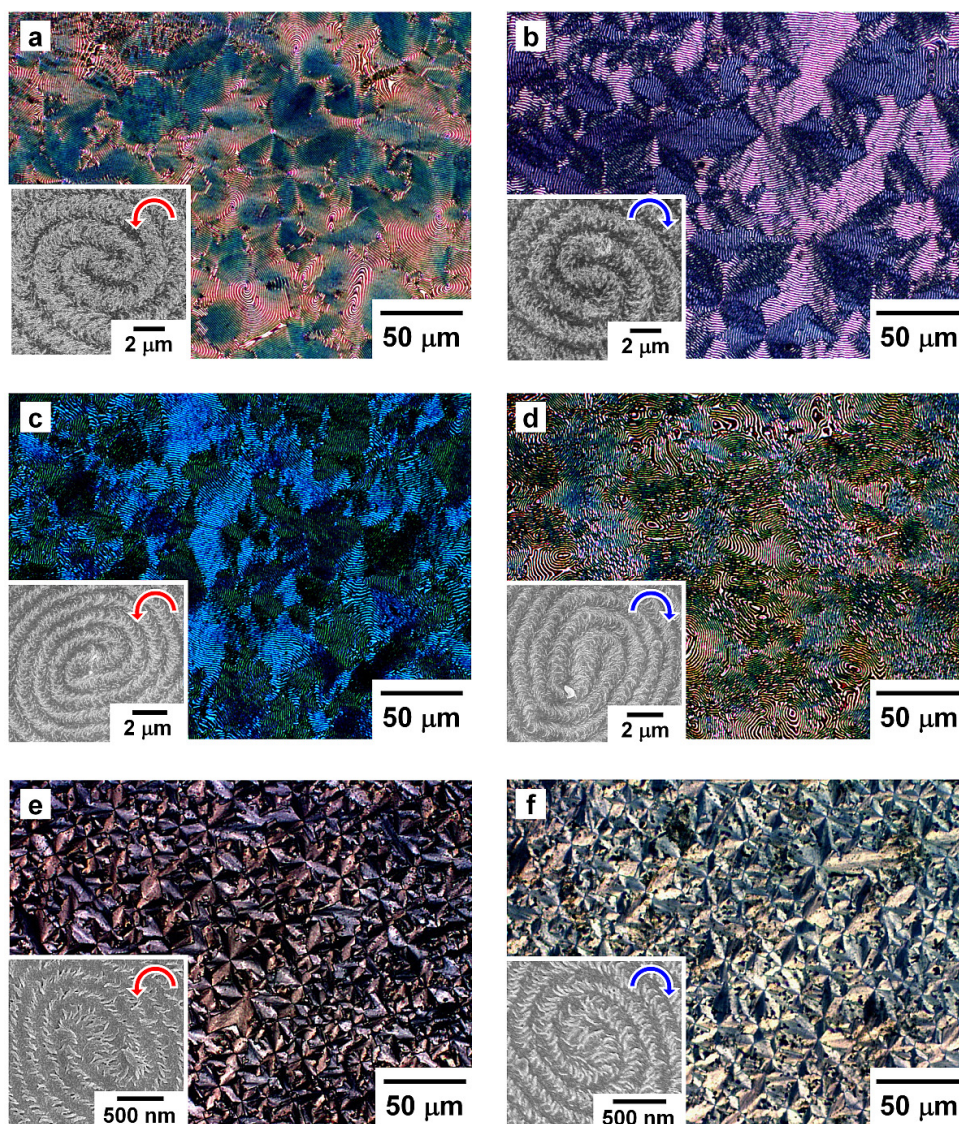


Figure 5. POM images of the oxidized H-PEDOT films prepared in N*-LCs using (*R*)- and (*S*)- (a,b) D1, (c,d) D2, and (e,f) D3 [polymerization; 5CB : chiral dopant : bis-EDOT : TBAP = 100 : 1 : 3 : 0.5, ITO glass (anode), ITO glass (cathode), 4 V, 5 min, 20 °C]. The insets show the magnified SEM images.

2.13. Carbonization of the H-PEDOT Films. Helical carbon films were produced via heat treatment of the H-PEDOT films at high temperatures. The XRD analyses for the Graphite-*O* and Graphite-*N* films showed that the Graphite-*O* has a higher

crystallinity than Graphite-*N* as described in previous reports.³³ Because of this, helical graphite films with a higher crystallinity were prepared using oxidized H-PEDOT films as precursors. To produce the helical carbon film, quartz and carbon plates were used as the substrates because of their high heat resistance. However, the difference in thermal shrinkage between the substrate and the H-PEDOT film during the heat treatment made it difficult to observe the screw directions of the spiral morphologies. In this work, the oxidized PEDOT film synthesized in ACN was used as an advanced substrate instead of quartz plate. The use of the oxidized PEDOT film as the carbonization substrate, which had almost the same thermal shrinkage as the oxidized H-PEDOT film, is anticipated to reduce the thermal shrinkage deformation during heat treatment. Therefore, the H-PEDOT film was transferred from the ITO glass substrate to the oxidized PEDOT film via a washing procedure and dried for several hours before carbonization. It was assumed that the carbon film prepared from the above H-PEDOT film would give an elemental analysis result very close to that of the carbon film prepared from the oxidized PEDOT film synthesized in ACN (Figure S8 in the Supporting Information).

2.14. Morphologies of the H-Carbon-*O* Films. Surprisingly, after the heat treatment at 800 °C, the morphology of the original oxidized H-PEDOT film was completely remained. SEM images of the H-Carbon-*O* films are shown in Figure 6. The H-Carbon-*O* films produced from the (*R*)- and (*S*)-PEDOT films showed left- and right-hand spiral morphology, respectively. The helical senses of the spirals are controllable by the chirality of the chiral dopant. The distances between the bundles were 0.13–1.6 μm can also be changing by the type and amount of the chiral dopants.

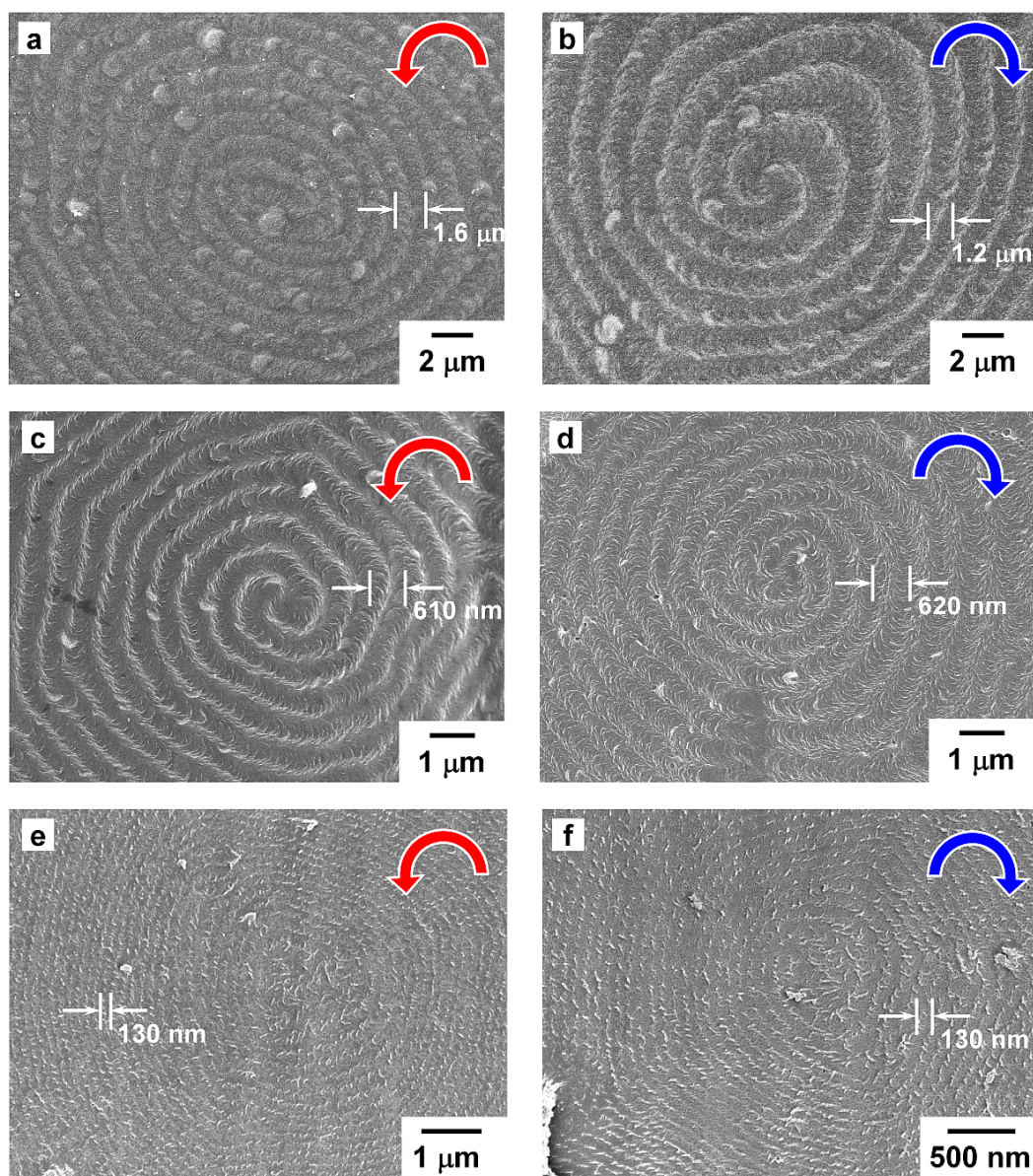


Figure 6. SEM images of the left- and right-handed H-Carbon-*O* films repared using (a) (*R*)- and (b) (*S*)-N*-LCs of system 1, (c) (*R*)- and (d) (*S*)-N*-LCs of system 2, and (e) (*R*)- and (f) (*S*)-N*-LCs of system 3.

2.15. Preparation and Morphologies of the Helical Graphite Films. Subsequently, the helical graphite films were produced via a heating process of the helical carbon films at 2600 °C (Figure 7). Figure 8 showed the SEM images of the H-Graphite-*O* films that were prepared using the N*-LC of systems 1, 2, and 3 containing the chiral dopant of (*R*)- and (*S*)-D1, D2, and D3. The graphite films prepared via heat treatment at 2600 °C have almost the identical spiral morphology from the H-PEDOT film and the H-Carbon-*O* film produced at 800 °C, i.e., large domains of left- and right-handed spiral morphologies containing fibril bundles. On average, the distances between the fibril bundles in the H-Carbon-*O* films decreased by 20% compared to these in the H-PEDOT films upon heat treatment at 800 °C. In contrast, the distances of the helical graphite films decreased by 50% compared to those of the helical carbon films after heat treatment at 2600 °C. These results show that the thermal shrinkage during graphitization is larger. The distances between the fibril bundles in the H-PEDOT, carbon, and graphite films are summarized in Table 3. The oxidized PEDOT film, as an advanced carbonization substrate, serves to reduce the thermal shrinkage deformation of the graphite film during heat treatment. This is why the graphite film prepared from the highly twisted H-PEDOT still preserves the morphology of the precursor after graphitization at 2600 °C.

Table 3. Half-helical pitches of the N*-LC systems and the distances between the fibril bundles of the helical PEDOT, carbon, and graphite films.

N*-LCs			distances between the fibril bundles (μm) ^a		
chiral dopants	system	half-helical pitch (μm)	helical PEDOT	helical carbon	helical graphite
di-substituted	D1	R: 1.6	1.6	1.6	0.82
		S: 1.6	1.5	1.2	0.63
	D2	R: 0.90	0.91	0.61	0.37
		S: 0.85	1.0	0.62	0.38
tetra-substituted	D3	R: 0.17	0.15	0.13	0.055
		S: 0.17	0.15	0.13	0.055

^a The distances were estimated from SEM images.

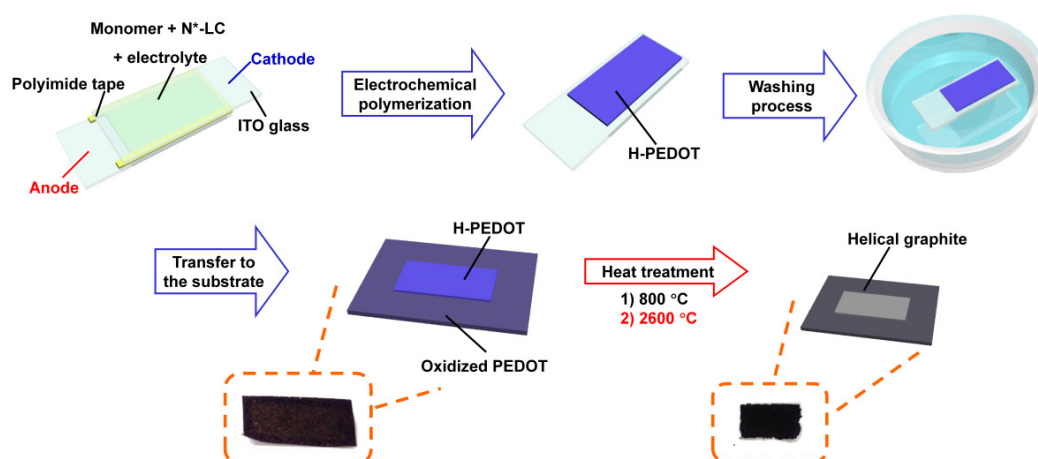


Figure 7. Schematic representation of the preparation of the helical graphite using an oxidized PEDOT film as a substrate.

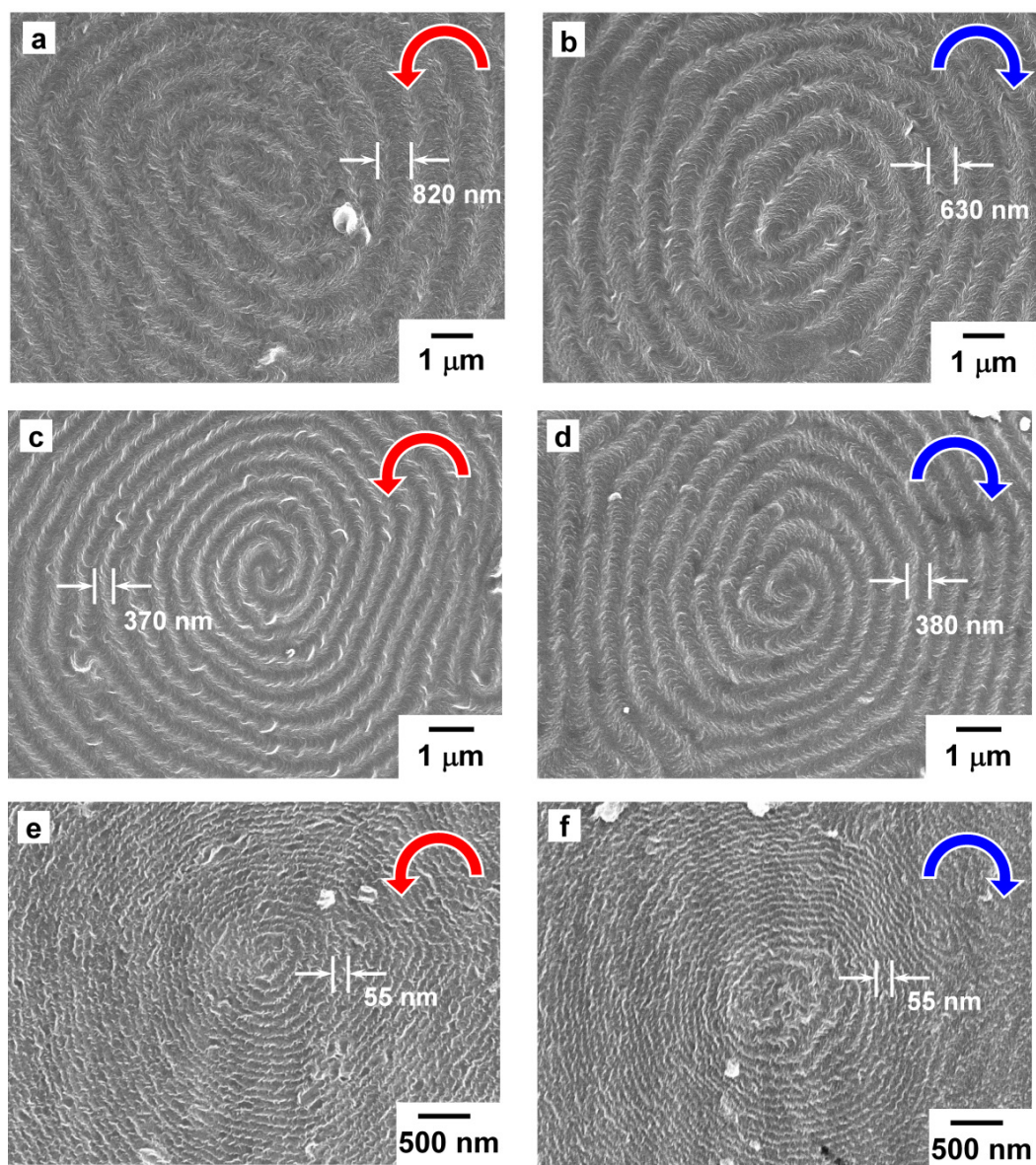


Figure 8. SEM images of the left- and right-handed H-Graphite-*O* films prepared using (a) (*R*)- and (b) (*S*)-N*-LCs of system 1, (c) (*R*)- and (d) (*S*)-N*-LCs of system 2, and (e) (*R*)- and (f) (*S*)-N*-LCs of system 3.

3. Conclusions

H-PEDOT films prepared in an N*-LC asymmetric reaction field via an electrochemical oxidative polymerization had clearly spiral morphologies consisting of fibril bundles. Three types of chiral dopants were used to control the distances between the fibril bundles and the screw direction in the spiral morphology. The (*R*)- and (*S*)-H-PEDOT films exhibited Cotton effects with mirror images in the CD measurement, irrespective of the neutral and oxidized form, upon optimization of the aging time and cooling rate of the N*-LC systems before polymerization. From the results of SEM observation, the spiral morphology of H-PEDOT film remained completely in the helical carbon and graphite films after the heat treatment. This is because of the advanced carbonization substrate, an oxidized PEDOT film. A graphite film with well-controlled helical morphologies may exhibit unique electrochemical properties characteristic of the helical structure, diamagnetism, and electrical conductivity.

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Chapter 2 Appendix

Materials and Measurements

1. Materials

2. Measurements

Polymerization of bis-EDOT in N*-LC

Supporting References

Supporting Figures

Materials and Measurements

1. Materials. The chemical compounds were purchased from commercially available sources and were used as received. The compounds, *n*-butyllithium (*n*-BuLi), hydrochloric acid (HCl), sodium (Na), sodium chloride (NaCl), sodium hydride (NaH), sodium hydrogen carbonate (NaHCO₃), sodium sulfate (Na₂SO₄), and triphenylphosphine (TPP) were purchased from Nacalai Tesque, Inc. The compounds, 4-cyano-4'-hydroxybiphenyl, 6-bromo-1-hexanol, 12-bromo-1-dodecanol, tetra-*n*-butylammonium perchlorate (TBAP), trimethylborate, 18-crown-6-ether, 4-cyano-4'-*n*-pentylbiphenyl (5CB), diethyl azodicarboxylate (DEAD), 3,4-ethylenedioxythiophene (EDOT), and tetrakis(triphenylphosphine)palladium(0) [(TPP)₄Pd] were purchased from Tokyo Chemical Industry Co., Ltd. The compounds, bromine (Br₂), calcium hydride (CaH₂), chloromethylmethylether, copper(II) chloride (CuCl₂), magnesium (Mg), and potassium carbonate (K₂CO₃) were purchased from Wako Pure Chemical Industries, Ltd.

Para-(*trans*-4-*n*-pentylcyclohexyl)bromobenzene, *para*-(*trans*-4-*n*-pentylcyclohexyl)phenol (PCH500), and cholesteryl oleyl carbonate were purchased from Kanto Chemical Co., Inc. The compounds, (*R*)-(+)- and (*S*)-(-)-1,1'-bi-2-naphthols (optical purity, 0.99) were purchased from commercially available sources. Acetone, acetonitrile (ACN), and chloroform (CHCl₃) (Nacalai Tesque, Inc.) were used as received. Tetrahydrofuran (THF) and dichloromethane (CH₂Cl₂) used in the reactions were distilled from sodium and calcium hydride as drying agents under argon gas before use, respectively. EDOT was distilled under reduced pressure in argon gas atmosphere before use (b.p. = ~200 °C/760 mmHg, 112 °C/20 mmHg). Indium-tin oxide (ITO) glass was purchased from Furuuchi Chemical Co. (10 Ω/cm²). Platinum (Pt) wire (Pt counter electrode for VC-2 cell) and mesh (Platinum gauze electrode 80 mesh) were purchased from BAS, Inc. A polyimide tape (P-221, thickness: 69 μm) was purchased from Nitto Denko, Co. NdFeB magnets (360 mT, 15 × 10 × 5 mm) were purchased from Niroku seisakusho Co., Ltd.

2. Measurements. Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using a JEOL EX-400 and an AL-400 NMR spectrometer. Chemical shifts are represented in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed at the Center for Organic Elemental Microanalysis of Kyoto University. Before the elemental analyses, the poly(3,4-ethylenedioxythiophene)s (PEDOTs) were dried through vacuum pumping for several hours at 90 °C (b.p. of ACN: 82 °C). The molecular ratio of doped perchlorate ion (ClO₄⁻) to EDOT unit in the PEDOT film (ClO₄⁻/EDOT) was calculated from the elemental analysis. The sum of all the

elements is assumed to be 100%. High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (ESI) and JEOL JMS-MS700 (EI).

The microscope observation was carried out under crossed nicols using a Carl Zeiss Axio Imager M1m polarizing microscope equipped with a Carl Zeiss AxioCam MRc5 digital camera and a temperature control system configured by a THMS600 heating and cooling stage, type 10002, connected to an LNP94/2 liquid nitrogen cooling system (Linkam). The chiral nematic liquid crystal (N*-LC) for observations with polarizing optical microscope (POM) was sandwiched between two cover glasses. The phase transition temperatures of LC were determined by POM.

The helical senses of the N*-LCs were determined through the miscibility test (contact method).¹⁻² The miscibility test is based on the observation of the mixing area between the N*-LC and the standard LC in POM. Cholesteryl oleyl carbonate is known to be a left-handed N*-LC (cholesteric LC), and therefore it is useful for the standard LC for the miscibility test. If the helical sense of the N*-LC is the same as that of the standard LC, the mixing area will be continuous. Otherwise, it will be discontinuous (shown as a Schlieren texture of the N-LC).

The helical pitches of N*-LCs were precisely evaluated by measuring the distance between Cano lines appearing on the surface of a wedge-type cell (EHC, KCRK-03, $\tan\theta = 0.0078$) under the POM.³⁻⁷ This method is based on the observation of the distance between the discontinuity lines that appear when the N*-LC is inserted into a cell with a thickness gradient. Meanwhile, when the helical pitch was smaller than 1 μm , it was evaluated with the selective light-reflection method at room temperature. The helical pitch was evaluated according to the equation, $p = \lambda_{\text{max}}/n$, where λ_{max} is the

center wavelength for the maximally reflected light, and n is the mean refraction index of N*-LC ($n \cong 1.5$).⁷⁻⁹

The helical twisting power (HTP; β_M) of chiral dopant, i.e., an ability to convert N-LC into N*-LC, was evaluated in N-LC of 5CB using, $\beta_M = (pcr)^{-1}$, where p is the helical pitch in micrometers, c is the molar concentration of the chiral dopant in the N*-LC represented as (mole of chiral dopant)/(mole of 5CB), and r is the enantiomeric purity of the chiral dopant; here, r is assumed to be 1.

Thermal behavior of PEDOTs was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with alumina pan. Before the TG-DTA measurements, the PEDOT films were dried through vacuum pumping for several hours at 90 °C.

The film thickness was measured using Nikon Digimicro digital length measuring system with DIGIMICRO MH-15M, DIGIMICRO STAND MS-5C, and DIGITAL READOUT UC-101.

The electrical conductivity of the PEDOT and carbon films was measured at room temperature using a low resistivity meter, Loresta GP with a MCP-TP06P probe (Mitsubishi Chemical Analytech).

Ultraviolet–visible (UV–vis) and circular dichroism (CD) spectra were measured using JASCO V570 and JASCO J820 spectrometers, respectively.

Optical purity of the chiral compounds were evaluated with specific rotation measured by JASCO P2300 polarimeter.

The accelerating voltage of field emission (FE)-SEM (JSM-7500F, JEOL) was 2–10 kV. The PEDOTs and carbon films were coated with Pt or Pt-Pd alloy using an ion

coater with type of JFC-1600 (JEOL) before measurements of SEM. The coating thickness was evaluated to be ca. 5 nm. The distance between the fibril bundles of the helical PEDOT (H-PEDOT) and carbon films was estimated from SEM images.

The electrochemical polymerization was performed using 0–30 V 2.5 A direct current (DC) power supply (CPS-3025L, CUSTOM).

The carbon films were prepared by using an electric furnace (KDF75, Denken). The graphite films were prepared by using a graphitization apparatus [SCC-U-80/150 (2P), Kurata-giken].

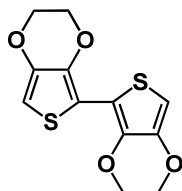
Carbonization and graphitization yields were evaluated using the equations, (weight of carbonized PEDOT)/(weight of PEDOT)×100 and (weight of graphitized film)/(weight of carbon film)×100, respectively.

Polymerization of bis-EDOT in N*-LC

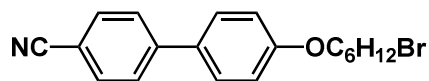
The H-PEDOT films were synthesized via electrochemical polymerizations in N*-LCs as asymmetric reaction fields. The N*-LC solutions were prepared by adding 1 mol % of D1, D2 or D3, 3 mol % of bis-EDOT, and 0.5 mol % of TBAP into 5CB. The bis-EDOT shows good affinity for N-LC due to its rod-like structure. The N*-LC solution was heated up to an isotropic phase temperature in order to dissolve the monomer, the electrolyte, and the chiral dopant completely in 5CB. The N*-LC solution containing the monomer was injected into a cell composed of sandwiched ITO glasses with a polyimide tape as a spacer. The spacer thickness was ~140 μm. The cell including the N*-LC solution was heated to 50 °C for a few minutes and then cooled to 20 °C with cooling rate of 5 °C/min to give the N*-LC with multidomain structure. The N*-LC was aged for 40 min. Figure 2 shows POM images of the

N*-LC solutions of systems 1, 2 and 3 including bis-EDOT and TBAP, before the electrochemical polymerizations. The N*-LC solution in the cell showed a fingerprint texture at 20 °C. The N*-LC solutions containing the monomer and the electrolyte showed no noticeable change in their optical texture (helical pitch) (see previous report¹⁰ for systems 1 and 3, and Figure S9 for system 2) and only a slight lowering of the transition temperature by 5–6 °C (see Figures 2 and S5). DC voltage of 4 V was applied to the cell for 5 min. Polymerization temperature was 20 °C. As the polymerization proceeded, the optical texture of the N*-LC solution became darker owing to the formation of polymer. As a result of the polymerization, a polymer film with dark blue color was deposited on the inner glass of the cell. It should be noted that the PEDOT films obtained are LC-free samples. The film is washed sequentially with ACN, hexane, and methanol in this order to remove the N*-LC electrolyte after the electrochemical polymerization. The film was dried through vacuum pumping for several hours.

