Macromolecules

Liquid Crystalline Polythiophene Bearing Phenylnaphthalene Side-Chain

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Supporting Information

ABSTRACT: Polythiophene bearing a 2-phenylnaphthalene side group at 3-position was synthesized from a 2,5-dibromothiophene monomer by two polymerization methods, i.e., Yamamoto dehalogenative polycondensation using Ni(cod)₂ and Ni-catalyzed chain-growth polymerization. Polymers prepared by the former method had good solubility for organic solvents, 6300–8400 g mol⁻¹ of number-average molecular weights, absorption bands at around 300 and 385 nm due to $\pi - \pi^*$ transitions at the phenylnaphthalene moiety and polythiophene backbone, a main fluorescence emission band at around 540 nm from the polythiophene backbone in solution and film state, and presence of enantiotropic liquid crystalline



phases which enabled to construct an arrayed state. On the other hand, the latter polymer showed considerably red-shifted absorption and emission bands at around 444 and 585 nm in solution and 509 and 720 nm in film state respectively, but had poor solubility and unresolved mesophases.

INTRODUCTION

Conjugated polymers bearing a liquid crystalline side-chain have been studied for the purpose of adding specific functionalities of birefringence, self-orientation, and induced anisotropy to semiconducting polymer backbones.^{1–3} They are prospective candidate of elaborate functional materials as well or better than main-chain type liquid crystalline conjugated polymers,^{4,5} because their electrical and optical properties are expected to be controlled by the molecular orientation of various liquid crystalline side chains and furthermore macroscopic alignment of them can be progressed by an external perturbation such as shear stress, electric or magnetic field.^{6–8}

Polythiophene derivatives have been drawing much attention for their wide-spreading potential of applications, such as organic light emitting diodes, ^{9–11} polymer solar cells, ^{12–15} and organic field effect transistors. ^{16,17} Therefore, they have also been investigated as π -conjugated backbone of the side-chain type polymer liquid crystals. For development of liquid crystallinity of polythiophenes, selective 2,5-polymerization of thiophene having mesogenic group at 3-position was crucial¹⁸ and several methods have successfully produced characteristic liquid crystalline polythiophenes, respectively.^{3,7,19–23} However, the excellent liquid crystalline polythiophenes, in which a fair percentage of insulating parts occupied, have faced a dilemma of sacrificing inherent electrical and optical properties of polythiophene. Replacement of the insulating side chains by semiconducting ones might be a solution and development strategy. Therefore, several conjugated polymers bearing semiconducting side chains have been synthesized and their basic properties were surveyed.²⁴

2-Phenylnapthalene derivatives have been received much attention as a calamitic liquid crystalline photoconductor with ambipolar and high carrier transport properties.^{25,26} It is considered that calamitic thermotropic liquid crystals are suitable as the side chain of polythiophene that should take a lamellar structure. In this paper, 2,5-dibromothiophene monomer having 2-phenylnaphthalene side chain at 3-position was prepared by two methods. The former is conventional 2,5-polymerization of 3-substituted polythiophenes using Ni(cod)₂ known as Yamamoto method²⁷ under different conditions to

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give two polythiophenes with different degree of polymerization (**PTPhN1a** and **PTPhN1b**) whose regioregularity of head-to-tail is uncontrolled, and the latter is Ni-catalyzed chaingrowth method^{28,29} to provide a 3-substituted polythiophene with high regioregularity of head-to-tail conformation, **PTPhN2**, as summarized in Scheme 1. Furthermore, basic

Scheme 1. Polymerization Methods



properties of these polymers were investigated by comparing their conformations, molecular weights, absorption-emission characteristics, and thermotoropic liquid crystalline behaviors.

EXPERIMENTAL SECTION

General Data. Average molecular weights of the polymers were determined by gel permeation chromatography (GPC) calibrated with polystyrene standards using THF as an eluent. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured with a JEOL JNM-ECS 400 at a resonance frequency of 400 MHz for ¹H and 100 MHz for ¹³C in CDCl₃ at room temperature. A Bruker AVANCE 600 was also used to measure NMR spectra at a resonance frequency of 600 MHz for ¹H and 150 MHz for ¹³C in chlorobenzene-*d*₅ at room



