Solubility control of regioregular 3-substituted polythiophenes bearing 2-phenylnaphthalene side chain by copolymerisation

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Abstract. Two types of 2,5-dibromothiophene monomers having a dodecyl chain and a 2-phenylnaphthalene one were randomly copolymerised in different feed molar ratio by Ni-catalysed chain-growth polymerisation method. Regioregularity of all polymers were sufficiently high (88-97%). Absorption λ_{max} due to π-π* transition of polythiophene backbones in solutions were observed at 444-451 nm for all polymers, which were almost similar to each other and typical of the optical characteristics of regioregular poly(3-alkylthiophene)s. The homopolymer of the latter monomer that had the phenylnaphthalene side group showed poor solubility to common organic solvents, i.e., it was insoluble in chloroform at room temperature and could dissolve only in hot solvents above 100 ºC. The copolymers, which had higher number average molecular weights (M_n), had better solubility than that of the homopolymer.

1. Introduction
Polythiophene and related derivatives having alkyl side chains have been studied worldwide energetically, while examples of studies about polythiophene derivatives having aromatic side groups with special functionalities such as liquid crystalline properties are limited so far. Recently, our group realised synthesising 3-substituted polythiophenes bearing a liquid crystalline and semiconducting 2-phenylnaphthalene moiety [1]. Polymers provided by the same 2,5-dibromo-3-substituted thiophene monomer but different polymerisation methods exhibited quite different properties. The polymers prepared by Yamamoto dehalogenative polycondensation method showed modest head-to-tail regioregularity, good solubility in organic solvents, large liquid crystalline domains, and wide energy gap (E_g) between HOMO and LUMO levels. In contrast, the polymers prepared by Ni-catalysed chain-growth polymerisation method showed better regioregularity, poor solubility, smaller liquid crystalline domains, and narrower energy gap. The latter polymers must have unique semiconducting properties of the regioregular poly(3-substituted thiophene) backbone and aggregated phenylnaphthalene side chain in an oriented state, however, the unexpected low solubility due to large intermolecular interaction holds up further investigations. In this study, 3-substituted thiophene bearing 2-phenylnaphthalene moiety was copolymerised with 3-alkylthiophene by the Ni-catalysed chain-growth polymerisation method in order to control solubility and regioregularity of poly(3-substituted thiophene)s bearing 2-phenylnaphthalene side chains, and basic properties of these polymers were investigated.
2. Experimental

2.1. Materials
One of the monomers, 2,5-dibromo-3-dodecylthiophene (M1), was synthesised along with well-established procedure from 3-bromothiophene [2,3], and the other monomer, 2,5-dibromo-3-[10-[6-(4-octylphenyl)naphthalene-2-yloxy]decyl]thiophene (M2), was prepared by the procedures described in our previous report [1]. Other chemicals used in this study were purchased from Kanto Chemical, Tokyo Chemical Industry, Nacalai Tesque, Sigma-Aldrich, and Acros Organics.

2.2. General procedure for the copolymerisation
All polymers were synthesised by Ni-catalysed chain-growth polymerisation method [4, 5]. The feed molar ratios of M1:M2 were settled as 1:0, 1:1, 1:3, 1:5, and 0:1, and resultant polymers were abbreviated P1:0, P1:1, P1:3, P1:5, and P0:1, respectively (Figure 1). Polymerisation was carried out under the conditions in the presence of the monomers (0.1 M (mol dm\(^{-3}\)), 2.0 M isopropylmagnesium chloride (iPrMgCl) in THF (1.05 eq), a Ni catalyst (0.02 eq), and LiCl (1-2 eq) in dry THF and under a N\(_2\) atmosphere.

Typical procedure was; the monomers (M1, M2) and LiCl were dissolved in dry THF. To the mixture, iPrMgCl (2.0 M) in THF was added at 0 °C, which was stirred at 0 °C for 1 h. After addition of [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl\(_2\)), an ice bath was removed and the reaction mixture was warmed up to room temperature slowly. After reacting 1-12h, the reaction was quenched by adding an aqueous HCl (5 M). The polymers were purified by precipitation from MeOH and acetone. For P1:1, P1:3, and P1:5, additional reprecipitation from hexane was performed. Similarly, P0:1 was further purified by reprecipitation from acetone/chloroform. Purple solids (40-62% yield) were obtained in all cases.