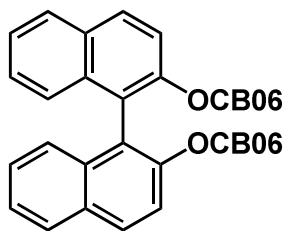
Synthesis

2,2'-Bis(3,4-ethylenedioxythiophene) (bis-EDOT)

To a three-necked round bottom flask containing 15 mL of anhydrous THF under argon purge was added 1.10 g (7.77 mmol) of EDOT. The solution was cooled to -78 °C by means of a dry ice/ethanol (EtOH) bath. To the solution was added 5 mL of *n*-BuLi (1.6 M in hexanes). The resulting solution was stirred for 45 min at -78 °C, after which, 1.11 g (8.23 mmol) of CuCl_2 was added in one portion. The solution was slowly heated up to 45 °C and stirred for a further 2 h. The solution was then poured into water to yield a dark green precipitate, which washed with dichloromethane, dissolved in chloroform and pass through a dry flash silica column using chloroform as the eluent. The crude product was further purified by recrystallization in EtOH affording a white solid with yield of 53% (0.59 g). Anal., calcd for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$: C, 51.05; H, 3.57; O, 22.67; S, 22.71. Found: C, 50.78; H, 3.61. MS (EI) calcd for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$: 282.00. Found: 282.0009. ^1H NMR (CDCl_3 , 400 MHz): δ 4.24 (m, 4H, $-\text{OCH}_2-$), 4.31 (m, 4H, $-\text{OCH}_2-$), 6.27 (s, 2H, ThH). ^{13}C NMR (CDCl_3 , 100 MHz): δ 64.5, 64.9, 97.4, 109.8, 136.9, 141.1.

4'-((6-bromohexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (CB06Br)

TPP (7.39 g, 28.2 mmol) and 4-cyano-4'-hydroxybiphenyl (5.00 g, 12.6 mmol) were added under argon gas into a 300 mL three-necked flask, dissolved in THF (40 mL). In the addition funnel, a mixture of DEAD (12.27 g, 40 wt % in toluene, 28.2 mmol), 6-bromo-1-hexanol (4.64 g, 25.6 mmol), and 10 mL of THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was stirred at room temperature for 24 h. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 , and the crude product was then purified by column chromatography using CHCl_3 as eluent. The product was recrystallized in ethanol and dried in vacuum, gave in 5.47 g, white and needle-shaped crystal (yield = 60%). Anal., calcd for $\text{C}_{19}\text{H}_{20}\text{BrNO}$: C, 63.70; H, 5.63; N, 3.91; Br, 22.30. Found: C, 63.91; H, 5.61; N, 3.94; Br, 21.52. MS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{BrNO}$: 357.07. Found: 357.07. ^1H NMR (CDCl_3 , 400 MHz): δ 1.53–1.56 (m, 4H, $-(\text{CH}_2)_2-\text{CH}_2\text{Br}$), 1.83–1.91 (m, 4H, $-(\text{CH}_2)_2-$), 3.43 (t, 2H, $J = 6.8$ Hz, $-\text{CH}_2\text{Br}$), 4.01 (t, 2H, $J = 8.0$ Hz, $-\text{OCH}_2-$), 6.99 (d, 2H, $J = 8.8$ Hz, *ortho*-PhH-O-), 7.53 (d, 2H, $J = 8.5$ Hz, *meta*-PhH-O-), 7.64 (d, 2H, $J = 8.28$ Hz, *meta*-PhH $\equiv\text{N}$), 7.69 (d, 2H, $J = 8.28$ Hz, *ortho*-PhH $\equiv\text{N}$). ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.31, 27.92, 29.07, 32.69, 33.69, 67.94, 110.16, 115.14, 119.07, 127.11, 128.36, 131.44, 132.58, 145.30, 159.76.

(R)-2,2'-CB06-1,1'-binaphthyl [(R)-D2]

(R)-D2 was synthesized as follows. The reagents CB06Br (1.57 g, 4.38 mmol), (*R*)-1,1'-bi-2-naphthol (0.50 g, 1.75 mmol), K_2CO_3 (1.23 g, 8.73 mmol), 18-crown-6-ether (catalyst amount, as phase transfer catalysts) and adequate acetone solvent (a little higher than the level of reagents) were added in a 100 mL flask. The solution was heated to 60 °C and refluxed under constant stirring for 24 hours. After evaporation of the solvent, the residue was washed with water and extracted with $CHCl_3$ (3×). The residue was dried over anhydrous Na_2SO_4 , and the crude product was then purified by column chromatography using $CHCl_3$ as eluent. The product was obtained by drying the viscous liquid in vacuum at 50 °C, gave in 1.39 g, white crystal (yield = 94%). Anal., calcd for $C_{58}H_{52}N_2O_4$: C, 82.83; H, 6.23; N, 3.33. Found: C, 82.68; H, 6.08; N, 3.34. MS (ESI) calcd for $C_{58}H_{52}N_2O_4$ $[M+Na^+]$: 863.38. Found: 863.38. 1H NMR ($CDCl_3$, 400 MHz): δ 0.92–1.55 (m, 16H, $-CH_2-$), 3.77 (t, 4H, $J = 6.6$ Hz, $-CH_2-O-$), 3.89–4.01 (m, 4H, $-O-CH_2-$), 6.92–7.92 (m, 28H, *PhH*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.42, 25.44, 28.97, 29.35, 67.96, 69.76, 110.17, 115.14, 116.02, 119.01, 120.95, 123.53, 125.57, 126.10, 127.08, 127.81, 128.31, 129.10, 129.39, 131.32, 132.58, 134.30, 145.29, 154.58, 159.83. $[\alpha]_D^{25} +16.2^\circ$ (*c* 1.00, $CHCl_3$).

(S)-2,2'-CB06-1,1'-binaphthyl [(S)-D2]

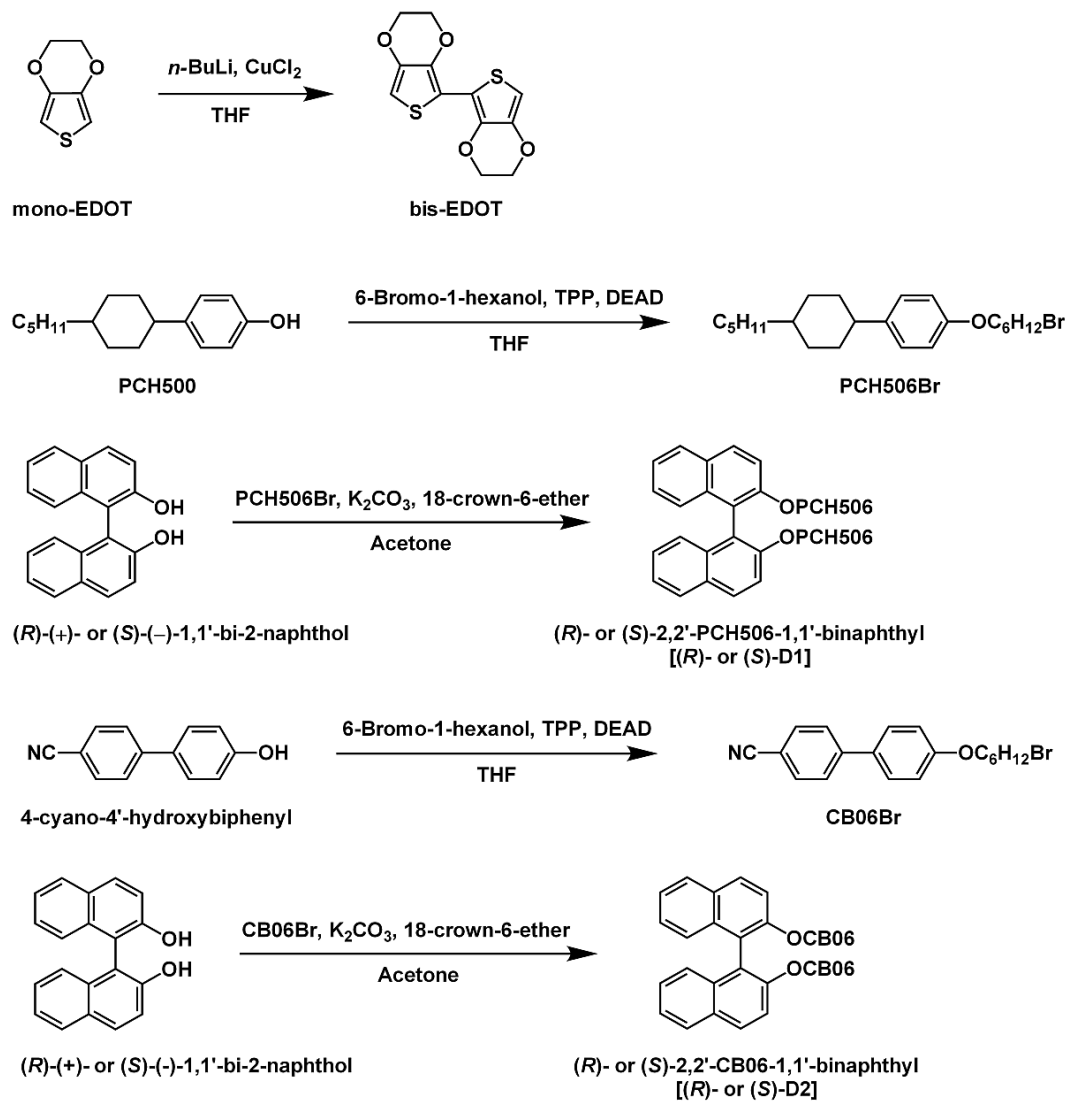
(S)-D2 was synthesized as follows. The reagents CB06Br (1.57 g, 4.38 mmol), (S)-1,1'-bi-2-naphthol (0.50 g, 1.75 mmol), K₂CO₃ (1.22 g, 8.73 mmol), 18-crown-6-ether (catalyst amount, as phase transfer catalysts) and adequate acetone solvent (a little higher than the level of reagents) were added in a 100 mL flask. The solution was heated to 60 °C and refluxed under constant stirring for 24 hours. After evaporation of the solvent, the residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄, and the crude product was then purified by column chromatography using CHCl₃ as eluent. The product was obtained by drying the viscous liquid in vacuum at 50 °C, gave in 1.11 g, white crystal (yield = 74%). Anal., calcd for C₅₈H₅₂N₂O₄: C, 82.83; H, 6.23; N, 3.33. Found: C, 82.70; H, 6.19; N, 3.35. MS (ESI) calcd for C₅₈H₅₂N₂O₄ [M+Na⁺]: 863.38. Found: 863.38. ¹H NMR (CDCl₃, 400 MHz): δ 0.92–1.55 (m, 16H, –CH₂–), 3.78 (t, 4H, *J* = 6.6 Hz, –CH₂–O–), 3.89–4.01 (m, 4H, –O–CH₂–), 6.92–7.92 (m, 28H, PhH). ¹³C NMR (CDCl₃, 100 MHz): δ 25.42, 25.44, 28.97, 29.35, 67.96, 69.75, 110.16, 115.13, 116.01, 119.07, 120.93, 123.52, 125.57, 126.10, 127.08, 127.81, 128.31, 129.10, 129.38, 131.31, 132.59, 134.28, 145.29, 154.57, 159.82. [α]_D²⁵₅₈₉ –16.7° (*c* 1.00, CHCl₃).

Supporting References

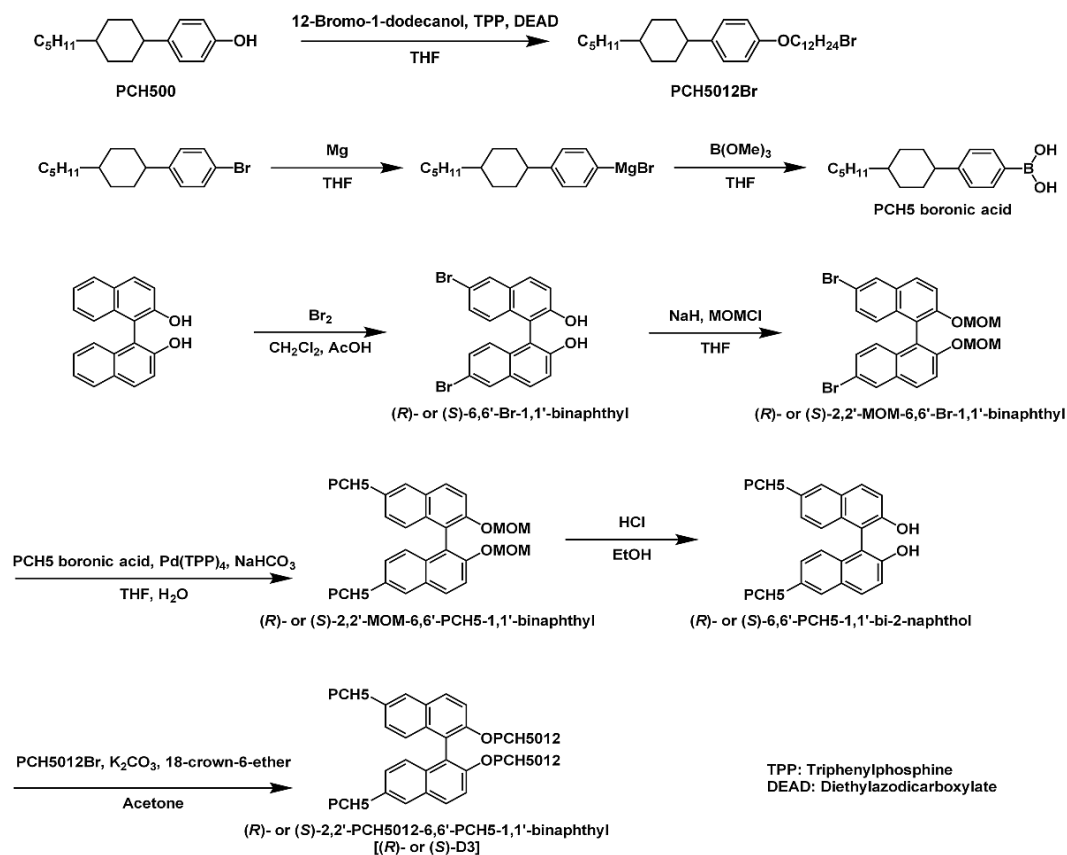
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Supporting Figures



(Continue)



Scheme S1. Synthetic routes of bis-EDOT and chiral dopants.

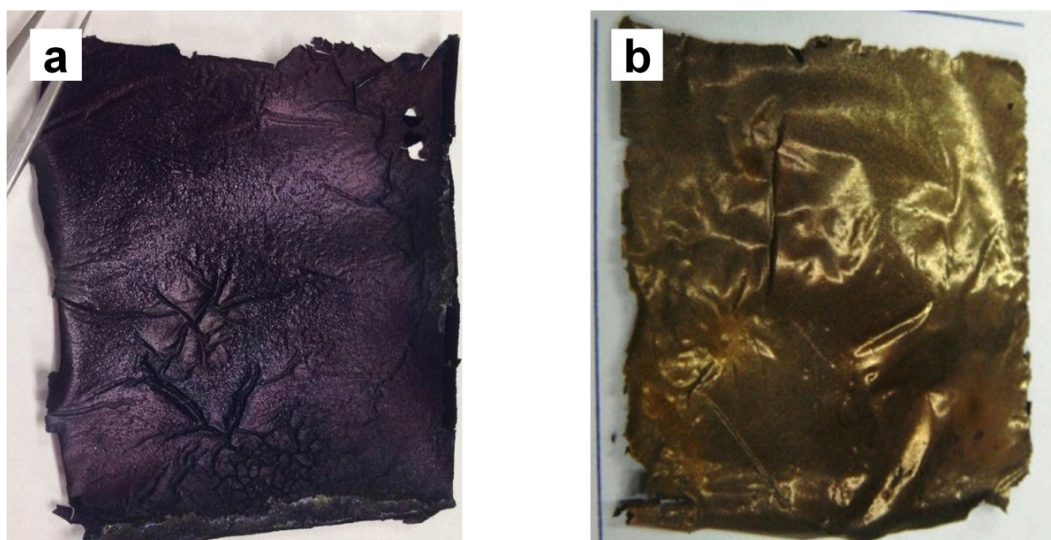


Figure S1. Photographs of the (a) oxidized [thickness: 67.7 μm , electrical conductivity (σ): 46 S/cm] and (b) neutral [thickness: 71.3 μm , σ : 1.1×10^{-4} S/cm] PEDOT films synthesized in ACN using mono-EDOT as a monomer [polymerization; mono-EDOT: 0.05 M, TBAP: 0.05 M, in ACN, ITO glass (anode), Pt mesh (cathode), 4 V, 30 min, room temperature] [de-doping; TBAP: 0.05 M, in ACN, Pt mesh (anode), ITO glass (cathode), 4 V, 20 min, room temperature].

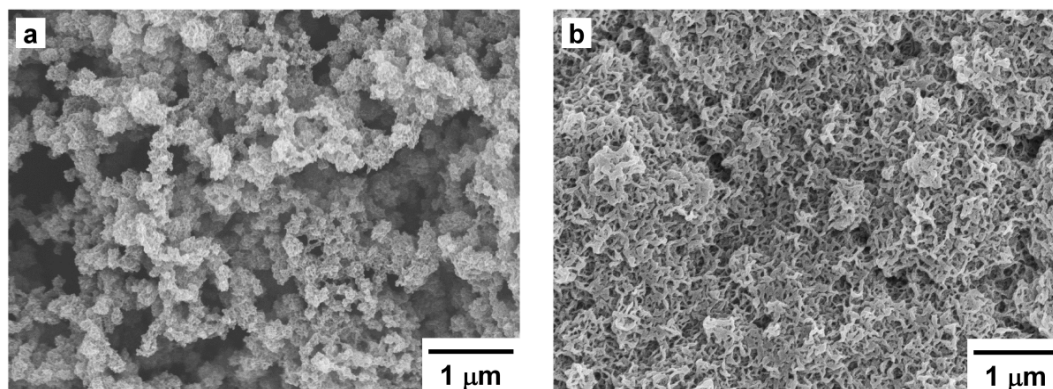


Figure S2. SEM images of the oxidized PEDOT films synthesized in ACN using (a) mono- and (b) bis-EDOT as monomers [mono- or bis-EDOT: 0.05 M, TBAP: 0.05 M, in ACN, ITO glass (anode), Pt mesh (cathode), 4 V, 20–30 min, room temperature].

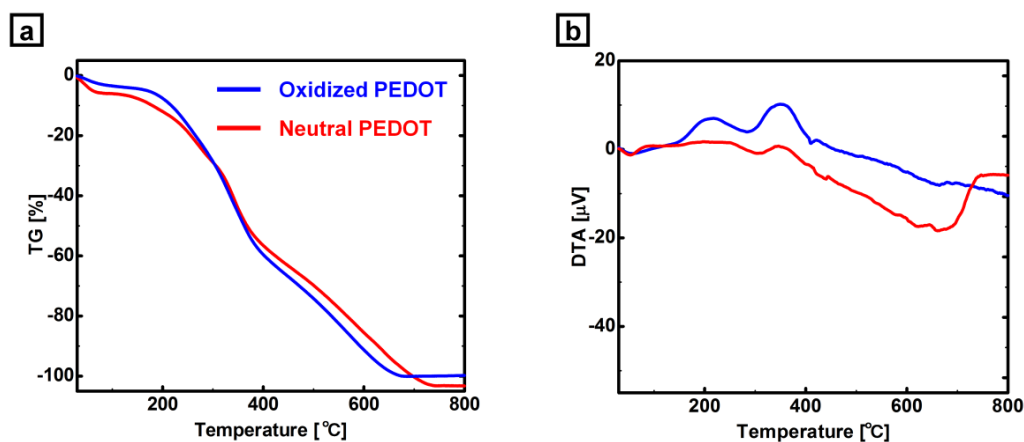


Figure S3. (a) TG and (b) DTA curves of the oxidized and neutral PEDOT films prepared using mono-EDOT as a monomer [polymerization; mono-EDOT: 0.05 M, TBAP: 0.05 M, in ACN, ITO glass (anode), Pt mesh (cathode), 4 V, 30 min, room temperature] [de-doping; TBAP: 0.1 M, in ACN, Pt mesh (anode), ITO glass (cathode), 4 V, 20 min, room temperature].¹¹

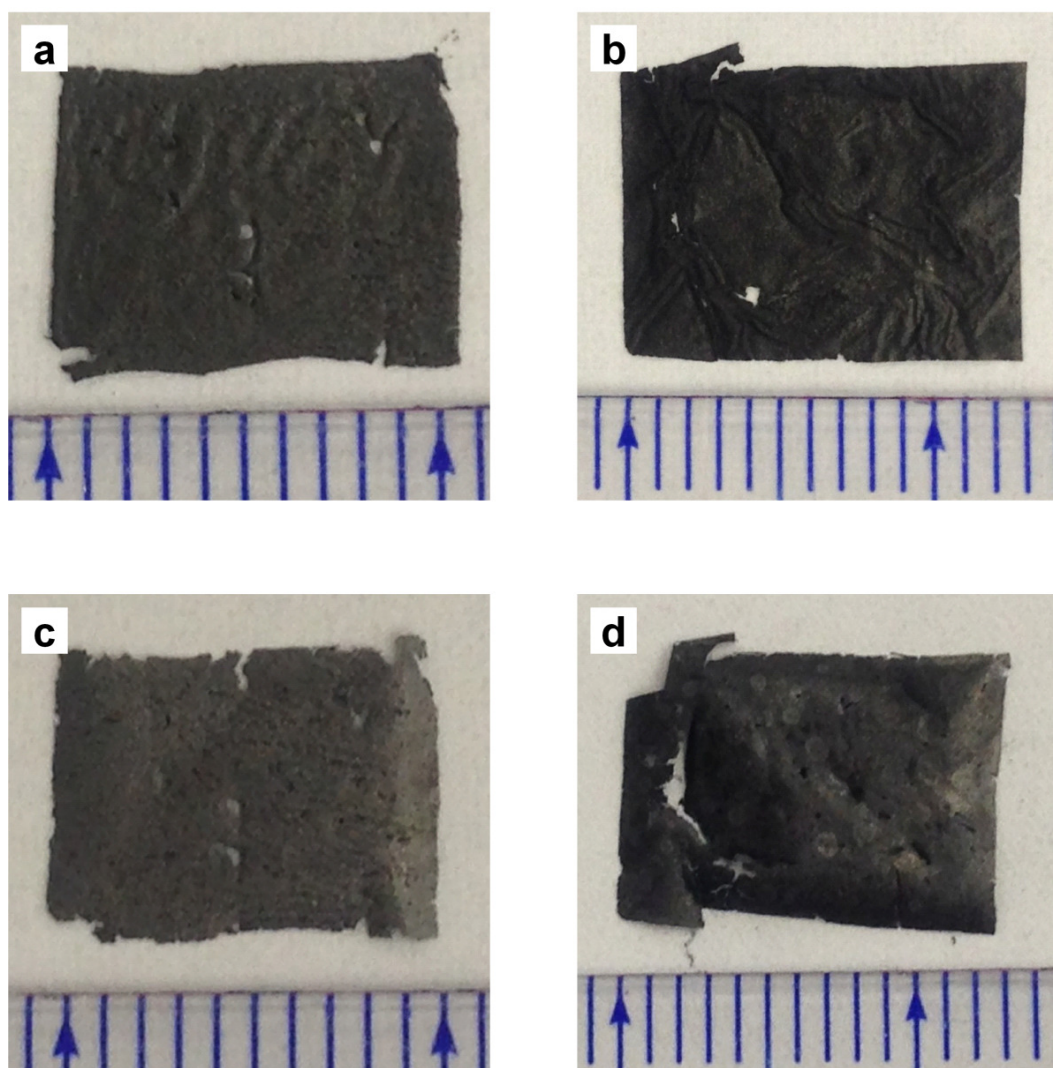


Figure S4. Photographs of the (a) Carbon-*O* [thickness: 43.5 μm , σ : 8.0×10^{-1} S/cm] and (b) Carbon-*N* [thickness: 32.6 μm , σ : 6.0×10^{-1} S/cm] films using mono-EDOT as a monomer. Photographs of the (c) Graphite-*O* and (d) Graphite-*N* films.

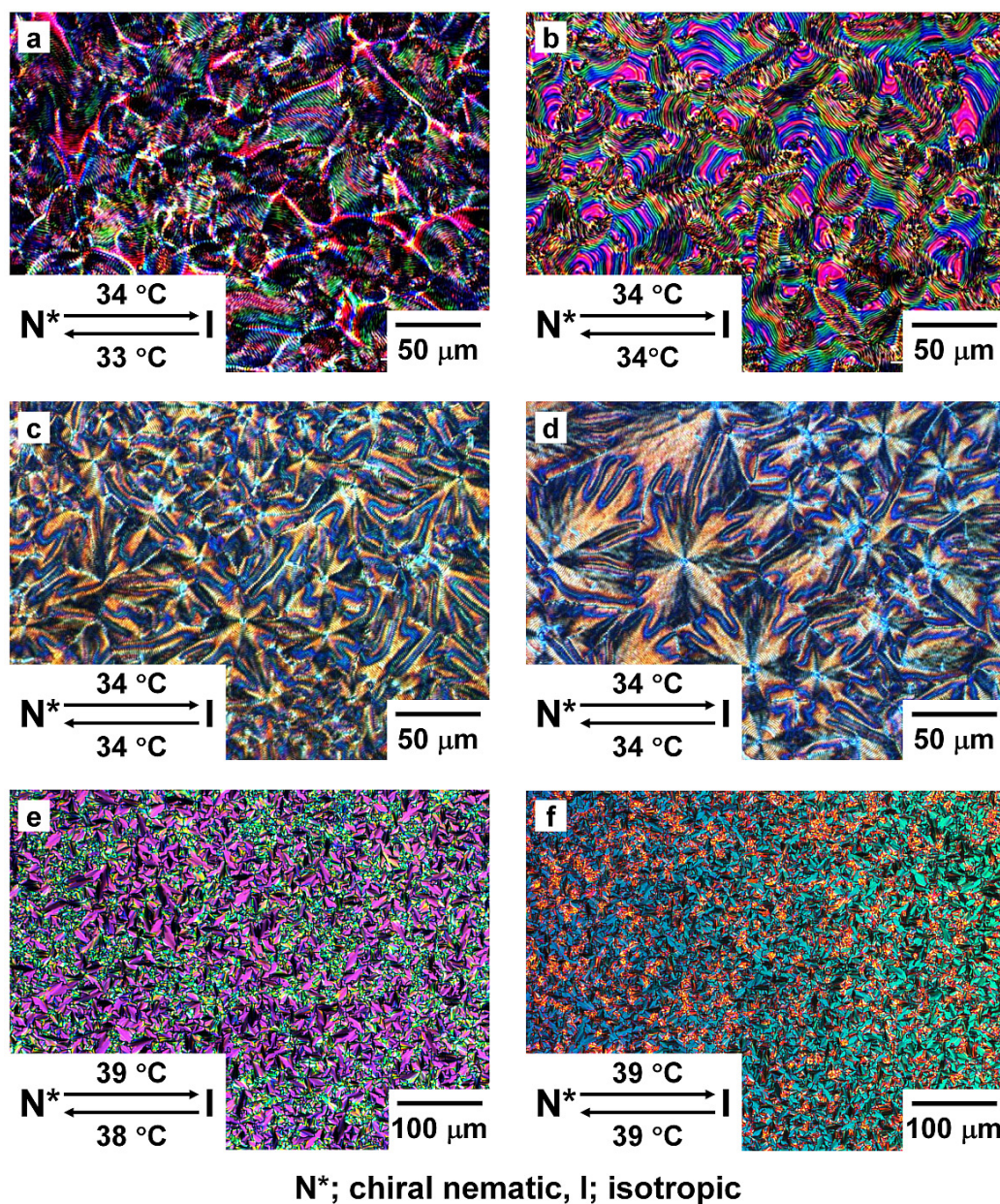


Figure S5. POM images of N*-LCs at 20 °C in cooling process prepared using (*R*)- and (*S*)- (a,b) D1, (c,d) D2, and (e,f) D3 [(a,b) system 1; 5CB : (*R*)- or (*S*)-D1 = 100 : 1 (mole ratio)] [(c,d) system 2; 5CB : (*R*)- or (*S*)-D2 = 100 : 1] [(e,f) system 3; 5CB : (*R*)- or (*S*)-D3 = 100 : 1].