temperature for PTPhN1b and at 120 °C for PTPhN2. IR spectra were recorded on a JASCO FT/IR 550 spectrometer. UV-vis absorption and photoluminescence (PL) spectra were recorded on a Shimadzu UV-3100PC and a Hitachi F-4500. The thermal properties of compounds were analyzed by differential scanning calorimetry (DSC) using SII EXSTAR 6000 at a heating/cooling rate of 10 °C min⁻¹. The optical textures of mesophases were observed by a Nikon ECLIPSE E 600 POL and a Nikon ECLIPSE LV 100 polarizing optical microscope (POM) with a Linkam TH-600PM thermocontroller. Xray diffraction (XRD) measurements were performed using a Rigaku RINT2100 and a PANalytical X'pert diffractometer with Cu-K_a radiation (λ = 1.5418 Å). Electrochemical measurements of drop-cast films of the polymers on an electrode were performed by cyclic voltammetry using a Hokuto Denko HB-305 function generator and a HAL3001 potentiostat equipped with a Pt disk electrode as the working electrode, a Pt plate as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The measurements were carried out at a scanning rate of 50 mV s^{-1} in acetonitrile (0.1 mol dm⁻³ Et₄NBF₄) under an Ar atmosphere. Ionization potentials (vs vacuum) of the polymers were estimated from the onset of their first oxidation peak (E_{onset}) in the cyclic voltammograms on the basis that ferrocene/ferrocenium is 4.8 eV below the vacuum level.^{30,31}

Materials. Following compounds shown in Scheme 2 were prepared according to methods described in a preceding report²⁴ with a little modification and the experimental details were described in Supporting Information; 2-(10-bromodecyloxy)tetrahydro-2H-pyran (1), 3-(10-tetrahydro-2H-pyran-2-yloxydecyl)thiophene (2), 3-thiophenedecanol (3), 2,5-dibromo-3-thiophenedecanol (4), 4-octyl-phenylboronic acid (5), 2-Methoxy-6-(4-octylphenyl)naphthalene (6). Other chemicals used in this study were purchased from Kanto Chemical Co., Inc., Tokyo Chemical Industry Co., Ltd., Nacalai Tesque Inc., Sigma-Aldrich Co., LLC., Merck & Co., Inc., or Acros Organics of Thermo Fisher Scientifics, and used without further purification unless stated. THF and DMF were purified by distillation according to common methods.

Synthesis. 2-(4-Octylphenyl)-6-hydroxynaphthalene (7). Into 6 (2.66 g, 7.68 mmol) in dry CH_2Cl_2 (100 mL) boron tribromide (15.3 mL, 1.0 mol dm⁻³ in CH_2Cl_2) was added dropwise under N₂ atmosphere at 0 °C. After stirring at room temperature overnight, water was poured into the reaction solution at 0 °C. The product was extracted with CH_2Cl_2 ,



washed with aqueous NaHCO₃ and water, and dried over anhydrous Na₂SO₄. Recrystallization from toluene gave 7 as a solid product (2.01 g, 78.8% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.89 (t, 3H), 1.28 (br, 10H), 1.66 (m, 2H), 2.66 (t, 2H), 5.04 (s, 1H), 7.12 (dd, 1H), 7.17 (d, 1H), 7.28 (d, 2H), 7.61 (d, 2H), 7.68–7.75 (m, 2H), 7.80 (d, 1H), 7.96 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 14.11, 22.67, 29.27, 29.38, 29.50, 31.53, 31.89, 35.63, 109.29, 118.09, 125.36, 126.25, 126.77, 127.02, 128.89, 129.18, 130.09, 133.61, 136.40, 138.42, 141.99, 153.39.

2,5-Dibromo-3-{10-[6-(4-octylphenyl)naphthalene-2-yloxy]decyl}thiophene (8). To a solution of 4 (1.06 g, 2.66 mmol), 7 (0.86 g, 2.59 mmol), and triphenylphosphine (0.85 g, 3.24 mmol) in dry THF (20 mL), diethyl azodicarboxylate (DEAD) (1.5 mL, 40% in toluene) was added at 0 °C, which was stirred at room temperature for 3 days. The product was purified by column chromatography on silica gel (CH₂Cl₂/hexane, 1:1) and recrystallization from acetone, which gave a colorless solid (1.18 g, 62.1% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.88 (t, 3H), 1.31 (br, 20H), 1.46–1.57 (m, 4H), 1.66 (m, 2H), 1.85 (m, 2H), 2.50 (t, 2H), 2.65 (t, 2H), 4.08 (t, 2H), 6.77 (s, 1H), 7.13-7.17 (m, 2H), 7.27 (d, 2H), 7.61 (d, 2H), 7.69 (dd, 1H), 7.75–7.78 (m, 2H), 7.94 (d, 1H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 14.10, 22.67, 26.09, 29.06, 29.24, 29.27, 29.32, 29.37, 29.43, 29.45, 29.50, 29.52, 29.54, 31.53, 31.89, 35.63, 68.05, 106.39, 107.92, 110.29, 119.36, 125.25, 125.93, 127.00, 127.09, 128.87, 129.12, 129.55, 130.95, 133.65, 136.22, 138.51, 141.88, 142.97, 157.14. Anal. Calcd for C38H48OSBr2: C 64.04, H 6.79, N 0.00. Found: C 63.89, H 6.52, N 0.06.