3. Results and discussion

3.1. Synthesis and characterisations of polymers
M1 and M2 in the feed molar ratios of 1:0, 1:1, 1:3, 1:5, and 0:1 were randomly polymerised by the Ni-catalysed chain-growth method [4, 5] to obtain regioregular poly(3-alkylthiophene)s (P1:0, P1:1, P1:3, P1:5, and P0:1) according a pathway shown in Figure 1. The number average molecular weights (M\(_n\)), weight average molecular weights (M\(_w\)), polydispersity indexes (M\(_w\)/M\(_n\)), number average degrees of polymerisation (dp), regioregularities, and actual compositon ratios of polymers were listed in Table 1. To determine M\(_n\) and dp of P0:1, \(^1\)H NMR spectrum in hot chlorobenzene-d5 was used because of its poor solubility to the gel permeation chromatography (GPC) eluent (THF) at ambient temperature [1]. Figure 2 shows \(^1\)H NMR spectra of the polymers. Average molecular weights of the polymers except P0:1, which were determined by GPC, were enough high and similar to those of poly(3-alkylthiophene)s provided by a similar method [6]. Average formula masses considered actual
Composition ratios of two units were used to calculate dp. The actual composition ratios of the copolymers were calculated from integration ratio between a well-separated $^1$H NMR peak at 4.0 ppm due to naphthoxy-linked methylene protons of the $\text{M2}$ unit (D) and overlapped peaks at 0.9 ppm due to terminal methyl groups of both monomer units (B and F). It is verified that reactivities of two monomers during polymerisation were almost same, because composition molar ratios of the polymers were quite similar with their initial feed molar ratios of the monomers. Regioregularities of the polymers were estimated similarly by the method in our previous report [1] considering integration values at methylenes A, C, and E in the $^1$H NMR spectra (Figure 2), and revealed to be high and similar each other except for $\text{P}_{0:1}$. The relatively low regioregularity observed for $\text{P}_{0:1}$ was attributed to its low molecular weight.

**Table 1.** Polymerisation results.

| Polymer | $M_n$ / kg mol$^{-1}$ | $M_w$ / kg mol$^{-1}$ | $M_w/M_n$ | dp | Regioregularity$^d$ / % | Composition ratio$^d$ |
|---------|-------------------|-----------------------|------------|----|------------------------|----------------------|
| $\text{P}_{1:0}$ | 11.0$^a$ | 14.8 | 1.34 | 43.9$^a$ | 97 | 1:0 |
| $\text{P}_{1:1}$ | 17.9$^a$ | 21.8 | 1.22 | 42.1$^a$ | 97 | 1:1.1 |
| $\text{P}_{1:3}$ | 15.9$^a$ | 21.0 | 1.32 | 33.0$^a$ | 96 | 1:3.4 |
| $\text{P}_{1:5}$ | 18.5$^a$ | 23.4 | 1.26 | 37.0$^a$ | 92 | 1:4.9 |
| $\text{P}_{0:1}$ | (4.09)$^b$ | | | | 88 | 0:1 |

$^a$ Determined by GPC calibrated with polystyrene standards using THF as an eluent.

$^b$ Estimated by $^1$H NMR spectrum [1].

$^c$ Number-average degree of polymerisation.

$^d$ Determined by $^1$H NMR spectra.

**Figure 2.** $^1$H NMR spectra of $\text{P}_{1:0}$ in CDCl$_3$ at rt, $\text{P}_{1:1}$ in CDCl$_3$ at 323K, $\text{P}_{1:3}$ in CDCl$_3$ at 323K, $\text{P}_{1:5}$ in chlorobenzene-d$_5$ at 373K, and $\text{P}_{0:1}$ in chlorobenzene-d$_5$ at 393K at a resonance frequency of 600 MHz.
3.2. Solubilities of polymers

Solubilities of the polymers were evaluated using chloroform which is popular and most often-used good solvent for conjugated polymers. Figure 3 is pictures of the polymer solutions in chloroform. Weight of polymer and volume of chloroform were determined 1.0 mg and 1.0 mL. All the polymers were purple in solid state but their colour changed to light orange when they were fully dissolved. After well mixing them at respective temperatures of ambient, 40 °C, 50 °C, and 60 °C, the mixing samples were left to stand at least 5 min at each temperature to check solubility. The homopolymer of M1, P1:0, was soluble in chloroform at room temperature as is well known. On the other hand, the homopolymer of M2, P0:1, did not dissolve even if it was heated at 60 °C in spite of its low molecular weight. Solubility of the copolymers was increased as increasing the content ratio of M1 unit, that is, P1:5, P1:3, and P1:1, dissolved completely at above 60 °C, 40 °C, and room temperature, respectively. From these results, it was found that the copolymerisation with 3-dodecylthiophene was effective for improving solubility of regioregular poly(3-substituted thiophene) bearing 2-phenylnaphthalene side group. It is suggested that the 3-dodecylthiophene (M1) unit encouraged dissolving and disturbing aggregation of the phenylnaphthalene side group. Differential scanning calorimetry (DSC) measurement at a heating/cooling rate of 10 °C/min was used to investigate phase transition behaviours of the polymers. Because of their high intermolecular forces in condensed states, the transition temperatures from isotropic liquid to the first less mobile phase of P1:0, P1:1, P1:3, P1:5, and P0:1 were clearly observed at 115 °C, 107 °C, 114 °C, 164 °C, and 171 °C, in the second cooling process of DSC thermograms. Although these phase transition temperatures are affected by molecular weights of polymers, it can be said that introduction of 3-dodecylthiophene (M1) unit was effective to improve fusibility of poly(3-substituted thiophene) bearing 2-phenylnaphthalene side group, P0:1.

| Polymer | rt | 40 °C | 50 °C | 60 °C |
|---------|----|-------|-------|-------|
| P1:0    | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) |
| P1:1    | ![Image](image5) | ![Image](image6) | ![Image](image7) | ![Image](image8) |
| P1:3    | ![Image](image9) | ![Image](image10) | ![Image](image11) | ![Image](image12) |
| P1:5    | ![Image](image13) | ![Image](image14) | ![Image](image15) | ![Image](image16) |
| P0:1    | ![Image](image17) | ![Image](image18) | ![Image](image19) | ![Image](image20) |

Figure 3. Pictures of polymer (1.0 mg) solutions in chloroform (1.0 mL).