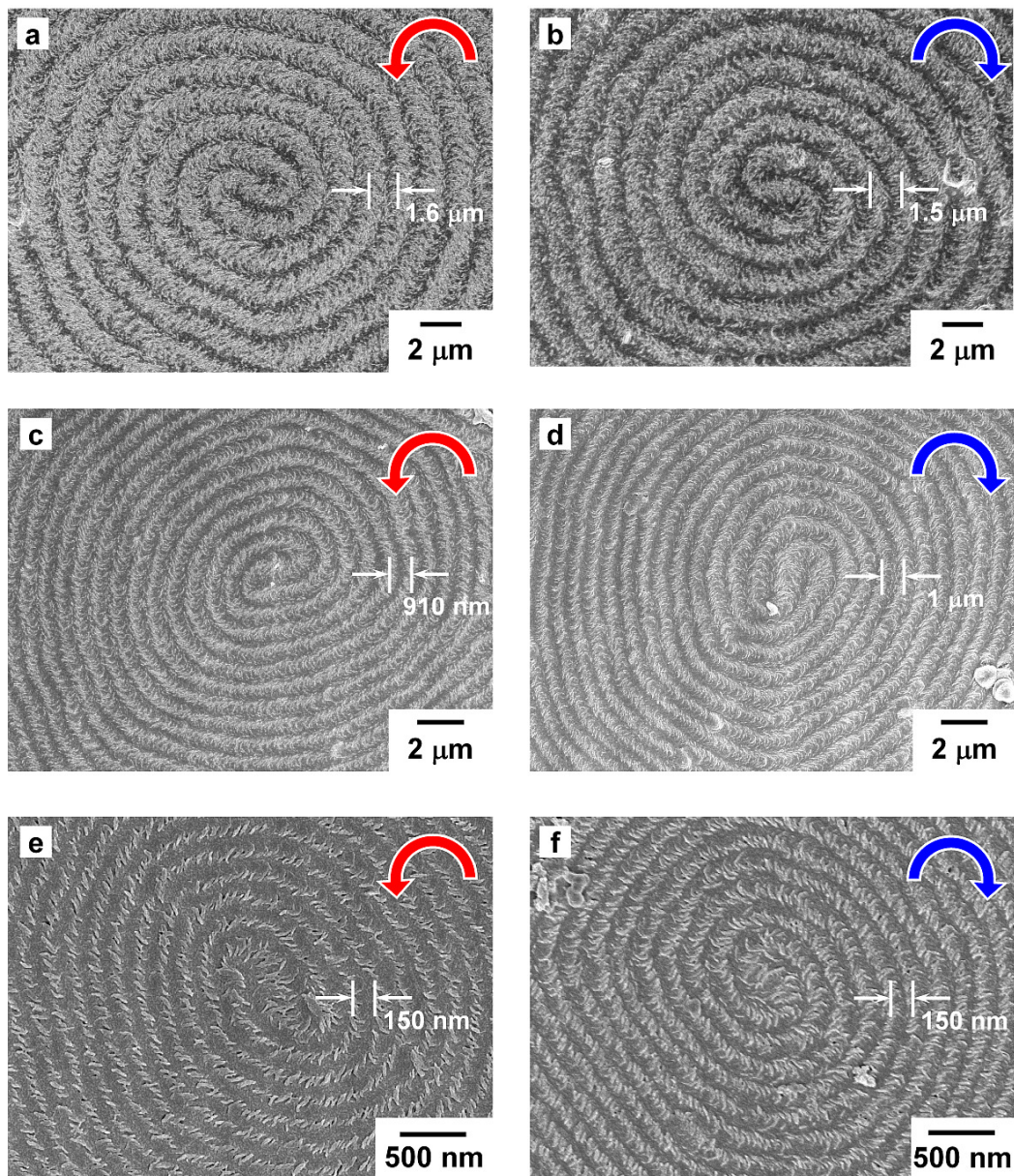


Figure S6. SEM images of the oxidized H-PEDOT films synthesized in N*-LCs using (R)- and (S)- (a,b) D1, (c,d) D2, and (e,f) D3 [polymerization; 5CB : chiral dopant : bis-EDOT : TBAP = 100 : 1 : 3 : 0.5, ITO glass (anode), ITO glass (cathode), 4 V, 5 min, 20 °C].

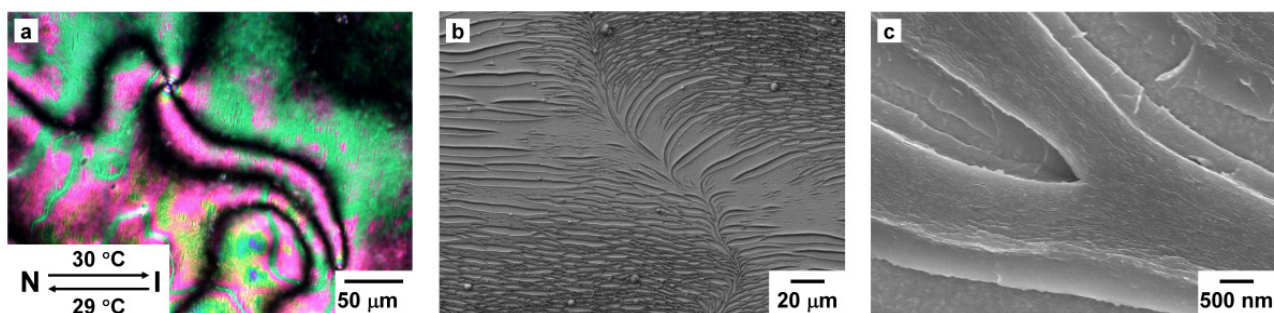


Figure S7. (a) POM image of N-LC system at 20 °C in cooling process. (b,c) SEM images of the oxidized PEDOT film synthesized in N-LC using bis-EDOT as a monomer [5CB : bis-EDOT : TBAP = 100 : 3 : 0.5, ITO glass (anode), ITO glass (cathode), 4 V, 5 min, 20 °C].



Figure S8. Photographs of (a) oxidized H-PEDOT film on the carbonization substrate (oxidized PEDOT film) and (b) these films after heat treatment at 2600 °C.

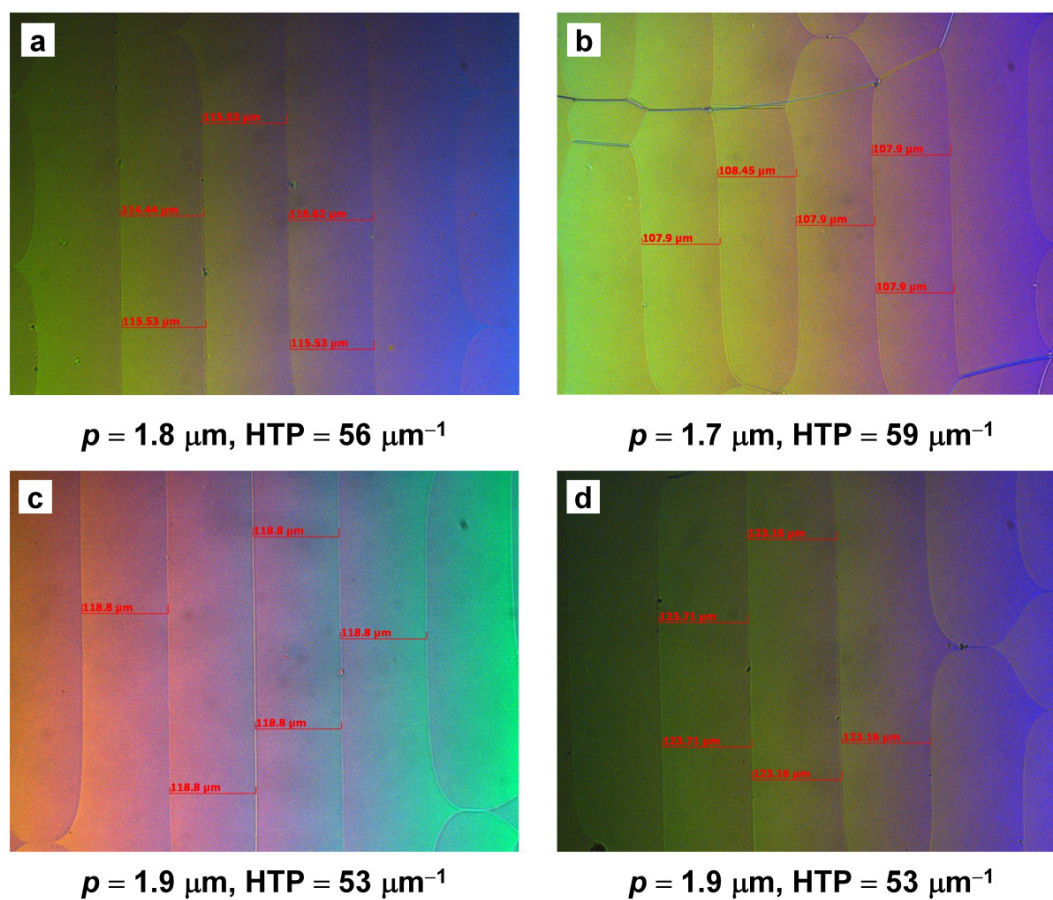


Figure S9. POM images of the N*-LC systems in Cano's wedge cell at 20 °C prepared using (a) (*R*)- and (b) (*S*)-D2 [system 2; 5CB : (*R*)- or (*S*)-D2 = 100 : 1]. POM images of N*-LC systems in Cano's wedge cell at 20 °C in cooling process prepared using (c) (*R*)- and (d) (*S*)-D2 [system 2; 5CB : (*R*)- or (*S*)-D2 : bis-EDOT : TBAP = 100 : 1 : 3 : 0.5].

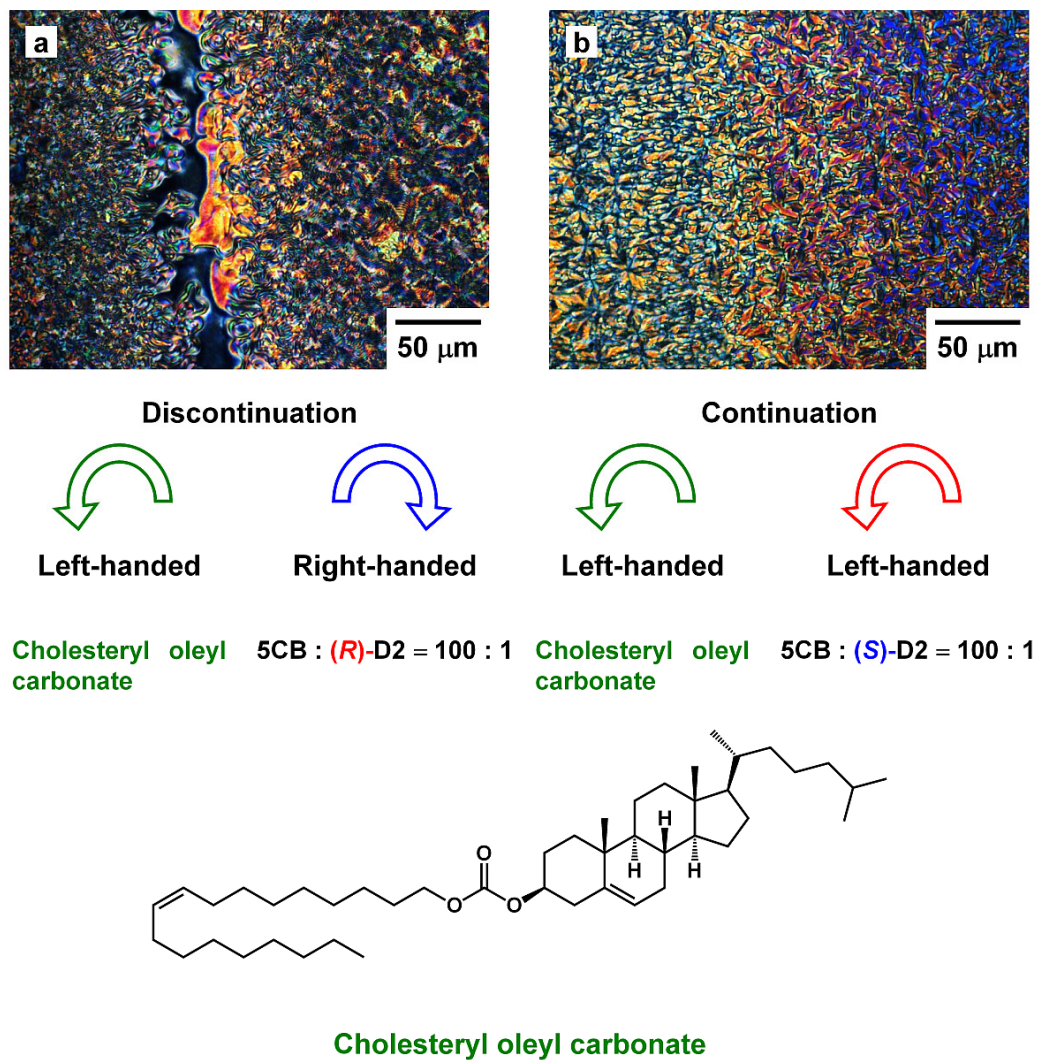


Figure S10. Miscibility tests between (a) (*R*)-N*-LC or (b) (*S*)-N*-LC and cholesteryl oleyl carbonate at 20 °C [system 2; 5CB : (*R*)- or (*S*)-D2 = 100 : 1].

Table S1. Screw direction of the chiral dopants and H-PEDOTs.

chiral dopants	helical sense of N*-LC ^a	helical sense of neutral H-PEDOT ^b	spiral of neutral and oxidized H-PEDOTs ^c
(<i>R</i>)-D1, (<i>R</i>)-D2, (<i>R</i>)-D3			
(<i>S</i>)-D1, (<i>S</i>)-D2, (<i>S</i>)-D3			

^a Helical senses of N*-LCs were determined by miscibility test. ^b Helical senses of H-PEDOT films were determined by CD measurements. ^c Screw directions of spirals of H-PEDOT films were determined by SEM images.

Chapter 3

Morphology-Controlled Carbonaceous and Graphitic Materials Prepared from Conjugated Polymers as Precursors through Solid-State Carbonization

1. Introduction

In modern carbon science, there are several newly discovered allotropes of carbon such as fullerenes, carbon nanotubes, and graphenes. There are also relatively classical carbon forms, such as diamonds, graphites, carbynes, and amorphous carbons, including carbon blacks. In the fundamental research of materials science, many types of carbon materials have been developed using various synthetic techniques for use in practical applications to satisfy future societal demands because of their exceptionally attractive properties. The carbonization of organic precursor materials is the simplest and the most basic technique for the facile production of carbon-rich materials [1]. The intrinsic properties of the carbon-based materials are largely dependent on the molecular structure and molecular ordering of the starting materials.

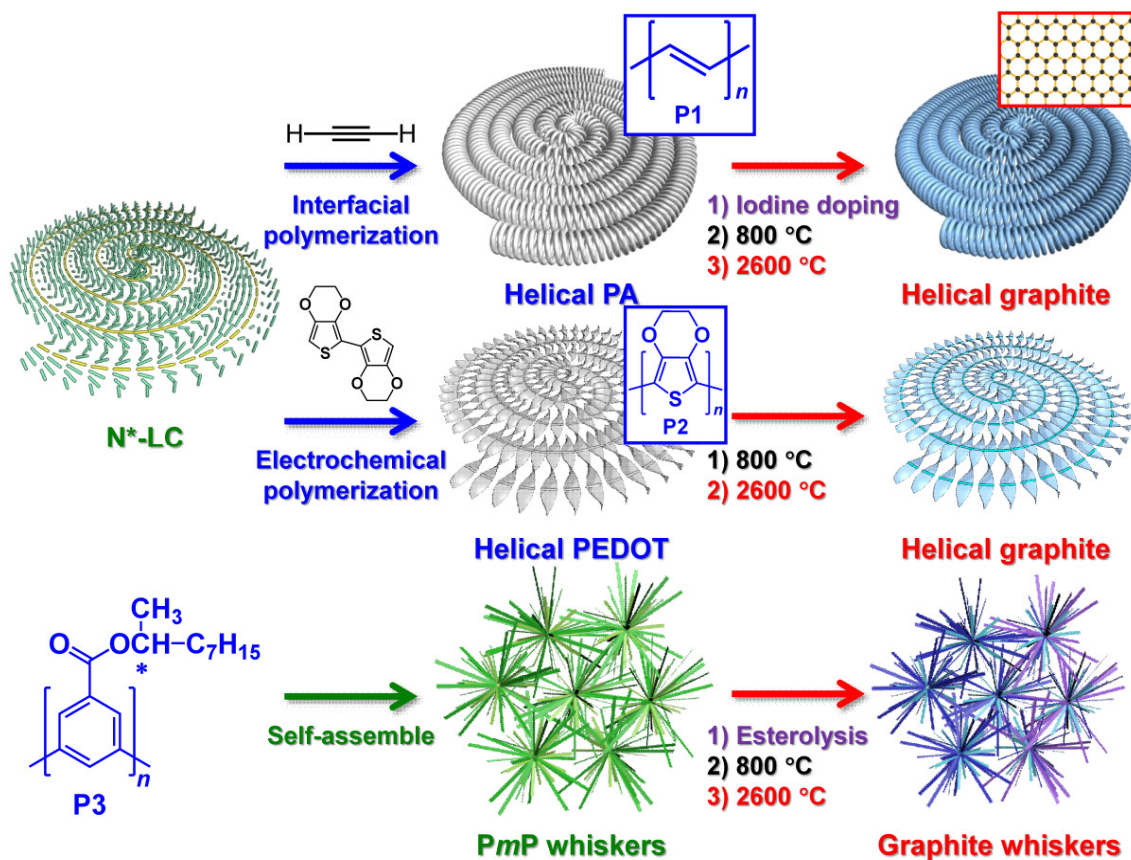
There are two major types of carbonization methods: vapor-phase carbonization and solid-state carbonization. One of the advantages of the solid-state carbonization of polymeric materials is its possibility of mass production on an industrial scale. This possibility has already been demonstrated by industrially produced polyacrylonitrile (PAN)-based and pitch-based carbon fibers [2]. The processability of polymeric materials, such as spinnability and stretchability, plays a crucial role in the production process. In contrast, although the vapor-phase growth process can produce the

previously described newly developed carbon materials, there are manufactural limitations for large-scale production because gaseous precursor molecules are currently employed for the carbonization method. Another advantage of the solid-state carbonization of polymeric materials is the potential of morphological controllability of the final carbon materials. In contrast to common polymeric materials, carbon materials are generally difficult to be precisely fabricated because they have less processability. In addition, the carbon materials prepared through vapor-phase carbonization are difficult to control morphologically.

If the morphology of polymeric precursor materials is retained even after solid-state carbonization at a high temperature, then morphology-controlled carbon materials can be produced. These morphology-controlled carbon materials at the meso-, micro-, and nanoscales are anticipated to possess unique functional properties derived from their morphology and might introduce a pathway for next-generation carbon-based electronics. The ability to perform organic-polymeric-precursor-controlled carbonization is important to achieve unique carbon materials [3]. The key challenges for the preparation of these advanced carbon materials is the precise control of the precursor morphology, as well as the prevention of thermal decomposition and gasification of the precursor during the heat treatment, because carbonization at high temperatures causes the decomposition reaction and volatilization of hydrocarbon gases, even under an inert atmosphere, destroying the morphology of the precursor polymer. Conjugated polymers have higher thermal stability than common vinyl polymers due to their rigid conjugated molecular chain structure; thus their use as starting materials for the preparation of advanced carbon materials should be a promising approach. In addition, conjugated polymers tend to form various polymer assemblies, including those

with a higher-order morphology due to their strong intra- and interchain π - π interactions during polymerization or annealing processes, as well as in a solution state.

In this chapter, the author briefly reviews recent advances in the preparation of carbonaceous and graphitic materials through carbonization and graphitization of conjugated polymeric materials by focusing on several aliphatic and aromatic conjugated polymers, such as polyacetylenes (PAs) (**P1**), polythiophene derivatives (**P2**), and polyphenylene derivatives (**P3**), as precursors in terms of morphologically controlling the carbon materials (Scheme 1). The author presents an overview of the following topics: (i) carbonaceous and graphitic materials prepared from conjugated polymers as carbonization precursors; (ii) macroscopically aligned carbon and graphite films prepared from iodine-doped stretchable PA films as precursors; (iii) helical carbon and graphite films prepared from iodine-doped helical PA films or ClO_4^- -doped helical polythiophene derivatives as precursors; and (iv) carbon and graphite whiskers prepared from self-assembled polyphenylene derivatives as precursors.

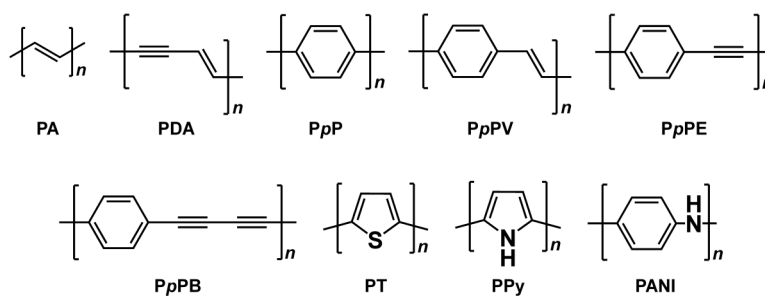


Scheme 1. Schematic representation of helical graphites prepared from helical PA and helical poly(3,4-ethylenedioxythiophene) (PEDOT), and graphite whiskers prepared from PmP derivatives.

2. Carbonaceous and graphitic materials prepared from conjugated polymers

Recently, many carbonaceous and graphitic materials with various morphologies, such as nanoparticles, nanofibers, nanotubes, mesoporous foams, anisotropic structures, and hierarchical helical structures, prepared through the heat treatment of various aliphatic or aromatic conjugated polymers as precursors have been reported. For example, the following precursor polymers have been proposed: PAs [4,5], polydiacetylenes (PDAs) [6–8], polyphenylenes [9–11,12b], poly(arylene vinylene)s

[13–16], poly(arylene ethynylene)s [17c,f,18], poly(arylene butadiynylene)s [17], polythiophenes (PTs) [12a,19–21], polypyrroles (PPys) [22,23b,24], polyanilines (PANIs) [23,25,26,27b,28], and two- or three-dimensional conjugated polymers [16,17f,18,19,27a] (Scheme 2). Because of the structural similarity between conjugated polymers and the graphene structure, the preparation of graphitic materials from conjugated polymers through solid-state carbonization might be the most facile and efficient procedure. Herein, representative examples from recent years are presented in terms of the following polymer structures.



Scheme 2. Chemical structures of the proposed precursor polymers used for the preparation of carbonaceous and graphitic materials.

2.1. Poly(diiododiacetylene)s

Goroff et al. reported the preparation of carbon nanofibers from poly(diiododiacetylene) (PIDA) (**P4**) nanofibers as precursors at 900 °C (Fig. 1) [6a]. The PIDA nanofibers were synthesized through the topochemical solid-state polymerization of diiodobutadiyne as a monomer within host–guest cocrystals at room temperature. Subsequently, they extended their approach to the chemical carbonization method in which a Lewis base, such as pyrrolidine, pyridine, or triethylamine, accelerates a deiodination reaction of PIDAs, enabling the formation of

carbon nanomaterials at room temperature [6b].

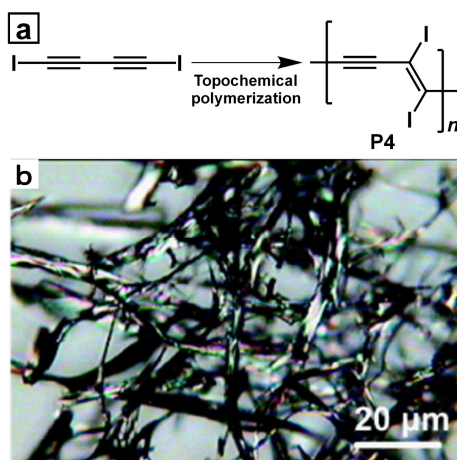
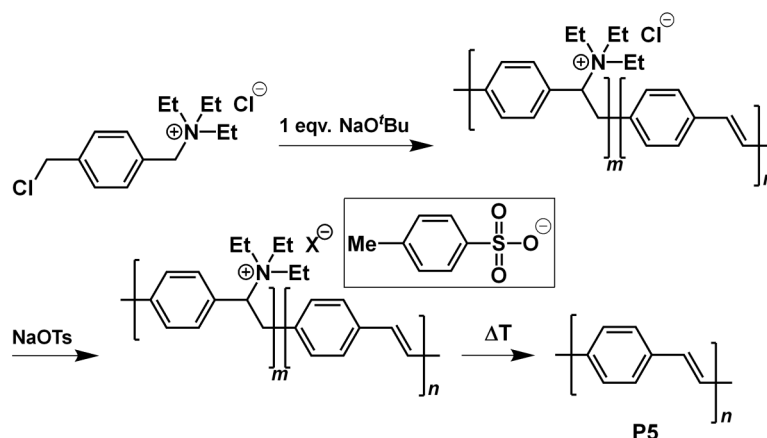


Fig. 1. (a) Synthesis of PIDA. (b) Photograph of the annealed PIDA fibers. Reproduced with permission from Ref. [6a]. Copyright (2011) American Chemical Society.