2-(4-Octylphenyl)-6-decyloxynaphthalene (PhN). 1-Bromodecane (95.0 μL, 0.46 mmol) and 7 (152 mg, 0.46 mmol) in acetone (4 mL) were refluxed for 3 days in the presence of K₂CO₃ (94 mg, 0.68 mmol). The mixture was washed with water/CH₂Cl₂ and the organic layer was dried over anhydrous Na₂SO₄. The product was purified by column chromatography on silica gel (CH₂Cl₂/hexane, 1:1) and recrystallization from hexane, yielding a colorless solid (92 mg, 42.6% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.88 (t, 3H), 1.28 (br, 24H), 1.50 (m, 2H), 1.66 (m, 2H), 1.85 (m, 2H), 2.65 (t, 2H), 4.07 (t, 2H), 7.13–7.18 (m, 2H), 7.27 (d, 2H), 7.61 (d, 2H), 7.69 (dd, 1H), 7.76 (d, 2H), 7.94 (d, 1H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 14.11, 22.67, 26.10, 29.25, 29.27, 29.33, 29.38, 29.42, 29.50, 29.57, 29.59, 31.54, 31.89, 35.62, 68.05, 106.33, 119.36, 125.25, 125.91, 126.99, 127.09, 128.86, 129.09, 129.54, 133.64, 136.18, 138.50, 141.86, 157.14.

Poly(3-{10-[6-(4-octylphenyl)naphthalene-2-yloxy]decyl}thiophene-2,5-diyl) (PTPhN). Method I: Nickel bis(cycloocadiene) (Ni(cod)₂) (235 mg, 0.85 mmol), 2,2'-bipyridine (bpy) (135 mg, 0.86 mmol), and 1,5-cyclooctadiene (cod) (96 µL, 0.78 mmol) in dry DMF (2 mL) were stirred at room temperature under N₂ atmosphere for 30 min. Then the monomer 8 (297 mg, 0.42 mmol) in dry THF (2 mL) was added into the catalyst solution, which was stirred at 80 °C for 3 days. The reaction mixture was poured into the solution of MeOH containing aqueous HCl, and the resultant precipitate was successively purified by reprecipitation from MeOH and acetone, respectively. PTPhN1a was obtained as a yellow solid (220 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.88 (br, 3H), 1.15–1.87 (m, 28H), 2.47-2.80 (m, 4H), 3.99 (br, 2H), 6.95-7.20 (m, 3H), 7.20-7.29 (br, 2H), 7.48-7.79 (m, 5H), 7.89 (br, 1H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 14.11, 22.67, 26.12, 29.28, 29.40, 29.50, 29.59, 30.61, 31.53, 31.89, 35.61, 67.98, 106.26, 119.31, 125.18, 125.84, 126.94, 127.09, 128.82, 129.06, 129.51, 133.63, 136.10, 138.43, 141.80, 157.10.

Similarly, the monomer 8 (205 mg, 0.29 mmol) in dry DMF (3.5 mL) was added into the solution of Ni(cod)₂ (252 mg, 0.92 mmol), 2,2'-bipyridine (149 mg, 0.95 mmol), and 1,5-cyclooctadiene (80 μ L, 0.58 mmol) in dry DMF (0.7 mL), and the reaction mixture was stirred at 80 °C for 3 days under N₂ atmosphere. The reaction mixture was precipitated from the MeOH containing aqueous HCl solution, and reprecipitated from MeOH and acetone, respectively, affording **PTPhN1b** as a yellow solid (151 mg, 95% yield). NMR spectra of **PTPhN1b** were identical with those of **PTPhN1a**.