3.3. Optical properties

UV-vis absorption spectra of the polymers in solution states and drop-cast films were shown in Figure 4 and Figure 5, and data of the UV-vis absorption λ\text{max} and photoluminescence (PL) λ\text{em} of the
polymers in solution and film states due to \( \pi-\pi^* \) transition were listed in Table 2. The absorption \( \lambda_{\text{max}} \) and PL \( \lambda_{\text{max}} \) of the polymers in solutions were observed at 444-451 nm and 579-588 nm, and they were similar each other and almost identical to the data of regioregular poly(3-dodecylthiophene) in a previous report [7]. On the other hand, the absorption \( \lambda_{\text{max}} \) of P0:1, P1:3, and P1:5, in films were hypsochromic shifted than that of P0:1, which might be due to effect of steric hindrance of the bulkier phenylnaphthalene side group than the dodecyl group (Figure 5). However, absorption edges of P1:1, P1:3, and P1:5, in films were little shifted from that of P0:1, which means that these copolymers have almost same bandgaps (\( E_g \)) as P0:1 has.

![Figure 4. UV-vis absorption spectra of P1:0 (black), P1:1 (red), and P1:3 (blue) in chloroform, and P1:5 (green), and P0:1 (orange) in o-dichlorobenzene.](image)

![Figure 5. UV-vis absorption spectra of drop-cast films of P1:0 (black), P1:1 (red), P1:3 (blue), P1:5 (green), and P0:1 (orange).](image)

| Polymer | UV-vis \( \lambda_{\text{max}}/\text{nm}^a \) | \( E_g/\text{eV} \) | PL \( \lambda_{\text{em}}/\text{nm}^a \) |
|---------|---------------------------------|-----------------|-----------------|
|         | Solution | Film | Solution | Film | Solution | Film |
| P1:0    | 445\(^b\) | 527,553 | 1.94 | 579\(^b\) | 727 |
| P1:1    | 451\(^b\) | 512 | 1.95 | 580\(^b\) | 692 |
| P1:3    | 447\(^b\) | 494 | 1.95 | 580\(^b\) | 628 |
| P1:5    | 451\(^c\) | 511 | 1.96 | 588\(^c\) | 714 |
| P0:1    | 444\(^c\) | 509 | 1.95 | 585\(^c\) | 720 |

\( a \) UV-vis \( \lambda_{\text{max}} \) and PL \( \lambda_{\text{em}} \) due to \( \pi-\pi^* \) transition of polythiophene backbone.

\( b \) In chloroform.

\( c \) In o-dichlorobenzene.

### 3.4. Energy levels

Energy levels of highest occupied molecular orbital (\( E_{\text{HOMO}} \)) of the polymers were estimated from the onset oxidation potentials of the polymers measured by cyclic voltammetry (CV), and Figure 6 shows the oxidation waves of the polymers. \( E_{\text{HOMO}} \) values of P1:0, P1:1, P1:3, P1:5, and P0:1 estimated from each onset potential were \(-4.91, -5.18, -5.24, -5.25, \) and \(-5.40 \text{ eV} \), although these polymers had almost same \( E_g \). The \( E_{\text{HOMO}} \) of P0:1 was deeper than that of P1:0 and the \( E_{\text{HOMO}} \) values of the copolymers were located between the homopolymers. This phenomenon implies that steric hindrance and/or some specific electronic interaction exist between the polythiophene backbone and the 2-phenylnaphthalene side group, which stabilises polythiophene backbone against oxidation.
4. Conclusions
A thiophene monomer, 2,5-dibromo-3-{10-[6-(4-octylphenyl)naphthalene-2-yloxy]decyl}thiophene (M2), was randomly copolymerised with 2,5-dibromo-3-dodecylthiophene (M1) by the Ni-catalysed chain growth method in order to improve solubility of regioregular poly(3-substitutedthiophene) with 2-phenynaphthalene side group. The copolymers, especially P1:1, realised much better solubility in organic solvents than P0:1 with maintaining high regioregularity. It is proved that insertion of the 3-dodecylthiophene moiety into a homopolymer structure of M2 can disturb aggregation between the 2-phenynaphthalene moieties and/or polythiophene backbone, effectively. In contrast, it is assumed that presence of the 2-phenynaphthalene moiety in the regioregular 3-substituted polythiophenes weakens π-stacking interaction between polythiophene backbones in consequence of steric effect of the bulky side chain in some degree, which lowered their $E_{\text{HOMO}}$ levels in spite of bearing similar regioregularity and $E_g$.

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Figure 6. Difference of onset potentials in oxidation waves of the polymers observed by CV in 0.1 M Et$_4$NBF$_4$/acetonitrile at a scan rate of 50 mV/s.