2.2. Poly(*para*-phenylene vinylene)s

Buchmeiser et al. reported the synthesis and carbonization of triethylammonium-based poly(*para*-phenylene vinylene) (PpPV) films [15]. The soluble and processable PpPVs were synthesized from an ammonium-based monomer using a method similar to a Gilch reaction under basic conditions (Scheme 3). The ammonium-based PpPVs with a larger counter anion of *p*-toluenesulfonate showed higher film-forming properties. The cast films were prepared by dissolving the ammonium-based polymers in dimethylsulfoxide; subsequently the solution was cast in polytetrafluoroethylene (PTFE) dishes. The insoluble PpPV (**P5**) films were prepared by annealing at 150 °C and were carbonized at up to 1800 °C, yielding carbon films.



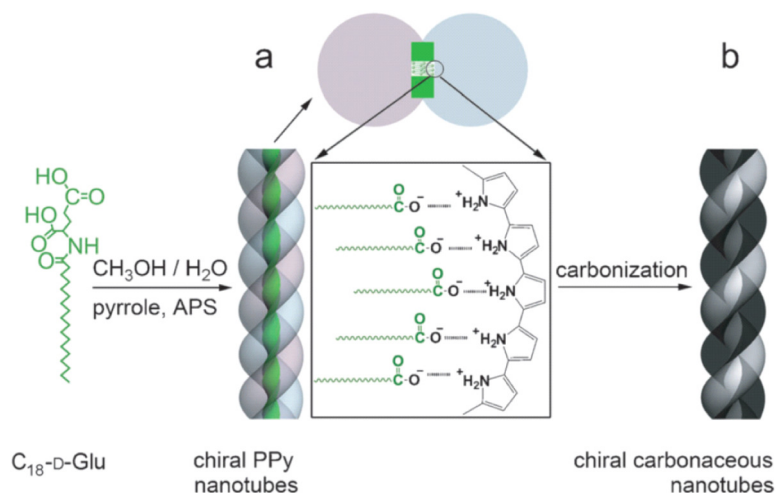
Scheme 3. Synthesis of ammonium-based *PpPV*.

2.3. Polypyrroles and polyanilines

Many studies on the carbonization of PPy and PANI have been reported, and they have been well reviewed by Ćirić-Marjanović et al. [23]. One of the advantages of using PPy and PANI as precursors is their facile introduction of doped nitrogen atoms into final carbon materials. It is well known that heteroatoms doped into carbon materials significantly affect their electrical, electromagnetic, and physicochemical properties of the materials. Here, representative cases are described as follows.

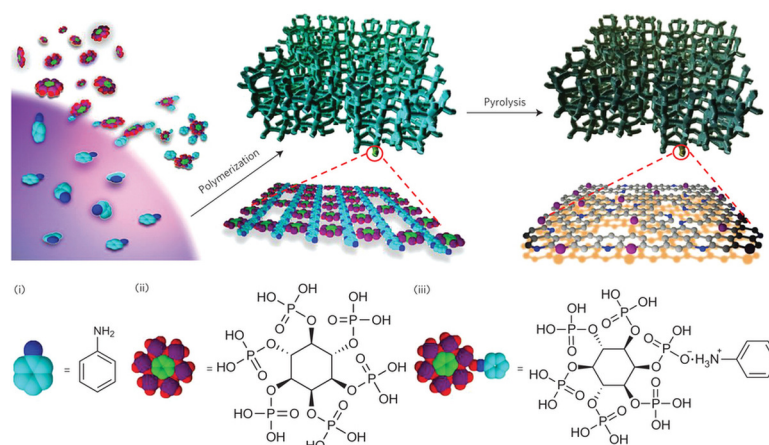
Che et al. prepared nitrogen-doped enantiopure chiral carbonaceous nanotubes with a helical morphology through the carbonization of self-assembled chiral PPy nanotubes at temperatures up to 950 °C (Scheme 4) [22]. The mesoporous helical PPy nanotubes were synthesized through a chemical oxidative polymerization templated by a self-assembly of enantiopure chiral amphiphilic *N*-acylamino acid molecules. Interestingly, the tubular and helical morphologies of the PPys were retained after heating at a high temperature. It was found from the solid-state diffuse reflectance circular dichroism (DRCD) measurements that the carbonized nanotubes showed

obvious optical activity. The chiral carbonaceous nanotubes showed distinct electrochemical reactivity for lithium intercalation; therefore, they are expected to be used in lithium ion batteries.



Scheme 4. Illustration of the synthesis of chiral PPy nanotubes and chiral carbonaceous nanotubes. (a) Chiral PPy nanotubes prepared by the self-assembly of $\text{C}_{18}\text{-D-Glu}$ (template) with ammonium persulfate as the initiator. (b) Chiral carbonaceous nanotubes prepared by the carbonization of chiral PPy nanotubes under an Ar atmosphere. Reproduced with permission from Ref. [22]. Copyright (2013) Wiley-VCH Verlag GmbH & Co.

Dai et al. reported a template-free method for three-dimensional nitrogen and phosphorus co-doped mesoporous nanocarbon (NPMC) foams through the heat treatment of PANI aerogels at temperatures up to 1100 °C synthesized in the presence of phytic acid (Scheme 5) [27b]. The NPMC foams with a large surface area showed efficient catalytic activity and long-term stability for oxygen reduction and oxygen evolution reactions as bifunctional air electrodes in primary and rechargeable zinc–air batteries.



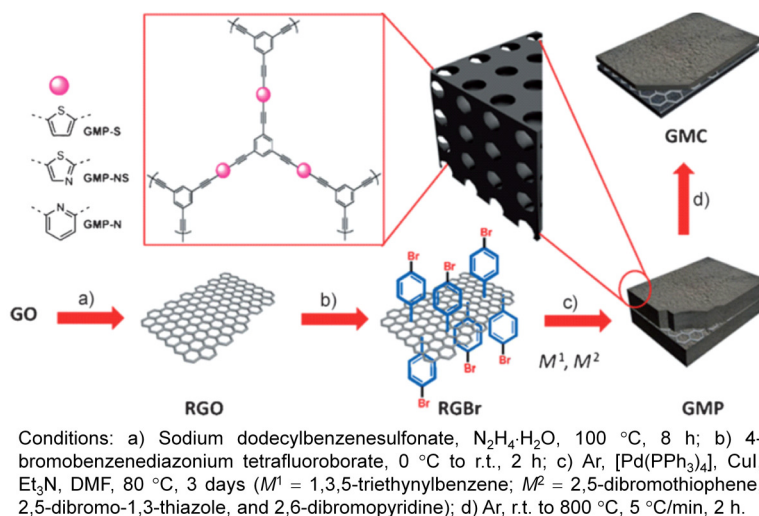
Scheme 5. Preparation of the NPMC electrocatalysts. Schematic illustration of the preparation process for the NPMC foams. An aniline (i)-phytic acid (ii) complex (iii) is formed, followed by oxidative polymerization into a three-dimensional PANI hydrogel cross-linked with phytic acids. Because each phytic acid molecule can complex with up to six aniline monomers, phytic acid can be used as the cross-linker and protonic dopant to directly form the three-dimensional PANI hydrogel network. The PANI hydrogel is freeze-dried into an aerogel and pyrolyzed in Ar to produce the NPMC. Reproduced with permission from Ref. [27b]. Copyright (2015) Macmillan publishers Ltd.

2.4. Conjugated microporous polymers

Among the porous materials, conjugated microporous polymers have recently attracted considerable attention because of their rigid conjugated three-dimensional network structures [29,30]. One of the feasible and direct ways of preparing porous carbon materials is to carbonize the conjugated microporous polymers as precursors. Zhang and Feng et al. reported heteroatom-doped two-dimensional porous carbons obtained via carbonization at 800 °C for graphene-based conjugated microporous

polymer sheets (GMPs) that were prepared through the grafting of conjugated microporous polymers on a graphene layer as the substrate in a two-dimensional manner (Scheme 6) [18a]. The conjugated microporous polymers were synthesized by polymerizing thiophene-, thiazole-, and pyridine-based monomers with a 1,3,5-triethynylbenzene monomer through a Sonogashira–Hagihara coupling reaction. The resulting graphene-based microporous carbons (GMCs) exhibited not only high efficiency as metal-free catalysts for the oxygen reduction reaction but also outstanding supercapacitive behavior.

Sulfur-doped microporous carbon materials were also prepared from thienylene-based aromatic conjugated polymer network precursors. The details are described in section 4.



Scheme 6. Preparation of GMPs and related GMCs. Reproduced with permission from Ref. [18a]. Copyright (2013) Wiley-VCH Verlag GmbH & Co.

3. Carbon and graphite films prepared from polyacetylene films

3.1. Macroscopically aligned carbon and graphite films prepared from stretchable polyacetylene films

Because an iodine-doped PA film showed metallic behavior as a component of its electrical properties, many conjugated polymers were designed and synthesized to achieve advanced semiconducting and/or conducting behavior [31]. The aliphatic PA is the most typical conjugated polymer and has the simplest structure with alternating single and double bonds. Due to its simple molecular structure without heteroatoms, PA has a higher carbon content (92.3%) than that of major precursor polymers, such as aliphatic PAN (~67.9%) and aromatic polyimide (PI) (~67.4%), for producing carbon products, i.e., industrially produced carbon fibers [2] and commercially available graphite films [32], respectively. The total production yield of the carbon fibers and graphite films is reported as high as 56% [33] and 50–55% [34,35], respectively. Because PA has a high carbon content, the theoretical carbonization yield should be higher than that of PAN and PI.

Several polymerization methods for the synthesis of PA films with controlled morphology have been developed. For example, PA films with macroscopically aligned morphology and hierarchical helical morphology have been achieved to date. The preparation of PA, carbon, and graphite films with helical morphology is discussed in sections 3 and 4. The macroscopically aligned PA films are simply prepared by drawing a stretchable PA film that is synthesized using the method of Naarmann and Theophilou [36], a solvent evacuation method [37], and an intrinsic nonsolvent method [38]. The electrical conductivity of the PA film was enhanced through a uniaxial alignment of the polymer chains, which was associated with the mechanical stretching

of the film following polymerization. Although the aligned PA films show high electrical conductivity along the stretching direction after doping, the critical disadvantage of PA films is their instability under atmospheric conditions. When a PA film is exposed to air, the conjugated molecular structure is easily oxidized and loses its conjugation. To overcome this issue, we decided to transform the unstable PA film into a stable carbon film. If the highly stretched PA film is used as a precursor, then the preparation of an anisotropic carbon film with enhanced electrical properties might be achieved.

Recently, we succeeded in preparing mechanically strong, electrically conductive and thermally stable single-component graphite films from iodine-doped stretchable PA films as precursors using a newly developed carbonization method called “morphology-retaining carbonization” [4]. The solvent evacuation method was used for the synthesis of the stretchable PA film. Iodine doping is the most important and indispensable procedure for preventing thermal decomposition and for retaining a fibril structure, as well as for retaining the original shape of the PA precursor film. Fig. 2 presents macroscopically aligned graphite films prepared from iodine-doped stretchable PA films using the morphology-retaining carbonization method. The graphite films were prepared through carbonization at 800 °C and then graphitization at a very high temperature of up to 3000 °C. The aligned graphite film prepared from the stretchable PA film presented a Laue X-ray diffraction (XRD) pattern in which graphitic crystal structures are aligned parallel to the stretching direction of the PA film. The anisotropic graphite film showed an enhancement in electrical conductivity along the stretching direction, exemplifying that an iodine-doped PA film is a highly efficient carbon source for producing graphite films. The present carbonization procedure

provides a graphite film with a total yield as high as 61–74% at up to 3000 °C, which is considerably higher than that of PAN-based carbon fiber and PI-based graphite film. The aligned graphite films might exhibit unique functional properties characteristic of the anisotropic structure and could be used in polymer electrolyte fuel cells or as an anisotropic carbon negative electrode material for lithium ion batteries.

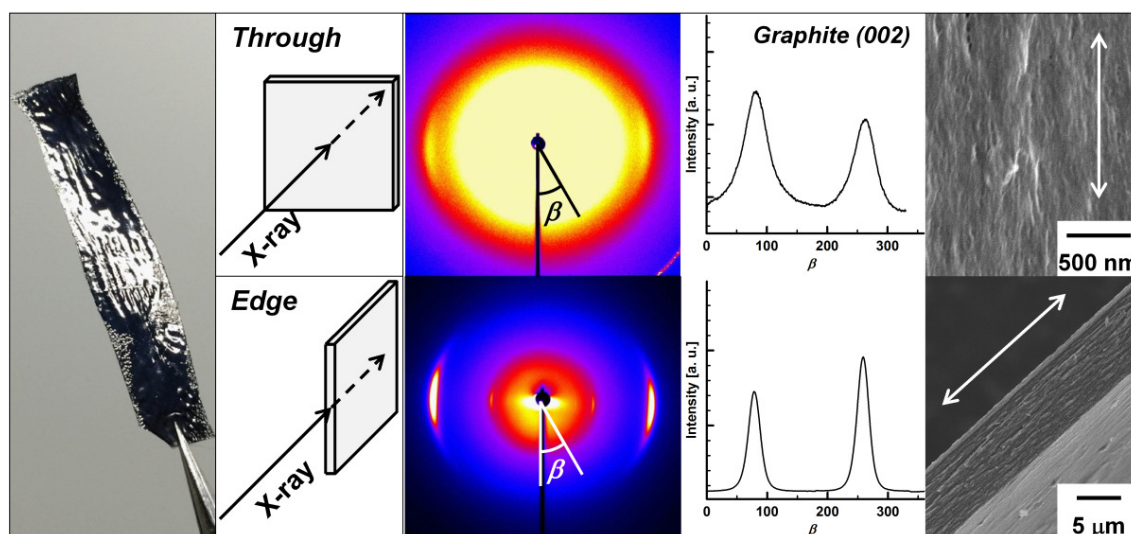


Fig. 2. Macroscopically aligned graphite films prepared from iodine-doped stretchable PA films using morphology-retaining carbonization. Reproduced with permission from Ref. [4]. Copyright (2015) American Chemical Society.

Note that the morphology-retaining carbonization method is possible for not only PA films but also cellulose papers as precursors. We reported the preparation of functional carbon papers from iodine-doped cellulose papers at temperatures up to 2600 °C [39]. We demonstrated that the iodine molecules doped in the cellulose paper prevent thermal decomposition of the paper and play an important role in retaining its entangled microfiber morphology.

3.2. Helical carbon and graphite films prepared from helical polyacetylene films

Previously, we succeeded in synthesizing PA films bearing a hierarchical helical fibril structure and a spiral morphology called “helical PA films” through an interfacial acetylene polymerization in chiral nematic liquid crystal (N*-LC) as an asymmetric reaction field [40]. The LC polymerization method is a useful technique for directly synthesizing conjugated polymers with an anisotropic structure during the polymerization reaction. The production of carbon films bearing a more complicated structure, including a hierarchical helical structure, remains challenging but is intriguing for the development of new carbon materials. Therefore, the use of a spontaneously ordered structure of LC molecules as an anisotropic reaction field for synthesizing conjugated polymer precursors should be a robust strategy to obtain this goal. If the morphology of the helical PA film is preserved even after the carbonization process, then the preparation of a carbon film consisting of hierarchical helical carbon fibrils can be expected. The helical carbon films are expected to be used in potential applications, such as graphene aggregates, carbon electrodes, and molecular magnets based on an induced solenoid magnetism, due to their helical structure and electrical conductivity.

Recently, we reported the preparation of helical graphite films from iodine-doped helical PA films as precursors through the morphology-retaining carbonization (Fig. 3) [5]. Importantly, the hierarchical helical fibril morphology of the helical PA film remained unchanged after the carbonization at 800 °C and the subsequent graphitization at 2600 °C. Note that the yield of the carbon film after the carbonization of the helical PA film was as high as approximately 80% of the weight of the helical PA film prior to iodine doping. Furthermore, the screw direction, degree of twist, and vertical or

horizontal alignment of the helical graphite film are well controllable by changing the sense and pitch of the helix, and the orientation of the N*-LC (Fig. 4). In particular, horizontally aligned helical graphite films were found to show an anisotropy in electrical conductivity in which the conductivity parallel to the aligned direction was higher than that perpendicular to the direction. The successful preparation of hierarchically controlled helical carbon and graphite films motivated us to extend the present method to aromatic conjugated polymers. The details are described in section 4.

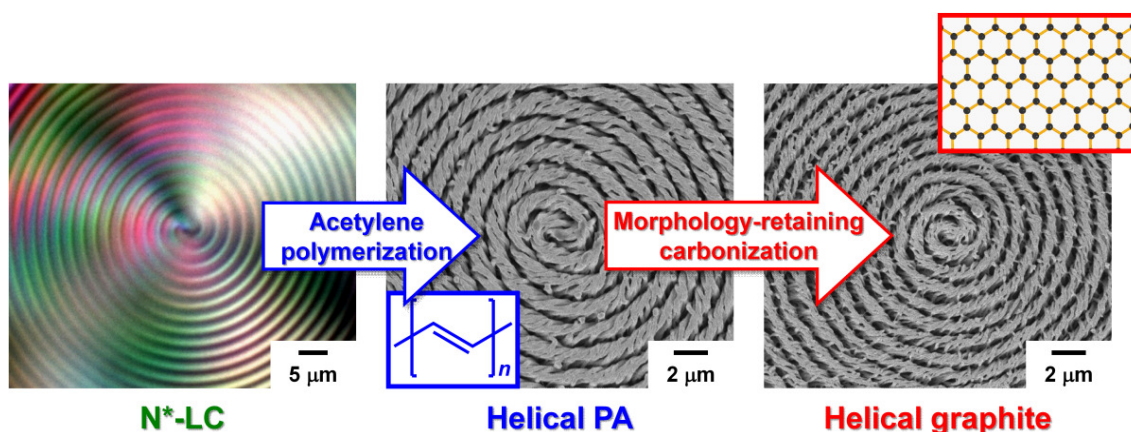


Fig. 3. Synthesis of helical PA films in N*-LCs and preparation of helical graphite films from iodine-doped helical PA films using morphology-retaining carbonization. Reproduced with permission from Ref. [5d]. Copyright (2011) American Chemical Society.

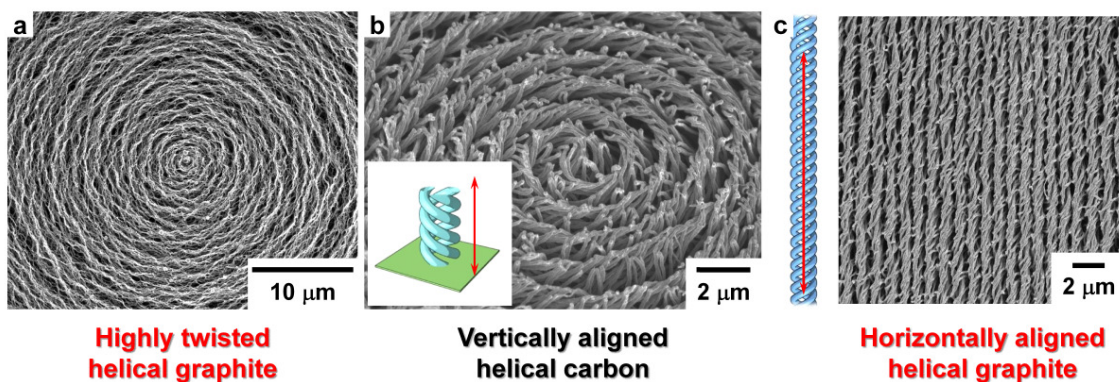


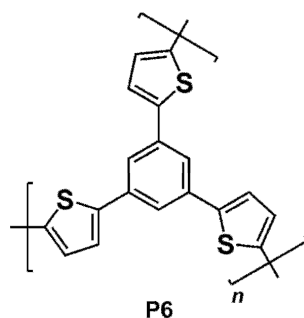
Fig. 4. SEM images of the (a) highly twisted helical graphite film, (b) helical carbon film with vertically aligned morphology, and (c) helical graphite film with horizontally aligned morphology. Reproduced with permission from Ref. [5d]. Copyright (2011) American Chemical Society.

Note that carbon films with N^* structural order were found to be prepared via another approach using cellulose materials as precursors. Recently, MacLachlan et al. reported N^* mesoporous carbon films with a high specific surface area that were prepared from nanocrystalline cellulose-silica composite films at 900 °C [41].

4. Helical carbon and graphite films prepared from helical polythiophene derivatives

The polymerization method in N^* -LC as a reaction field is a versatile technique and is applicable to not only aliphatic PAs but also aromatic conjugated polymers. For example, helical poly(3,4-ethylenedioxythiophene) (PEDOT) films synthesized in N^* -LC through an electrochemical oxidative polymerization show a clear spiral morphology on the film surface, a feature that is also possessed by helical PA films [42]. The electrochemical polymerization is a convenient technique and is safer than the

interfacial acetylene polymerization; it can also be performed under mild conditions. In addition, helical PEDOT films show bisignate Cotton effects in their CD spectra, which are characteristic of the formation of an interchain helically π -stacked structure. Because helical PEDOT films have hierarchical one-handed helical surface morphology, they are regarded as a promising candidate precursor polymer film for preparing other types of helical graphite films. The intrinsic rigid main chain of aromatic conjugated polymers will suppress their thermally decomposition and will afford high thermal stability during the heat treatment. It should be noted that Schmidt et al. reported microporous sulfur-doped carbon materials obtained by carbonization at 600–1000 °C for thienylene-based aromatic conjugated polymer network precursors, poly[1,3,5-tris(thienyl)benzene] (**P6**), synthesized through a chemical oxidative polymerization [19]. They claimed that the carbon materials are expected to be used as a promising support material for the immobilization of metal nanoparticles.



Recently, we succeeded in preparing helical graphite films from ClO_4^- -doped helical PEDOT films as precursors synthesized through asymmetric electrochemical polymerization (Fig. 5) [20]. Fig. 5(b) presents polarizing optical microscope (POM) and scanning electron microscope (SEM) images of the neutral helical PEDOT films synthesized in N^* -LC with a helical pitch as narrow as 341 nm. The SEM image shows a spiral morphology composed of a fibrous structure. It was found from XRD

analyses of the graphite films prepared from the ClO_4^- -doped and undoped PEDOT films at 800 °C and the subsequent graphitization at 2600 °C that the former has a higher crystallinity than the latter. This is because of the difference in crystallinity between the doped and undoped PEDOT films as precursors. The closely packed polymer chains stabilized by the doped ClO_4^- ions in the PEDOT film will effectively cross-link during the heating process. As a result, the graphitized PEDOT film with high crystallinity is prepared from the doped PEDOT film. Surprisingly, the helical morphology of the ClO_4^- -doped helical PEDOT film remained unchanged after the carbonization at 800 °C and the subsequent graphitization at 2600 °C. The helical graphite film has nearly the same surface morphology as that of the original helical PEDOT film and that of the helical carbon film, except for the presence of thermal shrinkage [Fig. 5(c)]. The present helical carbon atoms containing a dopant amount of sulfur atoms might exhibit unique electrochemical properties, characteristic of the helical structure, and electrical conductivity.

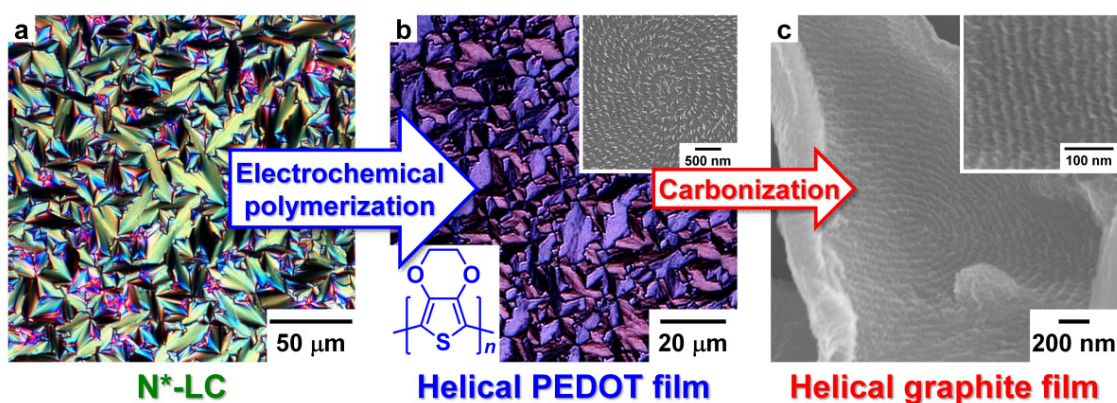


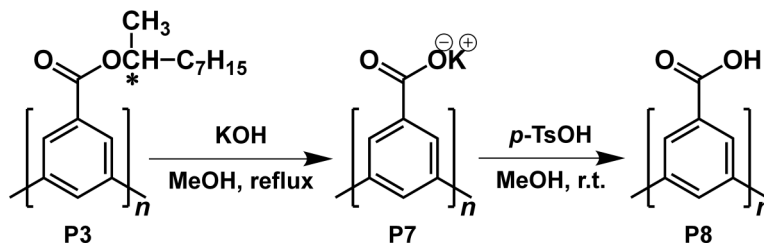
Fig. 5. POM images of the (a) N*-LC and (b) helical PEDOT film. (c) SEM image of the PEDOT-based helical graphite film. Reproduced with permission from Ref. [20]. Copyright (2014) Wiley-VCH Verlag GmbH & Co.

5. Carbon and graphite whiskers prepared from polyphenylene derivatives

Whiskers are filamentous materials with defect-free structures and high aspect ratios. Among the various whisker materials consisting of metallic, inorganic, and organic materials, carbon whiskers can be a promising candidate material for the fabrication of lightweight composite materials with high mechanical properties. Previously, we synthesized poly(*meta*-phenylene) (*PmP*) derivatives (**P3**) with racemic or chiral alkyl groups in the side chains [43]. The *PmP* derivatives present intrachain helical π -stacking ability and self-assemble to form polymer whiskers in which the columns consisting of a hexagonal columnar packed structure are uniaxially aligned parallel to the long axis of the whisker. Furthermore, a macroscopic alignment of the polymer whiskers is possible using an oriented substrate. However, it is difficult to prepare carbon and graphite whiskers via carbonization of the *PmP* whiskers because the self-assembled structure will dissociate during the heat treatment due to its long aliphatic solubilizing side chains. If the whisker morphology of the *PmP* derivative is preserved even at high temperatures, then the carbon and graphite whiskers can be produced.

Recently, we prepared carbon and graphite whiskers using the *PmP*-based polymer whiskers as precursors [11]. First, we prepared *PmP* films with a whisker morphology by annealing the *PmP* derivative, and then we synthesized *PmP* whiskers bearing carboxylic acid moieties (**P8**) through an esterolysis reaction of the polymer whisker film (Scheme 7). The desubstitution reaction is the most important procedure because flexible chiral alkyl chains easily fuse at high temperatures, resulting in the loss of the whisker morphology [44]. The carbon and graphite whisker films were then prepared from the **P8** films through carbonization at 800 °C and subsequent graphitization at

2600 °C, respectively. Fig. 6 presents carbon and graphite whiskers prepared from self-assembled *PmP* derivatives with an intrachain helically π -stacked structure.