Method II: Into the monomer 8 (252 mg, 0.35 mmol) and LiCl (18 mg, 0.4 mmol) in dry THF (1.5 mL), was added iPrMgCl (2.0 mol dm⁻³ in THF, 180 μ L) at 0 °C, which was stirred at 0 °C for 1 h. After addition of dry THF (2.0 mL), the part of the reaction mixture (0.5 mL) was sampled for analysis of metalated intermediates.³² Then 1.3bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl₂) (4 mg, 0.008 mmol) was added to the reaction mixture, which was stirred at room temperature overnight. After addition of an aqueous HCl solution, the reaction mixture was extracted with chloroform for several times to obtain a polymer-dispersed organic layer, which was washed with water and dried over CaCl₂. The product dissolved in hot o-dichlorobenzene was reprecipitated from MeOH, acetone, and chloroform/acetone, affording PTPhN2 as a purple solid (104 mg, 62% yield). ¹H NMR (600 MHz, chlorobenzene- d_5 , δ ppm): 0.87 (t, 3H), 1.33 (br, 20H), 1.47 (m, 4H), 1.66 (br, 2H), 1.77 (br, 2H), 2.54 (m), 2.61 (br, 2H), 2.88 (m), 3.99 (br, 2H), 6.96-7.25 (m, 5H), 7.55 (br, 2H), 7.57-7.68 (m, 3H), 7.87 (br, 1H). ¹³C NMR (150 MHz, chlorobenzene-d₅, δ ppm): 13.94, 22.81, 26.57, 29.48, 29.68, 29.75, 29.87, 29.96, 30.65, 30.82, 31.44, 32.13, 35.93, 68.81, 108.07, 119.59, 125.57, 125.80, 126.12, 126.24, 127.35, 127.48, 128.00, 128.41, 128.50, 128.58, 128.69, 128.77, 128.83, 128.96, 129.10, 129.21, 129.27, 129.43, 129.54, 129.62, 129.83, 130.05, 134.42, 135.50, 134.85, 136.859, 139.19, 141.99, 157.96.

Estimation of Regioregularity and Degree of Polymerization by ¹H NMR. Regioregularity (rr) of the 3-substituted polythiophenes (content of head-to-tail linkages in the polymer chains) was estimated from integration values of α -methylene proton signals of a head-to-tail linkage at about 2.8 ppm (I_{ht}) and a head-to-head linkage at about 2.58 ppm (I_{hh}) using an equation, rr = $I_{ht}/(I_{ht} + I_{hh})$, by ¹H NMR analysis.³ Practically, in the cases of PTPHN1a and PTPHN1b measured in CDCl₃ with the JEOL JNM-ECS 400, $I_{\rm hh}$ was roughly determined by subtracting overlapping integration of α -methylene protons (2H) at 2.61 ppm of the (4-octylphenyl)naphthalene moiety from total integration of signals in the region of 2.47-2.65 ppm. In the cases of ¹H NMR analysis of **PTPHN1b** and **PTPHN2** in chrorobenzene- d_5 measured with the Bruker AVANCE 600, rr was more properly calculated using eq 1 with I'_{ht} (2.95–2.77 ppm), I'_{hh} (2.77–2.65 ppm), and an integration value of α -methylene protons of polymer terminals (I'_{term}) (2.58–2.40 ppm).^{34,35} Similarly, number-average degree of polymerizations (dp) of PTPHN1b and PTPHN2 were estimated using eq 2 with these integration values.

$$rr = I'_{ht} / (I'_{ht} + I'_{hh} + I'_{term})$$
(1)

$$dp = (I'_{ht} + I'_{hh} + I'_{term})/I'_{term}$$
(2)

RESULTS AND DISCUSSION

Synthesis. Synthetic routes for the monomer 8, model liquid crystal (PhN), and polymers (PTPhN) are summarized in Scheme 2. 2,5-Dibromothiophene derivative 4 was synthesized from 3-bromothiophene and the THP protected 10-bromodecanol 1 by Kumada-Tamao-Corriu cross coupling,³⁶ followed by dibromination with NBS. On the other hand, phenylnaphthalene derivative 7 was prepared from 2bromo-6-methoxynaphthalene and 5 by Suzuki-Miyaura cross coupling³⁷ and successive ether cleavage reaction. The monomer 8 was synthesized from the thiophene moiety 4 and phenylnaphthalene moiety 7 by Mitsunobu reaction.³⁸ The model liquid crystal, 2-phenylnaphthalene derivative PhN, was also synthesized by Williamson reaction of 1-bromodecane and 7 for the purpose of comparison with the polymers. PTPhN1a and **PTPhN1b** were obtained by polymerization of the monomer 8 by Yamamoto method²⁷ (method I) in DMF-THF and in DMF, respectively. PTPhN2 was obtained from the same monomer 8 by Ni-catalyzed chain-growth polymerization method^{28,29} (method II).

General Properties. The polymerization results and average molecular weights and rr of **PTPhN1** and **PTPhN2** are summarized in Table 1. **PTPhN1a** and **PTPhN1b** exhibited

Table 1. Polymerization Results and Average Molecular Weights and Regioregularity of the Polymers

polymer	yield/%	$M_{\rm n}/{\rm g}~{\rm mol}^{-1}~(M_{\rm w}/M_{\rm n})$	dp ^a	$\mathrm{rr}/\%^b$
PTPhN1a	95	$6300 (1.24)^c$	11.4 ^c	(30)
PTPhN1b	95	8400 (1.62), ^c 4650 ^d	15.2, ^c 8.4 ^d	29.9 (30)
PTPhN2	62	4090 ^d	7.4^{d}	76.3

^{*a*}Number-average degree of polymerization. ^{*b*}Regioregularity determined by 600 MHz (and 400 MHz) ¹H NMR. ^{*c*}Determined by GPC. ^{*d*}Determined by ¹H NMR.

good solubility for organic solvents such as chloroform and THF at room temperature, while PTPhN2 was insoluble in such solvents, but soluble in hot chlorobenzene or hot odichlorobenzene. The GPC analysis showed that the numberaverage molecular weight (M_n) and polydispersity (M_w/M_n) were 6300 g mol⁻¹ and 1.24 for PTPhN1a and 8400 g mol⁻¹ and 1.62 for PTPhN1b, respectively. GPC analysis of PTPhN2 was not carried out because of the insolubility for the THF eluent. Head-to-tail content (rr) of PTPhN1 could be roughly estimated to be about 30% from ¹H NMR spectra at 400 MHz in CDCl₂ in the region of 2.2–3.2 ppm for α -methylene protons of 3-substituted polythiophene. In order to compare rr between PTPHN1 and PTPHN2, it was precisely examined by 600 MHz ¹H NMR in chlorobenzene- d_5 at room temperature for PTPhN1b and at 120 °C for PTPhN2 (Figure 1). A sharp and strong peak at about 2.61 ppm is assigned to α -methylene protons of the 4-octylphenylnaphthalene moiety (B), and the other signals are due to α -methylene protons of the 3substituent moiety of various thiophene units (A). Signals observed between 2.95 and 2.76 ppm (A1), 2.76-2.65 ppm (A_2) , and 2.58–2.40 ppm (A_3) are assigned to regionegular units, regioirregular ones and chain-end ones, respectively. 33-35 From these integration areas, rr of PTPhN1b and PTPhN2 could be estimated from eq 1 (see Experimental Section) to be 29.9% and 76.3% . On the basis of this NMR analysis, numberaverage degree of polymerization (dp) and M_n of PTPhN1b and PTPhN2 can be estimated using eq 2 with these integration values (see Experimantal Section). Interestingly, $M_{\rm n}$ values of two polymers estimated by NMR are in the range of 4000-5000 g mol⁻¹ and are not so much different. Considerable difference between M_n for PTPhN1b obtained by respective two methods is due to overestimation of $M_{\rm n}$ usually observed in rigid poly(3-alkylthiophene)s by GPC.³⁹

Consequently, the characteristic poor solubility of **PTPhN2** compared to **PTPhN1** was suggested to be caused by the higher rr, probably which caused strong intermolecular interaction between the main chains and side chains. Other than the NMR investigation, the good rr for **PTPhN2** is also supported by the fact that an intermediate, 3-substituted 2-bromo-5-chloromagnesiothiophene, produced 4 times larger than a 5-bromo-2-chloromagnesio derivative in the initial stage.³² which was confirmed by ¹H NMR analysis of the sampling according to the procedure described in the Experimental Section. The poor solubility of **PTPhN2** brought about precipitation of polymeric products in an early stage of polymerization, which rather lowered dp than expected from the molar ratio of the monomer/Ni catalyst about 44 and at the same time lowered rr.



Figure 1. ¹H NMR (600 MHz) spectra of **PTPhN1b** (a) at room temperature and **PTPhN2** (b) at 120 °C in chlorobenzene- d_s in the range 2.2–3.2 ppm.

Photoabsorption and Fluorescence Properties. UVvis absorption spectra of the polymers in solution and in thin solid film state are shown in Figure 2 and Figure 3, and their



Figure 2. Normalized UV-vis spectra of chloroform solutions of PTPhN1a (black solid line), PTPhN1b (black dashed line), PhN (black dotted line), and an *o*-dichlorobenzene solution of PTPhN2 (red solid line).

optical data of absorption and PL are summarized in Table 2. Absorption spectra of **PTPhN1a** and **PTPhN1b** were basically same in solution and in film state, and showed two characteristic absorption bands due to $\pi - \pi^*$ transition of the phenylnaphthalene moiety in the ultraviolet region around 300 nm and polythiophene backbones in the visible light region around 385 nm. The assignment is considered reasonable in comparison with spectrum of **PhN** shown in Figure 2. The