Scheme 7. Scheme for side-chain defunctionalization.

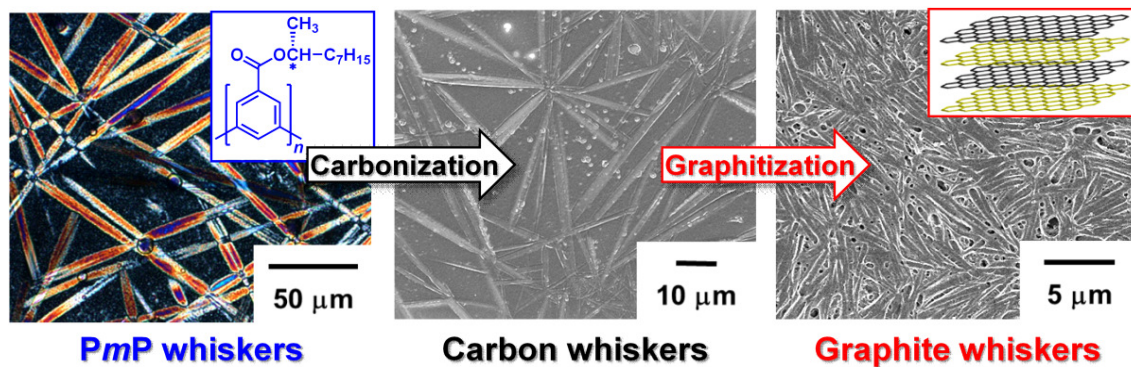


Fig. 6. Carbon and graphite whiskers prepared from self-assembled *PmP* derivatives. Reproduced with permission from Ref. [11]. Copyright (2015) American Chemical Society.

Furthermore, the carbon and graphite films with a macroscopically aligned whisker morphology were prepared from highly aligned *PmP* whisker films (Fig. 7). The aligned polymer whisker film was prepared by annealing **P3** on the oriented PTFE substrate [45]. The **P8** films with an aligned whisker morphology were then prepared by removing side chains via the esterolysis process. Finally, the aligned **P8** films were carbonized and subsequently graphitized, yielding macroscopically aligned carbon and graphite whisker films, respectively. The aligned carbon whisker films showed an

electrical anisotropy, in which the conductivity parallel to the aligned direction was higher than that perpendicular to the direction.

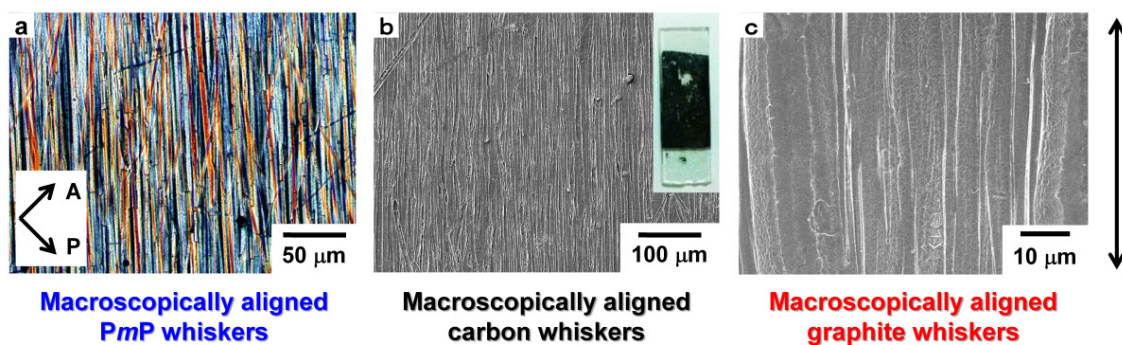


Fig. 7. (a) POM image of the PmP film with aligned whisker morphology. SEM images of the (b) carbon and (c) graphite films with aligned whisker morphology. Reproduced with permission from Ref. [11]. Copyright (2015) American Chemical Society.

6. Summary and outlook

We reviewed the recent progress in the solid-state carbonization of conjugated polymers as precursors by focusing on their potential for producing unique carbonaceous and graphitic materials with controlled morphology.

Section 2 described recent developments regarding various conjugated-polymer-based carbonaceous and graphitic materials in terms of a precursor molecular structure. Section 3 revealed that iodine doping is effective for increasing carbonization yield and for retaining the morphology of PA films by focusing on the preparation of macroscopically aligned carbon and graphite films from highly stretched PA films as precursors using morphology-retaining carbonization. Section 4 focused on the preparation of helical carbon and graphite films with hierarchically arranged fibril and spiral morphologies from doped helical PA and PEDOT films as precursors.

Section 5 discussed the heat treatment of self-assembled *PmP* derivatives, which affords filamentous graphitic materials, such as carbon and graphite whiskers. It was also discussed that the esterolysis process of the *PmP* derivatives is the indispensable procedure for retaining the *PmP* whisker morphology during the heat treatment.

Finally, note that the primary benefit of using conjugated polymers and solid-state carbonization is that the present carbonization method allows the design of the properties and morphological functions of carbon materials by selecting the molecular structure and morphology of precursor polymers with structural diversity. Thus, the active control of the porosity, crystallinity, conductivity, and electrochemical reactivity of the conjugated-polymer-based carbons through the flexible and customized production approach is one of the challenging aspects to be considered in this area. Further improvements in efficiency and effectiveness for the production of these advanced carbon materials, e.g., carbonization yield, through in-depth investigations of the carbonization mechanism and the effect of additives during the heat treatment are also important future challenges. Hence, we believe that this approach is readily applicable to a wide range of other conjugated polymeric materials with given morphologies.

Acknowledgments

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Chapter 4

Aligned Carbon and Graphite Fibers Prepared from Solid-State Polymerized Poly(3,4-ethylenedioxythiophene) Single Crystals and Their Applications for Supercapacitors

Solid-state polymerization, a polymerization method without initiators, catalysts, or solvents, was developed in the 1960s for preparing polydiacetylene single crystals.^{1,2} Years later, Wudl and co-workers reported that highly ordered poly(3,4-ethylenedioxythiophene) (PEDOT) could be prepared from 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) crystals simply by heating for several hours.^{3,4} This facile reaction stimulated research towards the synthesis of various highly conducting polymers, such as polythiophene⁵⁻⁷ and polyselenophene^{8,9} derivatives. The close intermolecular halogen...halogen interactions in the structurally preorganized monomer were considered to play a pivotal role in the solid-state polymerization, which was investigated using X-ray diffraction (XRD). Furthermore, PEDOT counter electrodes for dye-sensitized solar cells, which were previously synthesized via chemical or electrochemical polymerization, have also been prepared using solid-state reactions.^{10,11} The merits of solid-state polymerization are not only the synthetic convenience but also the ability to produce a highly crystalline and ordered polymer.

Recently, self-assembled helical poly(*meta*-phenylene) (PMP) derivatives have been

used as carbonization precursors for preparing carbon and graphite whiskers with randomly oriented morphologies.^{12,13} The macroscopically aligned PMP whiskers were produced by annealing the polymers on aligned substrates or drawing the polymers in the fluid state. Although the aligned whiskers showed a quite high degree of orientation in the scanning electron microscopy (SEM) images, the structural order parameter was only 0.16, which was determined by analyzing an azimuthal-angle profile of the Laue XRD pattern. On the other hand, macroscopically aligned graphite films with remarkable mechanical and electrical properties have been produced from iodine-doped stretchable polyacetylene (PA) films as carbonization precursors via a method named “morphology-retaining carbonization”, with the resulting films showing a high structural order parameter of 0.77.¹⁴ However, preparation of single-component graphite films required harsh conditions due to the difficult operation of interfacial acetylene polymerization and the poor stability of the aliphatic π -conjugated polymer.

Recently, helical carbon and graphite films with well-controlled left- and right-handed spiral morphologies have been prepared from helical PEDOT films through heat treatment at 800 and 2600 °C using a novel carbonization substrate.^{15,16} Helical PEDOT films used as stable carbonization precursors were synthesized via electrochemical polymerization in an asymmetric liquid crystal reaction field under ambient conditions. Helical graphite films with unique morphologies were expected to provide outstanding electrochemical and electromagnetic properties. However, the crystallinities of these graphite films were far from satisfactory. XRD and Raman measurements indicated the crystallinity of the graphite films prepared from PEDOT film was lower than that those prepared from PA films. This difference partially came

from the dissimilarity in crystallinity between the PEDOT and PA films used as carbonization precursors.

Carbon and graphite fibers have been widely used in aerospace, civil engineering and competitive sports products because of their profound properties, such as high hardness, good strength, strong chemical and temperature resistance, light-weight qualities, and low thermal expansion. However, carbon fibers are relatively expensive compared to other similar fibers such as fiberglass or plastic fibers. Highly ordered poly(diiododiacetylene) nanofibers prepared via topochemical polymerization were carbonized at 900 °C which recently reported by Goroff and co-workers.¹⁷ In this study, PEDOT fibers prepared via solid-state polymerization were used as novel carbonization precursors. If the highly ordered crystalline structures of solid-state polymerized PEDOT (SSP-PEDOT) fibers were preserved during heat treatment, then carbon and graphite fibers bearing high crystallinity and high structural order parameters could be produced. Here, we report a new approach to preparing oriented graphite fibers without time-consuming pretreatments, such as the use of aligned substrates or mechanical stretching. Furthermore, the performance of the carbon films prepared from SSP-PEDOTs for supercapacitor applications was investigated through electrochemical tests.

The monomers used for solid-state polymerization in this study, DBEDOT and 5,5'-dibromo-2,2'-bis(3,4-ethylenedioxythiophene) (*DBbis*EDOT) were synthesized by the direct halogenation of 3,4-ethylenedioxythiophene and 2,2'-bis(3,4-ethylenedioxythiophene), respectively (Scheme S1 in Supporting Information). Recrystallization in ethanol afforded DBEDOT as a colorless needle

crystal that was soluble in various organic solvents, such as hexane, chloroform, and acetone. The preparation of SSP-PEDOT was performed at 60 °C for 1–7 days in a closed Schlenk flask. During the polymerization, DBEDOT retained almost the same fiber morphology, only with a color change from colorless to metallic dark blue (Figure S1 in the Supporting Information). Fine acicular polymer crystals aggregated to form a single SSP-PEDOT fiber (Figure S2 in the Supporting Information). To remove the extra bromine from the SSP-PEDOT fibers, Soxhlet extraction was carried out for 24 h using CHCl_3 . Based on the results of TG/DTA measurements (Figure S3 in the Supporting Information), using a reaction time of 7 days was found to be an appropriate polymerization condition for a complete monomer consummation. The SSP-PEDOT fibers after Soxhlet extraction yielded the following elemental analysis data: C, 36.75; H, 2.80; S, 16.21; and Br, 17.14. The molecular ratio of the doped bromide ion (Br^-) to the EDOT units in the SSP-PEDOT fibers (Br^-/EDOT) was calculated to be $[\text{EDOT}(\text{Br}^-)_{0.42}]_n$. Next, dedoped SSP-PEDOT fibers were prepared via treatment with a hydrazine solution (50%, 10 mL/g) in acetonitrile (200 mL/g) at room temperature for 2 days. The molecular ratio of the doped Br^- to the EDOT unit in the dedoped SSP-PEDOT fibers (Br^-/EDOT) was calculated to be $[\text{EDOT}(\text{Br}^-)_{0.13}]_n$ based on elemental analysis, which indicated that 70% of the bromine had been removed during the dedoping process (Table S1 in the Supporting Information). However, it was difficult to maintain the shape of the SSP-PEDOT fibers when they were completely dedoped at higher reaction concentrations. On the other hand, DB*bis*EDOT was a yellow solid which was heated at 80 °C for 7 days without any color change. Solid-state polymerization probably did not occur for DB*bis*EDOT because the $\text{Br}\cdots\text{Br}$ distances between adjacent molecules in DB*bis*EDOT was not short enough.

Carbon fibers were prepared from doped and dedoped SSP-PEDOT fibers via thermal treatment at 800 °C (10 °C/min, 1 h) using an electric furnace. The carbonization yields of the doped and dedoped SSP-PEDOT fibers were 31 and 38%, respectively. No residual bromine remained in the carbon fibers prepared from both doped and dedoped SSP-PEDOT fibers (Table S2 in the Supporting Information). Subsequently, the carbonized fibers were graphitized at 2600 °C (20 °C/min, 30 min) using graphitization equipment with yields of 79 (doped) and 71% (dedoped). The fiber shape of SSP-PEDOT remained unchanged during the heat treatment process, irrespective of whether the SSP-PEDOT fibers were doped or dedoped (Figure S4 in the Supporting Information). The electrical conductivity of the graphite fiber when measured via four-point probe method was on the order of 10^2 S/cm along the fiber axis. This value was 10 times higher than the conductivity of the graphite film prepared from electrochemically synthesized PEDOT films.^{15,16}

Figure 1 shows the results of XRD analysis of the carbon and graphite fibers prepared using doped and dedoped SSP-PEDOT as the carbonization precursors. First, the carbon and graphite fibers were ground into powder for measurement. The XRD patterns of the carbon powder produced at 800 °C showed very weak crystalline reflections, indicating that the carbon samples existed in an almost amorphous state. After graphitization at 2600 °C, the graphite powder showed sharp (002) peaks of graphitic crystals, suggesting that the degree of crystallinity increases with increasing temperature. The crystal size in the *c*-axis (L_c) of the graphite powder prepared from doped SSP-PEDOT was estimated to be 14.5 nm from the (002) plane ($d = 3.4$ Å) of the XRD pattern, which suggests that 42 graphite layers formed the crystalline structures

based on the d_{002} -spacing and the L_c value. On the other hand, the L_c value of the graphite powder prepared from dedoped SSP-PEDOT was estimated to be 13.6 nm from the (002) plane ($d = 3.4 \text{ \AA}$) of the XRD pattern, which suggests that 40 graphite layers formed the crystalline structures. Although the L_c value of graphite powder produced from doped SSP-PEDOT was slightly larger, there was no significant difference between the doped and dedoped SSP-PEDOT because the graphite fibers were ground into powder for the measurements. Notably, the graphite fibers prepared from conjugated polymer PEDOT possessed large L_c values, which were close to the L_c of commercially available Kish graphite powder (Table S3 in the Supporting Information).

Figure 1c,d presents XRD patterns of the graphite fibers produced from doped SSP-PEDOT in the through and edge directions. In-plane orientation degree of the graphitic crystallites in the graphite fiber was estimated by using the intensity ratio of the (002) plane and the (100)/(101) planes ($I_{002}/I_{100\ 101}$). The XRD pattern of the graphite fiber prepared from doped SSP-PEDOT showed a much larger $I_{002}/I_{100\ 101}$ ratio of 341.1 in the edge direction compared to the ratio of 0.8 in the through direction, indicating that the graphene layers tended to be parallel to the surface of the aggregates of fine acicular graphite crystals. A similar result was observed in the case of graphite fibers prepared from dedoped SSP-PEDOT, with $I_{002}/I_{100\ 101}$ ratios of 241.6 and 2.2 in the edge and through directions, respectively (Figure 1e,f). The L_c values of the graphite fibers prepared from doped and dedoped SSP-PEDOTs were estimated to be 31.6 and 16.6 nm in the edge direction, which suggests that 95 and 50 graphite layers formed the crystalline structures, respectively. It follows that the graphite fiber prepared from the doped SSP-PEDOT had a higher crystallinity than that of the fibers

prepared from the dedoped SSP-PEDOT. This difference in crystallinity was also found between the graphite films produced from the doped and dedoped PEDOT films produced through electrochemical polymerization.^{15,16} The Br^- ions in doped SSP-PEDOT made the polymer chains more closely packed, leading to a more ordered structure. The closely packed polymer chains could therefore easily cross-link during carbonization. In addition, the ordered polymer structures of doped SSP-PEDOT were probably disturbed during the chemical dedoping process.

Figure 1h shows the Laue XRD pattern of the graphite fiber prepared from doped SSP-PEDOT in the edge direction and the azimuthal-angle profile based on the (002) reflection of the XRD pattern. The equatorial reflection of the highly anisotropic pattern was calculated to be 3.3 Å, which was assigned as the distance between the graphene layers. The remarkably high orientation factor of the graphite fiber of 0.82–0.85 suggests that the graphene layers were uniformly aligned parallel to the graphite fiber along the long axis and to the surface of the aggregates of fine acicular graphite crystals.

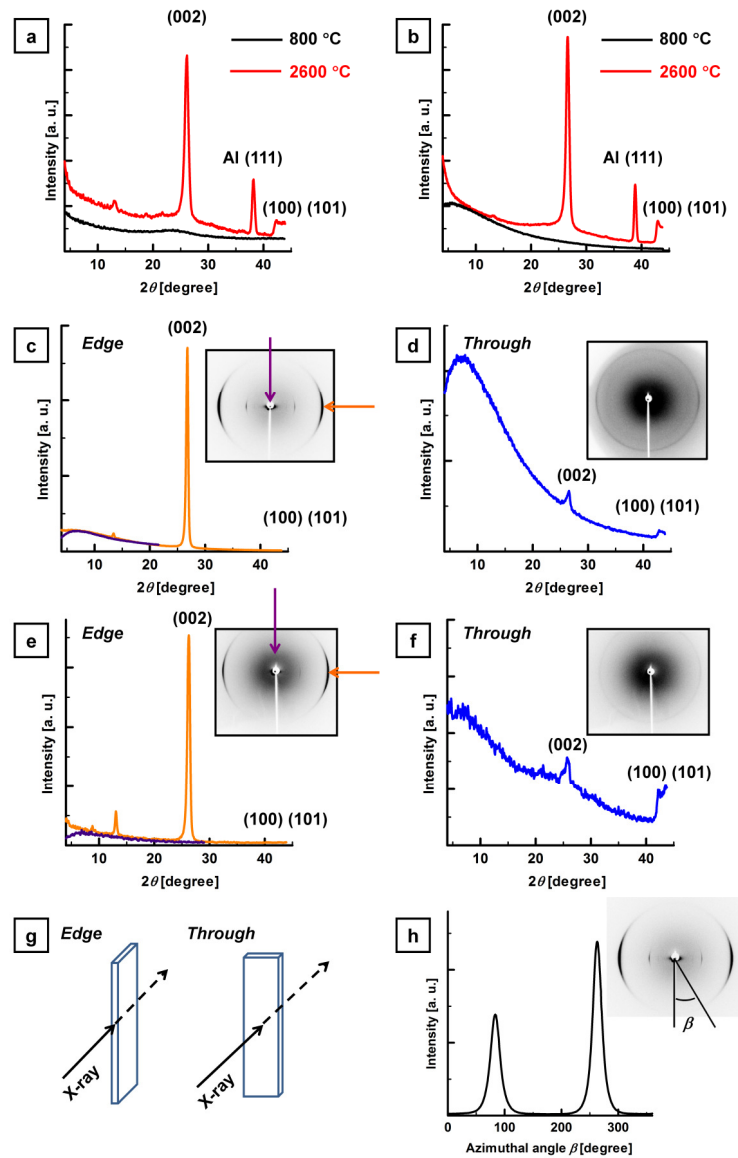


Figure 1. XRD patterns of (a) doped and (b) dedoped SSP-PEDOTs carbonized at 800 °C and graphitized at 2600 °C in powder form. Doped SSP-PEDOT fiber graphitized at 2600 °C in the (c) edge and (d) through directions. Dedoped SSP-PEDOT fiber graphitized at 2600 °C in the (e) edge and (f) through directions. (g) Sample configuration for XRD measurements. (h) Azimuthal-angle profiles based on the (002) reflection of the XRD pattern. The inset presents the Laue XRD pattern of the doped SSP-PEDOT fiber graphitized at 2600 °C.

Figure 2 shows Raman scattering spectra of carbon and graphite fibers produced using the doped and dedoped SSP-PEDOT as carbonization precursors. The Raman spectra of the doped and dedoped SSP-PEDOT fibers carbonized at 800 °C revealed a broad disorder band (D-band) and a graphite band (G-band) at 1350–1357 and 1579–1585 cm^{-1} , respectively. After graphitization at 2600 °C, the D- and G-bands decreased and increased in intensity, respectively, indicating the development of crystallinity from an almost amorphous structure in the graphite fibers. The sharp Raman bands observed at 2694–2698 cm^{-1} in both the doped and dedoped graphite fibers were assigned to a 2D-band, which is often found in graphite materials.¹⁷ The crystal sizes in the a -axis (L_a) of the graphite fibers prepared from the doped and dedoped SSP-PEDOT were estimated to be 17.9 and 10.9 nm from the Raman spectra, respectively. In contrast, the L_a value of Kish graphite powder was 17.1 nm, which is of the same degree as the L_a of graphite fibers. The crystal size of the graphite fibers prepared from SSP-PEDOT was also higher than that of the graphite films prepared from electrochemically polymerized PEDOT, which had an L_c value of 5.5 nm and an L_a value of 8.1 nm.¹⁵

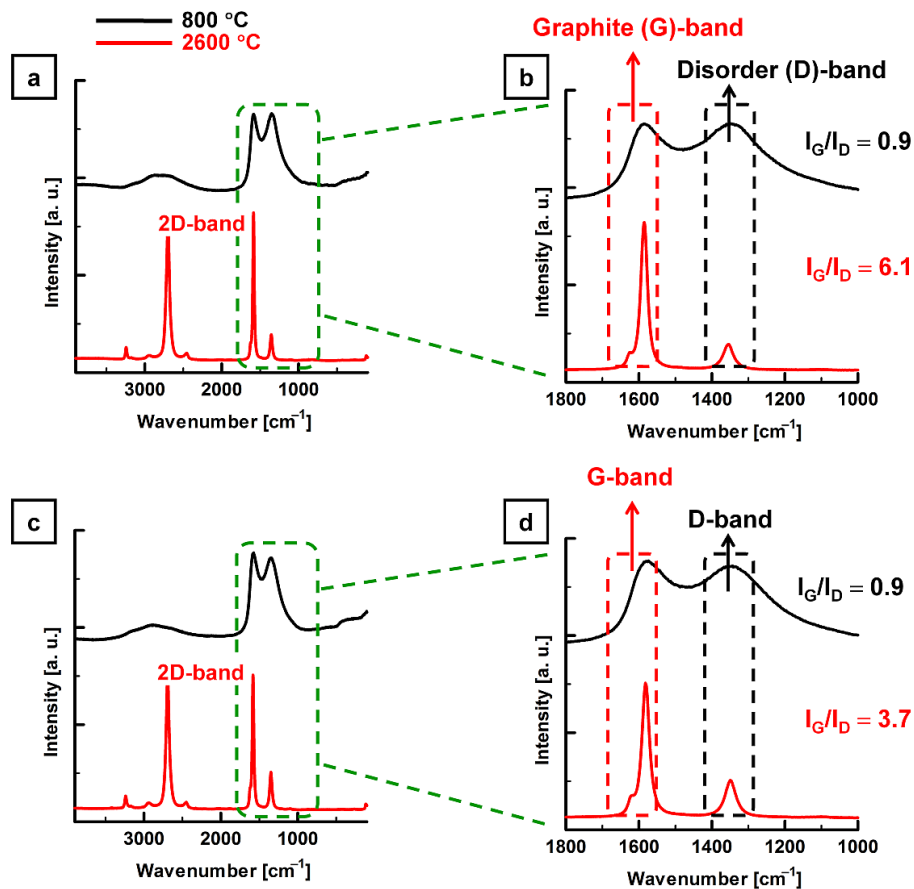


Figure 2. Raman scattering spectra of the carbon (black) and graphite (red) fibers prepared from (a,b) doped and (c,d) dedoped SSP-PEDOT.

Figure 3 shows SEM images of the carbon and graphite fibers in the through and edge directions. First, oriented plate morphologies along the fiber axis were observed in the through direction. After graphitization, the plate morphologies were reduced due to thermal shrinkage during the heat treatment at 2600 °C. Second, layer morphologies that aligned along the fiber axis were found in the edge direction. From the results of XRD analysis, Raman scattering, and SEM observations, a figure of the structural configuration of the graphite fibers was generated and is shown in Figure 4.

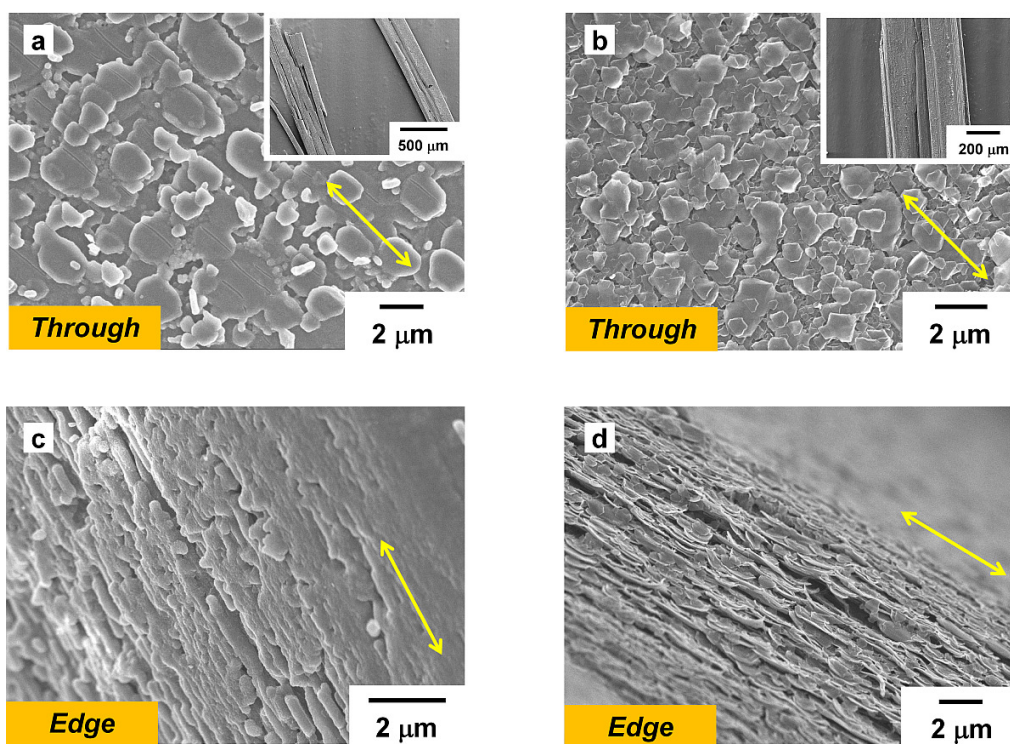


Figure 3. SEM images of the (a,c) carbon and (b,d) graphite fibers prepared from doped SSP-PEDOT in the (a,b) through and (c,d) edge directions. The arrows indicate the aligned directions of the fibers.

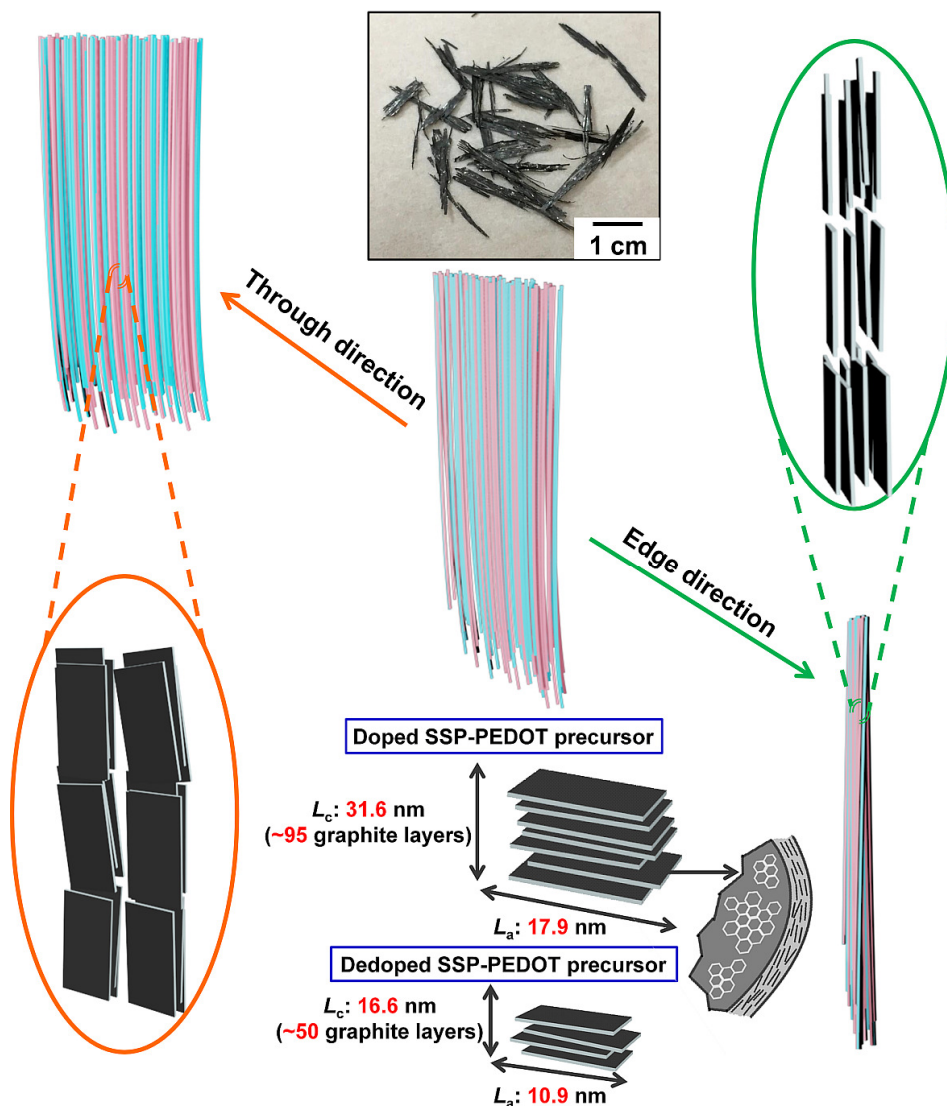


Figure 4. Structural configuration of the graphite fibers.

Furthermore, the capacitance performance of the carbon film prepared from SSP-PEDOT with an amorphous structure and a porous morphology for supercapacitor applications was investigated through electrochemical tests. The DBEDOT monomer in CHCl_3 was spin-coated on a glass substrate at 600 rpm for 15 s and 1000 rpm for 30 s. After evaporating the solvent, the colorless DBEDOT film was heated at 80 °C for 24 h,

yielding a dark blue SSP-PEDOT film. By utilizing a higher polymerization temperature, the polymerization time was shortened. The SSP-PEDOT film was removed from the glass substrate and then carbonized at 800 °C for 1 h. The carbon powder prepared from SSP-PEDOT was mixed with polytetrafluoroethylene (60 wt%) and carbon black (Super P) with a ratio of 80:10:10 wt%. The mixture was subsequently pressed onto a piece of nickel foam at room temperature.¹⁹ After drying process at room temperature for 12 h, a working electrode was prepared with 2.8–4.8 mg of active materials on the current collector. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) were carried out at room temperature in a three-electrode configuration using a 1 M NaOH aqueous solution as the electrolyte for the evaluation of the capacitance of the carbon film samples. Figure 5a shows the cyclic voltammograms of the carbon film obtained at scan rates from 10 to 500 mV/s. A quasi-rectangular shape with a slight slope was observed at all scan rates, suggesting slight deviations from the ideal electric double-layer capacitive behavior. The specific gravimetric capacitance increased from 4.9 F/g (scan rate at 500 mV/s) to 31.7 F/g (10 mV/s), as was calculated from the voltammograms (Table S4 in the Supporting Information). Figure 5b shows GCD curves at current densities from 0.1 to 5 A/g within a potential window of −1–0 V. Typical triangular shapes were observed, and the specific capacitance values were calculated at different current densities. The highest specific capacitance of 54.4 F/g was attained at lowest current of 0.1 A/g. When the current was increased to a high density of 5 A/g, the specific capacitance remained at 8.6 F/g (Table S4 in the Supporting Information), indicating good rate capability. These results were compared with cellulose-derived supercapacitors prepared from filter paper at a heating temperature of 1300 °C, which provided a

specific gravimetric capacitance value of 28.9 F/g (current density at 1 A/g),²⁰ thus indicating that the carbon films produced from SSP-PEDOT have significant potential to be used as supercapacitor electrodes. By increasing the heat treatment temperature, using acidic electrolytes, as well as optimizing the sample preparation, carbon films with higher specific capacitance and improved performance could be expected.

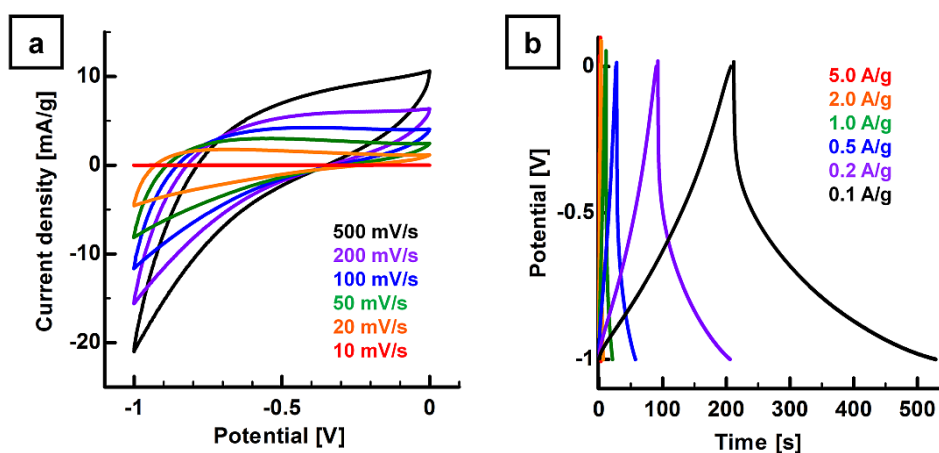


Figure 5. (a) CV and (b) GCD curves of the carbon films prepared from doped SSP-PEDOT at 800 °C obtained at various scan rates and current densities, respectively.

In summary, a novel approach for preparing graphite fibers with remarkably high crystallinity, structural order parameters, and electrical conductivity was developed using SSP-PEDOT fiber as a carbonization precursor. In this process, no time-consuming pretreatments, such as aligning substrates or a mechanical-stretching, were required. Graphite fibers prepared from doped SSP-PEDOT afforded a high orientation factor of up to 0.85, providing a higher crystallinity than those prepared from the dedoped polymer. Furthermore, carbon films produced from SSP-PEDOT

treated at 800 °C showed good capacitance performance in a basic electrolyte, which indicates a new direction for the usage of SSP-PEDOT. Engineering conducting wires with highly ordered structure and thermal stability might be one of the most promising applications of the graphite fibers.

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Chapter 4 Appendix**Materials and Measurements****1. Materials****2. Measurements****Synthesis****Supporting References****Supporting Figures****Materials and Measurements**

1. Materials. The chemical compounds were purchased from commercially available sources and were used as received. The compound, acetic acid (CH_3COOH), sodium hydrogen carbonate (NaHCO_3), sodium sulfate (Na_2SO_4), hydrazine monohydrate, and sodium hydroxide (NaOH) were purchased from Nacalai Tesque, Inc. The compound, *N*-bromosuccinimide (NBS) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Tokyo Chemical Industry Co., Ltd. Aluminum powder was purchased from Nilaco Co., Ltd. Carbon black (Super P, conductive, 99+ %) was purchased from Alfa Aesar. Polytetrafluoroethylene preparation (60 wt %, dispersion in H_2O) was purchased from Aldrich. Kish graphite powder was purchased from commercially available source. Acetone, acetonitrile (ACN), ethanol (EtOH), and chloroform

(CHCl₃) (Nacalai Tesque, Inc.) were used as received. EDOT was distilled under reduced pressure in argon gas atmosphere before use (b.p. = ~200 °C/760 mmHg, 112 °C/20 mmHg). Nickel foam was purchased from MTI Corporation. Platinum (Pt) wire counter electrode was purchased from Metrohm Autolab. RE-61AP reference electrode for alkaline solution was purchased from BAS, Inc.

2. Measurements. Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-d using a JEOL EX-400 and an AL-400 NMR spectrometer. Chemical shifts are represented in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed at the Center for Organic Elemental Microanalysis of Kyoto University. The molecular ratio of doped bromine ion (Br⁻) to EDOT unit in the PEDOT fiber (Br⁻/EDOT) was calculated from the elemental analysis. The sum of all the elements is assumed to be 100%. High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (ACPI).

Thermal behavior of PEDOTs was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with alumina pan. Before the TG-DTA measurements, the PEDOT fibers were dried through vacuum pumping for several hours.

The fiber thickness was measured using Nikon Digimicro digital length measuring system with DIGIMICRO MH-15M, DIGIMICRO STAND MS-5C, and DIGITAL READOUT UC-101.

The electrical conductivity of the graphite fiber was measured at room temperature

using a low resistivity meter, Loresta GP with a MCP-TP06P probe (Mitsubishi Chemical Analytech).

X-ray diffraction (XRD) measurements were performed with a Rigaku ultra X18 diffractometer. XRD patterns were recorded with an X-ray generator with Ni filtered $\text{CuK}\alpha$ radiation (40 kV/300 mA: $\lambda = 1.54 \text{ \AA}$) and a flat-plate camera (RINT2500, Rigaku). The sample-to-film distance was 100 mm calibrated using a (111) face of aluminum ($d = 2.33787 \text{ \AA}$) and exposure time was 1–2 h. The diffraction pattern was recorded on an imaging plate and scanned by a RAXIA-Di imaging plate reader at 100 μm resolution. The crystal size along the c -axis (L_c) of the graphite film was estimated from the (002) diffraction peak of the XRD pattern by means of the Scherrer equation, $L = K\lambda/\beta\cos\theta$, where K is the shape factor and adopted to be 0.94, λ is the X-ray wavelength, β is the peak width at half maximum in radians, and θ is the Bragg angle.¹ The degree of orientation of the graphite fiber was estimated using Hermans' (second-order) orientation factor (f) based on the (110) and (200) reflections of the pattern using the equation $f = (\langle 3\cos^2 \varphi \rangle - 1)/2$, where φ is the peak width at half-maximum for the azimuthal-angle profile.²

Raman spectra were obtained at room temperature by backscattering method, using a spectroscopy with a triple monochromator and a charge-coupled device (CCD) detector cooled by Peltier device (NRS-2100 or NRS-4100, JASCO). A 100 mW argon ion laser with a wavelength of 514.5 nm was used. An exposure time was 40 sec (10 sec $\times$ 4). The crystal sizes along the a -axis (L_a) of the carbon and graphite fibers were estimated from the Raman spectra by means of the equation, $L_a = 4.35(I'_D/I'_G)^{-1}$, where I'_D and I'_G are integrated intensities of the D-band and G-band, respectively.^{3,4} I'_D and I'_G are peak intensities of the D-band and G-band, respectively. The Raman spectra

were fitted with a mixed Gaussian-Lorentzian function using the software PeakFit®.

Ultraviolet–visible–NIR (UV–vis–NIR) spectrum was measured using JASCO V570.

Infrared (IR) absorption spectra of PEDOT fibers were measured in powdery solid state with a JASCO FT (Fourier transform)-IR 4200 spectrometer using transmission mode, KBr method.

The accelerating voltage of field emission (FE)-SEM (JSM-7500F, JEOL) was 2–10 kV. The DBEDOT and SSP-PEDOT fibers were coated with Pt or Pt-Pd alloy using an ion coater with type of JFC-1600 (JEOL) before measurements of SEM. The coating thickness was evaluated to be ca. 5 nm.

The carbon fibers were prepared by using an electric furnace (KDF75, Denken). The graphite fibers were prepared by using a graphitization apparatus [SCC-U-80/150 (2P), Kurata-giken].

Carbonization and graphitization yields were evaluated using the equations, (weight of carbonized PEDOT)/(weight of PEDOT)×100 and (weight of graphitized fiber)/(weight of carbon fiber)×100, respectively.

Spin coater (Opticoat MS-A150, MIKASA Corp.) was used for preparing DBEDOT monomer films on glass substrates.

Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed with μAUTOLAB III potentiostat/galvanostat.

The specific capacitance values calculated from CV (C_v) results are based on equation

$$C_v = \frac{\int_{E_1}^{E_2} i(E) dE}{2(E_2 - E_1) \nu}$$

where $\int_{E_1}^{E_2} i(E) dE$ is the total voltammetric charge obtained by integration of positive

and negative sweep, E_1 and E_2 are potential limits, m is the mass of sample, and v is the scan rate.

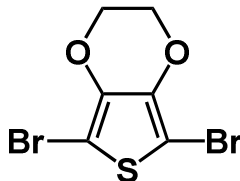
The specific capacitance values calculated from GCD (C_m) results are based on equation

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m},$$

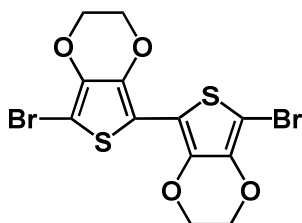
where the I is discharge current, Δt is the discharging time, ΔV is the potential drop during the discharge process in the range of $V_{\max}$ and $V_{\min}$, and m is the mass of the sample.

Synthesis

2,5-Dibromo-3,4-ethylenedioxythiophene (DBEDOT)



To a stirred solution of EDOT (3.0 g, 21.1 mmol) dissolved in 2 : 1 solvent mixture of distilled CHCl_3 (60 mL) and acetic acid (30 mL) was added by slowly NBS (9.38 g, 52.7 mmol) under argon atmosphere. The mixture was allowed to stir for 4 h at room temperature and quenched with water. The organic layer was separated, and the water layer was extracted with CHCl_3 ($\times 3$). The combine CHCl_3 extract was neutralized with NaHCO_3 solution, washed with distilled water, and dried with anhydrous sodium sulfate. The filtered solution was passed through a dry flash silica column using CHCl_3 as the eluent. The crude product was further purified by recrystallization in EtOH affording a white crystalline solid with yield of 55% (3.5 g). Anal., calcd for $\text{C}_6\text{H}_4\text{Br}_2\text{O}_2\text{S}$: C, 24.02; H, 1.34; Br, 53.28; O, 10.67; S, 10.69. Found: C, 24.15; H, 1.33; Br, 52.15; S, 10.70. MS (APCI) calcd for $\text{C}_6\text{H}_4\text{Br}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}^+]$: 298.84. Found: 298.84. ^1H NMR (CDCl_3 , 400 MHz): δ 4.27 (s, 4H, $-\text{OCH}_2$). ^{13}C NMR (CDCl_3 , 100 MHz): δ 64.9, 84.6, 140.1.

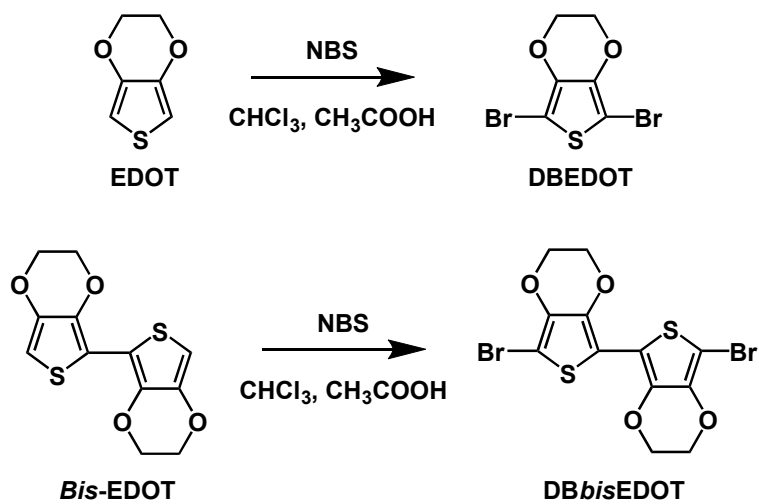
5,5'-Dibromo-2,2'-bis(3,4-ethylenedioxythiophene) [DBbisEDOT]

To a stirred solution of 2,2'-bis(3,4-ethylenedioxythiophene) (*Bis*-EDOT) (1.5 g, 5.3 mmol) dissolved in 2 : 1 solvent mixture of distilled CHCl_3 (30 mL) and acetic acid (15 mL) was added by slowly NBS (2.4 g, 13.3 mmol) in the dark at 0 °C under argon atmosphere. The mixture was allowed to stir for 4 h at 0 °C and quenched with water. The organic layer was separated, and the water layer was extracted with CHCl_3 ($\times 3$). The combine CHCl_3 extract was neutralized with NaHCO_3 solution, washed with distilled water, and dried with anhydrous sodium sulfate. The filtered solution was passed through a dry flash silica column using CHCl_3 as the eluent. The crude product was further purified by recrystallization in EtOH affording a yellow solid with yield of 51% (1.2 g). Anal., calcd for $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}_4\text{S}$: C, 32.75; H, 1.83; Br, 36.31; O, 14.54; S, 14.57. Found: C, 32.65; H, 1.86; Br, 35.53; S, 14.59. MS (APCI) calcd for $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}^+]$: 438.83. Found: 438.83. ^1H NMR (CDCl_3 , 400 MHz): δ 4.28 (s, 8H, $-\text{OCH}_2$).

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Supporting Figures

**Scheme S1.** Synthetic routes of DBEDOT and DBbisEDOT.

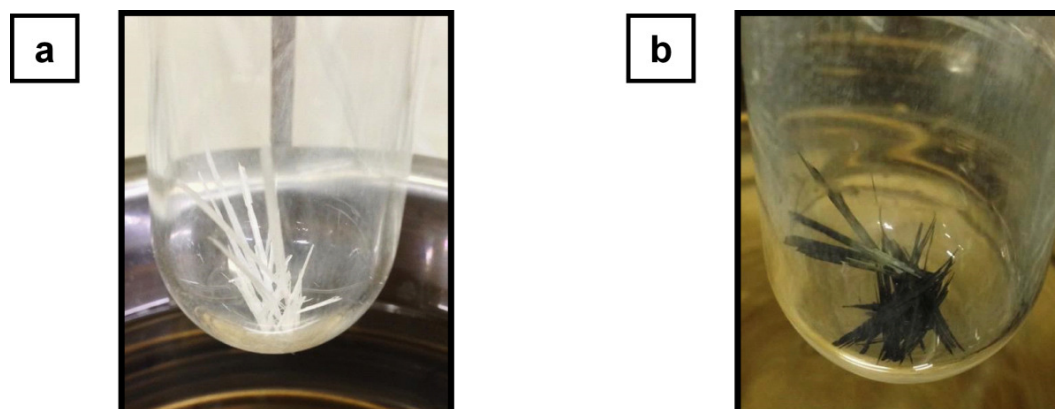


Figure S1. Photographs of the (a) DBEDOT and (b) SSP-PEDOT fibers.

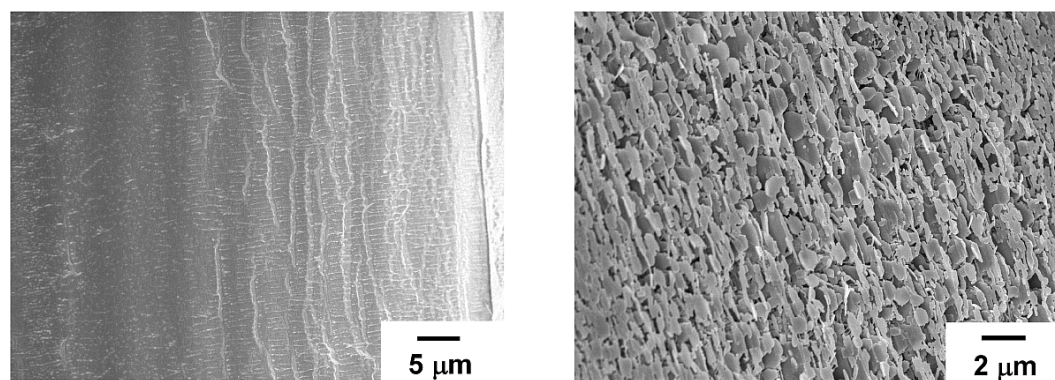


Figure S2. SEM images of the DBEDOT (left) and doped SSP-PEDOT (right) fibers.

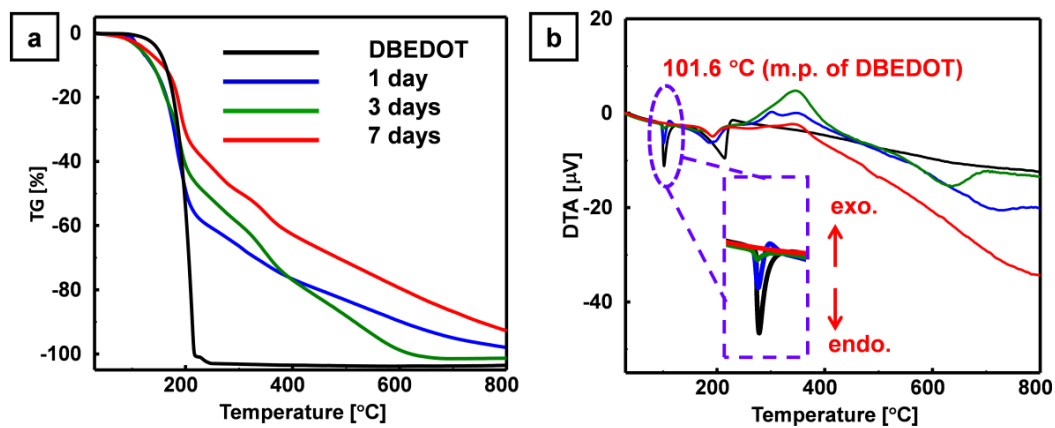


Figure S3. (a) TG and (b) DTA curves of DBEDOT and doped SSP-PEDOT fibers with various polymerization time.

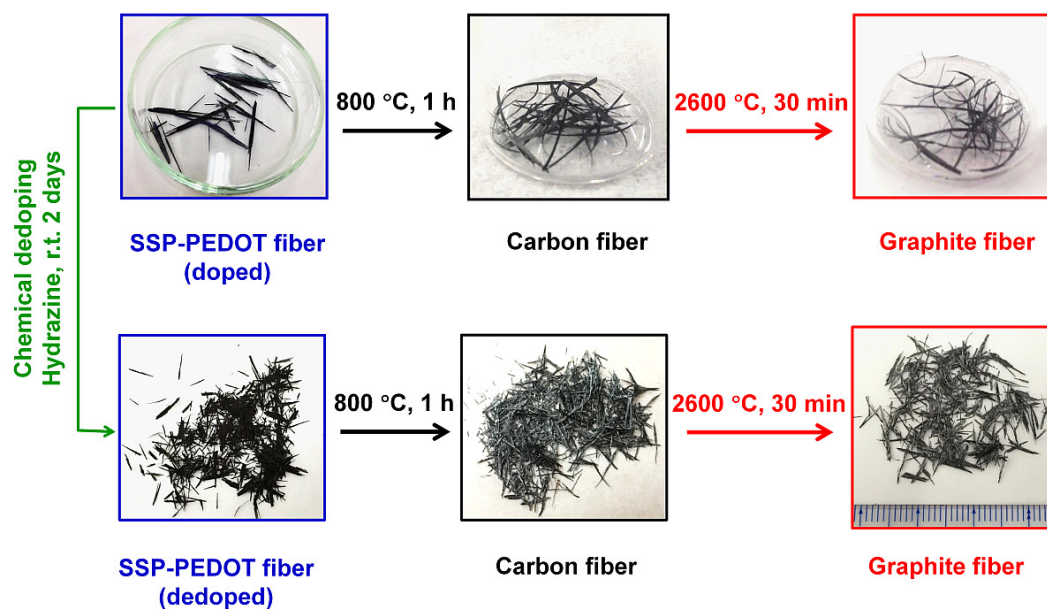


Figure S4. Photographs of the SSP-PEDOT, carbon, and graphite fibers.

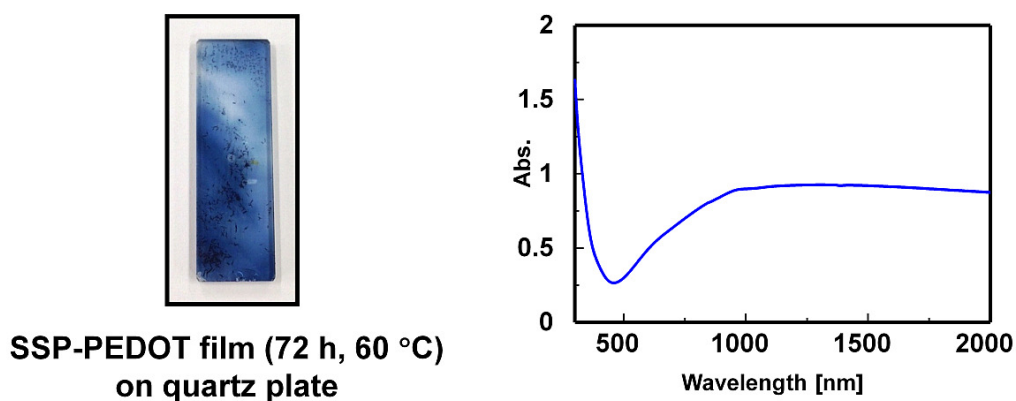


Figure S5. Photograph (left) and UV-vis-NIR spectrum (right) of the doped SSP-PEDOT film on quartz plate.