Figure 3. UV–vis spectra of a pristine film (black solid line) and an annealed film heat treated at 140 °C (black dashed line) of **PTPhN1b** and pristine film of **PTPhN2** (red solid line, *y* axis is Abs. (arbitrary unit)) on a quartz glass plate.

latter band observed in the region rather blue-shifted than usual 3-substituted polythiophenes and little difference between absorption λ_{\max} in solution and film state suggest that π conjugation of the polythiophene backbones is significantly restricted by the large side chains and their rr. A little bathochromic and hyperchromic shift of the latter band observed for PTPhN1b by comparison with PTPhN1a is due to longer π -conjugation of the higher molecular weight polymer. These results suggest that polymerization performed successfully. In contrast, the latter band of PTPhN2 was considerably bathochromic shifted compared to PTPhN1 especially in the film states. The absorption λ_{max} of PTPhN2 in CHCl₃ (444 nm) suggests that the $\pi - \pi^*$ transition energy is lower than those of regioirregular poly(3-alkylthiophene)s (λ_{max} = 428 nm)³³ and a regionegular octamer of 3-octylthiophene $(\lambda_{\text{max}} = 422 \text{ nm})^{40}$ and higher than that of regionegular poly(3-hexylthiophene $(\lambda_{\text{max}} = 456 \text{ nm})$,³³ Considering this, the optical characteristic of PTPhN2 is basically corresponding to the estimated rr (76.3%) and dp (7.4). Optical bandgaps (E_{σ}) between energy levels of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) of PTPhN1 and PTPhN2 estimated from absorption edge in the film state were 2.25 and 1.86 eV, respectively. E_{HOMO} of PTPhN1a and PTPhN1b were estimated at about -5.50 eV from onset oxidation potential of their cyclic voltammograms, and consequently, E_{LUMO} were calculated being about -3.25 eV from the values of $E_{\rm g}$ and $E_{\rm HOMO}$. In the same way, $E_{\rm HOMO}$ and E_{LUMO} of **PTPhN2** were estimated to be -5.34 and -3.46 eV. These results indicate that PTPhN2 has not only the narrower E_{α} but also larger electron accepting ability and lower ionization ability than PTPhN1.

When **PTPhN1** are excited with light energies at 256, 296, and 387 nm, they showed a characteristic emission band around 540 nm in chloroform (Figure 4) and 550 nm in the film state. The PL band is due to emission from the polythiophene backbone and not from the phenylnaphthalene moiety, which



Figure 4. Normalized PL spectra of chloroform solutions of PTPhN1b excited at 256 nm (black solid line), 296 nm (red solid line), 387 nm (blue solid line), PhN excited at 296 nm (black dotted line), and *o*-dichlorobenzene solution of PTPhN2 excited at 444 nm (black dashed line).

can be confirmed by comparing with PL spectra of poly(3hexylthiophene) polymerized under the same conditions (λ_{max} = 550 nm in chloroform) and **PhN** (λ_{max} = 369 nm in chloroform). This result suggests that Förster resonance energy transfer⁴¹ efficiently occurs from the phenylnaphthalene side group to the polythiophene backbone in the solution and film states taking into consideration that the PL band of the phenylnaphthalene side group overlaps with the absorption band of the polythiophene main chain. On the other hand, **PTPhN2** showed an emission peak from polythiophene backbones at 585 nm in solution and 720 nm in film state, which are almost same with those of regioregular poly(3hexylthiophene).³³

Liquid Crystalline Behavior. Thermal behavior of PTPhN and PhN was investigated by temperature-controlled POM and DSC, and the DSC thermograms are shown in Figure 5 and phase transition temperatures and changes of enthalpy (ΔH) of the polymers and PhN are summarized in Table 3. The DSC analysis showed that the phase transitions for PTPhN1a and PTPhN1b were enantiotropic. The POM analysis revealed that all mesophases of PTPhN1 showed fan-shaped textures typical of smectic phases (Sm), and sizes of domains were respectively large about several tens of μm regardless of their different average size of molecular weights (Figure 6a,b). PTPhN1a made a fan-shaped texture at around 115 °C under heating process, and it was changed into a broken one at about 122 °C. Further heating to 149 °C led to disappearance of the birefringence, which corresponds to transition into isotropic liquid phase (Iso). On the other hand, PTPhN1b showed one distinct smectic liquid crystalline phase, and the phase transition temperatures of glass phase (G)-Sm and Sm-Iso were higher than those of PTPhN1a. These results suggest that the higher molecular weight heightens phase transition temperatures of PTPhN1, while the higher polydispersity

Table 2. Optical Properties and Energy Levels of the Polymers

	UV-vis $\lambda_{\rm max}/{\rm nm}$		PL $\lambda_{\rm max}/{\rm nm}$				
polymer	solution	film ^c	solution	film ^c	$E_{\rm g}/{ m eV}^d$	$E_{\rm HOMO}/{\rm eV}^e$	$E_{\rm LUMO}/{\rm eV}^{f}$
PTPhN1a	385 ^a	386	534 ^a	550	2.25	-5.51	-3.26
PTPhN1b	387 ^a	387	541 ^a	559	2.25	-5.50	-3.26
PTPhN2	444 ^b	509	585 ^b	720	1.86	-5.34	-3.46

^{*a*}In chloroform. ^{*b*}In *o*-dichlorobenzene. ^{*c*}Drop-cast films on a quartz plate. ^{*d*}Calculated from absorption edge of the films. ^{*e*}Estimated from onset of the oxidation peak from cyclic voltammerty. ^{*f*}Calculated from HOMO level and the optical bandgap.



Figure 5. DSC thermograms of PTPhN1a (a), PTPhN1b (b), PTPhN2 (c), and PhN (d) in the second sweeps with a scan rate of 10 $^{\circ}$ C min⁻¹.

Table 3. Phase Transition Temperatures and Changes of Enthalpy of Compounds^{a,b}

	phase transition temperature/°C (ΔH /J g ⁻¹) ^c			
compound	heating process	cooling process		
PTPhN1a	G 115 (6.7) SmE 122 (10.4) SmA 149 (19.9) Iso	Iso 146 (-19.4) SmA 118 (-8.2) SmE 111 (-5.9) G		
PTPhN1b	G 143 (19.9) Sm 157 (16.7) Iso	Iso 151 (-17.4) Sm 132 (-16.3) G		
PTPhN2	G 124^d Sm 192^d Iso	Iso 171 ^{<i>d</i>} Sm 115 ^{<i>d</i>} G		
PhN	K 76 (16.1) SmE 83 (7.9) SmB 106 (9.8) SmA 127 (21.4) Iso	Iso 123 (-21.5) SmA 103 (-8.4) SmB 79 (-10.1) SmE 69 (-15.6) K		

^{*a*}Abbreviations: K, crystal; G, glass state; SmA, B, E, defined smectic phases as A, B, E; Sm, unresolved smectic phases; Iso, isotropic liquid. ^{*b*}Liquid crystalline phases were determined by DSC, POM, and XRD. ^{*c*}Determined from second DSC traces at a scan rate of 10 °C min⁻¹. ^{*d*}Approximate transition temperatures of undefined mesophases.

makes phase transitions indistinct. Meanwhile, **PTPhN2** did not show any distinct mesophases both in DSC and POM analyses, and the observed POM texture was a polygonal (Figure 6c). This is ascribed to the strengthened interactions between main chains as well as side mesogenic groups caused by the high rr.

The phase transition behaviors of **PTPhN1** thought to be dominantly affected by liquid crystalline properties of the phenylnaphthalene side chain. As listed in Table 3, **PhN** showed three enantiotropic smectic phases (SmE, SmB, SmA) between crystal phase (K) and Iso, whose behavior is similar to those of series of phenylnaphthalene liquid crystals reported previously.⁴² The ΔH of phase transition from Sm to Iso was within 17–20 J g⁻¹ for **PTPhN1** and 21 J g⁻¹ for **PhN**, which approximately equated to 10 kJ mol⁻¹. Although **PTPhN1a** and **PTPhN1b** had different phase transition temperatures and different number of distinct mesophases, their total ΔH between G and Iso are almost equal to 37 J g⁻¹ in the heating process and -34 J g⁻¹ in the cooling one. These results suggest that similar change of molecular arrangement occurs at the side chain moieties in **PTPhN1** between the states of G and Iso.



Figure 6. Polarized optical micrographs of **PTPhN1a** at 128 °C in the heating process (a), **PTPhN1b** at room temperature after isotropic phase transition, annealing at 140 °C, and successive rapid cooling (b), and **PTPhN2** at room temperature after isotropic phase transition, annealing at 150 °C, and rapid cooling (c).