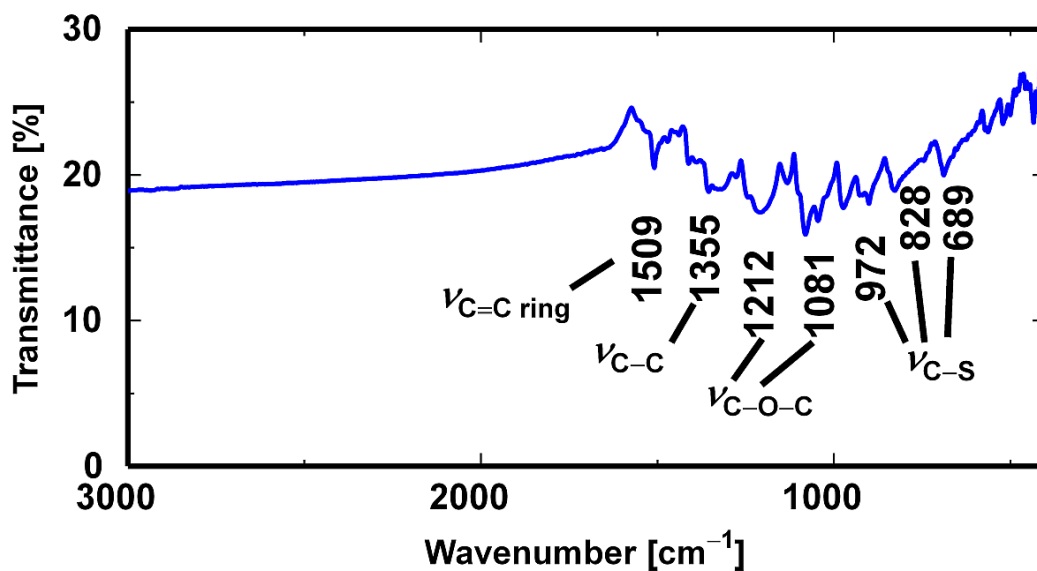


Figure S6. IR absorption spectrum of doped SSP-PEDOT fibers.

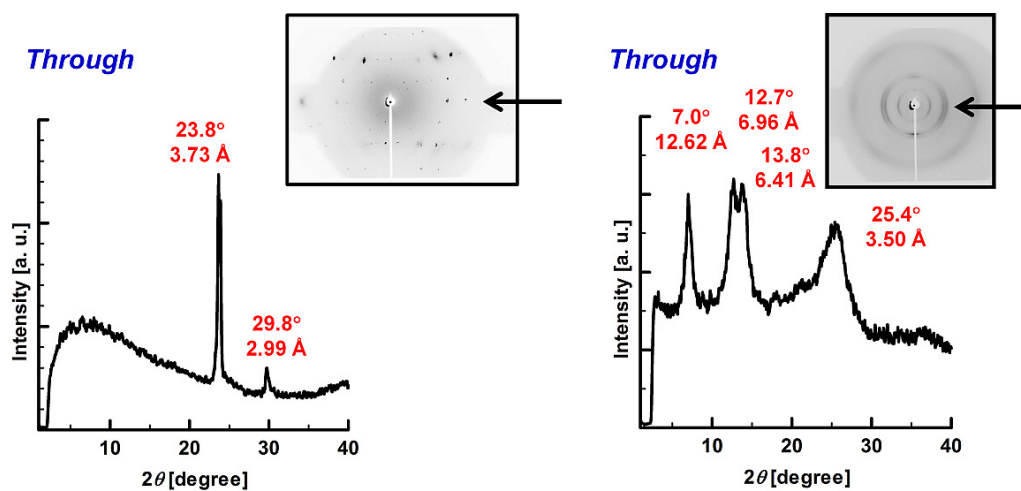


Figure S7. XRD patterns of the DBEDOT (left) and doped SSP-PEDOT (right) fibers in the through direction.

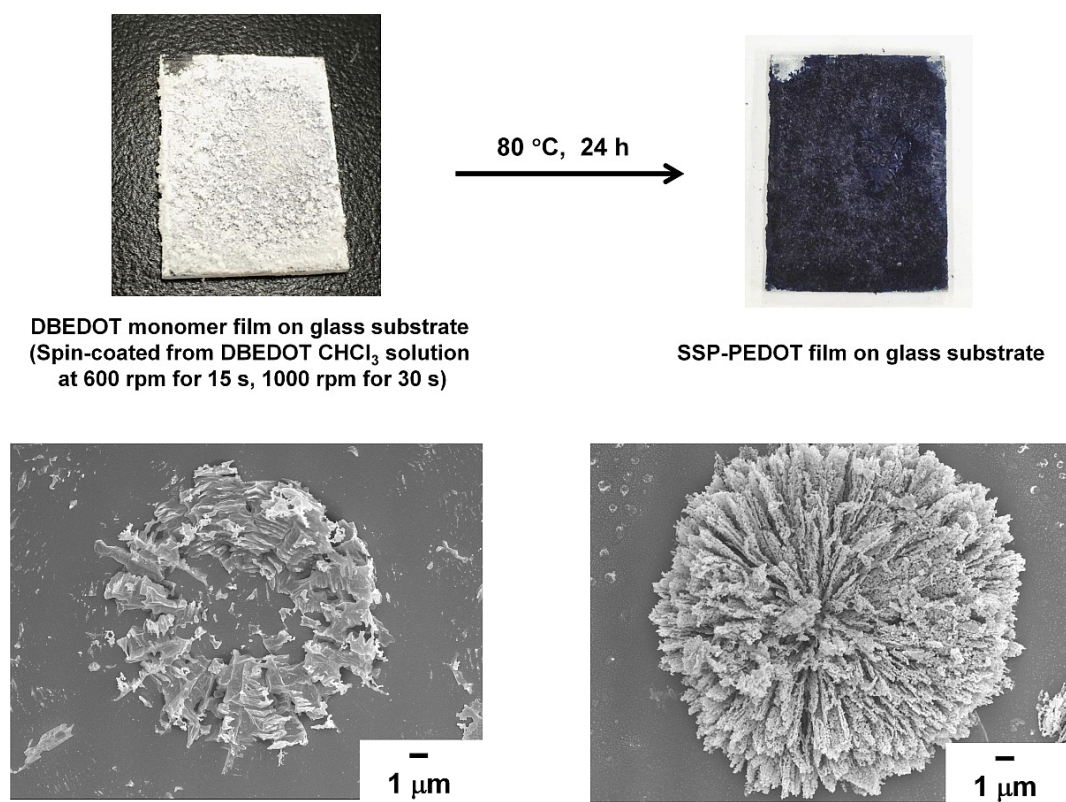


Figure S8. Photographs (upper) and SEM images (lower) of the DBEDOT and doped SSP-PEDOT films.

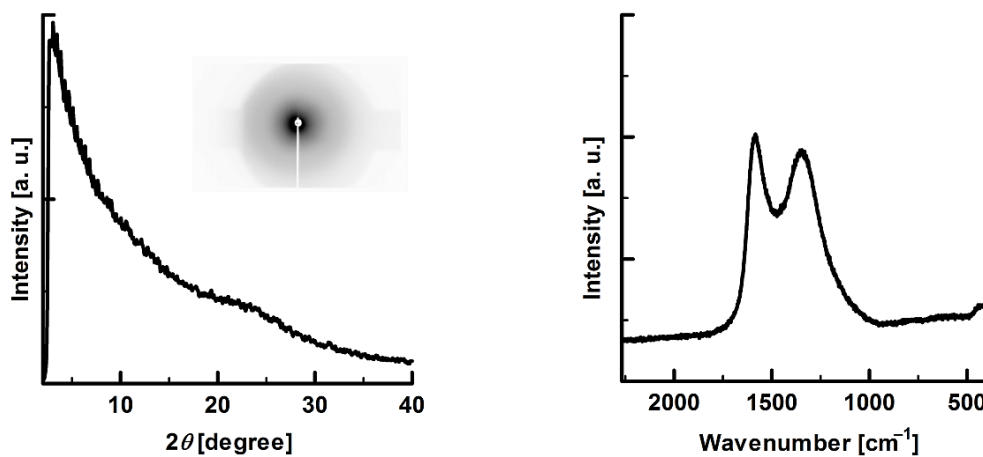


Figure S9. XRD patterns (left) and Raman scattering spectrum (right) of the carbon powder prepared at 800 °C for electrochemical tests.

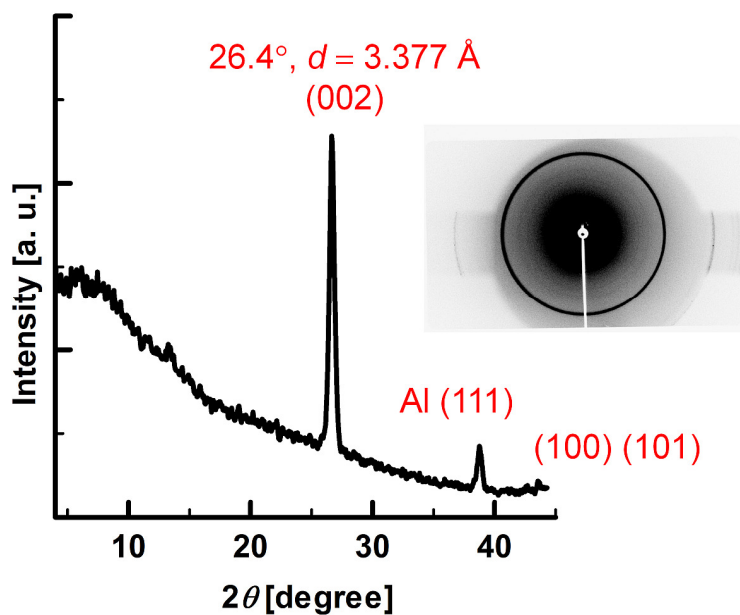


Figure S10. XRD patterns of the kish graphite powder.

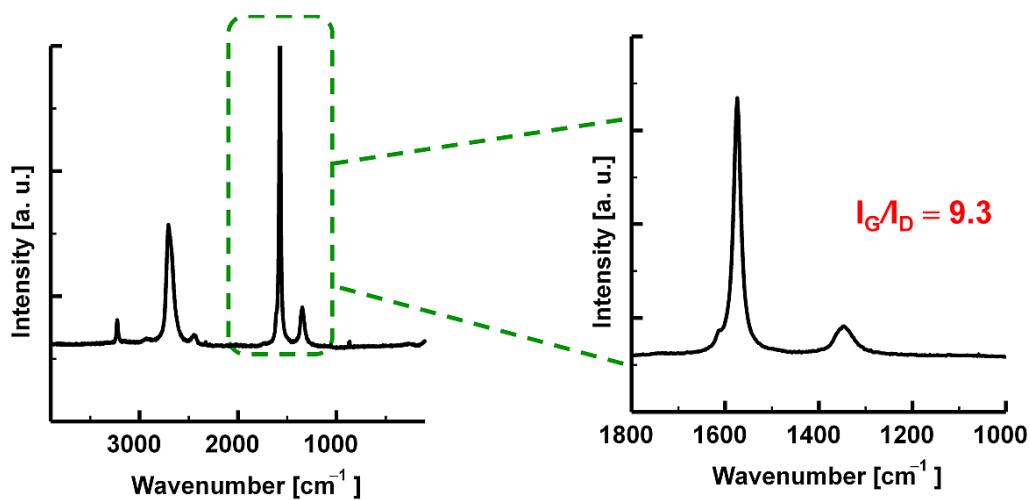


Figure S11. Raman scattering spectra of the kish graphite powder.

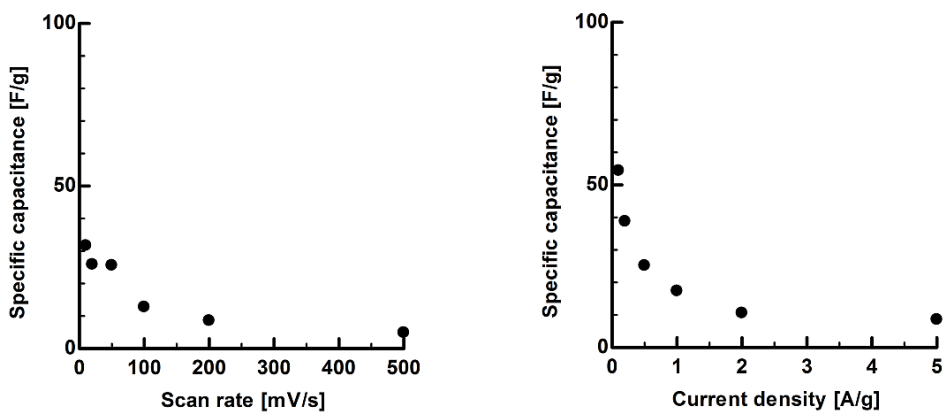


Figure S12. Relationships between specific capacitance and (left) scan rate based on the CV curves and (right) current density based on GCD curves of the carbon films prepared from the doped SSP-PEDOT at 800 °C.

Table S1. Elemental analysis results of SSP-PEDOTs with various polymerization time.

Reaction time	Yield	C, %	H, %	S, %	Br, %	Calculated formula
1 day	80%	25.92	1.73	11.37	50.11	[EDOT(Br ⁻) _{1.77}] _n
7 days	74%	29.89	1.86	13.32	38.49	[EDOT(Br ⁻) _{1.16}] _n
7 days (Soxhlet)	56%	36.75	2.80	16.21	17.14	[EDOT(Br ⁻) _{0.42}] _n
dedoping	64%	36.84	3.35	17.32	5.62	[EDOT(Br ⁻) _{0.13}] _n

Table S2. Carbonization yields and elemental analysis results of carbon and graphite fibers prepared from doped and dedoped SSP-PEDOTs.

Precursor	Heat-treatment temperature (°C)	Yield	C, %	H, %	S, %	Br, %
Doped SSP-PEDOT	800	31%	78.82	0.25	18.75	0
	2600	79%	99.52	0	—	—
Dedoped SSP-PEDOT	800	38%	81.49	0.25	14.62	0
	2600	71%	100.00	0	—	—

Table S3. The structural parameters estimated from XRD patterns and Raman scattering spectra of graphite fibers as well as those of kish graphite and graphite film.

Precursor	Form (direction)	d_{002} (Å)	$d_{100\ 101}$ (Å)	$I_{002}/I_{100\ 101}$	L_c (nm)	Number of graphite layers	I'_G/I'_D	L_a (nm)
Doped SSP-PEDOT	Fiber (edge)	3.3	2.1	341.1	31.6	95	5.4	17.9
	Fiber (through)	3.5	2.1	0.8	–	–		
	In powder	3.4	2.1	10.8	14.5	42		
Dedoped SSP-PEDOT	Fiber (edge)	3.3	2.1	241.6	16.6	50	3.7	10.9
	Fiber (through)	3.4	2.1	2.2	–	–		
	In powder	3.4	2.1	14.6	13.6	40		
Kish graphite	In powder	3.3	2.1	44.0	17.0	50	8.6	17.1
Doped PEDOT ⁵	In film	3.5	2.1	23.5	5.5	16	1.9	8.1

Table S4. The summary of specific capacitances on the basis of the CV and GCD curves of the carbon film.

Scan rate (mV/s)	10	20	50	100	200	500
C_v (F/g)	31.7	25.9	25.6	12.8	8.6	4.9
Current density (A/g)	0.1	0.2	0.5	1.0	2.0	5.0
C_m (F/g)	54.4	38.8	25.2	17.4	10.6	8.6

bromine (Br₂), calcium hydride (CaH₂), chloromethylmethylether, copper(II) chloride (CuCl₂), magnesium (Mg), and potassium carbonate (K₂CO₃) were purchased from Wako Pure Chemical Industries, Ltd.

Chapter 5

Carbon and Graphite Films Prepared from Iodine Doped Enzymatically Synthesized Amylose Films as Carbonization Precursors

Polysaccharide is a biological polymer, which plays important roles in the storage of energy and composition of the structure of living creature. Cellulose, starch, and chitin were widely studied as the most abundant homopolysaccharide because of their biodegradability. Recent years, preeminent antibacterial and mechanical properties of cellulose–chitosan^{1,2} and chitosan–amylose^{3–5} blend films attracted the attention of researchers. However, these studies were carried out on composite films with chitosan acid salts and plasticizers. An additives free film was desirable for the study on the physicochemical properties.

Nearly monodisperse^{6–8} and no branching⁹ enzymatically synthesized amylose (ESA) were prepared from a maltooligosaccharide as primer and glucose 1-phosphate as a substrate. The molecular weight of the synthetic amylose ESA could be controlled by changing the concentration of primer and of glucose-1-phosphate or the reaction time. These results indicate that the ESA is a suitable material for basic research such as solution physics of amylose. Furthermore, films prepared from water-soluble high molecular weight ESA show properties of well transparency and gas barrier, which are expected to be used as food wrapping and optical films.

Recently, we succeeded in preparing mechanically strong, electrically conductive and

thermally stable single-component graphite films from iodine-doped stretchable polyacetylene (PA) films as precursors using a newly developed carbonization method called “morphology-retaining carbonization”.^{10,11} The solvent evacuation method was used for the synthesis of the stretchable PA film. Iodine doping is the most important and indispensable procedure for preventing thermal decomposition and for retaining a fibril structure, as well as for retaining the original shape of the PA precursor film. The morphology-retaining carbonization method is possible for not only PA films but also cellulose papers as precursors. The author reported the preparation of functional carbon papers from iodine-doped cellulose papers at temperatures up to 2600 °C.¹² The author demonstrated that the iodine molecules doped in the cellulose paper prevent thermal decomposition of the paper and play an important role in retaining its entangled microfiber morphology.

It is well known that amylose will change its color to deep blue in the presence of iodine. The iodine molecules are considered to slip inside of the amylose coil. Iodine used as stabilizer for producing carbon products from potato starch and chitosan was reported by Miyajima and co-workers.¹³ In this study, iodine doped ESA with strictly controlled molecular weight was used as carbonization precursors for preparing carbon and graphite films. The relation between the conditions of iodine doping, which is a precursor treatment, and the carbonization yield were discussed and the possibility of application as supercapacitor was investigated. This approach will be able to broaden application of polysaccharide and even the swill processing.

Enzymatically synthesized amylose sample, A-900, was provided from Ezaki Glico Co., Ltd. (Osaka, Japan), which was prepared according to the method of Waldmann *et*

al.^{8,14} The sample was further purified by ethanol precipitation. The M_w s and M_w/M_n s of amylose, were measured by size exclusion chromatography-multi angle laser light scattering measurements on an HPLC system as described previously¹⁵ and determined to be $M_w = 900,000$ and $M_w/M_n = 1.10$. ESA films prepared by casting the amylose solution as reported previously¹⁶ and as described briefly as follows. 9.0 g of A-900 was dissolved in 180 mL of hot water (5 %) and heated at 120 °C for 10 min. The hot solution was filtrated through a glass filter. Then the filtrate was casted on a base film and dried at 60 °C. The thicknesses of these films were 60–100 μm .

The A-900 film yielded the following elemental analysis: C, 44.45; H, 6.22; and O, 49.34. The moisture measurement result of amylose films at 130 °C indicates water content of the film is about 8% (Figure 1a). Figure 1b shows TG and DTA curves of A-900 film. The first mass loss is attributed to the dehydration, and two mass losses from 300 to 600 °C are attributed to the thermal decomposition and oxidation of polymer. The mechanical property of A-900 film (100 μm) was evaluated through tensile test at room temperature. The tensile strength is about 64 Mpa and the tensile modulus is 2.8 GPa (Figure 2).

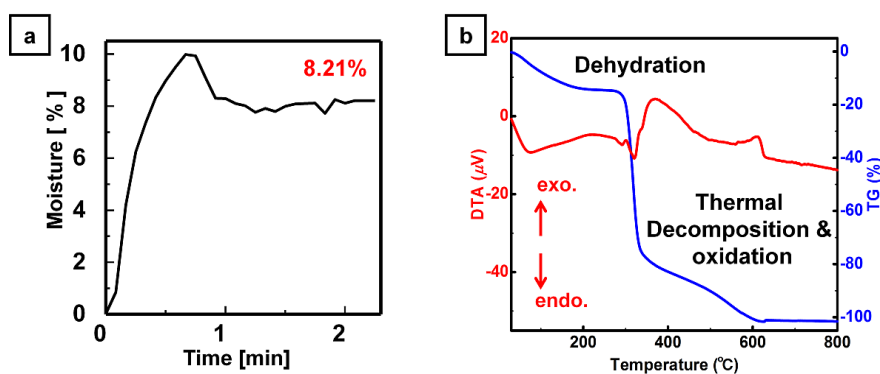


Figure 1. (a) Moisture measurement and (b) TG and DTA curves of A-900 films.

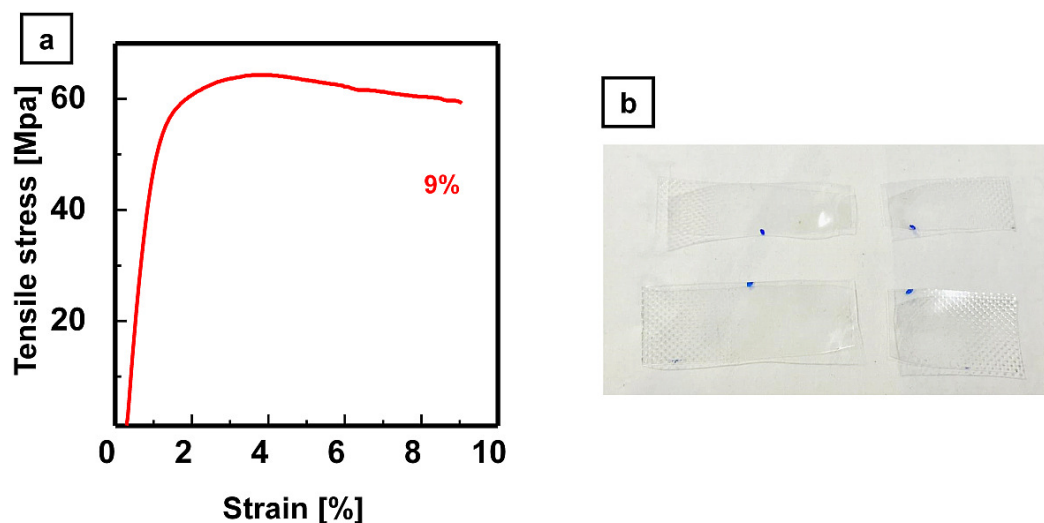


Figure 2. (a) The stress-strain curves for A-900 film. (b) Photographs of the A-900 films after the measurement.

At first, two types of doping methods were used for preparing iodine-doped ESA films. One is vapor-phase reaction (iodine: 0.5 g) at room temperature for 20 days (A-900-V). The colorless film turned to light yellow after reaction. The other is liquid-phase reaction (iodine: 0.5 g) in menthol and water solution (volume ratio 2 : 1) for 3 days at room temperature (A-900-L). The film turned to dark purple-black color after reaction (Figure 3). Figure 4 shows the optical spectra in UV-vis and CD of A-900, A-900-V, and A-900-L films. Both A-900-V, and A-900-L show absorption bands at 300 and 360 nm after iodine doping. However, the absorption band and Cotton effect at 510 nm only appeared in the A-900-L film indicated that the structure of A-900 was changed after liquid phase reaction.

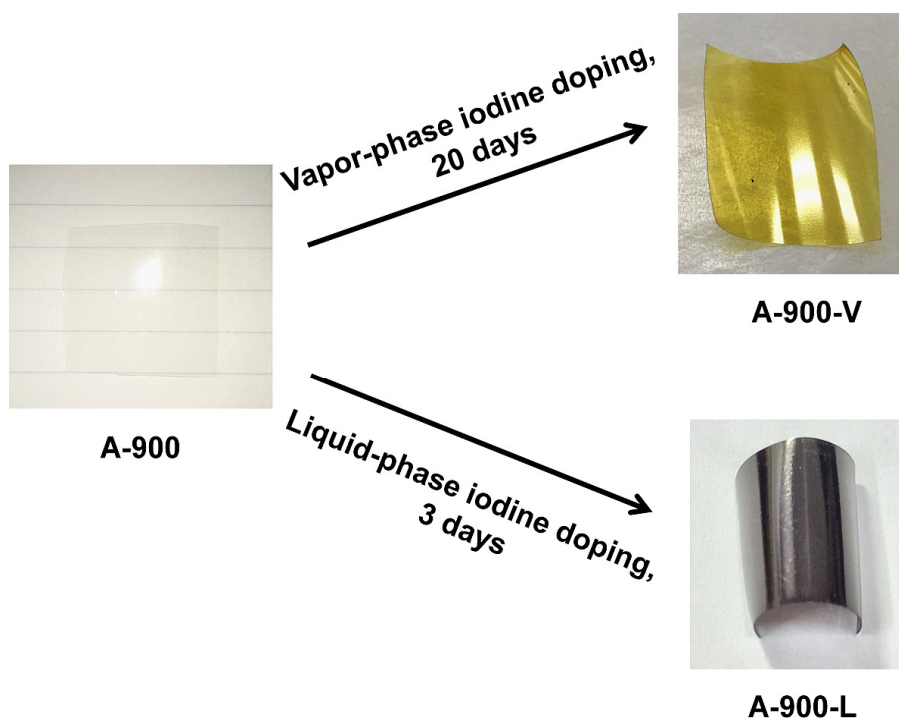


Figure 3. Preparation of A-900-V and A-900-G.

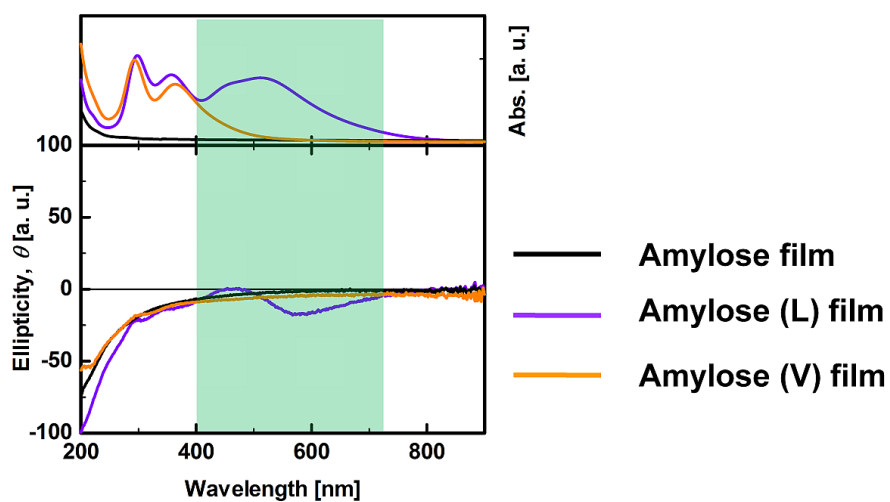


Figure 4. UV-vis and CD spectra of the A-900, A-900-V, and A-900-L films.

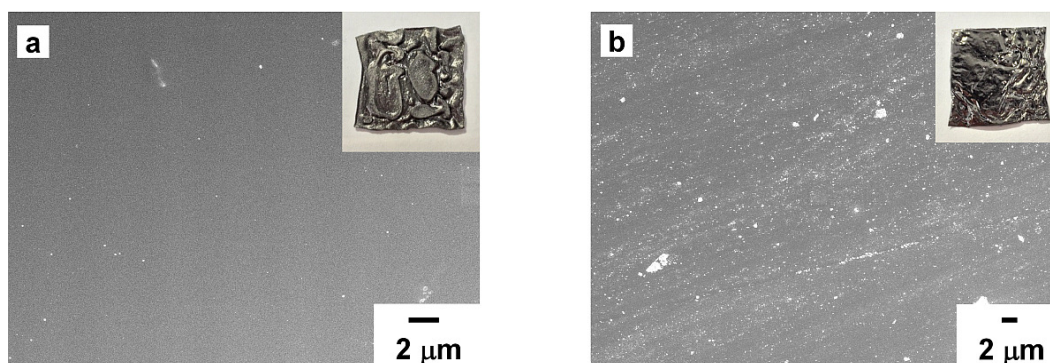


Figure 5. SEM images of carbon films prepared from (a) A-900-V and (b) A-900-L.