A typical molecular arrangement of PTPhN1 was predicted from X-ray diffraction (XRD) observations of a pristine dropcast film and an annealed sample of PTPhN1b on a Si substrate. The annealed sample was prepared by heat-treating at 175 °C (Iso) of the pristine film, cooling down and annealing at 140 °C (Sm) for several minutes, and rapidly cooling down to room temperature in a G state. As shown in Figure 7, the polymer film samples showed two characteristic XRD signal patterns, and the annealing sharpened and intensified both signals with enhancement of molecular arrangements. The former is a series of sharp peaks at $2\theta = 2.5^{\circ}$ ($c \approx 35$ Å), 4.8 and 7.4 due to a layered distance of the phenylnaphthalene side chains, which is assigned to Miller indices, (001)-(003). The layer spacing of ca. 35 Å is almost corresponding to a length of the side chain moiety in the most extended conformation. As a result, the layered distance should be equivalent to interchain distance of the polythiophene backbones. The latter is distinct peaks at $2\theta = 19.3^{\circ}$ and 20.7° on broad multiple signals around



Figure 7. XRD spectra of pristine (red) and annealed (black) films of **PTPhN1b** and a suggested molecular arrangement.

 $15-30^{\circ}$, which is sum of the signals due to distances of phenylnaphthalene moieties taking SmE domains involving reflections such as (200), (020), (110), (220) with lattice constants of a = 9.2 Å and b = 8.6 Å. Therefore, a layered π -stacked distance between polythiophene sheets should come to be 4.3 Å. **PTPhN1a** and **PTPhN2** in G state basically showed same XRD signal pattern of the pristine film of **PTPhN1b**. In addition, heat treatment of **PTPhN1a** at 125 °C changed the pattern to typical of SmA showing a layer distance (36 Å) read from a sharp peak at $2\theta = 4.8^{\circ}$ and an intermolecular distance (4.6 Å) between the mesogenic side chains read from a broad signal at $2\theta = 19.3^{\circ}$, while the pattern was almost invariant against thermal annealing for **PTPhN2**.

Furthermore, comparison of the UV-vis absorption spectra of the pristine and annealed films of **PTPhN1b** (Figure 3) showed that the annealed film had a stronger absorbance at around 400 nm due to the polythiophene backbone and weaker absorbances at around 250 and 300 nm due to the phenylnaphthalene moiety relative to those of the pristine film. These results also support the molecular orientation of **PTPhN1** illustrated in Figure 7, because the perpendicular oriented phenylnaphthalene moiety on a substrate hard to absorb perpendicular incident radiation and, in contrast, the parallel oriented polythiopehene backbones with torsion angles in some degree are favorable for the light absorption.

CONCLUSIONS

2-Phenylnaphthalene liquid crystals that are ambipolar carrier transporting semiconductor were introduced into 3-position of thiophene as the side chain functionality. The synthesized thiophene monomer was polymerized by Yamamoto method using $Ni(cod)_2$,²⁷ and also polymerized by chain-growth method using $Ni(dppp)Cl_2$.^{28,29} **PTPhN1a** and **PTPhN1b** prepared by the former method under the different conditions were well soluble in organic solvents, and the observed general characteristics of $M_{\rm n}$ (6000–9000 g mol⁻¹), absorption $\lambda_{\rm max}$ (ca. 385 nm), and PL emission λ_{max} (530–560 nm) were ordinary for 3-substituted polythiophenes obtained by this method. PL spectral analysis of PTPhN1 in solution and solid states suggested that energy transfer from the phenylnaphthalene side-chain to the polythiophene backbone effectively occurred by the Förster mechanism. PTPhN1 showed smectic mesophases between G and Iso in the enantiotropic phase transitions. From the total ΔH of phase transitions, changes of molecular arrangements of PTPhN1 along the phase transitions were revealed to be intrinsically same, while their transition temperatures were different. The molecular arrangement of PTPhN1b in the liquid crystalline

phase was examined by XRD and UV-vis spectroscopies with a cooled sample in glassy state. The patterns of XRD signals and the anisotropy of UV-vis absorbance suggested that the phenylnaphthalene side chains vertically oriented against to the polythiophene backbones to construct a polymer array. The observed distance of smectic layer ($c \approx 35$ Å) of the side chains is thought to correspond to the distance between the polythiophene backbones. In addition, a lamellar structure made by sheets of the rigid polymer backbones and interdigitated flexible side chains are suggested to take a SmE arrangement. Consequently, the arrayed PTPhN1 in the smectic states are expected to be reflected by the semiconducting characteristics of phenylnaphthalene liquid crystals,^{25,26,42} because the mesophases observed for PTPhN are basically caused by aggregation of the phenylnaphthalene side chains. On the other hand, PTPhN2 prepared by the latter method is expected to have good photoabsorption and semiconducting characteristics due to the fairly high regioregularity of polythiophene backbones. However, this attempt brought about production of the extremely low soluble polymer and its phase transition behaviors were obscure as observed in DSC and POM in spite of having M_n comparable to **PTPhN1**, which is a dilemma should be overcome by considering intermolecular interactions between polymer main chains as well as side groups.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures of compounds (1-6) and ¹H NMR spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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