Carbon films were prepared from A-900, A-900-V, and A-900-L films via heat treatment at 800 °C (10 °C/min, 1 h) using an electric furnace. After heat treatment, the A-900 film without iodine doping fused and lost the film state (Figure S1 in Supporting Information). On the other hand, the carbonization yields of the A-900-V and A-900-L films were 20 and 25%, respectively. From SEM observation, carbon films prepared from A-900-V and A-900-L films as carbonization precursors showed smooth morphologies (Figure 5).

In order to improve the carbonization yield, a new iodine doping method was developed by combine the vapor and liquid doping conditions. The A-900 film was first infiltrated in menthol and water solution (volume ratio 2 : 1) for 5 s, and then put under vapor-phase doping (iodine: 0.5 g) at room temperature for 24 h (A-900-LV). The film applied a dark purple-black color after reaction. Carbonization yield of the A-900-LV was 30% higher than other two carbonization precursors. From SEM observation, the morphology of carbon film prepared from A-900-LV film as carbonization precursors showed similar smooth morphologies as others (Figure 6). All of the A-900 films with iodine doping retained the film state after heat-treatment,

which indicated that iodine play an important role during the carbonization processes.

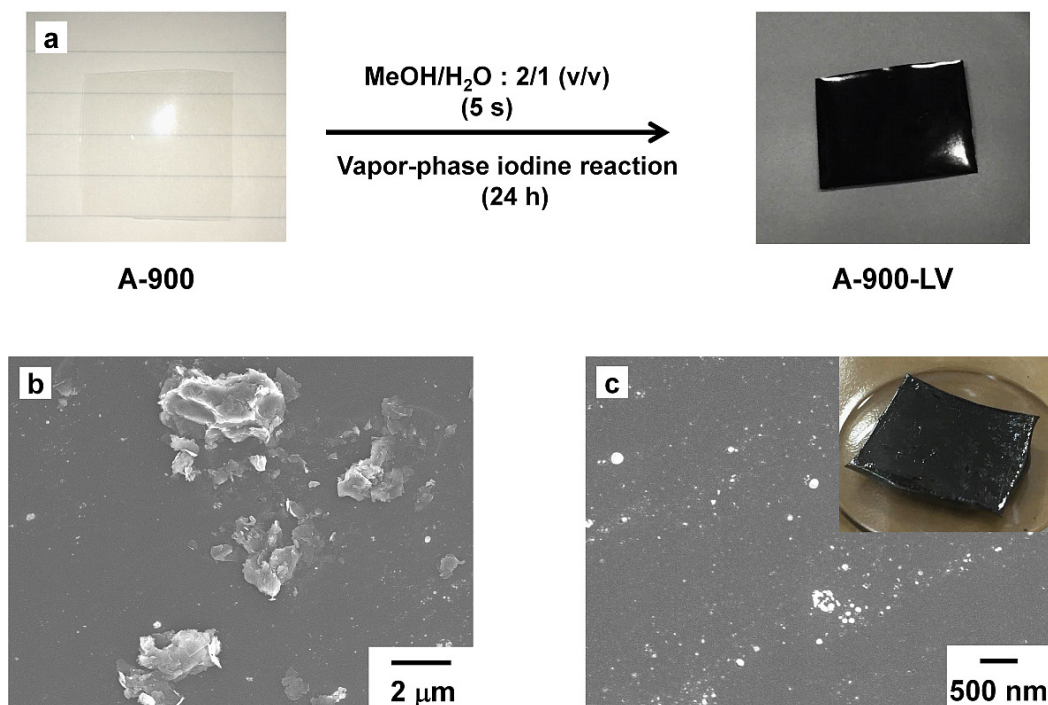


Figure 6. (a) Preparation of A-900-LV. (b,c) SEM images of carbon films prepared from A-900-LV.

Subsequently, the carbonized films were graphitized at 2600 °C (20 °C/min, 30 min) using graphitization equipment with yields of 23%. Bulk density of graphite films prepared from A-900-V, A-900-L, and A-900-LV were 0.42, 0.10, and 0.08 g/cm³, respectively. The graphite films yielded the following elemental analysis: C, 100 and H, 0. The film shape of A-900 was kept completely during the heat treatment process, irrespective of the iodine doping conditions. Figure 7 show SEM images of graphite films prepared from 3 kinds of A-900. Porous morphologies were observed in all of the graphite films. Figure 8 presents XRD patterns of the graphite films after heat treatment at 2600 °C, the graphite films show (002) peaks ($d = 3.4 \text{ \AA}$) of graphitic

crystals, implying that the degree of crystallinity should increase with increasing temperature.

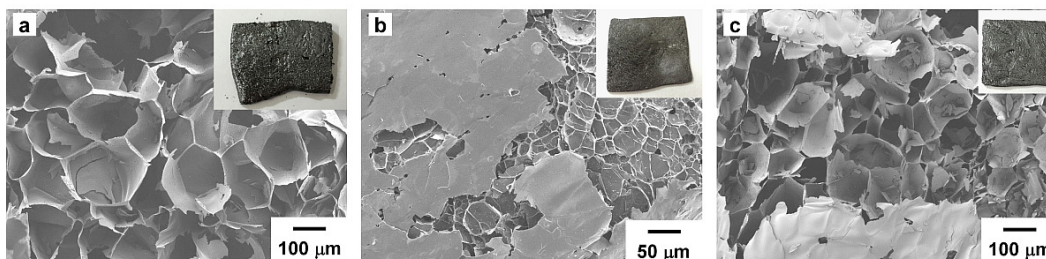


Figure 7. SEM images of graphite films prepared from (a) A-900-V, (b) A-900-L, and (c) A-900-LV.

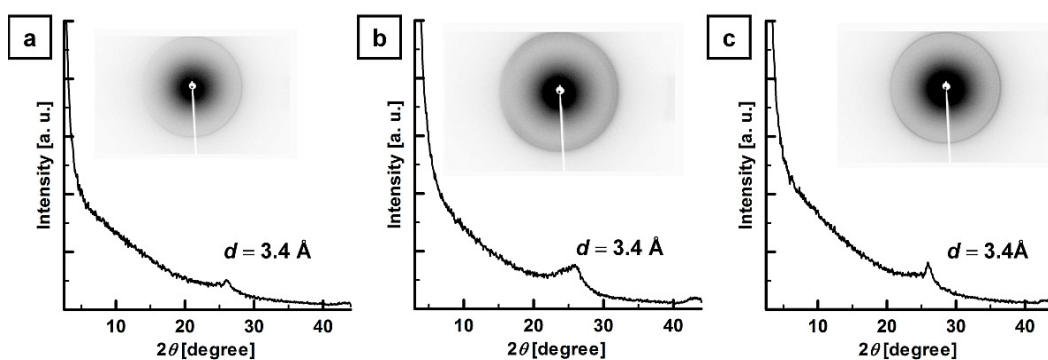


Figure 8. XRD patterns of graphite films prepared from (a) A-900-V, (b) A-900-L, and (c) A-900-LV.

Furthermore, performance of graphite film prepared from A-900 films with porous morphologies for supercapacitor applications was investigated by electrochemical tests. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) were carried out at room temperature in a three-electrode configuration using 5 M KCl aqueous solution as the electrolyte for the evaluation of capacitance of the carbon film sample. Figure 9

shows cyclic voltammograms of the carbon films with scan rate from 10 to 500 mV/s. A quasi-rectangular shape with a slight slope was observed at all scan rates, suggesting some deviations from the ideal electric double-layer capacitive behavior. The specific gravimetric capacitance increased from 1.6 F/g (scan rate at 500 mV/s) to 5.9 F/g (10 mV/s) calculated from the voltammograms (Table 1). Figure 10 shows GCD curves at current density from 0.1 to 5 A/g within a potential window of -1 – 0 V. Typical triangular shapes were observed and the specific capacitance values were calculated at different current densities. The specific capacitance of 8.1 F/g was attained at low current of 0.1 A/g. When the current increased to a high density of 5 A/g, the specific capacitance still remained to 11.0 F/g, indicating good rate capability. These results were one order lower than the cellulose-derived supercapacitors prepared from filter paper at heating temperature at 1300 °C, which provide specific gravimetric capacitance value of 28.9 F/g (current density at 1 A/g).¹⁷ With decreasing of heat treatment temperature, using acid electrolytes, and also by optimization of the sample preparation, carbon film with a higher specific capacitance value and better performance could be expected.

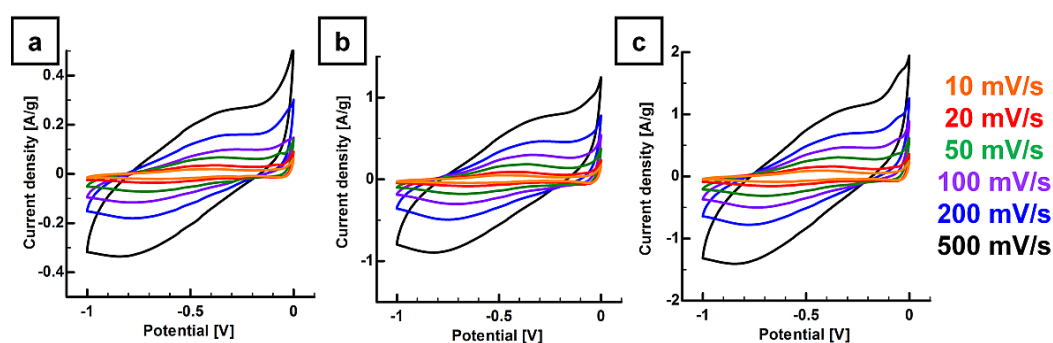


Figure 9. CV curves of graphite films prepared from (a) A-900-V, (b) A-900-L, and (c) A-900-LV with various scan rates.

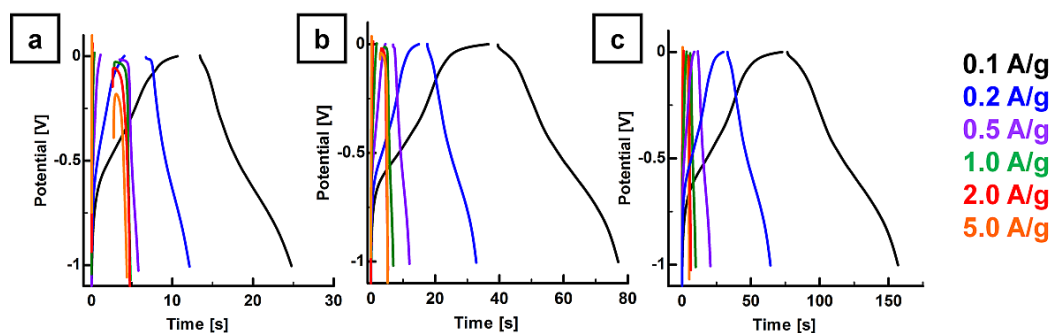


Figure 10. GCD curves of graphite films prepared from (a) A-900-V, (b) A-900-L, and (c) A-900-LV with various scan rates.

Table 1. The summary of specific capacitances on the basis of the CV and GCD curves of the graphite film.

Scan rate (mV/s)		10	20	50	100	200	500
C_v (F/g)	M1	1.4	1.2	1.0	0.7	0.6	0.4
	M2	3.2	2.9	2.3	1.9	1.5	1.1
	M3	5.9	5.1	4.0	3.1	2.4	1.6
Current density (A/g)		0.1	0.2	0.5	1.0	2.0	5.0
C_m (F/g)	M1	1.1	1.1	1.1	2.0	4.2	8.0
	M2	3.8	3.1	2.6	2.8	4.2	11.5
	M3	8.1	6.3	4.6	4.1	5	11.0

In summary, a novel approach for preparing carbon and graphite films was developed using iodine doped ESA with strictly controlled molecular weight as carbonization precursors. All of the ESA films with iodine doping retained the film state after heat-treatment, which indicated that iodine play an important role during the carbonization processes. The carbonization yield of the ESA films can be controlled

by changing the condition of iodine doping process. The possibility of application as supercapacitor was investigated. This approach will be able to broaden application of polysaccharide and even the swill processing.

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Chapter 5 Appendix

Materials and Measurements

1. Materials

2. Measurements

Synthesis

Supporting References

Supporting Figures

Materials and Measurements

1. Materials. The chemical compounds were purchased from commercially available sources and were used as received. The compound, potassium chloride (KCl) were purchased from Nacalai Tesque, Inc. Carbon black (Super P, conductive, 99+ %) was purchased from Alfa Aesar. Polytetrafluoroethylene preparation (60 wt %, dispersion in H₂O) was purchased from Aldrich. EtOH were used as received. Nickel foam was purchased from MTI Corporation. Nickel plate was purchased from Nilaco Co., Ltd. Platinum (Pt) wire counter electrode was purchased from Metrohm Autolab. RE-61AP reference electrode for alkaline solution was purchased from BAS, Inc.

2. Measurements. Thermal behavior of A-900 was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with alumina pan.

The film thickness was measured using Nikon Digimicro digital length measuring system with DIGIMICRO MH-15M, DIGIMICRO STAND MS-5C, and DIGITAL READOUT UC-101.

The electrical conductivity of the carbon film was measured at room temperature using a low resistivity meter, Loresta GP with a MCP-TP06P probe (Mitsubishi Chemical Analytech).

X-ray diffraction (XRD) measurements were performed with a Rigaku ultra X18 diffractometer. XRD patterns were recorded with an X-ray generator with Ni filtered $\text{CuK}\alpha$ radiation (40 kV/300 mA: $\lambda = 1.54 \text{ \AA}$) and a flat-plate camera (RINT2500, Rigaku). The exposure time was 1–2 h. The diffraction pattern was recorded on an imaging plate and scanned by a RAXIA-Di imaging plate reader at 100 μm resolution.

Ultraviolet–visible (UV–vis) and circular dichroism (CD) spectra were measured using JASCO V570 and JASCO J820 spectrometers, respectively.

Infrared (IR) absorption spectra of A-900 films were measured in powdery solid state with a JASCO FT (Fourier transform)-IR 4200 spectrometer using transmission mode.

The tensile tests of the A-900 films was performed at room temperature using a TENSILON RTG-1210 (A&D) with a load cell of 500 N at a displacement rate of 0.05 mm/min for the tensile test. The specimens for the tensile test were 4–12 mm wide (w), and the chuck distance (L_t) was 5 mm. The tensile strength (σ_t) and modulus (ε_t) were calculated using, $\sigma_t = f_t/wt$ and $\varepsilon_t = f/\delta$, respectively, where f_t is the maximum load, t is the specimen thickness, and f/δ is the initial linear slope of the load displacement curve.

The accelerating voltage of field emission (FE)-SEM (JSM-7500F, JEOL) was 2–10 kV. The A-900 films were coated with Pt or Pt-Pd alloy using an ion coater with type of JFC-1600 (JEOL) before measurements of SEM. The coating thickness was

evaluated to be ca. 5 nm.

The carbon films were prepared by using an electric furnace (KDF75, Denken). The graphite films were prepared by using a graphitization apparatus [SCC-U-80/150 (2P), Kurata-giken].

Carbonization and graphitization yields were evaluated using the equations, (weight of carbonized A-900)/(weight of A-900)×100 and (weight of graphitized film)/(weight of carbon film)×100, respectively.

Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed with μAUTOLAB III potentiostat/galvanostat.

The specific capacitance values calculated from CV (C_v) results are based on equation

$$C_v = \frac{\int_{E_1}^{E_2} i(E) dE}{2(E_2 - E_1)mv},$$

where $\int_{E_1}^{E_2} i(E) dE$ is the total voltammetric charge obtained by integration of positive and negative sweep, E_1 and E_2 are potential limits, m is the mass of sample, and v is the scan rate.

The specific capacitance values calculated from GCD (C_m) results are based on equation

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m},$$

where the I is discharge current, Δt is the discharging time, ΔV is the potential drop during the discharge process in the range of $V_{\max}$ and $V_{\min}$, and m is the mass of the sample.

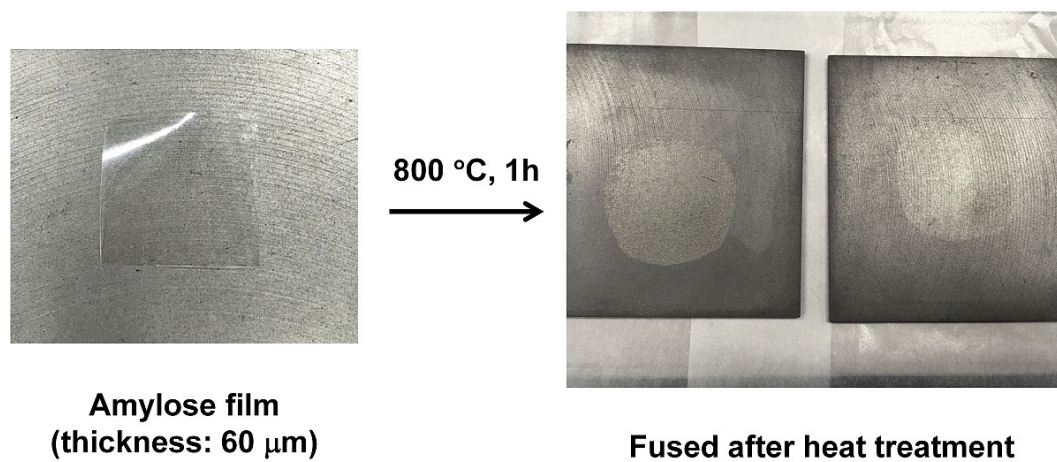
Supporting Figures

Figure S1. Photographs of A-900 without iodine doping before (left) and after (right) heat treatment.

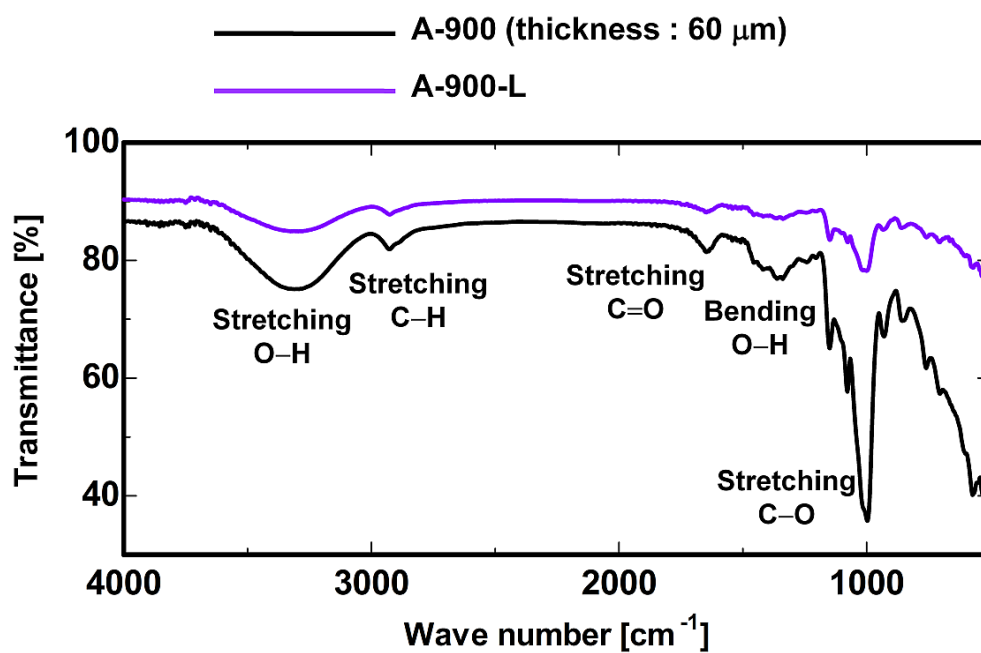


Figure S2. IR absorption spectra of A-900 and A-900-L films.

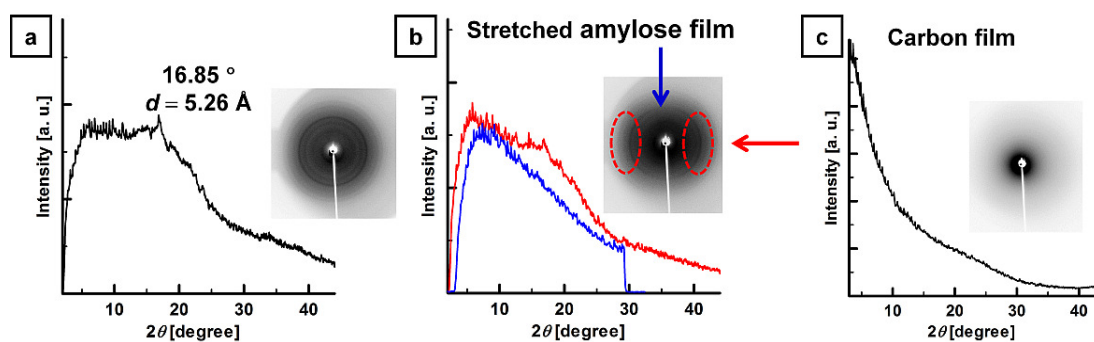


Figure S3. XRD patterns of (a) A-900, (b) stretched A-900, and (c) carbon film prepared from A-900-LV at 800 $^\circ\text{C}$.

General Conclusion

In *Chapter 1*, the author have prepared carbon and graphite whiskers with not only randomly but also macroscopically aligned morphologies from self-assembled PMP derivatives as carbonization precursors. The XRD profiles and Raman scattering spectra indicated that graphitic crystallization proceeded further in the carbon films though heat treatment at 2600 °C. The aligned carbon whiskers showed anisotropic electrical conductivity. It was also demonstrated that the esterolysis process is a new approach to retain the morphologies of precursors during heat treatment and could be used for other π -conjugated polymers as carbonization precursors. Thus, the prepared aligned whisker-type carbon and graphite films might be useful for anisotropic electrical materials with thermal stability and for engineering conducting wires based on microsize assemblies.

In *Chapter 2*, H-PEDOT films prepared in an N*-LC asymmetric reaction field via an electrochemical oxidative polymerization had clearly spiral morphologies consisting of fibril bundles. Three types of chiral dopants were used to control the distances between the fibril bundles and the screw direction in the spiral morphology. The (*R*)- and (*S*)-H-PEDOT films exhibited Cotton effects with mirror images in the CD measurement, irrespective of the neutral and oxidized form, upon optimization of the aging time and cooling rate of the N*-LC systems before polymerization. From the results of SEM observation, the spiral morphology of H-PEDOT film remained completely in the helical carbon and graphite films after the heat treatment. This is because of the advanced carbonization substrate, an oxidized PEDOT film. A graphite

film with well-controlled helical morphologies may exhibit unique electrochemical properties characteristic of the helical structure, diamagnetism, and electrical conductivity.

In *Chapter 3*, the author reviewed the recent progress in the solid-state carbonization of conjugated polymers as precursors by focusing on their potential for producing unique carbonaceous and graphitic materials with controlled morphology.

Section 2 described recent developments regarding various conjugated-polymer-based carbonaceous and graphitic materials in terms of a precursor molecular structure. Section 3 revealed that iodine doping is effective for increasing carbonization yield and for retaining the morphology of PA films by focusing on the preparation of macroscopically aligned carbon and graphite films from highly stretched PA films as precursors using morphology-retaining carbonization. Section 4 focused on the preparation of helical carbon and graphite films with hierarchically arranged fibril and spiral morphologies from doped helical PA and PEDOT films as precursors. Section 5 discussed the heat treatment of self-assembled PmP derivatives, which affords filamentous graphitic materials, such as carbon and graphite whiskers. It was also discussed that the esterolysis process of the PmP derivatives is the indispensable procedure for retaining the PmP whisker morphology during the heat treatment.

In *Chapter 4*, a novel approach for preparing graphite fibers with outstanding crystallinity, structural order parameter, and electrical conductivity was developed using SSP-PEDOT fiber as carbonization precursors without any time-consuming pretreatments such as aligned substrates or a mechanical-stretching procedure. Graphite

fibers prepared from the doped SSP-PEDOT provide higher crystallinity than the dedoped one, which afford high orientation factor of up to 0.85. Furthermore, carbon film produced from SSP-PEDOT at heat treatment at 800 °C shows good capacitance performance in base electrolytes, which carve out a new direction for the usage of SSP-PEDOT. Engineering conducting wires with highly ordered structure and thermal stability might be one of the most anticipated applications of the graphite fibers.

In *Chapter 5*, a novel approach for preparing carbon and graphite films was developed using iodine doped ESA with strictly controlled molecular weight as carbonization precursors. All of the ESA films with iodine doping retained the film state after heat-treatment, which indicated that iodine play an important role during the carbonization processes. The carbonization yield of the ESA films can be controlled by changing the condition of iodine doping process. The possibility of application as supercapacitor was investigated. This approach will be able to broaden application of polysaccharide and even the swill processing.

List of Publications

- 1) Yan, B.; Matsushita, S.; Suda, K.; Akagi, K.

Macroscopically Aligned Carbon and Graphite Whiskers Prepared from Poly(*m*-phenylene) Derivatives with Helicene-like Helical Structures.

Chem. Mater. **2015**, 27, 2973–2980.

(*Chapter 1* is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in *Chem. Mater.*, copyright © American Chemical Society after peer review. To access the final edited and published work see the following website:

<http://pubs.acs.org/doi/abs/10.1021/acs.chemmater.5b00303>)

- 2) Yan, B.; Matsushita, S.; Akagi, K.

An Advanced Method for Preparation of Helical Carbon and Graphitic Films Using a Carbonization Substrate.

Chem. Mater. **2016**, 28, 8781–8791.

(*Chapter 2* is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in *Chem. Mater.*, copyright © American Chemical Society after peer review. To access the final edited and published work see the following website:

<http://pubs.acs.org/doi/abs/10.1021/acs.chemmater.6b04355>)

- 3) Matsushita, S.; Yan, B.; Kyotani, M.; Akagi, K.

Morphology-controlled Carbonaceous and Graphitic Materials Prepared from Conjugated Polymers as Precursors through Solid-state Carbonization.

Synth. Met. **2016**, *216*, 103–112.

(*Chapter 3* is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in *Synth. Met.*, copyright © 2015 Elsevier B.V. after peer review. To access the final edited and published work see the following website:

<http://dx.doi.org/10.1016/j.synthmet.2015.09.010>)

- 4) Yan, B.; Matsushita, S.; Akagi, K.

Aligned Carbon and Graphite Fibers Prepared from Solid-State Polymerized Poly(3,4-ethylenedioxythiophene) Single Crystals and Their Applications for Supercapacitors.

(*Chapter 4* is the unedited Author's version of a Submitted Work that will be accepted for publication after peer review.)

- 5) Yan, B.; Matsushita, S.; Suzuki, S.; Kitamura, S.; Kaiho, T.; Akagi, K.

Carbon and Graphite Films Prepared from Iodine Doped Enzymatically Synthesized Amylose Films as Carbonization Precursors.

(*Chapter 5* is the Author's version of an Unsubmitted Work that will be submitted for publication.)